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Chemical Technology Division

**EXPLORATORY TESTS OF WASHING RADIOACTIVE SLUDGE SAMPLES
FROM THE MELTON VALLEY AND EVAPORATOR
FACILITY STORAGE TANKS AT ORNL**

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ABSTRACT

Exploratory tests were initiated to wash radioactive sludge samples from the Melton Valley Storage Tanks and evaporator facility storage tanks at the Oak Ridge National Laboratory. The sludge washing tests look promising, but the funding was canceled before this preliminary experiment could be completed. It was possible to wash the sludges and detect common inorganic anions, cations, and radioactive materials in the wash solutions. Preliminary information concerning anion constituents and general behavior trends of the sludge constituents during washing are noted. The actual data reported here are incomplete, and, therefore, should be considered as merely an indicator of the behavior of the sludges. Additional experimental work is recommended.

This work was performed in support of (1) the design of the proposed Waste Handling and Packaging Plant, and (2) research and development activities in formulating waste management alternatives.

EXPLORATORY TESTS OF WASHING RADIOACTIVE SLUDGE SAMPLES FROM THE MELTON VALLEY AND EVAPORATOR FACILITY STORAGE TANKS AT ORNL

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1. INTRODUCTION

Exploratory tests were initiated to wash radioactive sludge samples from the waste storage tanks at the Oak Ridge National Laboratory (ORNL). The purpose was to provide preliminary information about (1) the anions in the sludge phase that are soluble in water or dilute acid (e.g., the anions in the interstitial liquid) and (2) the solubilities of sludge constituents in water under process conditions. The experiments were terminated before completion due to changing priorities by the Department of Energy (DOE). This memorandum was prepared primarily for documentation purposes and presents the incomplete data.

Studies have been conducted to determine the chemical, radiochemical, and physical properties of the radioactive liquid wastes and sludges in the Melton Valley Storage Tanks (MVSTs) and the storage tanks at the low-level waste (LLW) evaporator service facility in Bethel Valley.^{1,2} This information is needed to develop process flow sheets and design systems for processing these wastes for disposal. Objectives included providing data in support of (1) the design of the proposed Waste Handling and Packaging Plant (WHPP), and (2) research and development (R&D) activities in developing waste management alternatives.

The studies performed from September 1989 to August 1990 provided a relatively extensive characterization of the cations, radioactive materials, and physical properties of the bulk sludge.^{1,2} This report documents additional studies performed on the sludges from September 1990 until the project was canceled in October 1990. Previous studies did not include an assay of anions (except carbonate), or experiments on the behavior of sludge constituents during washing. The determination of anions in the sludge phase is a problem area. The preferred analytical technique, ion chromatography, requires that the sludge solids

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first be placed in solution. Yet the use of a strong acid to dissolve the sludge samples places severe limitations on the ions that can be determined by ion chromatography. A new ion chromatograph with a special column for high nitrate samples was installed in the High Radiation Level Analytical Laboratory in the summer of 1990. This instrument offered capabilities for the determination of some anions in the sludge that were not available when the samples were first collected. Another area of interest is the solubilities of sludge constituents in water under process conditions. For the WHPP design, it has been proposed that solids be transported from the waste tank to the plant by using water, in addition to the liquid waste, as the transport fluid. There is also interest in the feasibility of separating the soluble sodium and potassium nitrate salts, which are present in the interstitial sludge liquid, from the transuranic (TRU) bearing solids as a means of reducing the quantity of TRU contaminated waste.

This report describes the first attempt at washing soft-sludge samples from six of the MVSTs and two of the evaporator facility service tanks, and one "hard" sludge sample (W31-H). Portions of the composite sludge samples that had been prepared for the earlier study were used in the washing tests. The methods used for sampling the tanks and preparing the composite samples as well as analytical data on the original sludge are given in ref. 1.

This report has not been designated for review in accordance with Waste Characterization Task QA Plan (QAP-X-89-WMRD-033, R0) because the work was preliminary, and funding was not available to complete the study.

2. BACKGROUND

A brief summary of the collection and handling of the samples and the general characteristics of the wastes are given in this section (for details see ref. 1).

2.1 SAMPLE COLLECTION AND HANDLING¹

During this project, 21 sludge samples and 22 liquid samples were collected from 6 of the MVSTs (tanks W-24 through W-28 and W-31) and 2 of the storage tanks at the evaporator service facility (W-21 and W-23).¹

The tanks are located in below-grade concrete vaults, and each is accessed by means of a 3-in.-diam pipe that penetrates the tank from the roof of the vault. Liquid samples were pulled by vacuum through Teflon tubing into the sample jars. A bottom-opening soft sludge sampler was used to collect a core of sludge up to 20-in. deep. The device consists of a detachable handle assembly and a hollow probe of clear polyvinyl chloride (PVC) pipe (1-in. ID) that can be controlled from above by the operator. The sludge layer was usually more than 20-in. deep. Samples were collected at successively lower layers to obtain a vertical profile of the tank contents. After the sludge sample had been collected, the handle was removed and the PVC tube capped, packaged, and transported to the analytical laboratory in a shielded carrier.

Sludge samples were unloaded from the carrier and placed in a hot cell. The samples were allowed to stand overnight in the PVC tubes to allow the solids to settle. Any liquid layer over the sludge was removed and the sludge (solids) transferred to a sample jar. The sample was stirred, and portions removed for waste characterization studies. Composite sludge samples representative of a complete vertical core were made up for the chemical and radiochemical analyses.¹ The composite samples were sonicated to ensure complete mixing.

A hard-sludge sampler was used to sample the thick material near the bottom of tank W-31. This device consists of a stainless-steel pipe with a machine-bevel cutting edge on the bottom and a detachable handle. (It is suitable only for very thick, sticky sludges.)

Dose rates (field survey) for the sludge samples in the PVC sampling tubes ranged from 1.2 to 2.5 R/h. Radiation fields were considerably higher near small samples dried in the laboratory; dose rates of up to 50 R per hour per gram at contact were observed. The increased dose was primarily due to low energy beta and alpha particles that had been

attenuated in the wet sludges. Sludge samples were handled in a hot cell, and small subsamples were removed for analysis in radiochemical hoods and glove boxes. Every effort was made to minimize the handling of dried samples in order to reduce both exposure and spread of contamination.

Because only sludge directly under the access point can be sampled, the samples may not be representative of other locations in the tank and should be considered as merely an indicator of the tank contents.

2.2 GENERAL WASTE CHARACTERISTICS¹

Bulk liquid wastes. The bulk liquid wastes in the storage tanks are essentially high pH (typically 11 to 13) sodium/potassium nitrate salt solutions. The nitrate concentration varies from 3 to 5 *M* with the average being about 4 *M*. The sodium concentration varies from 61 to 110 g/L and the potassium concentration from 8 to 78 g/L. The waste solutions are about 0.08 *M* in chloride; five tank solutions contained measurable concentrations of dissolved carbonate (0.1 to 0.4 *M*; 1.4 *M* for tank W-23 bulk liquid). The concentrations of the heavy metals (e.g., U, Th, RCRA metals) as well as the iron and aluminum are in the low parts-per-million range, as would be expected from the insolubilities of the hydroxides and carbonates.*

The bulk liquid in Tank W-21 was acidic (pH of 0.6) at the time the tank was sampled.** This aqueous waste contained significantly higher levels of calcium, magnesium, and heavy metals than did the waste in the other tanks.

