

TREATMENT OF RADIOACTIVE WASTES FROM  
DOE UNDERGROUND STORAGE TANKS

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# TREATMENT OF RADIOACTIVE WASTES FROM DOE UNDERGROUND STORAGE TANKS

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## ABSTRACT

Bench-scale batch tests have been conducted with sludge and supernate tank waste from the Melton Valley Storage Tank (MVST) Facility at Oak Ridge National Laboratory (ORNL) to evaluate separation technology processes for use in a comprehensive sludge processing flow sheet as a means of concentrating the radionuclides and reducing the volumes of storage tank waste at national sites for final disposal. This paper discusses the separation of the sludge solids and supernate, the basic washing of the sludge solids, the acidic dissolution of the sludge solids, and the removal of the radionuclides from the supernate.

## I. INTRODUCTION

At several national sites, USDOE is responsible for radioactive and hazardous wastes that are stored in tanks and which must be retrieved, treated, and disposed. To accomplish this, it is necessary to minimize the amount of wastes to avoid further costs and continued management of the wastes. Separation technology provides one approach to reducing the large volumes of storage tank wastes to smaller volumes of more concentrated and well-defined wastes. Two major components of tank wastes are supernatants (also referred to as supernates) and sludge (solids).

Previous and ongoing experimental work at several locations has identified a number of processes that will partition specific components in the sludges and supernates.<sup>1,2,3</sup> Many of these processes have not been tested on an actual tank waste, and the optimal subset of these processes has not been selected and shown to work together. This paper addresses the separation of the solids and supernate, the washing of the solids, the acid dissolution of the solids, the partitioning of the transuranic (TRU) components from the acid solutions, and the removal of the radionuclides from the supernate solutions. The bench-scale testing of the known processes in hot tests on actual wastes is the best way to ensure that the individual process technologies will achieve the required degree of performance in an integrated system.

Our approach is first to separate the supernate and the sludge to obtain a partial separation of the fission products and the TRU components. The soluble radionuclides will be removed from the supernate using ion exchangers or sorbents, leaving a low-level liquid waste (LLLW). The sludge solids will then be dissolved in appropriate acidic solutions, and the TRU components will be separated from other remaining radionuclides and nonradioactive waste components by solvent extraction.

## II. SLUDGE CHARACTERISTICS

Samples of sludge and supernate (~5 L total) were retrieved from tank W-25 at the MVST facility at ORNL and transferred to a stainless steel tank for mixing and storage in a hot cell. After a thorough mixing for 18 h and then while mixing continued, two samples of the equilibrated stock sludge were poured into 250-mL polypropylene bottles to be characterized and to be used in a leaching study. The samples were centrifuged for 30 min at 4450 x g to separate the sludge liquid and the wet sludge solids. The sludge liquid was a deep yellow color, and the wet sludge solids were light brown.

Analyses showed that the specific gravities of the sludge, the centrifuged wet sludge solids, and the decanted sludge liquid were 1.362, 1.53, and 1.206 g/mL, respectively. Samples of sludge and centrifuged wet sludge solids were air dried to constant weights to determine the total solids contents; they were 0.464 and 0.590 g/g, respectively. The average total solids content for the sludge liquid samples was 0.285 g/g; this was determined by drying samples

of sludge liquid to constant weights in a drying oven at 95°C. The average volume ratio of the decanted sludge liquid to the wet sludge solids was 1:1. The pH of the sludge liquid was 13.

Air dried samples of centrifuged wet sludge were analyzed to determine the concentrations of radionuclides and other metals. The results are provided in Table 1. Similar analyses of sludge samples taken from tank W-25 in 1989, which was reported by Sears, et. al.,<sup>4</sup> are also provided for comparison. The concentrations of the radionuclides were corrected for 4.5 y decay to make the results comparable. The values obtained for both the radionuclides and the other metals in the current study were larger than those obtained in the Sears' study, especially the aluminum, thorium, and uranium. The anion concentrations are in process of being determined in the present study.

