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NEPTUNIUM DISPOSAL TO THE SAVANNAH RIVER SITE TANK FARM

D. D. Walker, W.G. Dyer, H. H. Elder, T. L. Fellinger, E. K. Hansen, M. R. Poirier, and S. H. Reboul

Westinghouse Savannah River Company
Aiken, South Carolina 29808

ABSTRACT

Researchers investigated the neutralization of an acidic neptunium solution from a Savannah River Site (SRS) processing canyon and the properties of the resulting slurry to determine the feasibility of disposal in the SRS tank farm. The acidic solution displayed no properties that precluded the proposed disposal route. Neutralization of the acidic neptunium forms a 4 wt % slurry of precipitated metal hydroxides. The insoluble solids consist largely of iron (92%) and neptunium hydroxides (2%). The concentration of soluble neptunium remaining after neutralization equaled 1.8 ± 0.6 mg`/L, much less than previous solubility measurements predicted. Researchers used an apparatus similar to an Ostwald-type viscometer to estimate the consistency of the neptunium slurry with the solids present. The yield stress and consistency of the 4 wt % slurry will allow transfer through the tank farm, although concentration of the insoluble solids above 4 wt % may cause significant problems due to increased consistency and yield stress. The consistency of the 4 wt % slurry is 7.6 centipoise (cP) with a yield stress less than 1 Pascal (Pa). The neptunium slurry, when combined with actual washed radioactive sludge, slightly reduces the yield stress and consistency of the sludge and produces a combined slurry with acceptable rheological properties for vitrification in the Defense Waste Processing Facility (DWPF).

INTRODUCTION

The Department of Energy decided to close the processing canyons at the Savannah River Site, including removing all process materials. The majority of neptunium recovered and purified in the 1980s will be converted to oxide and transferred to Oak Ridge National

Laboratory for future production of plutonium-238. However, during closure operations for H Canyon, processing of irradiated uranium fuel yields small quantities neptunium-237. The small quantity (52 kg) and low purity of this neptunium makes it unattractive for recovery for production of Pu-238. Thus, the disposal option for these impure neptunium solutions to the tank farm is under consideration.

A preliminary engineering assessment identified transfer of the neptunium to a washed sludge tank as the preferred option. This option localizes the neptunium in a tank from which the primary outlet is vitrification in the DWPF. Transfer of neptunium to any other part of the tank farm would increase the soluble neptunium in feed to the Saltstone Facility. The higher neptunium concentrations would likely exceed Saltstone waste acceptance criteria for neptunium.

However, addition of the neptunium solutions to a washed sludge tank poses several technical uncertainties, including transferring a neutralized slurry from H Canyon to the washed sludge tank, soluble neptunium concentration in tank heels that do not reach the washed sludge tank, changes in composition and rheological properties of the washed sludge, and changes in glass composition and processing. This report discusses results of investigations into the neutralization and transfer of neptunium slurry. None of the results preclude the transfer of the neutralized solution to the tank farm.

EXPERIMENTAL

Researchers analyzed portions of the acidic neptunium solution obtained from a storage tank in the SRS processing canyon. Routine methods available within the Analytical Development Section of the Savannah River Technology Center were used for the major components. Actinides were analyzed by a combination of alpha spectroscopic, gamma spectroscopic, and inductively coupled mass spectroscopic methods. Table I lists results of the analyses.

Researchers neutralized aliquots of the acidic neptunium solution using concentrated NaOH solution (18 ± 1 M, density 1.513 g/mL) prepared from reagent grade NaOH pellets. NaOH solution was added in 0.1 mL increments at a rate simulating the expected duration in canyon operations (1-3 hours). The solids were filtered, washed, and dried at ambient temperature (23 ± 3 °C) by drawing air through the filter for 4 days. The damp solids were analyzed by x-ray diffraction and scanning electron microscope methods. The damp solids were further dried at 115 °C and portions dissolved in aqua regia were analyzed to determine metal content. Table II lists results of the analyses of the solids.