Sludges. The sludges are not homogeneous and vary in consistency and color. The consistency of soft-sludge samples that had been sonicated ranged from "similar to prepared mustard" to "like peanut butter with gritty particles." Two tanks (W-27 and W-31) contained a layer of "hard" sludge in addition to soft sludge. The designation of hard or soft sludge was made at the sampling point and refers to the type of sampler used to collect the sludge.

The total solids content of the bulk soft sludges (i.e., the precipitated solids plus the interstitial liquid), based on the weight of residue after drying a measured volume of sample

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*RCRA = Resource Conservation and Recovery Act.

**After the tanks were sampled for this study, the waste in Tank W-21 was neutralized to a pH of 7.

overnight at 115°C, were about 400 to 500 mg/g. The sludges thus contain 50 to 60% water. This does not include any water of crystallization that might be associated with the precipitated solids. In the study of four soft-sludge samples by Ceo et al., it was found that the undissolved solids were 22-25 wt %, while the dissolved solids (i.e., salts dissolved in the interstitial liquid) were 24-29 wt % of the bulk sludge.² The hard sludge in tank W-31 was approximately 96 wt % solids.¹

The principal metals found in the sludges were sodium, potassium, calcium, magnesium, uranium and thorium. Based on the total metals determined, the sodium and potassium combined are typically 40 to 60 wt %; the calcium averages about 30%; magnesium averages about 5%; and the uranium plus thorium, 4 to 20%. The sludges contain low levels of aluminum (0.1 to 0.8 % of bulk sludge) and iron (0.1 to 0.25 %), as well as traces of RCRA metals.

The soft sludges typically contain 0.4 to 2 wt % inorganic carbon as carbonate [0.3 to 1.5 (avg. 0.7) mol of carbonate per kilogram of sludge]. Eight of the soft sludge samples contained about 1 mol of calcium per mole of carbonate; two sludges (W25-S and W28-S) contained more moles of calcium than carbonate. The total organic carbon content of the sludges was typically in the range of 0.2 to 0.8 wt %. Very little of the organic matter suggested to be present by the total organic carbon analyses was accounted for by the Environmental Protection Agency (EPA) regulatory procedures.

Based on the history of the wastes, the interstitial liquid in the sludge phase is expected to be primarily a concentrated sodium/potassium nitrate salt solution. However, because of liquid waste transfers and a lack of mixing in the tanks, the sludge liquid may not have the same composition as the bulk liquid taken from the same tank. As an example, for Tank W-21, the pH of the bulk liquid was 0.6, while the pH of the sludge liquid was 7.

Alpha emitters (TRU waste) and beta-gamma emitters. Wastes that are contaminated with TRU alpha emitters with half-lives greater than 20 years and activities greater than 3700 Bq/g (100 nCi/g) at the time of assay are classified as TRU wastes.³ All of the composite sludge samples except the soft sludge in tank W-31 were identified as TRU wastes. If the sludge from tank W-31 were dried, then the solid residue would also be classified as a TRU waste.

In general, little or no alpha activity was observed in the basic liquid phases in the tanks. The liquid samples were all non-TRU solutions; their salt residues, if dried, would also be non-TRU.

The most abundant beta-gamma emitters observed were ^{137}Cs and ^{90}Sr and their short-lived daughters ^{137}Ba and ^{90}Y , respectively. Gamma-active europium isotopes were observed in the sludges but were not detected in the liquid phase of any tanks that were basic.

3. EXPERIMENTAL

Samples of the sludges were washed twice with water followed by a dilute nitric acid wash of the water-insoluble solids. A relatively large quantity of wash solution (~50 to 100 mL per g of starting sludge) was used in an effort to wash the soluble species from the precipitated solids while limiting the number of handling steps. The acid wash was performed in two steps starting with 2 M HNO₃. More concentrated acid was then added bringing the final concentration to 4 M HNO₃. Most of the sludge solids dissolved readily (within 10 min) in 2 M HNO₃ leaving relatively little solid residue (visual observation). Washing tests were conducted at room temperature. Some analyses were performed on the wash solutions.

Portions of the composite sludge samples that had been prepared for the earlier study (see ref. 1) were used in the washing tests. The samples had aged 7 to 12 months before the washing tests were performed, and their condition was uncertain. The samples contained some granular material. A few grains of granular material on the rim of the jar might have prevented the lid from sealing to be airtight. This would result in loss of water by evaporation over time and possibly some sorption of CO₂ from the air. Two of the soft-sludge samples (W27-H1-S and W31-S) and the "hard" sludge sample (W31-H) had dried (i.e., lost water).*

The Analytical Chemistry Division (ACD) request numbers for the sludge washing experiments are IPA6374, IPA6375, TRU9370, and TRU9415. This information is useful for retrieval of data from the ACD data management system.**

3.1 SLUDGE WASHING

Approximately a 1-2 g aliquot of sludge sample was weighed into a jar and 100 mL of distilled water was added. The jars were placed on a rotating tumbler, and tumbled by

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*The materials used in the washing tests of W27-H1-S and W31-S were actually subsamples that had been stored in the sample room. The main supplies of these samples in the hot cell might have a different composition from the material used in these washing tests.

**The washing of sample W25-S was a preliminary test of the method feasibility for detecting anions, and was not entered into the ACD data management system.

hand for about 30 min. The solids settled reasonably well (within ~10 min), although there was a little "milky" cast to the supernatant liquid. The physical appearance of the sludge samples and the first water wash phases are summarized in Table 1. After washing with water, the solids had the appearance of sand with a few black particles. A small amount of a foamy, clear layer was observed floating over the supernate in about half the tests.

The mixture was filtered, the wash solution was reserved for analysis, and the solid residue air dried on the filter at room temperature for about 1.5 h and weighed. The foamy layer disappeared when the liquid was filtered.

The filter was washed with distilled water to transfer the solid residue from the water wash to the tumbling jar, the volume brought to 100 mL, and the washing procedure repeated: tumble for about 30 min, filter, air dry for about 1.5 h, and weigh. (A new filter was used.) The solids again had the appearance of sand with a few black specks. The foamy layer was also observed in the second water wash, if it was observed in the first wash.

The filters from the second water wash were washed with 50 mL of 2 M HNO_3 to transfer the solid residue to the tumbling jar, and the mixture tumbled for 10 min, and examined visually. Most of the sludge appeared to have dissolved in the 2 M HNO_3 . At this time, 50 mL of 6 M HNO_3 was added, bringing the acid wash to 4 M HNO_3 . The mixture was tumbled for 10 min, examined visually, and tumbled for an additional 40 min. The mixture was filtered, the acid wash solution was reserved for analysis, and the filter was air dried for about 1.5 h and weighed. The residue from the acid wash was removed (scraped) from the filter with spatula, and weighed again on weighing paper. In some cases, there was some discoloration of the filter, but the amount of residue was too small to recover with a spatula.

In the washing tests of sample W25-S sludge, a centrifuge was used for the solid/liquid separations (rather than a filter) and the solids were not air-dried between washes. In other respects, the procedure was the same as in the other experiments. A brown emulsion layer was observed, which clarified to a foamy layer similar to that observed in other tests.

