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Washing and Alkaline Leaching of Hanford Tank Sludges: A Status Report

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Summary

This report describes the sludge washing and caustic leaching tests conducted at Pacific Northwest Laboratory (PNL) in FY 1994 under the Sludge Treatment and Extraction Technology Development Task of the Tank Waste Remediation System (TWRS) Pretreatment Technology Development Project. The highlights from this work were as follows.

- Three sludge washing and alkaline (caustic and carbonate) leaching tests were performed using sludge from single-shell tank (SST) B-201. Portions from two core samples (26 and 27) were examined. The two cores behaved similarly, although some differences were observed. Of the major sludge components only Na was effectively removed from the sludge by washing and alkaline leaching. Listing the various sludge components in the order of decreasing weight percent in the untreated sludge, the percentages of each component removed by sludge washing and alkine leaching were as follows: Bi (0 to 5%), Na (97 to 99%), Mn (0%), Si (30 to 60%), La (0 to 3%), Fe (1%), Ca (0 to 4%). The behaviors of Al, Cr, and P were of interest with respect to the volume of high-level waste (HLW) glass produced in the disposal of the Hanford single-shell tank (SST) wastes. The percentages of each of these component removed by sludge washing and alkaline leaching were 16 to 46% for Al, 50 to 74% for Cr, and 15 to 46% for P. Little TRU material was found in the wash and caustic leach solutions, but some was found in the carbonate leachate. If the sludge wash solution and the caustic leach solutions were combined and concentrated to 5 M Na, the TRU concentration would be $\sim 1 \times 10^{-3}$ μCi/mL and the ^{90}Sr concentration would be $< 10^{-3}$ μCi/mL.

- A sludge washing and caustic leaching test was performed using sludge from SST U-110. In this test, a portion of U-110 sludge was washed with 0.1 M NaOH at room temperature, then was leached with a solution consisting of 3 M NaOH and 2 M Na_2CO_3 at 1) 100°C and 2) ~20°C while sonicating. Sonication had little effect on improving removal of the various sludge constituents, however, this test yielded very promising results. Washing the sludge with 0.1 M NaOH at room temperature removed 89 to 92% of the P from the sludge, while leaching with 3 M NaOH/2 M Na_2CO_3 removed an additional 8 to 9% of the P; thus, $\geq$97% of the P was removed from the U-110 sludge. Very little Al was removed in the 0.1 M NaOH wash, but a total of 84% of the Al had been removed after caustic leaching. The only other measured sludge components removed were Cr and B. For Cr, 64 to 73% was removed in the wash, but $\leq$11 was removed in the caustic leach. For B, $\geq$82% was removed in the wash step. Little TRU material was found in the wash and leach solutions. Less than 2.3% of the TRU material was present in these solutions. Similarly, little (1.5%) ^{90}Sr was removed from the sludge during washing and caustic leaching. If the sludge wash solution and the caustic leach solutions were combined and concentrated to 5 M Na, the TRU concentration would be $< 2.4 \times 10^{-4}$ μCi/mL and the ^{90}Sr concentration would be 0.17 μCi/mL.

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1.0 Introduction

Methods are being developed to treat and dispose of the large volumes of radioactive defense wastes currently stored in underground tanks at the U. S. Department of Energy's (DOE) Hanford Site in southeastern Washington State. The current baseline scenario for the treatment and disposal of these wastes involves partitioning the wastes into a small volume of high-level waste (HLW) and a relatively large volume of low-level waste (LLW). The HLW will be immobilized in borosilicate glass and disposed of in a geologic repository, while the LLW will be immobilized in a yet undefined glass waste form, which will likely be disposed of at the Hanford Site.

Because of the assumed high cost of HLW immobilization and disposal, pretreatment methods are being developed to minimize the volume of HLW requiring vitrification. Pacific Northwest Laboratory (PNL)[a] is investigating several options for pretreating the radioactive wastes stored in underground tanks at the Hanford Site. The pretreatment methods under study for the tank sludges include: 1) simply washing the sludges with dilute NaOH, 2) performing caustic leaching (as well as washing) to remove certain wash components,[b] and 3) dissolving the sludges in acid and extracting key radionuclides from the dissolved sludge solutions. The data collected in this effort will be used to support the March 1998 decision on the extent of pretreatment to be performed on the Hanford tank sludges. This document describes sludge washing and caustic leaching tests conducted in FY 1994 . These tests were performed using sludges from single-shell tanks (SST) B-201 and U-110. A summary is given of all the sludge washing and caustic leaching studies conducted at PNL in the last few years (Section 4.0).

(a) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

(b) This is the current baseline approach.

2.0 Sludge Washing and Alkaline Leaching of SST B-201 Sludge

The waste contained in tank B-201 is believed to be primarily lanthanum fluoride decontamination waste (Hill and Simpson 1994). This waste was generated in the final Pu concentration steps conducted in the bismuth phosphate process for Pu production (Cleveland 1970). Two composite samples of tank B-201 sludge were examined. These composites represented two core samples (26 and 27) taken from this tank. For two of the sludge washing and caustic leaching tests, the composites from cores 26 and 27 were dried to a constant weight at 80°C. The samples were dried to avoid uncertainties associated with differing initial water contents of the wastes. For the third test, a composite of core 26 was treated without drying as a control to determine whether preliminary drying alters the leachability of sludge components in any significant way. The procedures followed are shown schematically in Figures 2.1, 2.2, and 2.3.

The sludge samples were washed twice with 0.1 M NaOH at 100°C. In the first wash, 5 mL of 0.1 M NaOH were used per gram of dry sludge, and in the second wash, 2 mL of 0.1 M NaOH were used per gram of dry sludge initially used. The washed sludge was leached twice with 3 M NaOH (5 h at 100°C per contact) and twice with 1 M K_2CO_3 (5 h at 100°C per contact). After each treatment (0.1 M NaOH wash, 3 M NaOH leach, and 1 M K_2CO_3 leach) the solids were washed with water to remove dissolved components from the interstitial liquid. The undissolved solids after each wash or leach step were separated by centrifuging and decanting the supernatant liquid. Samples of the untreated sludge, the wash and leach solutions, and the washed and leached sludge were submitted for analysis.

The mass loss for each core sample was similar, with about 30% of the solids dissolved by washing and alkaline leaching. The measured elemental compositions of the core 26 and core 27 composite samples are presented in Table 2.1 and Table 2.2, respectively. The composition of each element per gram of sludge was determined in two ways. First, the untreated sludge was analyzed directly ("direct analysis" in Tables 2.1 and 2.2). Second, the amount of a given element found in each wash and leach solution was added to the amount found in the leached sludge, and the total was then divided by the weight of sludge used in the test ("summation method" in Tables 2.1 and 2.2). In order to reduce any discrepancies due to incomplete sample drying, the data have also been normalized by reporting the concentration of each element per gram of Bi present in the sludge. (Bismuth is expected to stay in the solid phase during these wash and leach operations.)

In general, there was reasonable agreement between the concentrations obtained through the summation method and the results obtained through direct analysis, and fairly good agreement between the results of the core 26 and core 27 samples. The most noticeable differences were the analyses for Ba, Mg, and Pb, which were not detected in core 27, but were present, albeit close to the detection limits, in core 26. The most abundant metallic element detected was Bi, which comprised 15-20 wt% of the initial dried sludge mass. Bismuth was followed in prevalence (by weight) by Na, Mn, Si, La, Fe and Ca, all of which were present in > 10% of the quantity of Bi in the sludge.

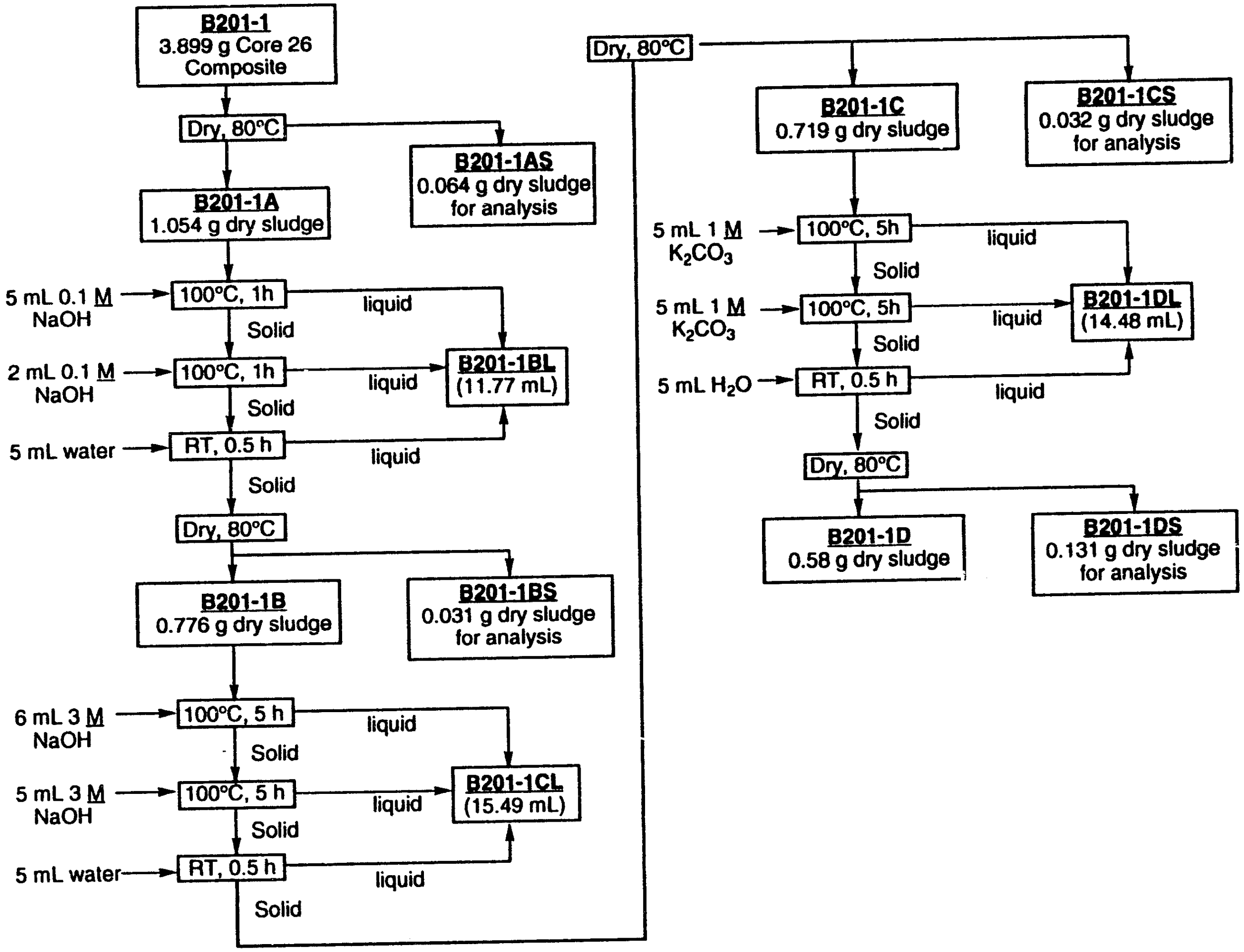

Figure 2.1. Schematic of B-201 (Core 26) Sludge Washing and Alkaline Leaching Test with Dried Sample