Figure 1 shows the glass apparatus (or "racetrack") used for demonstrating the relative flow characteristics of slurries at different solids loadings. The racetrack consisted of a reservoir at the top to hold the slurry sample, a stopcock to initiate flow, and a coiled section through which the slurry flows. The coiled tubing (3 mm inside diameter) measured 15.5 cm long and 2.2 cm diameter and contained 24 loops. A measured sample was placed in the reservoir and the stopcock opened. The time required for the reservoir to drain was measured using a stopwatch. The initial runs with a new fluid and dry racetrack yielded significantly higher efflux times compared to subsequent runs and were not included in the data reduction. All tests were conducted at ambient temperature (21 ± 2 °C). After determining the efflux time was linear with samples sizes between 10 and 30 mL, samples of 15 (±3) mL were used in further testing and the efflux times were linearly corrected to a 15 mL sample volume. The racetrack was calibrated with four solutions: water, two silicone oil standards (Cole-Parmer, Viscosity Reference Standards S3 and S6), and a salt solution (3 M NaOH and 3 M $NaNO_3$). The viscosity of the salt solution was measured in a calibrated Cannon-Fenske viscometer (Cannon Instrument Co., Model 50, Serial #U-428).

Table III lists the racetrack measurements of the consistency of the neptunium slurries at 2.2, 4.0, and 6.7 wt % insoluble solids. Personnel measured the yield stress of a settled slurry with a Haake Model RV20/M5 rheometer calibrated with an oil standard at 25 °C. The neptunium slurry sample was loaded into a settling cup and allowed to settle undisturbed for 4 days prior to using a vane-type rheometer head to measure the settled solids yield stress. The maximum yield stress, or shear strength, was 5.2 Pa. A flow curve (yield stress vs. yield rate) of a homogenized sample was measured using a ramp from 0 to 1000 sec^{-1} in 5 minutes, hold at 1000 sec^{-1} for 1 minute, and ramp from 1000 to 0 sec^{-1} in 5 minutes. Table IV shows the sample was somewhat non-Newtonian. Plotting of the Newtonian and Bingham Plastic results against the actual data show that either model accurately describes the results. The flow curve data shows that the yield stress is very low (< 1 Pa) after the material is mixed or sheared.

A flow curve for washed radioactive sludge from Sludge Batch 2 was measured. The sludge sample (90 mL) was mixed with neptunium slurry (3 mL) in the ratio expected in the tank farm and the flow curve was remeasured. A third measurement was made after adding ~3mL of 0.01M NaOH solution to simulate potential flush water additions resulting from the neptunium transfer. The data were curve fitted using the Bingham Plastic model between a shear rate of $86s^{-1}$ to $1100s^{-1}$. Table V lists the results.

RESULTS AND DISCUSSION

Researchers neutralized several aliquots of neptunium solution by a procedure simulating the conditions expected during canyon operations. Enough NaOH was used to neutralize acidic components and leave an excess an excess hydroxide concentration of 0.6 M. The excess hydroxide is required to inhibit corrosion of the carbon steel storage tanks in the SRS tank farm. The reaction proceeded as expected with the generation of heat, precipitation of solids, and changes in solution color. No gas evolution or foaming occurred.

Solids precipitation occurred locally during the initial addition of NaOH, but the solids dissolved as the solution was mixed. Precipitated solids became persistent after approximately 100 minutes from the start, which corresponds to the addition of enough NaOH to neutralize the free acid. Immediately prior to observation of persistent solids, the color of the solution changed from dark green to reddish orange. Solids precipitation caused a noticeable increase in the slurry viscosity as evidenced by a decrease in the rotational rate of the stir bar used to mix the slurry. The viscosity appeared to peak after approximately 135 minutes, after which it decreased slightly during the final 15 minutes. The improved mixing at the end possibly results due to dilution of the slurry following complete precipitation of solids or due to passing the isoelectric point (typically pH 6 to 8) where slurries exhibit their most viscous properties.