Most of the sludges dissolved in the cold acid wash leaving little visible residue on the filter. The indications from the visual examination were that most of the sludge that was going to dissolve went into solution in the 2 M HNO_3 step. One possible exception was W31-H (a "hard" sludge), where some may have dissolved in the 4 M HNO_3 step.

Table 1. Physical appearance of sludge samples and water wash phases

Sample	Starting sludge	Water wash 1	
		Supernate	Solids ^a
W21-S	Brown/yellow sludge	Light yellow	Brown/yellow
W23-S	Brown/yellow sludge	Gray ^b	Brown/yellow
W24-S	Brown/yellow sludge	Light yellow	Brown/yellow
W26-S	Brown/yellow sludge	Yellow gray ^b	Brown/yellow
W27-H1-S	Light brown; dry	Gray ^b	Brown/gray
W28-S	Brown/yellow sludge	Yellow	Yellow
W31-S	Light brown; dry, clear chips	Yellow gray ^b	Brown/yellow
W31-H	Brown; dry	Cloudy, murky	Brown

^aAppearance of sand with black particles.

^bA small amount of a foamy, clear layer was observed floating over the supernate.

Air drying at room temperature was not sufficient to dry the filters to constant weight, and no meaningful residue weights were obtained. The filters containing the residues were not oven-dried because of the possibility that heating might affect the solubility properties in the subsequent washing steps.

3.2 ANALYTICAL MEASUREMENTS

Anions in the wash solutions were determined using the new Dionex Model 4506 ion chromatograph with the AS2 column. This column retains nitrate strongly permitting the determination of fluoride, chloride, nitrite, phosphate, and sulfate in samples with a large excess of nitrate. It was necessary to dilute the wash solutions for ion chromatography analysis. The first water wash was diluted 1 mL/10 mL, and the acid wash by 0.1 mL/10 mL. The second water wash was run directly.

Other analytical methods are described in Appendix B of Ref. 1 with some adjustments for concentration. Cations were determined by inductively coupled plasma atomic emission spectroscopy (ICP). Most cation analyses were run directly on the wash solutions. However, for the sodium and potassium analyses, the first water washes were diluted 0.2 mL/2 mL. Potentiometric titration was used to measure the pH. For the total solids determination, 10 mL of the wash solution was quantitatively transferred to a preweighed evaporating dish, evaporated to dryness at 115°C for 16 h, and weighed. The radiochemical characterization included gross alpha, gross beta, gamma spectrometry, and actinides by alpha spectrometry. The ^{241}Am alone is based on gamma spectrometry, while the combined $^{239}\text{Pu}/^{241}\text{Am}$ was determined by alpha spectrometry.

4. RESULTS AND DISCUSSION

4.1 ANALYTICAL RESULTS

Soft-sludge samples from six of the MVSTs (tanks W-24 through W-28 and W-31) and two of the concentrate storage tanks (W-21 and W-23) at the evaporator service facility (W-21 and W-23), as well as one hard sludge sample (W31-H) were washed twice with water followed by an acid wash using the methods described in Sect. 3.1. Portions of the composite sludge samples, that had been prepared for the earlier study (see ref. 1), were used in the washing tests. The resulting wash solutions were analyzed for anions, selected cations (Na, K, Ca, Mg), gross alpha, gross beta, gamma emitters (by gamma spectroscopy), pH, and total solids. (Residues were not analyzed, except for the determination of gamma emitters in some of the acid-insoluble residues.)

The analytical data for the sludge washing experiments are presented in Tables 2-10. The sample identification code includes the tank identification code (e.g., W21, W23, etc.) followed by a hyphen and a phase identification (S = soft sludge; H = hard sludge). All washing and residue data are reported relative to the starting weight of sludge. The less than symbol (<) means that the constituent was not detected, and the limit of detection is reported. A dash (-) means that the analysis was performed and the constituent was not detected. A blank indicates that the analysis was not performed. Solid residues from the acid leach were analyzed as solids by gamma spectroscopy when sufficient material was recovered.*

General trends and observations concerning the behavior of the sludges in the washing experiments are discussed in Sect. 4.2. There are uncertainties in the data with respect to the cation/anion balance and mass balance (see Sect. 4.3). The data should therefore be considered as merely an indicator of the behavior of the sludges. Additional experimental work is necessary before definitive quantitative statements can be made.

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*The project had requested that the acid-insoluble residues be examined by x-ray fluorescence, however, this instrument was not operational at the time of the experiment.

Table 2. Analytical data for washing sludge sample W21-Sa,b

Characteristic		Dissolved in wash			Bulk sludge ^b
		Water wash 1	Water wash 2	Acid wash	
Miscellaneous data					
pH		7.2	7.8		7
Total solids	(mg/g)	172	7.8	217	511
Process metals					
Ca	(mg/kg)	6.5e+03	1.5e+03	6.4e+03	4.5e+04
K	(mg/kg)	1.3e+04	4.5e+03	1.4e+04	8.5e+03
Mg	(mg/kg)	5.9e+02	2.2e+02	<1.1e+00	9.6e+03
Na	(mg/kg)	5.8e+04	2.0e+03	2.0e+03	4.8e+04
Anions					
Carbonate	(mg/kg)				6.00e+04
Chloride	(mg/kg)	1.4e+03	3.9e+01	1.5e+03	
Fluoride	(mg/kg)	-	-	-	
Nitrate	(mg/kg)	2.5e+05	5.7e+03		
Nitrite	(mg/kg)	6.4e+02	-	-	
Phosphate	(mg/kg)	-	-	6.7e+03	
Sulfate	(mg/kg)	1.0e+04	8.6e+02	-	
Beta/gamma emitters					
Gross beta	(Bq/g)	2.9e+05	8.7e+03	4.1e+06	3.36e+06
⁶⁰ Co	(Bq/g)	9.8e+02	1.3e+02	9.0e+04	8.07e+04
¹³⁴ Cs	(Bq/g)	2.6e+03	1.2e+02	<6.0e+02	6.99e+03
¹³⁷ Cs	(Bq/g)	1.7e+05	6.7e+03	5.0e+04	2.49e+05
¹⁵² Eu	(Bq/g)	1.1e+03	<3.0e+02	1.5e+06	1.30e+06
¹⁵⁴ Eu	(Bq/g)	<4.0e+02	<2.0e+02	6.6e+05	4.77e+05
¹⁵⁵ Eu	(Bq/g)	<4.0e+02	<1.0e+02	1.9e+05	1.33e+05
Alpha emitters					
Gross alpha	(Bq/g)	8.3e+01	3.3e+01	8.3e+04	1.29e+05
²³³ U	(Bq/g)			3.8e+03	8.13e+03
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/g)			8.7e+03	2.49e+04
²⁴¹ Am	(Bq/g)	<3.0e+02	<1.0e+02	1.3e+04	
²³⁸ Pu/ ²⁴¹ Am	(Bq/g)			1.7e+04	5.13e+04
²⁵² Cf	(Bq/g)			8.3e+01	
²⁴⁴ Cm	(Bq/g)			4.4e+04	4.46e+04

^aAll washing data are reported relative to the starting sludge weight.