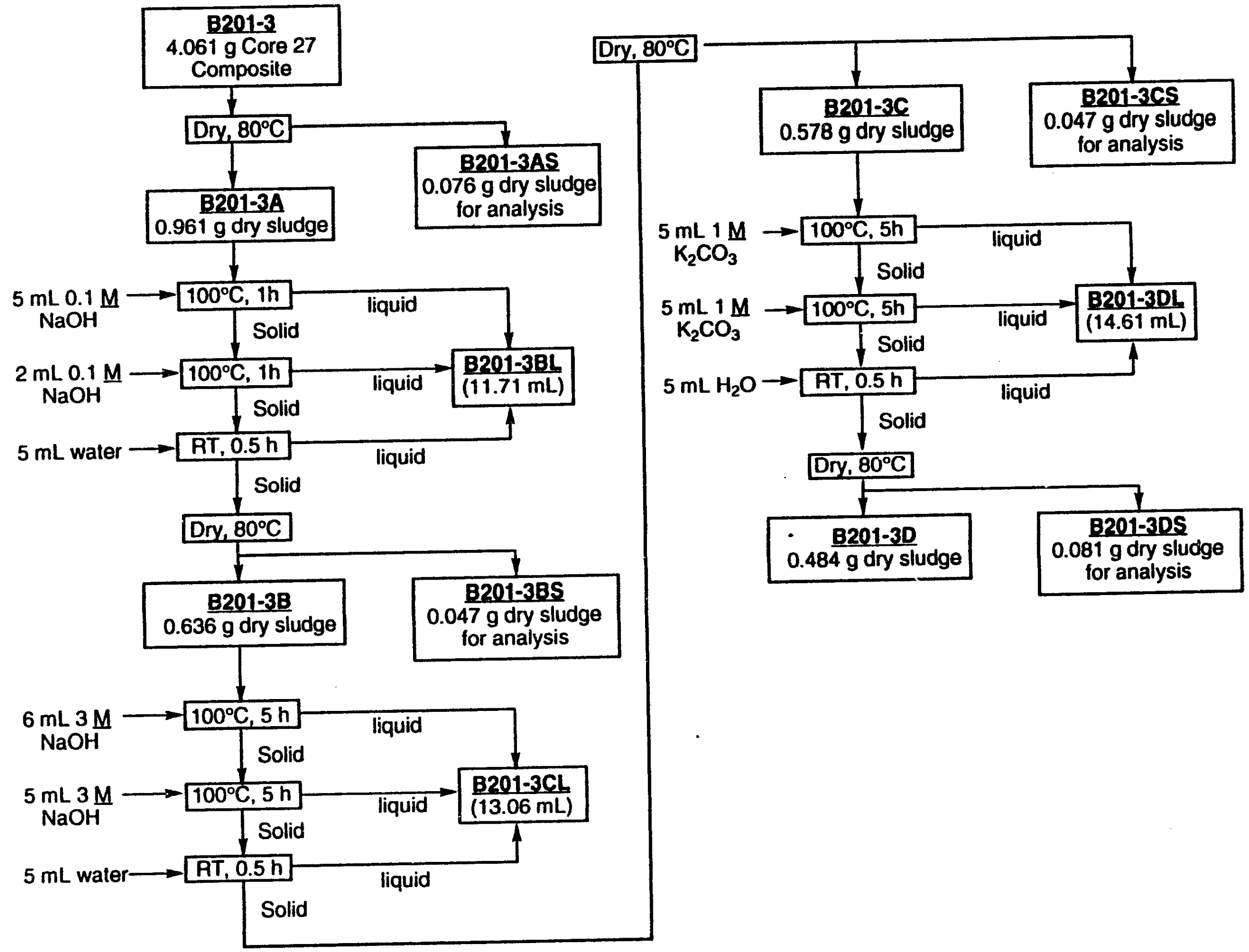

Figure 2.2. Schematic of B-201 (Core 27) Sludge Washing and Alkaline Leaching Test with Dried Sample

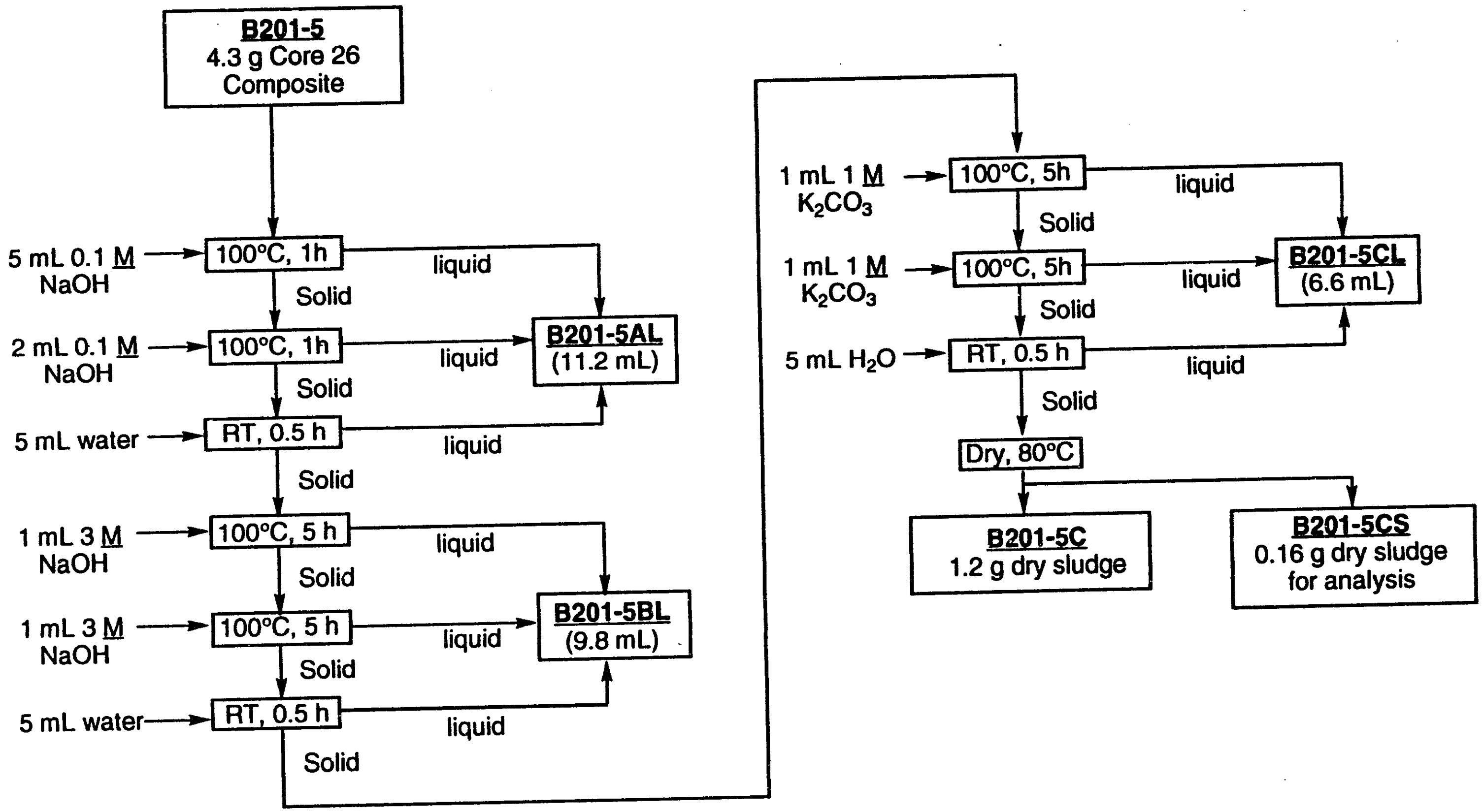

Figure 2.3. Schematic of B-201 (Core 26) Sludge Washing and Alkaline Leaching Test with Wet Sample

Table 2.1. Composition of Core 26 Composite Sample from Tank B-201

	g/g Dry Sludge			g/g Bi		
	Summation Method[(a)]			Summation Method[(a)]		
	Maximum	Minimum	Direct Analysis[(b)]	Maximum	Minimum	Direct Analysis[(b)]
Al	7.6E-03	7.7E-03	8.2E-03	5.3E-02	5.2E-02	4.7E-02
Ba	5.8E-04	6.8E-04	4.0E-04	4.0E-03	4.6E-03	2.3E-03
Bi	1.4E-01	1.5E-01	1.8E-01	1.0E+00	1.0E+00	1.0E+00
Ca	2.4E-02	2.4E-02	2.7E-02	1.6E-01	1.6E-01	1.6E-01
Cr	6.5E-03	6.5E-03	6.3E-03	4.5E-02	4.4E-02	3.6E-02
Fe	2.4E-02	2.4E-02	3.0E-02	1.7E-01	1.6E-01	1.7E-01
La	3.0E-02	3.0E-02	3.1E-02	2.1E-01	2.0E-01	1.8E-01
Mg	4.4E-03	5.4E-03	3.5E-03	3.1E-02	3.7E-02	2.0E-02
Mn	4.4E-02	4.3E-02	4.5E-02	3.0E-01	2.9E-01	2.5E-01
Na	(c)	(c)	8.3E-02	(c)	(c)	4.7E-01
P	1.2E-02	1.2E-02	1.1E-02	8.5E-02	8.2E-02	6.0E-02
Pb	2.6E-03	3.1E-03	1.6E-03	1.8E-02	2.1E-02	9.0E-03
Si	3.4E-02	3.4E-02	4.3E-02	2.4E-01	2.3E-01	2.4E-01
Sr	1.5E-03	1.6E-03	1.5E-03	1.1E-02	1.1E-02	8.7E-03
Ti	8.3E-04	8.7E-04	1.1E-03	5.7E-03	5.9E-03	6.2E-03

(a) For the summation method, the quantity of each component per gram of sludge was determined by summing the amount of each component found in the wash, the acidic dissolving solutions, and the undissolved residue and dividing the total found by the mass (in grams) of sludge used in the test. Two cases were considered. First, when the concentration of a given element was below the detection limit, the concentration of that element was assumed to be zero. Second, when below the detection, the detection limit was used as the concentration. In this way, maximum and minimum concentration values were obtained.