Following neutralization, the solids were separated from the aqueous phase by filtration, washed slightly with 0.1 M NaOH, and partially dried at ambient temperature (23 ± 3 °C). Table I lists the results of analyses of the filtrate and Table II lists the results for the damp solids. The ~13 wt % yield of damp solids exceeded the expected value of ~4 wt % and indicated significant amounts of water remained. Further drying at 115 °C reduced the solids yield to ~6 wt %. The presence of 14 wt % sodium in the dried solids and $NaNO_3$ in the damp solids suggests incomplete washing occurred and soluble salts remained in the damp solids.

X ray diffraction analysis revealed the solids are largely amorphous, although a small fraction appeared as magnetite and sodium nitrate. Chemical analysis showed iron as the major constituent, with lesser amounts of aluminum, chromium, neptunium, nickel, and manganese. Sodium and sulfur were also present, probably due to incomplete washing to remove the aqueous phase (i.e, sodium salts of nitrate and sulfate). Some or all of the aluminum may have been present for the same reason. The composition of the solids is consistent with the expected precipitation of the metals under alkaline conditions.

The aqueous phase analyses showed the expected loss of metals found in the solids. Iron, chromium, neptunium, nickel, and manganese precipitate as expected. In addition, the analyses showed approximately 70% of the uranium precipitated. The final concentration of neptunium in the filtrate equaled 1.8 mg/L, much lower than the expected solubility of ~100 mg/L.[1] The low concentration likely reflects a non-equilibrium condition due to the rapid precipitation in the presence of a large amount of iron hydroxide.

Based on complete precipitation of iron (as $Fe(OH)_3$), neptunium (as Np_2O_5), chromium (as $Cr(OH)_3$), nickel (as $Ni(OH)_2$), and manganese (as MnO_2) in the original neptunium solution, the theoretical insoluble solids concentration in the final neutralized solution equals 4.0 wt %. The solids (by weight) are approximately 92% iron hydroxide, 4% chromium hydroxide, 2% nickel hydroxide, and 2% neptunium oxide. Magnesium also precipitates but comprises less than 0.5% of the solids weight.

Figure 1 shows the "racetrack" apparatus constructed to demonstrate the relative flow characteristics of slurries at different solids loadings. The inside diameter of the glass tubing (3 mm) exceeds the particle diameter of the insoluble solids, thus allowing use with slurries containing particles that would plug the small diameter tubes in Ostwald or Canon-Fenske viscometers.[2] The racetrack apparatus requires only 15 mL of sample compared to 60 to 90 mL required for the cup and rotor viscometer discussed below. The time required to empty the cup was measured for various solutions. Calibration of the apparatus with standards of known viscosity allowed conversion of the efflux time to viscosity.

Researchers prepared three neptunium slurries at 2.2, 4, and 6.7 wt % insoluble solids by allowing the solids to settle in a 4 wt % slurry, decanting clear supernate from one sample to concentrate the insoluble solids to 6.7 wt %, and adding the decant solution to another slurry to dilute it to 2.2 wt %. Table III lists the results of the racetrack tests. The neptunium slurry, as precipitated at 4.0 wt % insoluble solids, flowed smoothly through the racetrack with an efflux time corresponding to a viscosity of 7.3 cP. This value closely approximates the result from the Haake viscometer discussed below (7.65 cP). The diluted slurry (2.2 wt %) also flowed smoothly (4.0 cP). These slurries drained with efflux times less than four minutes. In contrast, the concentrated slurry (6.7 wt %) did not flow smoothly, flowed slower with time, and, after 5 minutes, the slurry did not reach the bottom of the racetrack.

Researchers measured the yield stress of a settled slurry, and the yield stress and consistency of a well-mixed slurry at 4 wt % insoluble solids and ambient temperature (20-23°C) using rotating vane and coaxial cylinder geometries with a Haake rheometer. The yield stress of settled solids were measured using a four-vane measuring head after settling for four days. The yield stress by this method was 5.2 Pa. Researchers homogenized the sample by hand mixing with the vanes, transferred the sample to a measuring cup, installed a cylindrical rotor, and measured the flow curve (shear rate vs. shear stress). The flow curve was analyzed assuming the slurry was either a Newtonian or a Bingham plastic fluid (Table IV). The Newtonian viscosity of 7.65 cP agrees closely with the racetrack results (7.3 ± 0.5 cP). The yield stress for the homogenized slurry was 0.21 to 0.55 Pa. As expected, this was much lower than the yield stress for settled solids.