### III. BASIC AND ACIDIC SLUDGE LEACHING RESULTS

A sequential washing and leaching test series was conducted to determine the removal of radionuclides by caustic washing and acid leaching of the solids. The results are given in Table 2. A 44.0-g sample of the centrifuged wet sludge solids, containing 970  $\mu\text{Ci}$   $^{137}\text{Cs}$  ( $3.6 \times 10^7$  Bq), 92  $\mu\text{Ci}$   $^{154}\text{Eu}$  ( $3.4 \times 10^6$  Bq), and 119  $\mu\text{Ci}$   $^{60}\text{Co}$  ( $4.4 \times 10^6$  Bq), was washed twice with 100 mL of 0.16 M sodium hydroxide. (The wet sludge solids contained about 26 g of air dried solids.) The mixing times were 5 and 23 h, respectively, on a rotator in the hot cell. Together, the dilute caustic washes removed only 54.4  $\mu\text{Ci}$  of the  $^{137}\text{Cs}$  from the wet sludge solids with about 81% of this being removed in the first wash. Only trace amounts of the  $^{154}\text{Eu}$  and  $^{60}\text{Co}$  were removed. The lack of europium and cobalt removal from the pH 13.2 washes was expected because these elements would likely be present as precipitated forms. On the other hand, the lack of cesium removal was unexpected because most cesium compounds are soluble in aqueous solutions. The percentage of the initial  $^{137}\text{Cs}$  removed was only 5.6%. Most of the cesium that was removed was probably present in the interstitial sludge liquid that was not physically removed by centrifugation. The cesium that remained after the caustic washes was presumably bound in the matrix of the solids. The mass of the wet sludge solids decreased from 44.0 g to 42.0 g and then to 41.8 g after these two washes. A portion of the weight loss resulted from the replacement of the high salt content interstitial liquid with 0.16 M NaOH leachant.

The washed, centrifuged, sludge solids were then leached by mixing for 5.6 h with 100 mL of 0.5 M nitric acid. The pH of the resulting solution was 7.56. This dilute acid leach removed about 12  $\mu\text{Ci}$  of  $^{137}\text{Cs}$  and trace amounts of cobalt and europium. The mass of the decanted wet sludge was 39.6 g.

In the next two leaching steps, the wet sludge solids were subsequently leached with 3 M nitric acid (100 mL each) for mixing periods of 70 and 50 h, respectively. The nitric acid concentration of the acid solution after the first leach was 1.3 M, and 2.68 M after the second leach. Of the 39.6 g of wet sludge solids, about 28.1 g remained after the first leach, and about 18.5 g remained after the second leach. The first leach removed 158  $\mu\text{Ci}$  of  $^{137}\text{Cs}$ , and the second leach removed 239  $\mu\text{Ci}$  of  $^{137}\text{Cs}$ , leaving 508  $\mu\text{Ci}$  in the remaining wet sludge solids. Over 80% of the  $^{60}\text{Co}$  and  $^{154}\text{Eu}$  was removed from the solids by the first 3 M acid leach, and less than 10% remained after the second leach. It was noted that a gelatinous precipitate appeared in the leachate from the first 3 M nitric acid wash after the solution stood for several days. This gelatinous material was postulated to be some form of silicic acid.

The remaining sludge solids from these leaches were mixed with 100 mL of 6 M nitric acid for 18 days. After mixing, the nitric acid concentration of the leachate was 5.69 M. This leaching step removed an additional 294  $\mu\text{Ci}$  of  $^{137}\text{Cs}$ , along with 1.6  $\mu\text{Ci}$  of  $^{154}\text{Eu}$  and 4.0  $\mu\text{Ci}$  of  $^{60}\text{Co}$ . The amount of  $^{137}\text{Cs}$  remaining in the sludge solids at this stage of the leaching process was 213  $\mu\text{Ci}$ . The mass of the centrifuged wet sludge solids was 20.4 g, which was 1.9 g more than was obtained for the previous leaching step. These solids were less rigid than those observed in the previous leaching steps and contained more liquid that could not be removed by an additional centrifugation and decantation step.