^bBulk sludge results were obtained prior to the washing experiment; mass balance may not be observed (see Sect. 4.3).

Table 3. Analytical data for washing sludge sample W23-Sa,b

Characteristic		Dissolved in wash			Residue ^c	Bulk sludge ^b
		Water wash 1	Water wash 2	Acid wash		
Miscellaneous data						
pH		11.9	9.4			
Total solids	(mg/g)	219	15	250		544
Process metals						
Ca	(mg/kg)	3.6e+01	3.9e+02	5.6e+03		5.5e+04
K	(mg/kg)	2.6e+04	3.7e+03	<2.5e+01		1.8e+04
Mg	(mg/kg)	<1.0e+00	<1.0e+00	<1.0e+00		1.6e+04
Na	(mg/kg)	8.1e+04	3.4e+03	+03		8.2e+04
Anions						
Carbonate	(mg/kg)					9.04e+04
Chloride	(mg/kg)	2.5e+03	1.4e+02	8.1e+02		
Fluoride	(mg/kg)	1.0e+02	1.5e+01	-		
Nitrate	(mg/kg)	8.1e+04	4.6e+03			
Nitrite	(mg/kg)	3.3e+03	8.1e+01	-		
Phosphate	(mg/kg)	-	-	1.6e+04		
Sulfate	(mg/kg)	3.0e+03	2.0e+02	-		
Beta/gamma emitters						
Gross beta	(Bq/g)	5.1e+05	2.8e+04	6.6e+06		6.67e+06
⁶⁰ Co	(Bq/g)	7.1e+02	1.3e+02	2.3e+05	3.8e+02	2.52e+05
¹³⁴ Cs	(Bq/g)	2.4e+03	6.6e+01	<2.2e+03	<1.0e+01	<6.5e+03
¹³⁷ Cs	(Bq/g)	4.7e+05	1.0e+04	4.7e+04	2.5e+02	4.95e+05
¹⁵² Eu	(Bq/g)	<1.5e+02	<1.8e+02	7.1e+05	1.1e+02	7.22e+05
¹⁵⁴ Eu	(Bq/g)	<1.5e+02	<8.0e+01	5.6e+05	1.0e+02	5.14e+05
¹⁵⁵ Eu	(Bq/g)	<5.7e+02	<1.1e+02	1.4e+05	2.1e+01	1.21e+05
Alpha emitters						
Gross alpha	(Bq/g)	5.4e+00	1.9e+01	2.2e+05		2.23e+05
²³³ U	(Bq/g)			8.9e+03		1.18e+04
²³⁹ Pu, ²⁴⁰ Pu	(Bq/g)			9.5e+03		1.18e+04
²⁴¹ Am	(Bq/g)	<3.3e+02	<7.0e+01	1.4e+04	<1.0e+01	
²³⁸ Pu/Am	(Bq/g)			3.2e+04		3.21e+04
²⁵² Cf	(Bq/g)			<2.2e+02		
²⁴⁴ Cm	(Bq/g)			1.4e+05		1.67e+05

^aAll washing data are reported relative to the starting sludge weight.

^bBulk sludge results were obtained prior to the washing experiment; mass balance may not be observed (see Sect. 4.3).

^cResidue was counted as a point source that was not equivalent to calibrated geometry; $\pm 50\%$ error is possible. Weight of residue recovered from filter was 3 mg/g sludge.

Table 4. Analytical data for washing sludge sample W24-S^{a,b}

Characteristic		Dissolved in wash			Bulk sludge ^b
		Water wash 1	Water wash 2	Acid wash	
<u>Miscellaneous data</u>					
pH		12.1	9.7		
Total solids	(mg/g)	179	100	105	487
Carbonate	M	0.004			
<u>Process metals</u>					
Ca	(mg/kg)	2.2e+02	1.8e+03	8.2e+03	2.9e+04
K	(mg/kg)	1.5e+04	1.2e+03	<3.5e+01	7.6e+03
Mg	(mg/kg)	1.8e+01	<1.0e+00	<1.0e+00	5.6e+03
Na	(mg/kg)	1.1e+05	2.7e+03	6.2e+02	6.9e+04
<u>Anions</u>					
Carbonate	(mg/kg)				3.32e+04
Chloride	(mg/kg)	2.2e+03	1.9e+02	2.9e+03	
Fluoride	(mg/kg)	-	-	-	
Nitrate	(mg/kg)	2.0e+05	3.8e+03		
Nitrite	(mg/kg)	1.3e+03	-	-	
Phosphate	(mg/kg)	-	-	1.8e+04	
Sulfate	(mg/kg)	2.1e+03	-	-	
<u>Beta/gamma emitters</u>					
Gross beta	(Bq/g)	2.9e+05	4.2e+04	2.9e+06	2.62e+06
⁶⁰ Co	(Bq/g)	1.0e+02	<5.0e+01	4.0e+04	3.39e+04
¹³⁴ Cs	(Bq/g)	6.1e+02	<5.0e+01	<1.0e+03	<6.2e+02
¹³⁷ Cs	(Bq/g)	1.8e+05	4.2e+03	5.0e+04	1.96e+05
¹⁵² Eu	(Bq/g)	<2.0e+00	<3.0e+02	6.9e+04	6.20e+04
¹⁵⁴ Eu	(Bq/g)	<2.0e+00	<2.0e+02	4.7e+04	3.60e+04
¹⁵⁵ Eu	(Bq/g)	<4.0e+00	<1.0e+02	1.4e+04	1.03e+04
<u>Alpha emitters</u>					
Gross alpha	(Bq/g)	2.6e+01	<2.0e+01	2.1e+04	2.34e+04
²³³ U	(Bq/g)			6.3e+01	5.15e+02
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/g)			1.1e+03	1.54e+03
²⁴¹ Am	(Bq/g)	<3.0e+02	<1.0e+02	3.2e+03	
²³⁸ Pu/ ²⁴¹ Am	(Bq/g)			3.9e+03	3.74e+03
²⁵² Cf	(Bq/g)			<5.0e+01	
²⁴⁴ Cm	(Bq/g)			1.2e+04	1.63e+04

^aAll washing data are reported relative to the starting sludge weight.

^bBulk sludge results were obtained prior to the washing experiment; mass balance may not be observed (see Sect. 4.3).

Table 5. Analytical data for washing sludge sample W25-S^a

Characteristic		Dissolved in wash			Bulk sludge ^b
		Water wash 1	Water wash 2	Acid wash	
<u>Miscellaneous data</u>					
pH					
Total solids	(mg/g)				531
<u>Process metals</u>					
Ca	(mg/kg)				3.8e+04
K	(mg/kg)				9.2e+03
Mg	(mg/kg)				5.9e+03
Na	(mg/kg)				6.6e+04
<u>Anions</u>					
Carbonate	(mg/kg)				1.96e+04
Chloride	(mg/kg)	1.8e+03	1.5e+02	8.2e+02	
Fluoride	(mg/kg)	5.6e+01	1.5e+01	4.9e+02	
Nitrate	(mg/kg)	2.5e+05	7.7e+03		
Nitrite	(mg/kg)	2.1e+03	7.6e+01	-	
Phosphate	(mg/kg)	-	-	3.1e+04	
Sulfate	(mg/kg)	1.4e+03	1.0e+02	-	

^aAll washing data are reported relative to the starting sludge weight.