Researchers measured flow curves on a portion of washed radioactive sludge (Sludge Batch 2)[3] mixed with 4 wt % neptunium slurry to determine the impact of the neptunium on the sludge rheological properties. The experiment compared flow curves for the washed sludge, sludge mixed with neptunium, and the sludge-neptunium mixture diluted with inhibited water (0.01 M NaOH). The neptunium and sludge were combined in a volume ratio corresponding to the expected transfer of 12,000 gallons of neptunium slurry into 360,000 gallons of washed sludge (volume ratio: 1:30). To account for flush water that may accompany the neptunium, a volume of 0.01 M NaOH equal to the neptunium slurry volume (i.e., volume ratios of flush water:Np slurry:washed sludge of 1:1:30) was added for the final measurement. The washed sludge sample contained 17.5 wt % insoluble solids.

Table V and Figure 2 show the results of modeling the slurries as Bingham plastics. The addition of the neptunium slurry and flush water thinned the sludge slurry. This is likely due to the net decrease in wt % insoluble solids caused by the two additions. All of the results fell within the DWPF operating region.

SUMMARY

Researchers investigated the neutralization of neptunium solution and the properties of the resulting slurry. Neutralization of the acid neptunium solution proceeds smoothly without complications. Metal hydroxide solids precipitate, producing a slurry containing 4 wt % insoluble solids. The insoluble solids are largely iron hydroxide (92%). Neptunium hydroxides or oxides comprise only 2% of the insoluble solids. A racetrack apparatus used to measure the consistency of slurries containing particles that could plug a small-bore Ostwald-type viscometer proved effective in estimating the neptunium slurry consistency. The rheological properties of the neptunium slurry (as precipitated at 4 wt % insoluble solids) will allow transfer through the tank farm. However, concentration of the insoluble solids above 4 wt % may cause significant problems due increased consistency and yield stress. The consistency of the 4 wt % slurry is 7.6 cP with a yield stress less than 1 Pa. Concentration to 6.7 wt % insoluble solids increases the yield stress and consistency, producing a slurry that does not flow through the racetrack apparatus, and suggesting potential problems during tank farm transfer. The neptunium slurry, when combined with actual washed radioactive sludge, slightly reduced the yield stress and consistency of the sludge and produced a combined slurry with acceptable rheological properties for DWPF processing.

TABLE I. Composition of Neptunium Solution before and after Neutralization

Component	Before Neutralization	After Neutralization
	Concentration (M)	
Free acid	4.9	--
Free hydroxide	--	0.60 ± 0.11
Nitrate	6.6	4.48 ± 0.22
Sulfate	1.29	0.84 ± 0.04
Na	0.58	6.6 ± 0.2
Fe	0.70	--
Al	0.23	0.109 ± 0.008
	Concentration (mg/L)	
Cr	1530	10.4 ± 0.6
Ni	855	<0.2
Mn	218	<0.1
Ca	112	0.53 ± 0.10
Zn	54	0.46 ± 0.16
Zr	28	<0.3
Np-237	1280	1.8 ± 0.6
Total U	44	9.2
	Concentration (d/m/mL)	
Cs-137	2.11×10^{6}	$1.38(\pm 0.04) \times 10^{6}$
Density (g/mL)	1.364	1.322

TABLE II. Composition of Precipitated Solids*

Component	Concentration (wt %)	Component	Concentration (wt %)
Al	1.6 ± 0.1	Na	14.2 ± 0.7
Cr	1.2 ± 0.1	Ni	0.62 ± 0.05
Fe	29.0 ± 2.4	S	2.4 ± 0.2
Mn	0.16 ± 0.01	Np-237	1.03 ± 0.07

* After drying to constant weight at 115 °C

TABLE III. Viscosity of Neutralized Neptunium Slurries from Racetrack Tests

Sample	Viscosity (cP)
2.2 wt % neptunium slurry	4.0 ± 0.3
4.0 wt % neptunium slurry	7.3 ± 0.5
6.7 wt % neptunium slurry	did not flow
3.7 wt % neodymium simulant	5.8 ± 0.4*

* This non-radioactive simulant was tested in a Canon-Fenske viscometer and ran twice successfully before plugging. The viscosity by this method was 7.5 ± 0.1 cP.