(b) A portion of the core 26 composite sludge sample used in this test was analyzed directly.

(c) Because of the relatively large amount of Na added as NaOH, the amount of Na in the sludge could not be determined accurately by the summation method.

Table 2.2. Composition of Core 27 Composite Sample from Tank B-201

	g/g Dry Sludge			g/g Bi		
	Summation Method[(a)]			Summation Method[(a)]		
	Maximum	Minimum	Direct Analysis[(b)]	Maximum	Minimum	Direct Analysis[(b)]
Al	4.0E-03	4.0E-03	6.5E-03	2.7E-02	7.6E-02	3.3E-02
Ba	6.8E-04	0.0E+00	0.0E+00	4.6E-03	0.0E+00	0.0E+00
Bi	1.5E-01	5.2E-02	1.9E-01	1.0E+00	1.0E+00	1.0E+00
Ca	2.4E-02	8.8E-03	2.4E-02	1.6E-01	1.7E-01	1.2E-01
Cr	6.5E-03	5.3E-03	7.0E-03	4.4E-02	1.0E-01	3.6E-02
Fe	2.4E-02	1.1E-02	3.4E-02	1.6E-01	2.1E-01	1.8E-01
La	3.0E-02	9.0E-03	3.0E-02	2.0E-01	1.7E-01	1.6E-01
Mg	5.4E-03	1.0E-03	0.0E+00	3.7E-02	2.0E-02	0.0E+00
Mn	4.3E-02	1.8E-02	5.4E-02	2.9E-01	3.4E-01	2.8E-01
Na	(c)	(c)	8.0E-02	(c)	(c)	4.1E-01
P	1.2E-02	6.9E-03	1.1E-02	8.2E-02	1.3E-01	5.7E-02
Pb	3.1E-03	9.4E-04	0.0E+00	2.1E-02	1.8E-02	0.0E+00
Si	3.4E-02	2.3E-02	3.0E-02	2.3E-01	4.4E-01	1.5E-01
Sr	1.6E-03	6.1E-04	1.9E-03	1.1E-02	1.2E-02	9.7E-03
Ti	8.7E-04	2.9E-04	7.0E-04	5.9E-03	5.4E-03	3.6E-03

(a) For the summation method, the quantity of each component per gram of sludge was determined by summing the amount of each component found in the wash, the acidic dissolving solutions, and the undissolved residue and dividing the total found by the mass (in grams) of sludge used in the test. Two cases were considered. First, when the concentration of a given element was below the detection limit, the concentration of that element was assumed to be zero. Second, when below the detection, the detection limit was used as the concentration. In this way, maximum and minimum concentration values were obtained.

(b) A portion of the core 26 composite sludge sample used in this test was analyzed directly.

(c) Because of the relatively large amount of Na added as NaOH, the amount of Na in the sludge could not be determined accurately by the summation method.

The percentages of each of the nonradioactive sludge components found in the wash, caustic leach, and carbonate leach solutions are found in Tables 2.3 and 2.4. The dominating feature of these results is the inefficient dissolution of most of the major elements in B-201 sludge. Only Na was effectively removed from the B-201 sludge by alkaline washing and leaching. The leached sludge contained ≤3% of the Na found in the untreated sludge.

Appreciable amounts of Cr (50 to 74%) were removed by the alkaline treatments. Because of the intense yellow color of the leach solutions, it is likely that most of the dissolved Cr was present as Cr(VI). The intensity of the yellow solutions qualitatively correlates with the amount of Cr dissolved according to the ICP analyses. However, partial dissolution of Cr(III) cannot yet be ruled out, since Cr(III) is known to have appreciable solubility at high OH^- concentrations (Rai, Sass, and Moore 1987).

Aluminum showed poor removal during these alkaline treatments, with a cumulative removal of roughly 55% (core 27) to 27% (core 26). As expected, most of this dissolution was accomplished by contact with 3 M NaOH; the treatments with 0.1 M NaOH and 1 M K_2CO_3 were ineffective at dissolving Al.

Table 2.3. Results from the B-201 Core 26 Sludge Washing and Alkaline Leaching Tests

	Component Dissolved, %							
	0.1 M NaOH Wash		3 M NaOH Leach		1 M K_2CO_3 Leach		Leached Sludge	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Al	1	0	16	16	1	0	84	82
Ba	2	0	11	0	2	0	100	84
Bi	0	0	3	0	1	0	100	96
Ca	0	0	2	0	1	1	99	97
Cr	33	33	15	15	2	2	50	50
Fe	1	1	0	0	0	0	99	99
La	0	0	1	0	0	0	100	98
Mg	2	0	14	0	3	0	100	80
Mn	0	0	0	0	0	0	100	100
Na	(a)	(a)	(a)	(a)	(a)	(a)	3	3
P	3	3	10	10	2	2	85	85
Pb	3	3	15	0	3	0	97	79
Si	8	8	28	28	4	4	60	60
Sr	1	0	3	0	1	0	100	95
Ti	1	0	4	0	1	0	100	94

(a) Because of the relatively large amount of Na added as NaOH, the percentage of Na dissolved from the sludge in each step could not be determined accurately. The percentage of Na reported for the leached sludge is based on that found initially in the sludge by direct analysis and that found in the leached sludge.

Table 2.4. Results from the B-201 Core 27 Sludge Washing and Alkaline Leaching Tests

	Component Dissolved, %							
	0.1 M NaOH Wash		3 M NaOH Leach		1 M K_2CO_3 Leach		Leached Sludge	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Al	2	0	39	38	5	5	56	55
Ba	11	0	13	0	15	0	0	0
Bi	1	0	2	0	2	0	100	95
Ca	1	1	1	0	2	2	97	96
Cr	41	41	24	24	9	9	26	26
Fe	0	0	0	0	0	0	99	99
La	1	0	1	0	1	0	100	97
Mg	10	0	11	0	13	0	100	66
Mn	0	0	0	0	0	0	100	100
Na	(a)	(a)	(a)	(a)	(a)	(a)	1	1
P	14	14	25	25	7	7	54	54
Pb	9	0	18	17	13	12	69	63
Si	10	10	55	55	5	5	30	30
Sr	2	0	3	0	3	0	100	92
Ti	2	0	3	0	3	0	100	92

(a) Because of the relatively large amount of Na added as NaOH, the percentage of Na dissolved from the sludge in each step could not be determined accurately. The percentage of Na reported for the leached sludge is based on that found initially in the sludge by direct analysis and that found in the leached sludge.

A result of special interest regarding minimizing the amount of glass formed from vitrifying the alkaline-leached sludge is the poor removal of P. A cumulative total of only 15% (core 26) to 46% (core 27) removal of P was observed. Both the dilute (0.1 M) hydroxide and the concentrated (3 M) hydroxide contacts removed P to an appreciable extent, with the strong caustic solution being roughly twice as effective as the dilute hydroxide solution. The carbonate leaching step was performed because P might be solubilized by phosphate metathesis with carbonate in salts such as calcium phosphate which cannot be metathesized with caustic (calcium is a large component in the B-201 sludge). But carbonate leaching was only marginally effective, with < 10% additional P removal being achieved.

The behavior of the radioactive components is summarized in Table 2.5. Except for Tc, (which was detected in only one core sample at close to its detection limits), the majority of radioactive components were not removed by these alkaline sludge treatments. Even for ^{137}Cs, which might be expected to be soluble under alkaline conditions, only 15-40% was removed by these treatments. The incomplete removal of ^{137}Cs by sludge washing, which was initially unexpected, has been observed for a number of tank samples (Lumetta, Rapko, Wagner, Carlson, and Barrington 1994, Lumetta, Wagner, Colton, and Jones 1993), so that now efficient Cs removal under alkaline conditions might be considered the exception rather than the rule. The other radionuclides showed little inclination to dissolve under alkaline treatment. Strontium-90 and ^{241}Am did not dissolve at all. Plutonium was solubilized to some extent by the carbonate leach step, with 15-25% of the Pu being dissolved. If the wash and alkaline (NaOH and K_2CO_3) leach solutions were combined and concentrated to 5 M Na plus K, the TRU concentration would be ~ 0.05 μCi/mL. Because of the partial Pu dissolution, and the lack of additional P removal, carbonate leaching of B-201 sludge is not recommended.

Table 2.5. Behavior of Radionuclides in the B-201 Sludge Washing and Alkaline Leaching Tests

Core 26	uCi/g Dry Sludge		Component Dissolved, %			
	Summation	Direct	0.1 M NaOH	3 M NaOH	1 M K2CO3	Residue
Total Alpha	2.13E+00	2.26E+00	0	0	26	74
$^{239,240}Pu$	2.99E+00	2.39E+00	0	0	25	75
^{99}Tc	Not Detected	Not Detected	–	–	–	–
^{90}Sr	6.63E+00	4.22E+00	0	0	0	100
^{137}Cs	7.65E-01	1.23E+00	22	12	5	61
^{241}Am[(a)]	6.43E-02	7.17E-02	0	0	0	100

Core 27	uCi/g Dry Sludge		Component Dissolved, %			
	Summation	Direct	0.1 M NaOH	3 M NaOH	1 M K2CO3	Residue
Total Alpha	1.93E+00	2.43E+00	0	0	15	85
$^{239,240}Pu$	2.46E+00	2.48E+00	0	0	14	86
^{99}Tc	Not Detected	3.50E-03	–	–	–	–
^{90}Sr	6.23E+00	6.26E+00	0	0	0	100
^{137}Cs	6.98E-01	1.55E-01	11	4	0	85
^{241}Am[(a)]	5.69E-02	5.85E-02	0	0	0	100

Wet Core 26	uCi/g Wet Sludge		Component Dissolved, %			
	Summation	Direct	0.1 M NaOH	3 M NaOH	1 M K2CO3	Residue
Total Alpha	1.26E+00	not done	0	0	0	100
$^{239,240}Pu$	1.17E+00	not done	0	0	0	100
^{99}Tc	2.17E-05	not done	100	0	0	0
^{90}Sr	1.64E+00	not done	0	0	0	100
^{137}Cs	1.68E-01	not done	29	0	13	59
^{241}Am[(a)]	2.74E-02	not done	0	0	0	100

(a) Am concentrations obtained by gamma spectroscopy.

The impact of initially drying the B-201 sludge on leaching behavior was also evaluated. Table 2.6 shows the elemental composition of the residue of a core 26 sample of B-201 sludge following the alkaline treatments described above. In one case, the sludge was dried at 80°C before treatment (dry sludge) and in the other instance the sludge sample was used as received (wet sludge). Little difference in the overall mass changes was observed if the initial weight loss due to drying is taken into account. Overall, little difference in the final composition is apparent, which indicates that the initial drying step had negligible impact on the alkaline treatment results.