Table 6. Analytical data for washing sludge sample W26-S^{a,b}

Characteristic		Dissolved in wash			Residue ^c	Bulk sludge ^b
		Water wash 1	Water wash 2	Acid wash		
<u>Miscellaneous data</u>						
pH		9.5	9.3			
Total solids	(mg/g)	145	123	211		449
<u>Process metals</u>						
Ca	(mg/kg)	9.2e+02	3.3e+02	6.2e+03		3.6e+04
K	(mg/kg)	2.8e+04	2.5e+03	<2.7e+01		1.5e+04
Mg	(mg/kg)	3.4e+02	3.0e+02	<1.0e+00		1.1e+04
Na	(mg/kg)	7.2e+04	4.7e+03	2.3e+03		5.1e+04
<u>Anions</u>						
Carbonate	(mg/kg)					6.00e+04
Chloride	(mg/kg)	2.1e+03	9.3e+01	8.6e+02		
Fluoride	(mg/kg)	1.2e+02	4.0e+01	-		
Nitrate	(mg/kg)	8.9e+04	7.9e+03			
Nitrite	(mg/kg)	1.6e+03	7.7e+01	-		
Phosphate	(mg/kg)	-	-	-		
Sulfate	(mg/kg)	2.3e+03	2.7e+02	-		
<u>Beta/gamma emitters</u>						
Gross beta	(Bq/g)	5.7e+05	2.8e+04	5.6e+06		5.70e+06
⁶⁰ Co	(Bq/g)	1.2e+03	2.4e+02	1.2e+05	2.1e+03	1.03e+05
¹³⁴ Cs	(Bq/g)	2.5e+03	1.7e+02	<2.1e+03	2.5e+01	2.97e+03
¹³⁷ Cs	(Bq/g)	6.3e+05	4.4e+04	2.3e+05	1.0e+04	6.84e+05
¹⁵² Eu	(Bq/g)	<2.2e+02	<1.7e+02	7.0e+05	7.0e+02	4.92e+05
¹⁵⁴ Eu	(Bq/g)	<1.8e+02	<1.1e+02	4.7e+05	4.8e+02	3.19e+05
¹⁵⁵ Eu	(Bq/g)	<6.8e+02	<2.0e+02	1.2e+05	1.2e+02	7.51e+04
<u>Alpha emitters</u>						
Gross alpha	(Bq/g)	4.0e+01	2.2e+01	9.3e+04		9.13e+04
²³⁵ U	(Bq/g)			8.1e+03		6.66e+03
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/g)			4.2e+03		5.11e+03
²⁴¹ Am	(Bq/g)	<3.9e+02	<1.2e+02	8.1e+03	6.6e+01	
²³⁸ Pu/ ²⁴¹ Am	(Bq/g)			1.3e+04		1.48e+04
²⁵² Cf	(Bq/g)			<1.0e+02		
²⁴⁴ Cm	(Bq/g)			5.8e+04		6.14e+04

^aAll washing and residue data reported relative to the starting sludge weight.

^bBulk sludge results were obtained prior to the washing experiment; mass balance may not be observed (see Sect. 4.3).

^cResidue was counted as a point source that was not equivalent to calibrated geometry; $\pm 50\%$ error is possible. Weight of residue recovered from filter was 31 mg/g sludge

Table 7 Analytical data for washing sludge sample W27-H1-Sa,b

Characteristic		Dissolved in wash			Residue ^c	Bulk sludge ^b
		Water wash 1	Water wash 2	Acid wash		
Miscellaneous data						
pH		11.0	9.5			
Total solids	(mg/g)	189	10	134		386
Process metals						
Ca	(mg/kg)	2.2e+03	8.7e+02	9.0e+03		3.8e+04
K	(mg/kg)	1.3e+04	1.8e+03	<3.9e+01		6.1e+03
Mg	(mg/kg)	<2.0e+00	<1.0e+00	3.3e+01		4.8e+03
Na	(mg/kg)	1.2e+05	5.1e+03	1.6e+03		7.1e+04
Anions						
Carbonate	(mg/kg)					2.62e+04
Chloride	(mg/kg)	3.3e+03	1.5e+02	1.9e+03		
Fluoride	(mg/kg)	1.2e+02	3.2e+01	-		
Nitrate	(mg/kg)	1.3e+05	7.6e+03			
Nitrite	(mg/kg)	2.8e+03	8.4e+01	-		
Phosphate	(mg/kg)	-	-	-		
Sulfate	(mg/kg)	1.7e+03	1.3e+02	-		
Beta/gamma emitters						
Gross beta	(Bq/g)	4.4e+05	1.8e+04	1.5e+06		1.44e+06
⁶⁰ Co	(Bq/g)	2.5e+02	4.0e+01	2.3e+04	5.9e+01	1.61e+04
¹³⁴ Cs	(Bq/g)	9.8e+02	<8.0e+01	<9.4e+02	<1.0e+01	<1.2e+03
¹³⁷ Cs	(Bq/g)	4.4e+05	1.2e+04	1.7e+05	3.1e+03	3.75e+05
¹⁵² Eu	(Bq/g)	<2.8e+02	<1.8e+02	2.9e+04	<4.0e+01	1.99e+04
¹⁵⁴ Eu	(Bq/g)	<1.6e+02	<1.6e+02	1.9e+04	<2.0e+01	1.26e+04
¹⁵⁵ Eu	(Bq/g)	<6.9e+02	<1.3e+02	5.6e+03	<2.0e+01	<3.4e+03
Alpha emitters						
Gross alpha	(Bq/g)	2.5e+00	3.9e+00	2.6e+04		2.25e+04
²³⁵ U	(Bq/g)			5.8e+02		5.18e+02
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/g)			1.3e+03		1.04e+03
²⁴¹ Am	(Bq/g)	<4.0e+02	<9.0e+01	4.3e+03	<2.0e+01	
²⁴¹ Pu/ ²⁴¹ Am	(Bq/g)			5.0e+03		4.4e+03
²⁵² Cf	(Bq/g)			<5.0e+01		
²⁴⁴ Cm	(Bq/g)			1.6e+04		1.60e+04

^aAll washing and residue data reported relative to the starting sludge weight.

^bBulk sludge results were obtained shortly after the sample had been collected. Sample material had dried (i.e., lost water) before the washing experiment was run.

^cResidue was counted as a point source that was not equivalent to calibrated geometry; $\pm 50\%$ error is possible. Weight of residue recovered from filter was 14 mg/g sludge.