To determine how much  $^{137}\text{Cs}$ ,  $^{154}\text{Eu}$ , and  $^{60}\text{Co}$  were present in the interstitial liquid associated with the remaining wet sludge solids after centrifugation, the wet sludge solids were rinsed with two 50-mL volumes of 6 M nitric acid. Each time, the sample was mixed for 10 min on a Vortex mixer prior to centrifuging. The composite rinses removed an additional 56  $\mu\text{Ci}$   $^{137}\text{Cs}$ , 0.3  $\mu\text{Ci}$   $^{154}\text{Eu}$ , and 0.7  $\mu\text{Ci}$   $^{60}\text{Co}$ . The remaining solids contained 157  $\mu\text{Ci}$

$^{137}\text{Cs}$ , 0.3  $\mu\text{Ci}$   $^{154}\text{Eu}$ , and 2  $\mu\text{Ci}$   $^{60}\text{Co}$ . The weight of the centrifuged wet solids was 19.1 g. A portion of these solids was air-dried to a constant weight, yielding a solid content of 0.2503 g/g. Based upon this value, the calculated final mass of air dried solids was 4.8 g.

The longer mixing time in the 6 M  $\text{HNO}_3$  leachings step probably resulted in the formation of silicic acid gel which stayed with the solids during centrifugation, causing the solids to retain more of the leachate. Based upon the mass of air-dried sludge solids at the beginning (26 g) and at the end (4.8 g) of the sequential basic and acidic leaching test series, about 81.5% of the initial air-dried solids was dissolved.

In summary (see Figure 1), the basic washes and acidic leaches removed 83.8%, 99.7%, and 98.5% of the  $^{137}\text{Cs}$ ,  $^{154}\text{Eu}$ , and  $^{60}\text{Co}$ , respectively. The leachability of cesium from the centrifuged wet solids appears to be directly related to the dissolution of the solids. The europium and cobalt were readily dissolved. Only the first 3 M  $\text{HNO}_3$  leachate developed a gel and only after several days after decantation. Gel formation also seems to have occurred during the mixing step with 6 M  $\text{HNO}_3$  which complicated the interpretation of the solids dissolution results.

Sludge dissolution studies are continuing to optimize the conditions for dissolving the sludge solids prior to separation of the TRU components using TRUEX solvent extraction.

#### IV. ION EXCHANGE REMOVAL OF CESIUM FROM SUPERNATE

Approximately one liter of supernate that was separately retrieved from the supernate layer above the sludge layer in tank W-25 of the MVST facility was used in adsorption studies to evaluate various ion exchangers for removing certain radionuclides, especially  $^{137}\text{Cs}$ . The specific gravity of the supernate was 1.232 g/mL; the pH was 12.62. Gamma counting revealed that the supernate contained 6.2  $\mu\text{Ci/mL}$   $^{137}\text{Cs}$ , 0.003  $\mu\text{Ci/mL}$   $^{154}\text{Eu}$ , and 0.17  $\mu\text{Ci/mL}$   $^{60}\text{Co}$ . The concentration of  $^{137}\text{Cs}$  in the supernate was a factor of 1.8 larger than the concentration of  $^{137}\text{Cs}$  in the sludge liquid. Analyses of the supernate showed that it was composed primarily of sodium and potassium nitrate, 3.39 M  $\text{Na}^+$  and 0.44 M  $\text{K}^+$ .