Table 2.6. Comparison of Wet vs Dry Sludge Residue Compositions from Composite Core 26 Samples from Tank B-201 After Sludge Washing and Alkaline Leaching

	g/g Dried Residue	
	Dried Core 26 Test	Wet Core 26 Test
Al	1.0E-02	1.2E-02
Ba	9.2E-04	6.8E-04
Bi	2.3E-01	2.6E-01
Ca	3.8E-02	4.2E-02
Cr	5.2E-03	7.1E-03
Fe	3.8E-02	4.5E-02
La	4.8E-02	5.6E-02
Mg	7.0E-03	5.8E-03
Mn	7.0E-02	7.3E-02
Na	3.1E-02	1.8E-02
P	1.7E-02	1.8E-02
Pb	3.9E-03	2.6E-03
Si	3.3E-02	5.9E-02
Sr	2.4E-03	2.7E-03
Ti	1.3E-03	1.5E-03

Anion analyses were performed on all solid residues and on all of the wash solutions obtained during the sludge washing and alkaline leaching sequence. The results for cores 26 and 27 are shown in Table 2.7. The very high detection limits in these anion analyses discourage detailed analysis and restrict the interpretation to a description of broad trends. Both sludge cores show similar initial features and appear to respond analogously to the sludge washing and alkaline leaching sequence.

The anion content of the untreated sludges is dominated by the presence of nitrate and fluoride, with chloride and nitrite present to a much lesser extent. Nitrate, nitrite and chloride respond similarly to the sludge washing and alkaline leaching sequence: the majority of each of these anions is removed by the 0.1 M NaOH sludge wash with residual amounts removed during the 3 M NaOH caustic leach. In all cases, the anion concentration was removed to below detection limits, with roughly a two order of magnitude decrease in nitrate being discerned.

Fluoride responded somewhat differently to the sludge washing and alkaline leaching sequence, with about half of the anion removed during the 0.1 M NaOH wash and about two thirds of the remainder being removed during the 3 M NaOH leach. This behavior suggests that caustic metathesis of some insoluble fluoride salt(s) occurred. The carbonate leach had little discernable influence, although some additional fluoride appeared to be removed, bringing the total residual fluoride concentration to below detection limits; a decrease of roughly two orders of magnitude.

Table 2.7. Ion Chromatography Analyses From the B-201 Core 26 and Core 27 Washing and Leaching Test

Core 26 Anion	Initial Sludge, $\mu g/g$	Concentration: 0.1 M NaOH Wash Step		3 M NaOH Leach Step		1 M K_2CO_3 Wash Step	
		Solution, $\mu g/mL$	Sludge, $\mu g/g$	Sludge, $\mu g/mL$	Sludge, $\mu g/g$	Sludge, $\mu g/mL$	Sludge, $\mu g/g$
F	16,400	7.5	10,000	<6.4	3,000	2.7	<1,450
Cl	3,700	2.1	<2,450	<0.25	<1,250	<0.5	<1,450
NO_2	3,000	2	<4,900	<0.5	<2,500	<1	<2,700
Br	<650	<0.5	<2,450	<0.25	<1,250	<0.5	<1,450
NO_3	110,000	58	6,000	0.9	<2,500	<1	<2,900
PO_4	<1,300	<1	<4,900	2.6	4,000	<1	<2,900
SO_4	2,000	<1	5,000	0.5	<2,500	<1	<2,900

Core 27 Anion	Initial Sludge, $\mu g/g$	Concentration: 0.1 M NaOH Wash Step		3 M NaOH Leach Step		1 M K_2CO_3 Wash Step	
		Solution, $\mu g/mL$	Sludge, $\mu g/g$	Sludge, $\mu g/mL$	Sludge, $\mu g/g$	Sludge, $\mu g/mL$	Sludge, $\mu g/g$
F	21,100	12.5	11,000	<6.4	4,000	<2.6	<3,750
Cl	4,100	2.7	<1,650	<0.5	<1,550	<0.5	<3,750
NO_2	4,000	3	<3,300	<1	<3,100	<1	<7,500
Br	<725	<0.5	<1,650	<0.5	<1,550	<0.5	<3,750
NO_3	99,000	73	4,000	<1	<3,100	<1	<7,500
PO_4	3,000	2	4,000	3	<3,100	<1	<7,500
SO_4	2,000	<1	4,000	<1	4,000	<1	8,000

A combination of relatively low concentrations and high detection limits resulted in anion analysis revealing little about the response of PO_4^{3-} and SO_4^{2-} to the sludge washing and alkaline leaching sequence. Some phosphate is detected in the 0.1 M NaOH wash and 3 M NaOH leach solutions with the core 26 sample and some phosphate is detected in the 3 M NaOH leach solution with the core 27 sample. This order of 3 M NaOH > 0.1 M NaOH > 1 M K_2CO_3 is consistent with the elemental analysis results (Tables 2.3 and 2.4), if P is present as PO_4^{3-}. In the case of sulfate, very little is revealed about from the anion analyses. Indeed, the relatively large concentration of SO_4^{2-} in the final residue of core 27 is internally inconsistent with the other anion analysis results. The detection of a small amount of sulfate in the caustic leach solution following contact with core 26 suggests that some sulfate may be removed during this step, but, again, the internal inconsistencies the analysis of the solids and the high detection limits prevent the drawing of any firm conclusion.

Particle size analyses were performed on both the untreated sludges and for the undissolved residues. The results were obtained both in terms of the number of particles present in a given size range and in terms of the volume (assuming that the particles are spheres) in a given size range and are summarized in Table 2.8 and Figures 2.4 through 2.11. By volume, cores 26 and 27 both show a broad range of particle sizes (0.05 to 70 μm), with core 27 weighed more heavily towards the upper ranges. In contrast, by number core 27 seems more weighed towards the lower end as compared with core 26, which seems to have a fairly narrow band of particles present. Following the alkaline treatments, the two samples differ somewhat in their response. Core 26 seems to have kept a broad range of particle sizes by volume similar to that seen before treatment, albeit reduced overall towards smaller particle sizes. For core 27, however, a very small and narrow band of particles sizes by volume is seen following treatment, with a substantial overall decrease in particle sizes. By number, core 26 shows little change in the >2 μm particle sizes, but a marked increase in the proportion of particles <2 μm in size. The most remarkable feature about core 27 is the complete loss of the small number of large (>6 μm) particles, and little other observed changes.

Table 2.8. Particle Size Data for B-201 Sludge Composites

Sample	Type of Analysis	Median (μm)	Mean (μm)	Mode (μm)
Core 26, Untreated	Number	0.8	1.1	0.7
Core 26, Untreated	Volume	15.4	16.4	30.1
Core 27, Untreated	Number	1	1.5	0.8
Core 27, Untreated	Volume	74.7	71.3	118.4
Core 26, Leached Sludge	Number	1	1.4	0.8
Core 26, Leached Sludge	Volume	10.5	12.6	19.5
Core 27, Leached Sludge	Number	1.1	1.4	1.25
Core 27, Leached Sludge	Volume	3.8	3.5	4.3

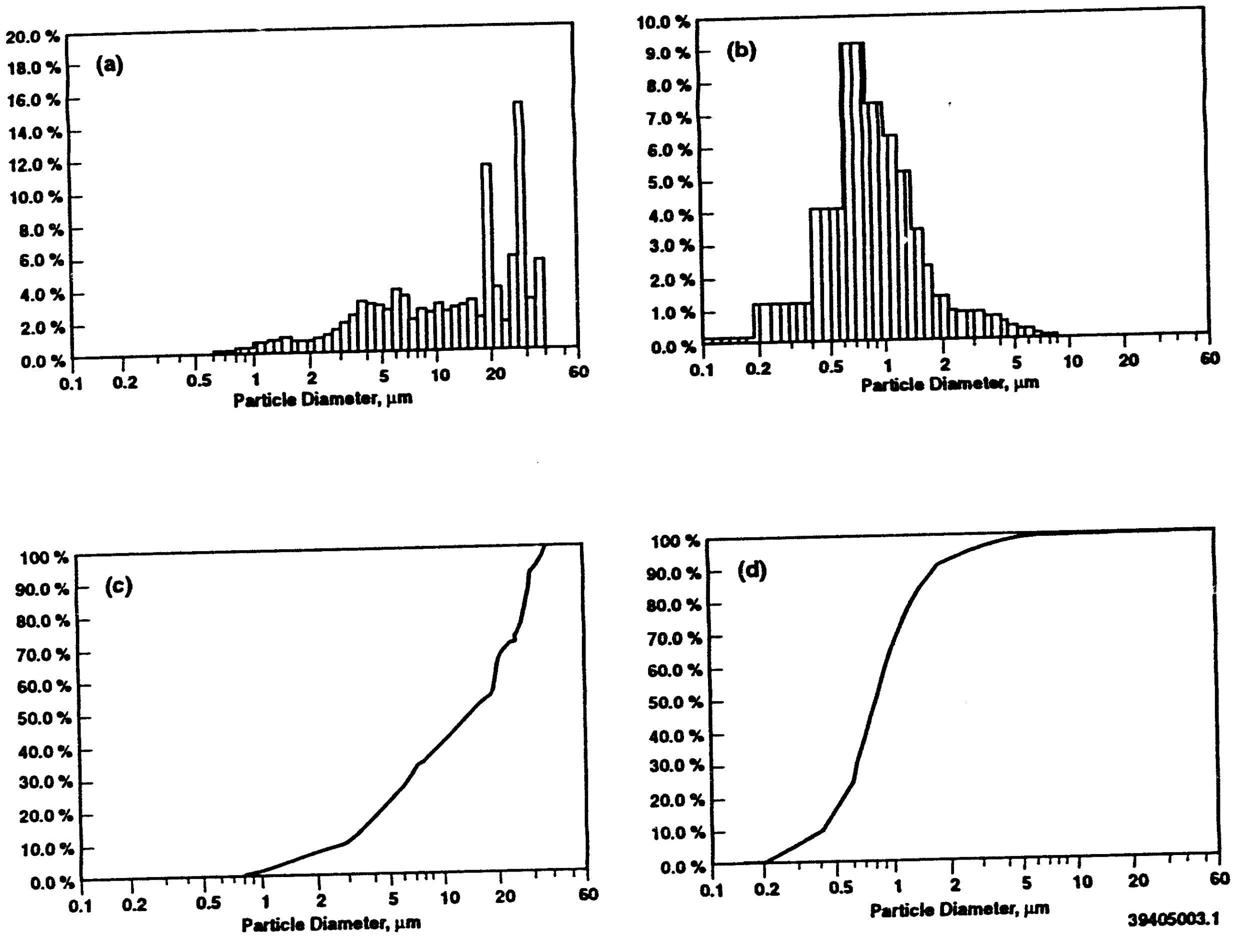

Figure 2.4. Particle Size Analysis of Dried Untreated B-201 Core 26 Sludge: a) Probability Volume Density Graph, b) Probability Number Density Graph, c) Probability Volume Distribution Graph, and d) Probability Number Distribution Graph