Table 8. Analytical data for washing sludge sample W2^{a,b}

Characteristic		Dissolved in wash			Bulk sludge ^b
		Water wash 1	Water wash 2	Acid wash	
<u>Miscellaneous data</u>					
pH		12.2	10.2		
Total solids	(mg/g)	202	15	227	533
Carbonate	M	0.006			
<u>Process metals</u>					
Ca	(mg/kg)	6.8e+03	2.1e+03	6.5e+03	5.7e+04
K	(mg/kg)	1.8e+04	1.8e+03	<2.8e+01	1.1e+04
Mg	(mg/kg)	2.0e+00	<1.0e+00	<1.0e+00	1.5e+04
Na	(mg/kg)	1.0e+05	2.4e+03	1.6e+03	6.6e+04
<u>Anions</u>					
Carbonate	(mg/kg)				1.81e+04
Chloride	(mg/kg)	2.3e+03	5.3e+01	1.3e+03	
Fluoride	(mg/kg)	-	-	-	
Nitrate	(mg/kg)	2.7e+05	5.4e+03		
Nitrite	(mg/kg)	6.3e+02	-	-	
Phosphate	(mg/kg)	-	-	8.5e+03	
Sulfate	(mg/kg)	9.9e+02	2.5e+02	-	
<u>Beta/gamma emitters</u>					
Gross beta	(Bq/g)	2.8e+05	7.3e+05	2.8e+06	2.40e+06
⁶⁰ Co	(Bq/g)	2.0e+02	<6.0e+01	9.7e+04	7.91e+04
¹³⁴ Cs	(Bq/g)	3.4e+03	<7.0e+01	<2.0e+03	<4.6e+03
¹³⁷ Cs	(Bq/g)	1.8e+05	3.5e+03	1.1e+04	1.94e+05
¹⁵² Eu	(Bq/g)	<2.0e+02	<3.0e+02	8.7e+05	7.18e+05
¹⁵⁴ Eu	(Bq/g)	<2.0e+02	<2.0e+02	4.4e+05	3.20e+05
¹⁵⁵ Eu	(Bq/g)	<4.0e+02	<1.0e+02	1.3e+05	9.70e+04
<u>Alpha emitters</u>					
Gross alpha	(Bq/g)	6.8e+01	4.4e+01	5.8e+04	5.39e+04
²³³ U	(Bq/g)			2.3e+03	3.56e+03
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/g)			2.7e+03	1.51e+03
²⁴¹ Am	(Bq/g)	<3.0e+02	<6.0e+01	8.4e+03	
²³⁸ Pu/ ²⁴¹ Am	(Bq/g)			9.0e+03	5.28e+03
²⁵² Cf	(Bq/g)			<8.0e+01	
²⁴⁴ Cm	(Bq/g)			3.7e+04	3.83e+04

^aAll washing data are reported relative to the starting sludge weight.^bBulk sludge results were obtained prior to the washing experiment; mass balance may not be observed (see Sect. 4.3).

Table 9. Analytical data for washing sludge sample W31-S^{a,b}

Characteristic		Dissolved in wash			Residue ^c	Bulk sludge ^b
		Water wash 1	Water wash 2	Acid wash		
Miscellaneous data						
pH		9.7	9.1			
Total solids	(mg/g)	476	19	58		369
Process metals						
Ca	(mg/kg)	1.2e+03	4.6e+02	1.1e+04		5.6e+03
K	(mg/kg)	3.0e+04	6.6e+03	<4.7e+01		7.9e+03
Mg	(mg/kg)	4.2e+02	7.4e+01	1.3e+03		8.7e+02
Na	(mg/kg)	2.8e+05	6.5e+03	1.2e+03		6.9e+04
Anions						
Carbonate	(mg/kg)					7.05e+03
Chloride	(mg/kg)	4.6e+03	7.5e+01	1.2e+03		
Fluoride	(mg/kg)	1.7e+02	2.9e+01	-		
Nitrate	(mg/kg)	3.7e+05	9.9e+03	-		
Nitrite	(mg/kg)	3.9e+03	7.8e+01	-		
Phosphate	(mg/kg)	-	-	-		
Sulfate	(mg/kg)	2.5e+03	-	-		
Beta/gamma emitters						
Gross beta	(Bq/g)	5.8e+05	3.4e+04	5.9e+06		3.18e+06
⁶⁰ Co	(Bq/g)	1.2e+03	6.4e+01	1.2e+04	1.3e+02	8.10e+03
¹³⁴ Cs	(Bq/g)	5.4e+03	1.1e+02	<1.0e+03	<1.0e+01	3.64e+03
¹³⁷ Cs	(Bq/g)	4.1e+05	9.8e+03	5.0e+04	1.1e+03	2.35e+05
¹⁵² Eu	(Bq/g)	<2.8e+02	<3.5e+02	1.9e+04	<4.0e+01	<1.7e+04
¹⁵⁴ Eu	(Bq/g)	<1.8e+02	<1.4e+02	8.7e+03	<3.0e+01	5.86e+03
¹⁵⁵ Eu	(Bq/g)	<7.5e+02	<1.6e+02	3.6e+03	<2.0e+01	<5.9e+03
Alpha emitters						
Gross alpha	(Bq/g)	2.8e+01	4.9e+01	4.1e+04		2.31e+04
²³³ U	(Bq/g)			6.5e+02		5.08e+02
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/g)			8.5e+02		8.78e+02
²⁴¹ Am	(Bq/g)	<4.3e+02	<1.0e+02	4.4e+03	2.0e+01	
²³⁸ Pu/ ²⁴¹ Am	(Bq/g)			4.3e+03		2.43e+03
²⁵² Cf	(Bq/g)			<5.0e+01		
²⁴⁴ Cm	(Bq/g)			3.0e+04		1.71e+04

^a All washing and residue data are reported relative to the starting sludge weight.

^b Bulk sludge results were obtained shortly after the sample had been collected. Sample material had dried (i.e., lost water) before the washing experiment was run.

^c Residue was counted as a point source that was not equivalent to calibrated geometry; $\pm 50\%$ error is possible. Weight of residue recovered from filter was 4 mg/g sludge.

Table 10. Analytical data for washing sludge sample W31-11^{a,b}

Characteristic		Dissolved in wash			Residue ^c	Bulk sludge ^b
		Water wash 1	Water wash 2	Acid wash		
<u>Miscellaneous data</u>						
pH		7.8	8.0			
Total solids	(mg/g)					964
<u>Process metals</u>						
Ca	(mg/kg)					6.2e+04
K	(mg/kg)					6.7e+03
Mg	(mg/kg)					3.1e+03
Na	(mg/kg)					4.8e+04
<u>Anions</u>						
Carbonate	(mg/kg)					1.10e+05
Chloride	(mg/kg)	3.2e+03	6.6e+01	2.9e+03		
Fluoride	(mg/kg)	-	-	-		
Nitrate	(mg/kg)	2.2e+05	4.2e+03			
Nitrite	(mg/kg)	5.8e+03	-	-		
Phosphate	(mg/kg)	-	-	-		
Sulfate	(mg/kg)	3.0e+03	5.2e+02	-		
<u>Beta/gamma emitters</u>						
Gross beta	(Bq/g)	4.4e+05	5.1e+04	3.4e+07		1.10e+07
⁶⁰ Co	(Bq/g)	6.7e+02	<3.0e+02	6.3e+04	1.1e+03	3.01e+04
¹³⁴ Cs	(Bq/g)	1.2e+03	<2.0e+02	<3.0e+03	2.6e+01	2.07e+03
¹³⁷ Cs	(Bq/g)	2.6e+05	2.0e+04	6.8e+05	1.4e+04	5.52e+05
¹⁵² Eu	(Bq/g)	<6.0e+02	<6.0e+02	4.8e+04	<7.0e+01	2.72e+04
¹⁵⁴ Eu	(Bq/g)	<3.0e+02	<3.0e+02	4.8e+04	<6.0e+01	2.07e+04
¹⁵⁵ Eu	(Bq/g)	<8.0e+02	<3.0e+02	1.3e+04	<6.0e+01	<8.7e+03
<u>Alpha emitters</u>						
Gross alpha	(Bq/g)	2.6e+01	2.2e+02	2.1e+05		8.95e+04
²³³ U	(Bq/g)			2.1e+03		2.05e+03
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/g)			7.7e+03		3.22e+03
²⁴¹ Am	(Bq/g)	<5.0e+02	<2.0e+02	1.1e+04	1.5e+02	
²⁴⁰ Pu/ ²⁴¹ Am	(Bq/g)			2.9e+04		1.12e+04
²⁵² Cf	(Bq/g)			<2.5e+02		
²⁴⁴ Cm	(Bq/g)			1.5e+05		6.89e+04

^aAll washing and residue data are reported relative to the starting sludge weight.