Batch tests were used to measure the distribution coefficients ( $D_s$ ) and percentage removals (% $R_s$ ) of cesium from MVST supernate with several ion-exchange materials. See Table 3. The  $D$  was calculated as follows:

$$D = [(C_i - C_p)/C_p][V/m] \text{ (units are mL/g).}$$

The  $D$  for cesium is an expression of the ratio of the mass of  $\text{Cs}^+$  ions sorbed on a gram of ion exchanger to the mass of  $\text{Cs}^+$  remaining in the supernate after a specified mixing time. The initial and final concentration  $^{137}\text{Cs}$  in the supernate are given as  $C_i$  and  $C_p$ , respectively. The ion exchangers tested included Duolite CS-100 (Rohm & Haas), formaldehyde/resorcinol resin (SRR) from Boulder Scientific Company, crystalline silicotitanate (CST) from Sandia National Laboratories, and granular potassium cobalt hexacyanoferrate which was prepared at ORNL using the Prout procedure.<sup>5</sup> In these experiments, 10 mL of supernate was mixed with 50 mg of exchanger in polypropylene centrifuge tubes for periods of 2, 24, 72, and 144 h. After mixing, samples of the supernate were centrifuged twice and filtered with 0.2  $\mu\text{m}$  filters before gamma counting. The  $D_s$  for cesium ranged from 35 to 44 mL/g (% $R = 15$  to 22) for the CS-100, from 641 to 764 mL/g (% $R = 78.7$  to 79.5) for the formaldehyde/resorcinol resin, 662 to 958 mL/g (% $R = 77.4$  to 83.8) for the crystalline silicotitanate, and from 26,000 to 46,200 mL/g (% $R = 99.3$  to 99.6) for granular potassium cobalt hexacyanoferrate (35 to 28 mesh). The distribution coefficients changed only slightly or not at all over the 144-h time period measured for each of the exchangers. The pH was measured after each test and there was little change from the initial pH of 12.6. Control tests were also run in which no exchanger was added to the supernate; there was no loss of cesium from the supernate.

Additional testing of sorbents is continuing to determine the best materials and optimal conditions for removing radioactive cesium from the supernate solutions in underground storage tanks at Oak Ridge, Hanford, and other DOE sites.

## REFERENCES

1. G. J. Lumetta, M. J. Wagner, R. J. Barrington, B. M. Papko, and C. D. Carlson, Sludge Treatment and Extraction Technology Development: Results of FY 1993 Studies, PNL-9387, UC-721, March 1994.
2. L. A. Bray, R. J. Elovich, and K. J. Carson, Cesium Recovery Using Savannah River Laboratory Resorcinol-Formaldehyde Ion Exchange Resin, PNL-7273 (UC-510), March 1990.
3. J. P. Bibler, R. M. Wallace, and L. A. Bray, "Testing a New Cesium-Specific Ion Exchange Resin for Decontamination of Alkaline High-Activity Waste," Waste Management '90, Vol. 2, R. G. Post, Ed, pp. 747-51 (1990).
4. M. B. Sears, J. L. Botts, R. N. Ceo, J. J. Ferrada, W. H. Griest, J. M. Keller, and R. J. Schenley, Sampling and Analysis of Radioactive Liquid Wastes and Sludges in the Melton Valley and Evaporator Storage Tanks at ORNL, ORNL/TM-11652, Sept. 1990.
5. W. E. Prout, E. R. Russell, and H. J. Groh, "Removal of Cesium from Aqueous Solutions by Ion Exchange," U. S. Patent 3,296,123, January 3, 1967.