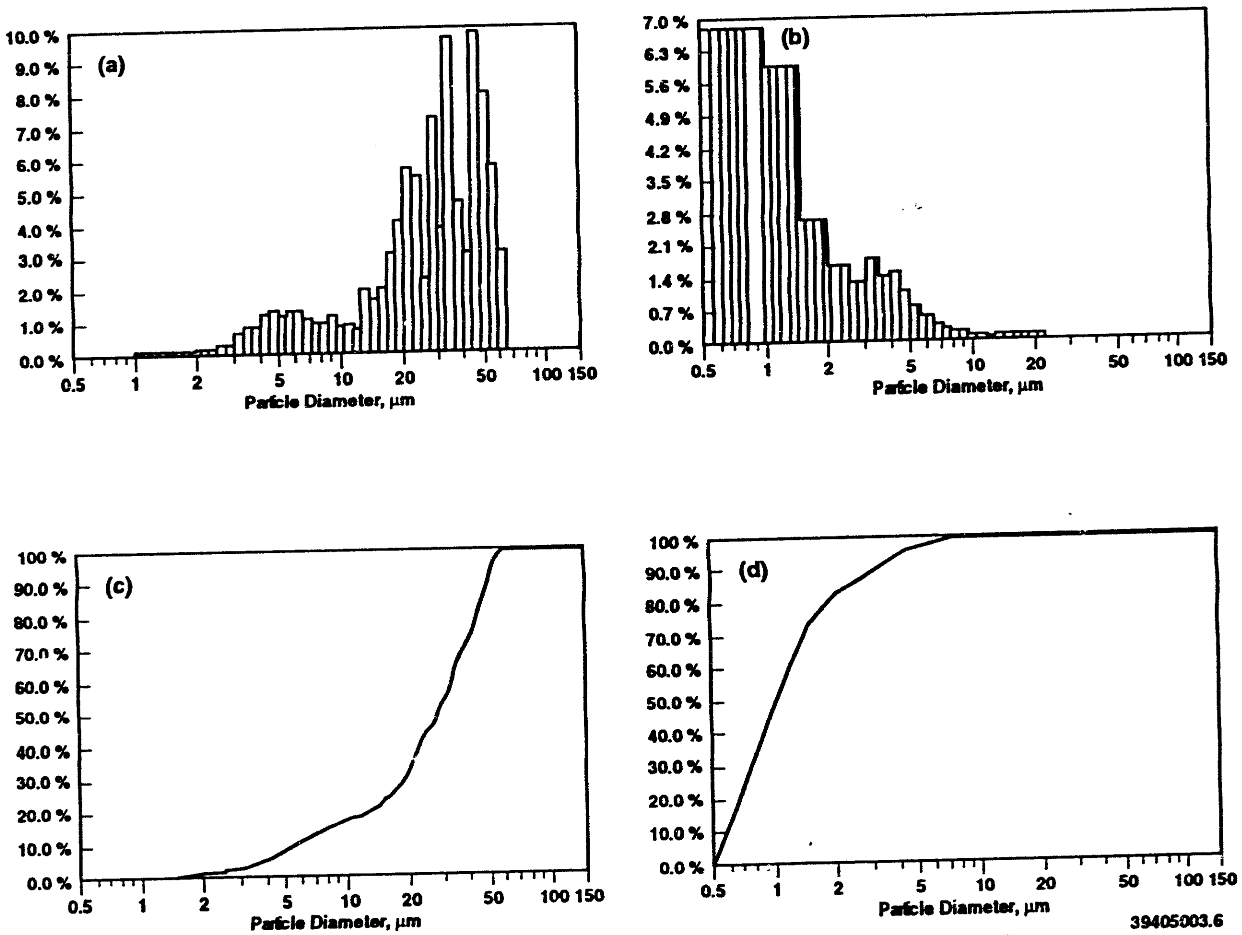

Figure 2.5. Particle Size Analysis of B-201 Core 26 Sludge After Washing With 0.1 M NaOH: a) Probability Volume Density Graph, b) Probability Number Density Graph, c) Probability Volume Distribution Graph, and d) Probability Number Distribution Graph

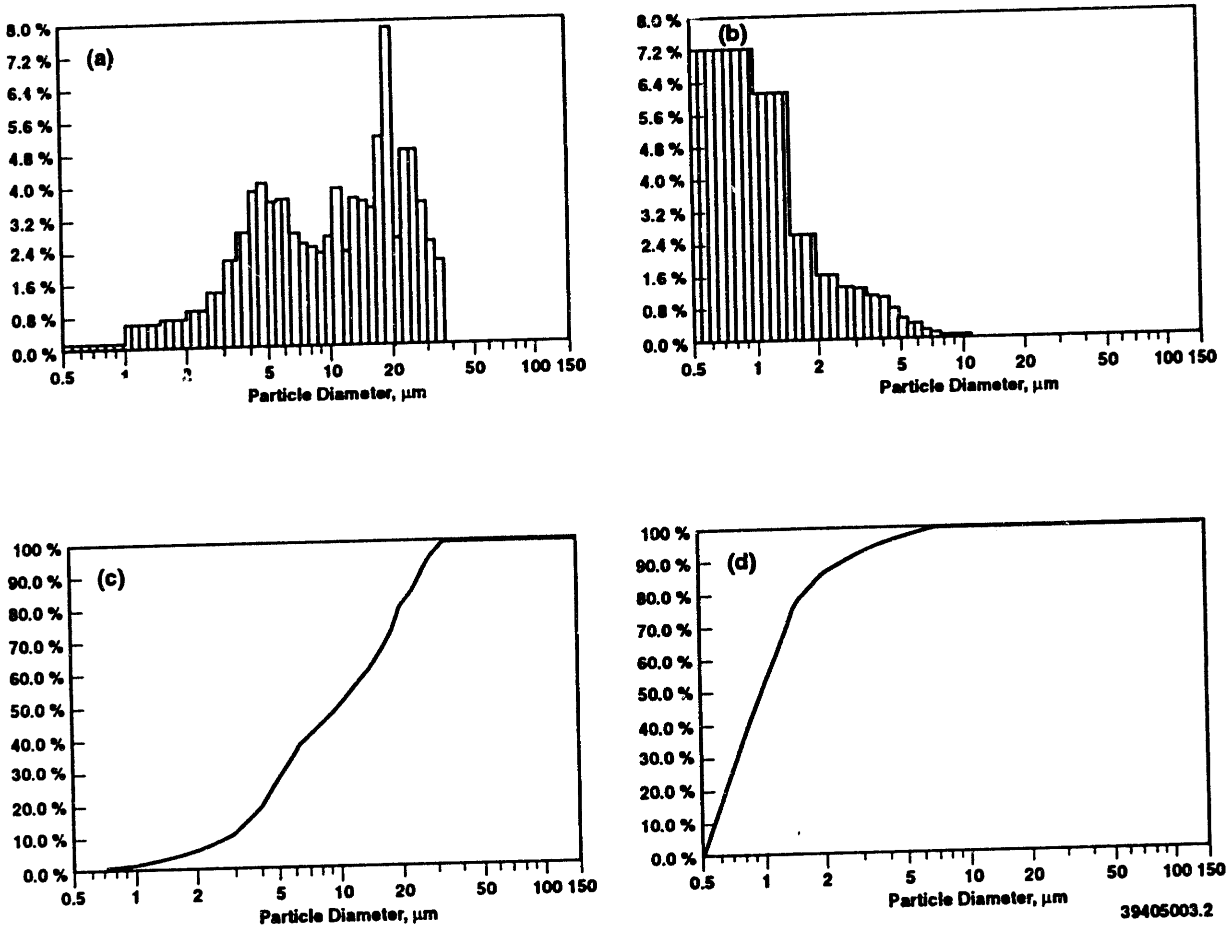

Figure 2.6. Particle Size Analysis of B-201 Core 26 Sludge After 3 M NaOH Leach: a) Probability Volume Density Graph, b) Probability Number Density Graph, c) Probability Volume Distribution Graph, and d) Probability Number Distribution Graph

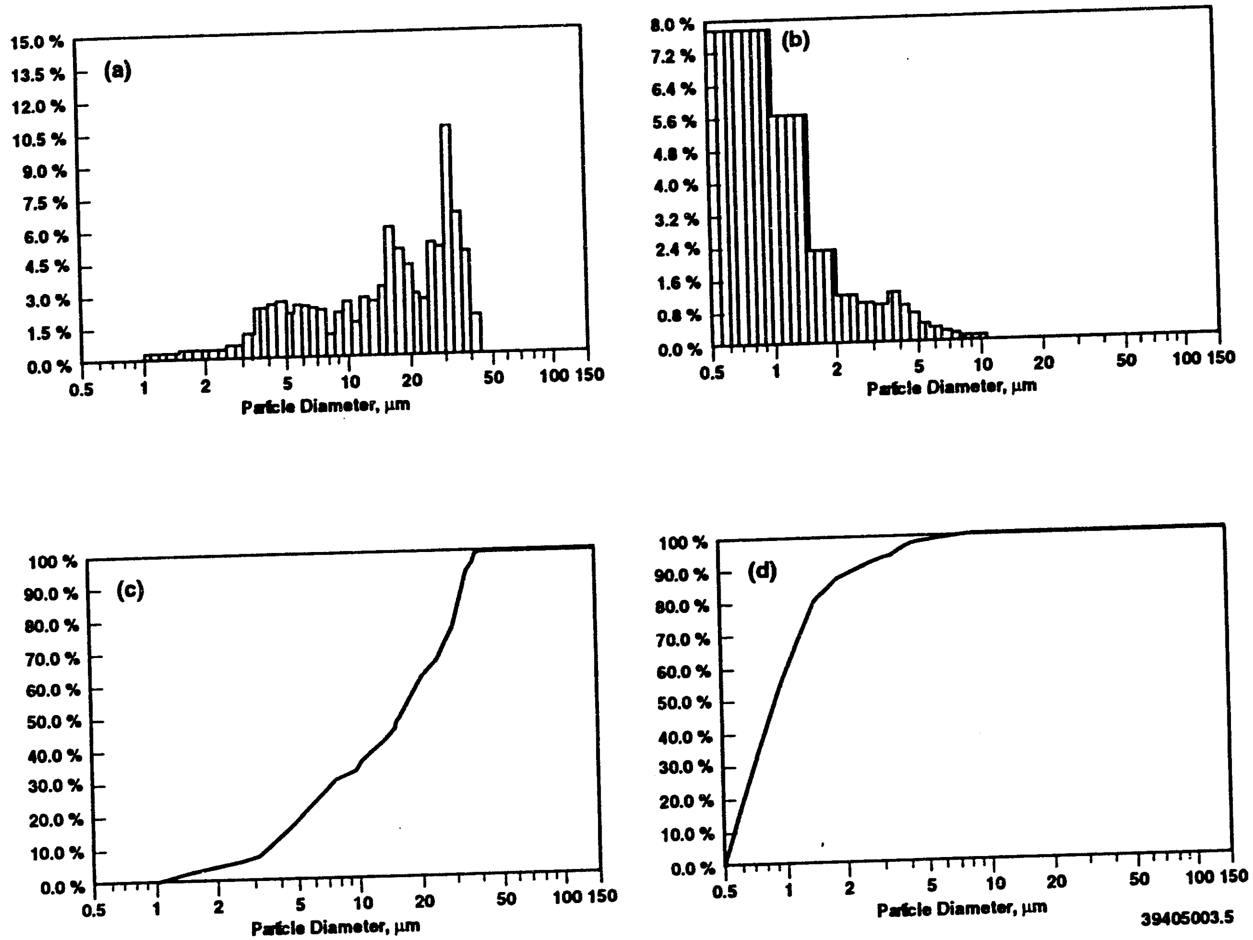

Figure 2.7. Particle Size Analysis of B-201 Core 26 Sludge 1 M K_2CO_3 Leach: a) Probability Volume Density Graph, b) Probability Number Density Graph, c) Probability Volume Distribution Graph, and d) Probability Number Distribution Graph