^bBulk sludge results were obtained shortly after the sample had been collected. This sample appeared to have dried to hard lumps and lost water before the washing experiment was run.

^cResidue was counted as a point source that was not equivalent to calibrated geometry; $\pm 50\%$ error is possible. Weight of residue recovered from filter was 36 mg/g sludge.

4.2 GENERAL TRENDS

The primary constituents in the water wash solutions are sodium/potassium nitrate salts. Most of the sodium and potassium were found in the first water wash (average, 94% for sodium and 90% for potassium, except sample W21-S). The water washes of most sludges were low in calcium and magnesium. A little calcium was found in the water washes of samples W21-S and W28-S. The bulk liquid over the sludge in these tanks also contained a little calcium.¹ The amount of material recovered in the second water wash was small, on the order of a few percent.

The pH of the first water wash was relatively high, generally in the range of 9.5 to 12, due to the basic nature of the sludges. The second water wash was usually slightly basic with a pH of about 9. The pH of the wash from sample W21-S was 7. This sludge came from the tank where the bulk liquid over the sludge was acidic ($\text{pH} < 1$), and the pH of the original sludge liquid was 7.

The principal anion found in the water wash solutions by ion chromatography was nitrate, as was expected. Low levels of chloride, nitrite, and sulfate were detected in the first water wash. Fluoride was found at low levels in the water washes of five sludges (W23-S, W25-S, W26-S, W27-H1-S, and W31-S). The acid washes of all sludge samples contained a little chloride, and five contained a little phosphate (W21-S, W23-S, W24-S, W25-S, and W28-S). An unknown peak with a retention time of 0.82-0.83 min was observed in the chromatograms of all the water and acid washes. A second unknown peak with a retention time of 9.55-9.68 min was observed in the acid washes. For comparison, the retention times for F^- , Cl^- , PO_4^{3-} and SO_4^{2-} were 0.55-0.57, 3.12-3.18, and 8.00-8.12, and 11.4-11.7 min, respectively. An additional unidentified peak was observed in the acid washes of W26-S and W-31-S at 7.90 and 7.85, respectively. The possibility of the 7.9-min peak being a phosphate peak that was slightly shifted was not investigated. The AS2 column is capable of determining low molecular weight organic acids such as acetate and a variety of other inorganic species, but the instrument was not calibrated for other species. The unknown peaks are small and would be minor constituents. (Carbonate cannot be determined by ion chromatography because a carbonate solution is used as the eluant with the AS2 column.)

Very little of the alpha activity dissolved in the water washes (<100 Bq/g of starting sludge in the first wash and <50 Bq/g in the second wash). The alpha emitters dissolved readily in the cold acid wash. The ^{137}Cs was distributed about 80% in the water washes and

20% in the acid wash. While most alkali metal salts are soluble, cesium is known to sorb on sediments in the environment, and it also appears to sorb on the sediments in the sludge to some extent. An average of 7% of the gross beta dissolved in the water washes. The primary contributor to the gross beta is ^{90}Sr and its short-lived daughter, ^{90}Y .¹ This indicates that most of the ^{90}Sr remained insoluble during the water washes. The curium isotopes and ^{60}Co also had a low solubility in the water washes (about 0.1 and 1%, respectively), but dissolved readily in the acid wash.

The soft sludges appeared to dissolve readily (within 10 min) in 2 M HNO_3 at room temperature leaving relatively little solid residue (visual observation). Most of the hard sludge W31-H dissolved in 4 M HNO_3 . The quantity of solid residue recovered from the filter (with a spatula) after the 4 M HNO_3 wash is given in the footnotes to the tables. This is not a quantitative technique, but it does provide an indication that the amount of residue was small. The sludges with the most residue were W26-S and W31-H (about 3 and 4%, respectively, of the starting sludge mass). If no residue weight is given, the amount was too small to recover. The ease with which the sludge solids dissolved and the low concentrations of anions other than nitrate in the acid wash indicate that the precipitated sludge solids are probably predominately carbonates and hydroxides. (Carbonate and hydroxide ions are not stable in acid solutions, and cannot be determined in the acid wash solution.)

4.3 UNCERTAINTIES

Condition of Samples. Characteristics of the bulk sludge (see ref. 1) have been included in the tables for information purposes. However, the results for the bulk sludge were obtained on fresh samples shortly after the samples were collected, and months prior to the sludge washing tests. The composition of the samples may have changed before the sludge washing tests were run. A mass balance may not be observed if the sample lost water during storage. This should be taken into consideration in comparing the sludge washing data with the bulk sludge results. The species of interest in sludge washing are nonvolatile and would still be present even if the sample lost water, but their concentrations would be higher.

Cation-anion balance. The cation-anion balances for the first water wash of the "A" sludge washing batch (W21-S, W24-S, and W28-S) are good considering that these are radioactive samples (see Table 11). However, for the "B" sludge washing batch (W23-S,

Table 11. Constituents dissolved in first water wash of sludge sampler^a

Characteristic	Batch A					Batch B			
	W25-S	W21-S	W24-S	W28-S	W31-H	W23-S	W26-S	W27-H1-S	W31-S
Weight of sludge (g)	2.9360	1.7934	1.4269	1.7652	0.5595	2.0331	1.8754	1.2880	1.0651
pH of wash water		7.2	12.1	12.2	7.8	11.9	9.5	11.0	9.7
Cations (mmol/g)									
Ca ²⁺		0.162	0.0055	0.170		0.001	0.022	0.055	0.030
K ⁺		0.332	0.384	0.460		0.665	0.716	0.332	0.767
Mg ²⁺		0.024	0.0007	<0.0001		<0.0001	0.014	<0.0001	0.017
Na ⁺		2.53	4.76	4.37		3.54	3.144	5.11	12.22
Cations found (equiv/g)		3.23	5.15	3.17		4.21	3.93	5.55	13.08
Anions (mmol/g)									
F ⁻	0.003	-	-	-	-	0.005	0.006	0.006	0.092
Cl ⁻	0.052	0.038	0.062	0.065	0.090	0.069	0.058	0.093	0.130
NO ₃ ⁻	0.046	0.014	0.028	0.014	0.127	0.072	0.034	0.060	0.085
SO ₄ ²⁻	0.014	0.106	0.022	0.010	0.032	0.032	0.024	0.018	0.026
NO ₂ ⁻	4.11	3.98	3.27	4.32	3.63	1.307	1.44	2.10	5.95
OH ⁻ (calc from pH)		-	0.72	0.90	-	0.39	0.002	0.078	0.005
CO ₃ ²⁻			0.23	0.34					
Anions found (equiv/g)		4.24	4.68	6.00	3.91	1.91	1.56	2.37	6.31
Dissolved solids (mg/g)		172	179	202		219	145	189	476
Mass of cations and anions found (mg/g)		337	362	432					

^aWashing data reported relative to starting weight of sludge.