TABLE IV. Rheology Flow Curve Data

Newtonian	**Viscosity (cp)**		**R^2**			
	Up	**Down**	**Up**	**Down**		
Run 1	7.86	7.38	0.9736	0.9964		
Run 2	7.88	7.50	0.9851	0.9969		
Average	7.87	7.44				
Average (up/down)	7.65					
Bingham Plastic	**Consistency (cp)**		**Yield Stress (Pa)**		**R^2**	
Run 1	6.92	7.05	0.63	0.22	0.9984	0.9993
Run 2	7.16	7.20	0.48	0.20	0.9985	0.9991
Average	7.04	7.13	0.55	0.21		

TABLE V. Yield Stress and Consistency from Washed Sludge Tests

Sample	Yield Stress (Pa)	Consistency (cP)
Washed sludge	7.79	6.0
Washed sludge + Np slurry	7.37	6.0
Washed sludge + Np slurry + flush water	6.53	5.5

FIGURE 1. Racetrack Apparatus

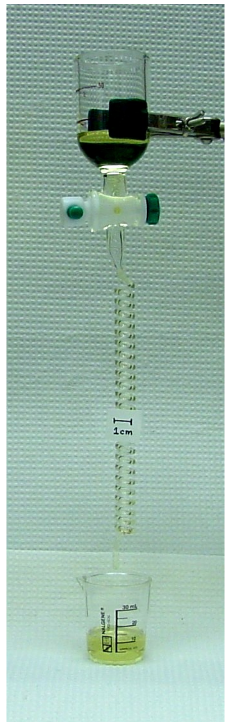
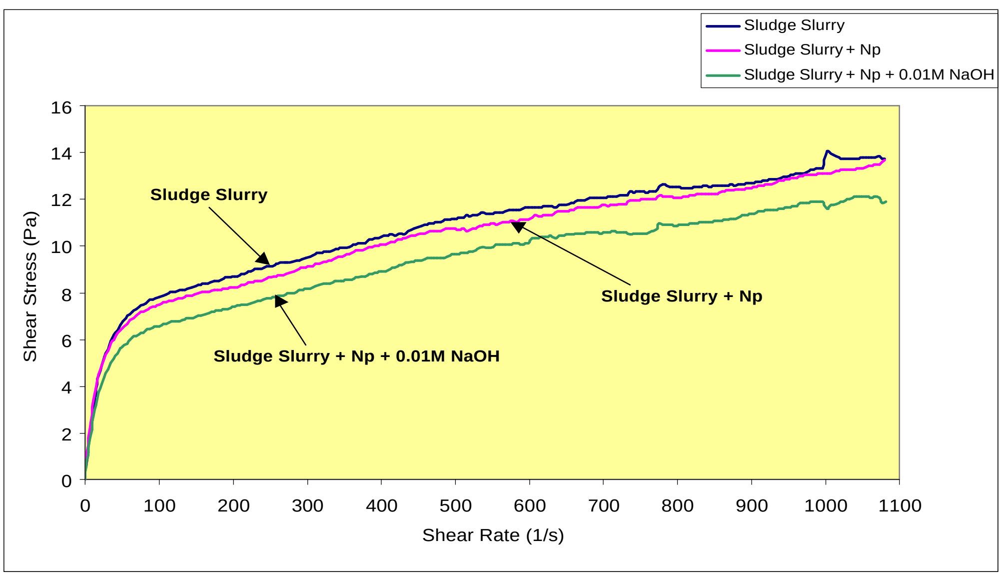


FIGURE 2. Flow Curves for Washed Sludge Mixtures



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