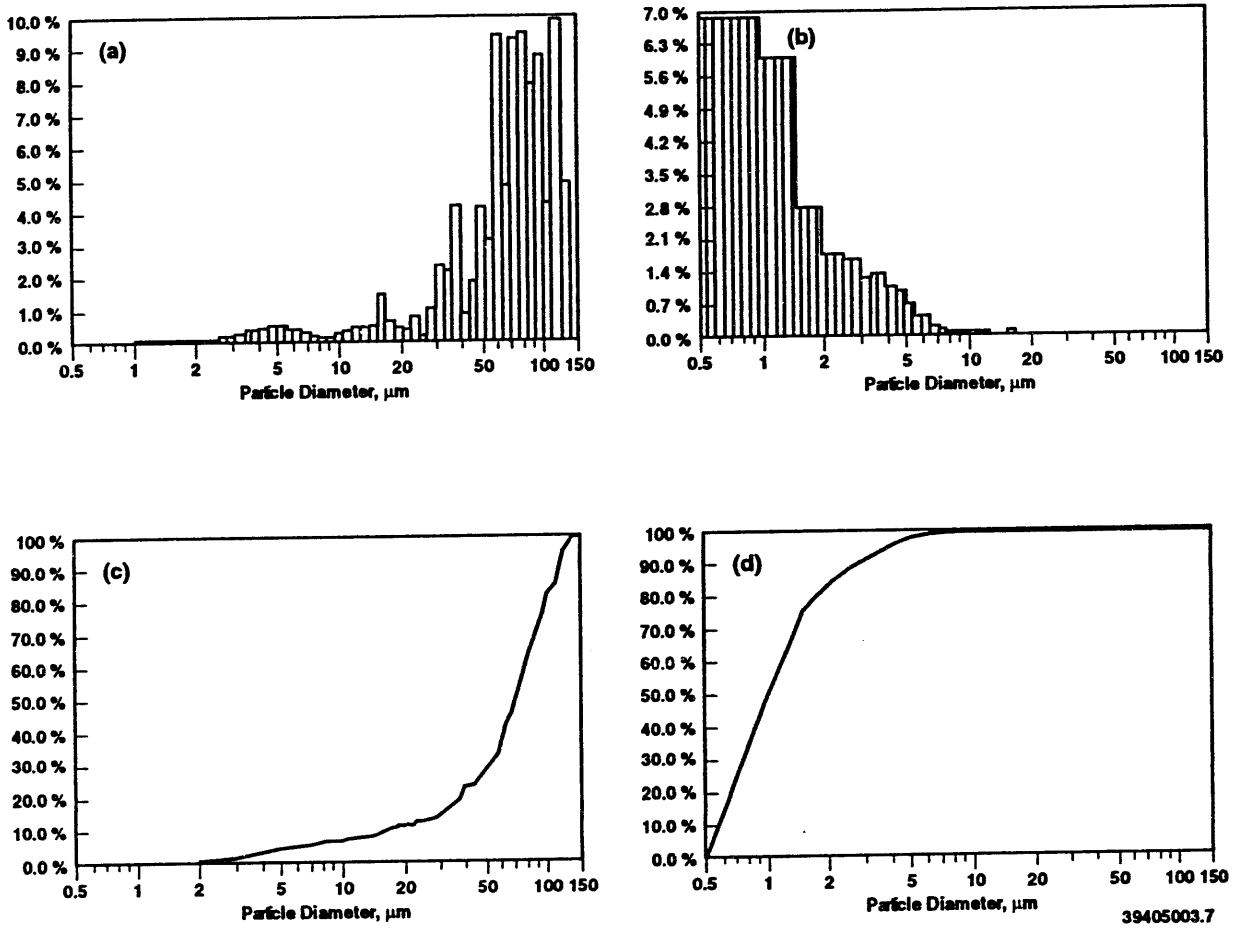

Figure 2.8. Particle Size Analysis of Dried Untreated B-201 Core 27 Sludge: a) Probability Volume Density Graph, b) Probability Number Density Graph, c) Probability Volume Distribution Graph, and d) Probability Number Distribution Graph

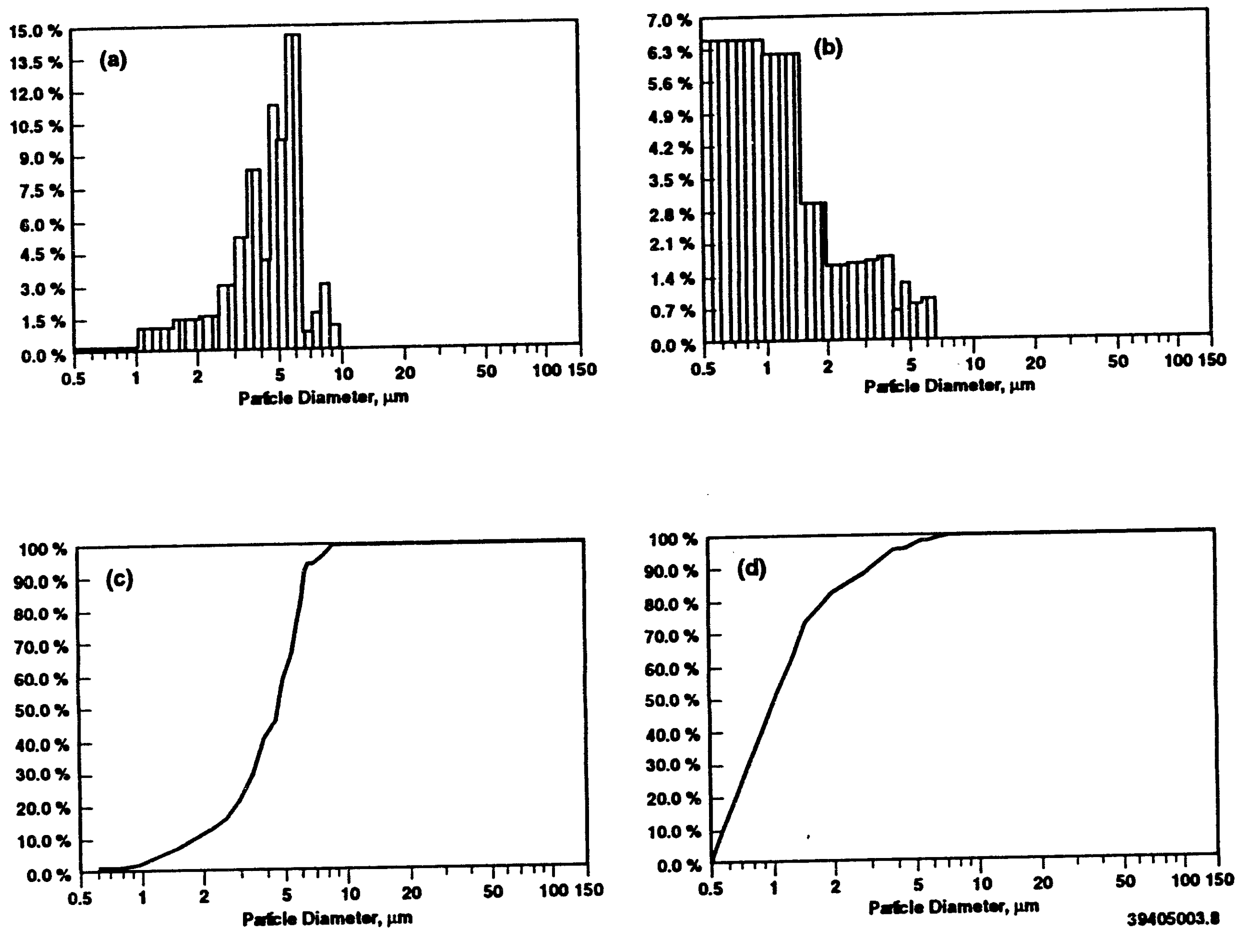

Figure 2.9. Particle Size Analysis of B-201 Core 27 Sludge After Washing With 0.1 M NaOH: a) Probability Volume Density Graph, b) Probability Number Density Graph, c) Probability Volume Distribution Graph, and d) Probability Number Distribution Graph