W26-S, W27-H1-S, and W31-S) the equivalents of cations are approximately double the equivalents of anions. Good cation-anion balances were obtained in the analyses of the bulk tank liquid wastes (see ref. 1, p. 44). The water wash solutions are chemically similar to the bulk liquid wastes only more dilute. Since the bulk liquids were diluted before analysis, concentration should not be a factor. Therefore, it should be possible to obtain acceptable ($\pm 25\%$) cation-anion balances for the first water wash solutions. A discrepancy of a factor of 2 raises the question of whether there might have been a dilution factor error. It seems likely that the cation/anion uncertainty could have been resolved by a few spot rechecks, and, if necessary, a carbonate analysis.

Comparison of sludge washing data with bulk sludge results. Relatively good agreement was obtained for the radioactive materials between the sludge washing experiments (i.e., the sum of the water and acid washes and residues) and the bulk sludge for five samples (W21-S, W23-S, W24-S, W26-S, and W28-S; see Table 12). The results for the radioactive materials in the sludge washing of the three samples that had dried (W27-H1-S, W31-S, and W31-H) were higher than for the bulk sludge, as would be expected for samples that had lost water during storage. (Note that the residues were not analyzed for alpha emitters.)

The comparison of the cations found in the washes with the composition of the bulk sludge is shown in Table 13. The sodium and potassium were consistently higher in the washing tests than in the analyses of the bulk sludge. This may be due in part to the samples losing water in storage. There is also some uncertainty about the analyses (see cation-anion balance above). In addition, the sodium and potassium analyses by ICP are not as accurate (about $\pm 20\%$) as some of the analyses.

Only about 30% of the calcium expected to be present was found in the washing experiments (Table 13). Most of the calcium is present as calcium carbonate (CaCO_3). Based on the chemical properties, it was expected that most of the calcium would be found in the acid wash. Most of the magnesium is also unaccounted for. One possibility for the missing calcium is that the calcium carbonate might have been present as a very fine precipitate (i.e., the milky color in the water wash before filtration). This very fine precipitate might have been trapped within the pores of the filter media used with the water washes and not recovered from the filters for the acid wash. There may also be some

Table 12. Comparison of radioactive materials found in sludge washing experiments with composition of bulk sludge

Sample	Ratio of radioactive materials found in sludge washes to bulk sludge ^a				
	Gross alpha	Gross beta	⁶⁰ Co	¹³⁷ Cs	¹⁵² Eu
W21-S	0.6	1.3	1.1	0.9	1.2
W23-S	1.0	1.1	0.9	1.1	1.0
W24-S	0.9	1.2	1.2	1.2	1.1
W26-S	1.0	1.1	1.2	1.3	1.4
W27-H1-S ^b	1.2	1.4	1.4	1.6	1.5
W28-S	1.1	1.3	1.2	1.0	1.2
W31-S ^b	1.8	2.0	1.6	2.0	NA ^c
W31-H ^b	2.3	3.1	2.2	1.8	1.8

^aSum of radioactive material found in water wash 1 + water wash 2 + acid wash + residue, divided by concentration in bulk sludge.

^bSample appeared to have dried prior to sludge washing experiment.

^cNA = not applicable.

Table 13. Comparison of selected cations found in sludge washing experiments with composition of bulk sludge

Sample	Ratio of cations found in sludge washes to bulk sludge ^{a,b}			
	Na	K	Ca	Mg
W21-S	1.3	3.7	0.3	0.08
W23-S	1.1	1.6	0.1	<0.001
W24-S	1.6	2.1	0.4	0.003
W26-S	1.5	2.0	0.2	0.06
W27-H1-S ^c	1.7	2.4	0.3	0.007
W28-S	1.6	1.8	0.3	<0.001
W31-S ^c	4.2	4.6	2.3	2.1

^aSum of cation found in water wash 1 + water wash 2 + acid wash, divided by concentration in bulk sludge.

^bFilters were not leached and no residue analyses performed.

^cSample appeared to have dried prior to sludge washing experiment.

calcium and magnesium in the residue from the acid wash. An acid leach of the filter media and residue is needed for a complete material balance.

Total solids analysis of wash solutions. For the "A" sludge washing batch, the mass of total solids in the first water wash determined by drying a 10 mL sample in the oven and weighing the residue was only about half the value obtained by summing the mass of all the cations and anions found (Table 11). For these dilute wash solutions, the cation and anion analyses are considered to be more accurate than the total solids analysis. The mass of the dried residue is small relative to the mass of the container. A total solids analysis of dilute wash solutions does not look promising as a method of following the progress of sludge washing tests. However, this observation should be confirmed by additional experiments.

4.4 DISCUSSION AND RECOMMENDATIONS

This was the first time an experiment to wash ORNL tank sludges was attempted. The sludge washing tests look promising, but the funding was canceled before this preliminary experiment could be completed. It was possible to wash the sludges and detect common inorganic anions, cations, and radioactive materials in the wash solutions. The actual data reported here are incomplete and there are some inconsistencies. The data should therefore be considered as merely an indicator of the behavior of the sludges. Additional experimental work is necessary before definitive quantitative statements can be made.

The data suggest that water could be used as the fluid to mobilize and transport the sludges without dissolving the TRU constituents. The pH of the first sludge wash (except tank W-21 sludge) would probably be high enough to keep the TRU and other heavy metals precipitated without the need to add additional base.

The preliminary studies indicate that the sodium/potassium nitrate salts in the sludge interstitial liquid can be separated from the TRU solids by water washing. Additional experiments with "neat" sludges, which had not been sonicated, and more realistic water wash to sludge ratios would be needed to provide useful information on washing efficiency.

ORNL has a number of collection tanks upstream of the LLW evaporator that have either been taken out of service or are anticipated to be removed from service under the pending Federal Facilities Agreement. The ease with which the MVST sludges dissolved in acid suggests that chemical dissolution might be considered as a method of removing sludges

from small tanks in preparation for decommissioning the tank. For small underground tanks, chemical dissolution followed by concentration of the waste at a central facility might be simpler than physical mobilization of the sludges.

Additional studies of washing the sludges are recommended. The initial studies should be with samples that have been sonicated to homogenize the samples so that experiments can be compared, and the analytical methods checked. The bulk sludge should be analyzed at about the same time as the sludge washing tests are performed to provide a reference standard for comparison. Data to be collected should include a cation/anion balance for the first water wash, leaching of the filter media, analysis of residues, and a mass balance and a radioactive materials balance vs. the starting bulk sludge. A range of conditions for both the water wash and the acid wash, as well as experiments with "neat" (i.e., unsonicated) sludges should be explored. Considerable development work on this procedure may be needed.

5. REFERENCES

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