Table 1. Analytical data for MVST W-25 sludge solids<sup>a</sup>

	Sears <sup>b</sup>	CDSSPP <sup>c</sup>
Radionuclides	(Bq/g)	(Bq/g)
<sup>137</sup> Cs	3.8e+05	1.4e+06
<sup>60</sup> Co	4.1e+04	1.3e+05
<sup>154</sup> Eu	6.6e+04	1.7e+05
<sup>90</sup> Sr	2.8e+06	1.6e+07
<sup>244</sup> Cm	5.3e+04	3.1e+05
<sup>239/240</sup> Pu	5.5e+03	2.4e+04
<sup>238</sup> Pu	1.4e+03	7.5e+04
Other metals	(mg/g)	(mg/g)
Al	5.3	25.8
Ba <sup>d</sup>	0.1	0.4
Ca	71.6	91.5
Cd <sup>d</sup>	0.02	0.05
Cr <sup>d</sup>	0.1	0.6
Fe	1.8	8.6
Hg <sup>d</sup>	0.08	BDL
K	17.3	14.0
Mg	11.1	13.5
Mn	BDL <sup>e</sup>	0.7
Na	124.0	110.0
Ni <sup>d</sup>	0.06	0.4
Pb <sup>d</sup>	0.4	2.0
Sr	0.3	5.6
Th	7.3	57.4
U	9.0	21.1

<sup>a</sup>Analytical results were based upon samples of air dried sludge solids that were dissolved in concentrated nitric acid by microwave digestion.

<sup>b</sup>The Sears' data<sup>1</sup> for the radionuclides were corrected for 4.5 y decay.

<sup>c</sup>CDSSPP = Comprehensive Demonstration of Sludge and Supernate Processing Program.

<sup>d</sup>RCRA metals.

<sup>e</sup>BDL = below detection limit.

Table 2. Sequential leaching data of MVST W-25 sludge<sup>a</sup>

Leaching Steps	Solids (g)	Mixing Time (h)	Radionuclide Content of Remaining Solids		
			<sup>137</sup> Cs (μCi)	<sup>60</sup> Co (μCi)	<sup>154</sup> Eu (μCi)
W-25 Sludge Sample	(80.0)		(1062)	(119)	(92.3)
↓					
Centrifuge <sup>b</sup>	44.0		970	118	92.2
↓					
0.16 <u>M</u> NaOH Leach	42.0	5	926	118	92.2
↓					
0.16 <u>M</u> NaOH Leach	41.9	22	916	118	92.2
↓					
0.5 <u>M</u> HNO <sub>3</sub> Leach	39.6	6	904	118	92.2
↓					
3 <u>M</u> HNO <sub>3</sub> Leach	28.1	70	746	24.3	16.4
↓					
3 <u>M</u> HNO <sub>3</sub> Leach	18.5	50	508	6.5	2.2
↓					
6 <u>M</u> HNO <sub>3</sub> Leach	20.4	432	213	2.5	0.6
↓					
6 <u>M</u> HNO <sub>3</sub> Rinses	19.1	20	157	1.8	0.3

<sup>a</sup>Procedure: 100 mL of indicated leachants were added to sludge solids and mixed at room temperature.

<sup>b</sup>The W-25 MVST sludge sample was centrifuged to separate the sludge solids from the sludge liquid.

Table 3. Batch adsorption data showing the effect of mixing time on the removal of cesium from MVST W-25 supernate.<sup>a</sup>

Sample <sup>b</sup>	Mixing Time							
	(2 h)		(24 h)		(72 h)		(144 h)	
	D	%R	D	%R	D	%R	D	%R
CS-100	35	20.0	34	15.0	42	20.0	44	22.0
SRS	763	79.3	736	79.5	764	79.2	641	78.7
CST	662	77.4	672	77.5	672	77.7	958	83.8
KCoFC <sup>c</sup> (Gr.)	46200	99.6	36900	99.5	36300	99.5	26000	99.3
Blank tube		0		0		0		

<sup>a</sup>Each batch test was conducted by mixing 50 mg of adsorber with 10mL of MVST W-25 supernate for the mixing times indicated. D = distribution coefficient in (mL/g) and %R = percentage removal.

<sup>b</sup>SRS - resorcinol-formaldehyde resin (425 - 595  $\mu$ m); CST - crystalline silicotitanate (fine powder); and KCoFC - granular potassium cobalt hexacyanoferrate (250 to 595  $\mu$ m).