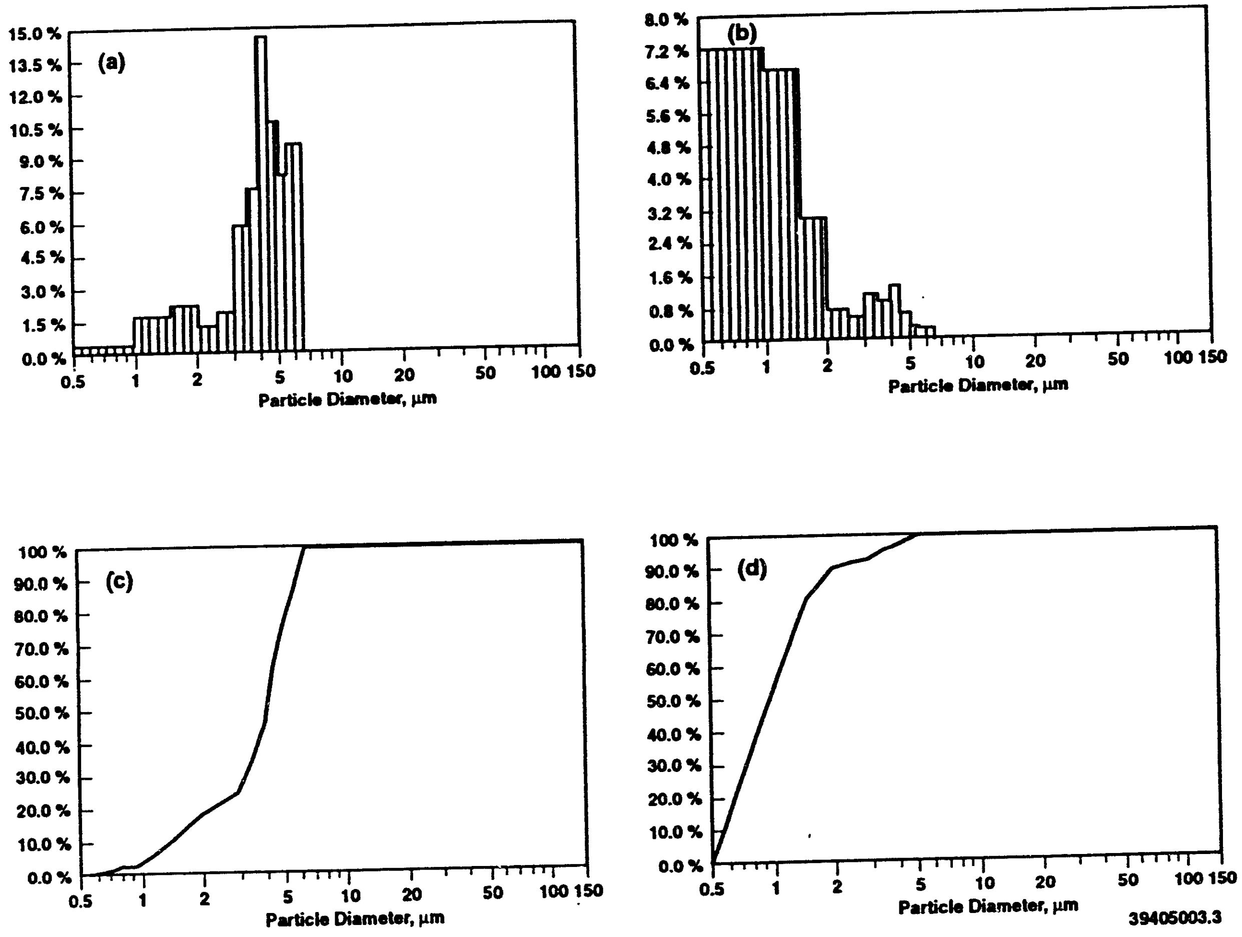

Figure 2.10. Particle Size Analysis of B-201 Core 27 Sludge After 3 M NaOH Leach: a) Probability Volume Density Graph, b) Probability Number Density Graph, c) Probability Volume Distribution Graph, and d) Probability Number Distribution Graph

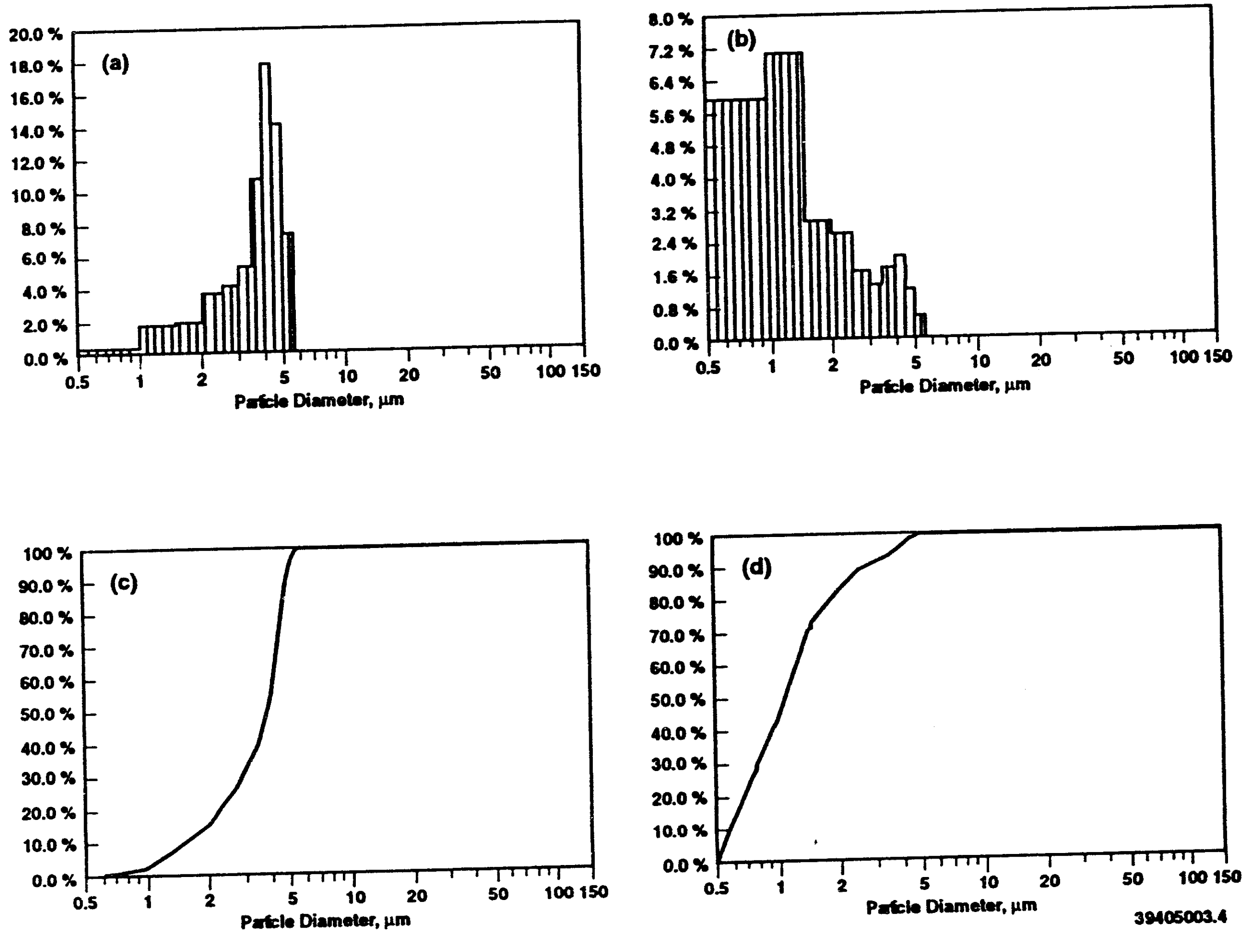

Figure 2.11. Particle Size Analysis of B-201 Core 27 Sludge 1 M K_2CO_3 Leach: a) Probability Volume Density Graph, b) Probability Number Density Graph, c) Probability Volume Distribution Graph, and d) Probability Number Distribution Graph

3.0 Sludge Washing and Alkaline Leaching of SST U-110 Sludge

The primary waste type stored in SST U-110 is the neutralized first-cycle decontamination waste from the bismuth phosphate process. Other wastes added to this tank include REDOX process HLW, cladding waste, and laboratory waste from the 222-S building (Hill and Simpson 1994). The U-110 sludge has a relatively high Al content.

Previous work with U-110 sludge indicated some inconsistencies in the amount of P removed from the sludge by washing or leaching. For example, when a portion of U-110 sludge was washed with 0.01 M NaOH at room temperature, ≥56%[(a)] of the P was removed (Lumetta, Wagner, Colton, and Jones 1993). However, when another portion of U-110 sludge was leached directly with 5 M NaOH at 100°C, only 35 to 49% of the P was removed from the sludge (Lumetta, Rapko, Wagner, Carlson, and Barrington 1994). Treatment of the caustic-leached U-110 sludge with a carbonate solution resulted in additional removal of P. In the current test, a portion of U-110 sludge was washed with 0.1 M NaOH, then was leached with a combined caustic/carbonate solution in an attempt to demonstrate complete P removal from the sludge.

The test procedure is described schematically in Figure 3.1. A dry[(b)] 0.57-g composite sample from core 14 was stirred for 1 h at room temperature with ~3 mL of 0.1 M NaOH. The mixture was centrifuged and the wash solution was decanted. The sludge was then washed in a similar manner with 2 mL of water to removed dissolved materials in the interstitial liquid. The washed sludge was stirred for 5 h at 100°C with 4 mL of a solution consisting of 3 M NaOH plus 2 M Na_2CO_3. After cooling, the mixture was centrifuged and the supernatant liquor (first leach solution) was decanted. Another 4 mL of 3 M NaOH/2 M Na_2CO_3 was added and the mixture was again stirred for 5 h at 100°C. After cooling to room temperature and centrifuging, the supernatant liquor was sampled for analysis (a total of 0.2 mL solution was withdrawn). To determine if ultrasonic methods would improve the leaching efficacy, the mixture was sonicated for 5 h at ~20°C. The mixture was then centrifuged and the leach liquor decanted (second leach solution). The leached sludge was washed twice with 3-mL portions of water to remove any dissolved materials in the interstitial liquid. The remaining sludge was dissolved by successive treatment with 1) 2 M HNO_3 and 2) 2 M HNO_3/1 M HF; both dissolution steps were conducted at 100°C.

(a) A value of 100% P removal by sludge washing was reported earlier (Lumetta, Wagner, Colton, and Jones 1993), but this value was found to be overstated upon subsequent analysis of the data. Taking ICP detection limits into account, the value of ≥56% was obtained. A complete reevaluation of the data from this earlier experiment is discussed in a separate report (Lumetta, G. J., R. J. Barrington, and M. J. Wagner. 1994. *Sludge Dissolution Laboratory Studies: Report for the Third Quarter FY 1994.* TWRSPP-94-050, Pacific Northwest Laboratory, Richland, Washington.)

(b) The composite U-110 sludge sample had dried under ambient conditions in the hot cell where it was stored.

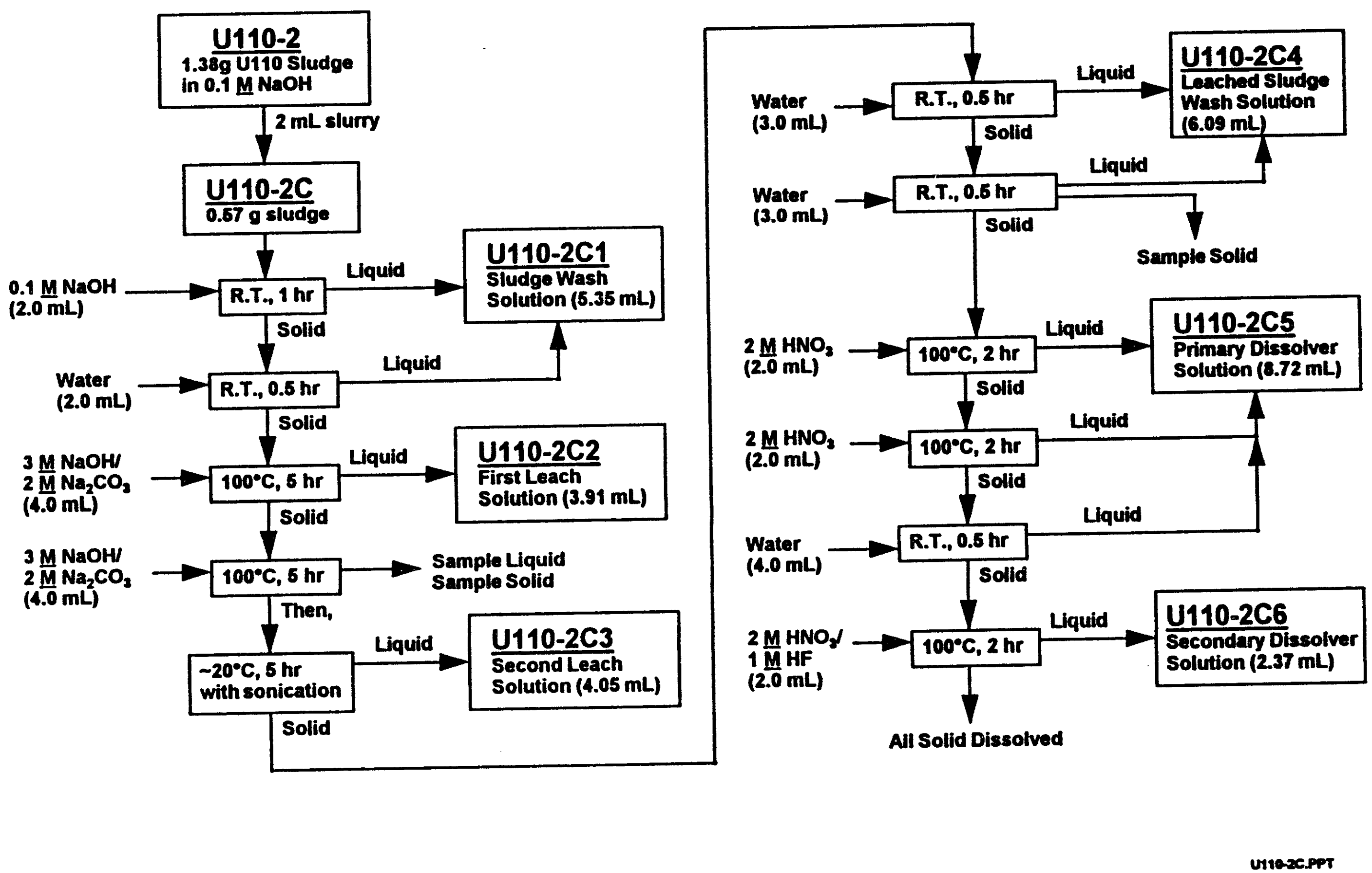

Figure 3.1. Schematic of U-110 Sludge Washing and Alkaline Leaching Test

The results for the nonradioactive sludge components are presented in Table 3.1. Except for Na, Al was the most abundant metallic element in the U-110 sludge, comprising ~20 wt % of the wet sludge. Little Al was removed by washing with 0.1 M NaOH, but a significant fraction (83%) was removed by leaching twice with 3 M NaOH/2 M Na_2CO_3. These findings are consistent with previous work (Lumetta, Wagner, Colton, and Jones 1993; Lumetta, Rapko, Wagner, Carlson, and Barrington 1994). The only other metallic element appreciably removed from the sludge was Cr. Most of the Cr (64 to 73%) was removed in the dilute NaOH wash step. Only a small portion of the Si was removed by washing and caustic leaching.

In this test with U-110 sludge, P was effectively removed from the sludge. Washing with 0.1 M NaOH removed ~90% of the P. Less than 2% of the P remained after the two caustic leaching steps.

In comparing to previous caustic leaching results (Lumetta, Rapko, Wagner, Carlson, and Barrington 1994), it appears that directly leaching U-110 sludge with high caustic results in less P removal than when the sludge is washed with dilute NaOH. There are at least two possible explanations for this observation. First, the interstitial liquid in the sludge might contain soluble phosphate that readily washes out when the sludge is washed at room temperature. Under these conditions (room temperature) metathesis of $Ca(OH)_2$ to $Ca_3(PO_4)_2$ would be expected to be slow. When the sludge was directly leached with high caustic, however, the temperature was 100°C. At this temperature, metathesis to $Ca_3(PO_4)_2$ might be more rapid, causing the phosphate to precipitate into the sludge as $Ca_3(PO_4)_2$. Second, $Na_7F(PO_4)_2 \cdot 19H_2O$ has been identified in U-110 sludge by x-ray diffraction (Jones et al. 1992). This salt has appreciable solubility in water, so it would be expected to be removed by sludge washing; however, the presence of a high concentration amount of Na would suppress dissolution by shifting the following equilibrium to the left.

$$Na_7F(PO_4)_2 \cdot 19H_2O(S) \leftrightharpoons 7Na^+(aq) + F^-(aq) + 2PO_4^{3-} + 19H_2O \qquad (3.1)$$

This could explain why less P dissolution occurred in the high caustic leach. Further work is needed to clarify the exact cause for these observations.

The behavior of sulfate ion was determined by ion chromatography. The wet U-110 sludge contained ~0.002 g SO_4^{2-}/g wet sludge; ≥65% of the SO_4^{2-} was removed in the wash step. The caustic-leached sludge contained ≤24% of the SO_4^{2-}.

The concentration of Na in the U-110 sludge sample was estimated to be ~0.5 g Na/g wet sludge. The caustic-leached U-110 sludge contained ~4% of the Na originally present. The leached sludge contained 1.7 g Na/g Fe.

Sonication provided marginal benefit to the alkaline leaching process. A comparison of the composition of the second leach solution before and after sonication is presented in Table 3.2. Slight increases in the amount of Al and P dissolved were observed, but good removal of these elements was achieved without sonication. No improvement in Si dissolution was achieved by sonicating.

Table 3.1. Results of Washing, Alkaline Leaching, and Dissolution of Tank U-110 Sludge

	g/g Dry Sludge		Amount of Component Found, %									
			Wash		First Leach Soln		Second Leach Soln		2 M HNO_3		2 M HNO_3/1 M HF	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Al	2.1E-01	2.1E-01	1	1	37	37	46	46	8	8	8	8
As	4.5E-04	2.1E-04	0	3	100	46	51	0	0	0	0	0
B	8.6E-04	7.1E-04	100	82	5	0	6	0	5	0	1	0
Ba	1.3E-04	7.4E-05	1	0	8	0	22	0	100	59	10	0
Bi	1.0E-02	8.0E-03	1	0	5	0	14	0	61	49	39	31
Ca	1.4E-03	1.2E-03	1	0	4	0	10	0	79	68	21	18
Cr	7.3E-04	6.4E-04	73	64	3	0	8	0	27	24	2	0
Fe	1.0E-02	1.0E-02	0	0	0	0	0	0	50	50	50	50
Mg	7.1E-04	2.1E-05	2	0	15	0	39	0	100	36	9	0
Mn	3.7E-03	3.6E-03	0	0	0	0	1	0	96	95	4	4
Ni	2.3E-04	5.3E-06	2	0	13	0	35	0	100	42	8	0
P	1.9E-02	1.8E-02	92	89	6	6	3	2	1	0	1	0
Si	1.1E-02	1.1E-02	6	5	4	4	4	3	4	0	87	83
Sr	4.3E-04	4.1E-04	0	0	1	0	3	0	97	93	3	3
Ti	3.3E-03	3.3E-03	0	0	0	0	0	0	82	81	18	18
U	1.4E-02	4.2E-04	2	0	15	0	39	0	100	36	9	0
V	1.8E-04	1.2E-04	1	0	6	0	100	76	13	0	4	0
Zn	1.4E-04	0.0E+00	2	0	14	0	38	0	33	0	13	0
Zr	2.1E-04	1.4E-04	1	0	5	0	13	0	11	0	100	70
SO_4^{2-}	2.2E-03	1.4E-03	100	65	4	0	7	0	19	0	5	0

Table 3.2. Comparison of the Composition of the U-110 Second Leach Solution Before and After Sonication

	Concentration, M	
	Before Sonication	After Sonication
Al	0.38	0.42
P	0.0015	0.0019
Si	0.0016	0.0016

Sonication of the leach mixture affected the particle size distribution of the sludge. Particle size data obtained at various points in the procedure are presented in Figures 3.2 to 3.4. For the untreated sludge (Figure 3.2), the number distribution indicated that nearly all the particles were less than 10-μm in diameter with the median particle diameter being 0.93 μm. On the other hand, the volume distribution indicated that 85% of the volume was occupied by particles greater than 10 μm in diameter, with a median particle size of 33 μm in diameter. After leaching twice with 3 M NaOH/2 M Na_2CO_3 at 100°C, the particle size number distribution had not significantly changed (compare Figures 3.2a and c to Figures 3.3a and c); the median particle diameter was 1.03 μm. However, the volume distribution had significantly changed (compare Figures 3.2b and d to Figures 3.3b and d). The entire sludge volume was occupied by particles with diameters less than 7 μm in diameter and the median particle diameter had decreased from 33 μm to 3.48 μm. Sonication reduced the particle size even further, giving a mixture of particles in which the number distribution was very similar to the volume distribution (Figure 3.4); the median particle diameter was 0.61 μm as determined from the number distribution compared to 0.79 μm as determined from the volume distribution.

The behavior of the radionuclides during the U-110 sludge washing and leaching test is presented in Table 3.3. Little TRU material was found in the wash and leach solutions. Less than 2.3% of the TRU material was present in these solutions; this equates to <0.009 μCi per gram (dry basis) of sludge processed. As expected from previous work with U-110 sludge (Lumetta, Wagner, Colton, and Jones 1993), the vast majority (>94.8%) of the TRU component was in the 2 M HNO_3 dissolved sludge solution. Similarly, little (1.5%) ^{90}Sr was removed from the sludge during washing and alkaline leaching. If the sludge wash solution and the alkaline leach solutions were combined and concentrated to 5 M Na, the TRU concentration would be <3.5 x 10^{-4} μCi/mL, the ^{90}Sr concentration would be 0.24 μCi/mL, and the ^{137}Cs concentration would be 0.09 μCi/mL. The resulting LLW form would likely meet the NRC Class C LLW criteria, but might exceed the Class A limits (10 CRF 61, 1988).

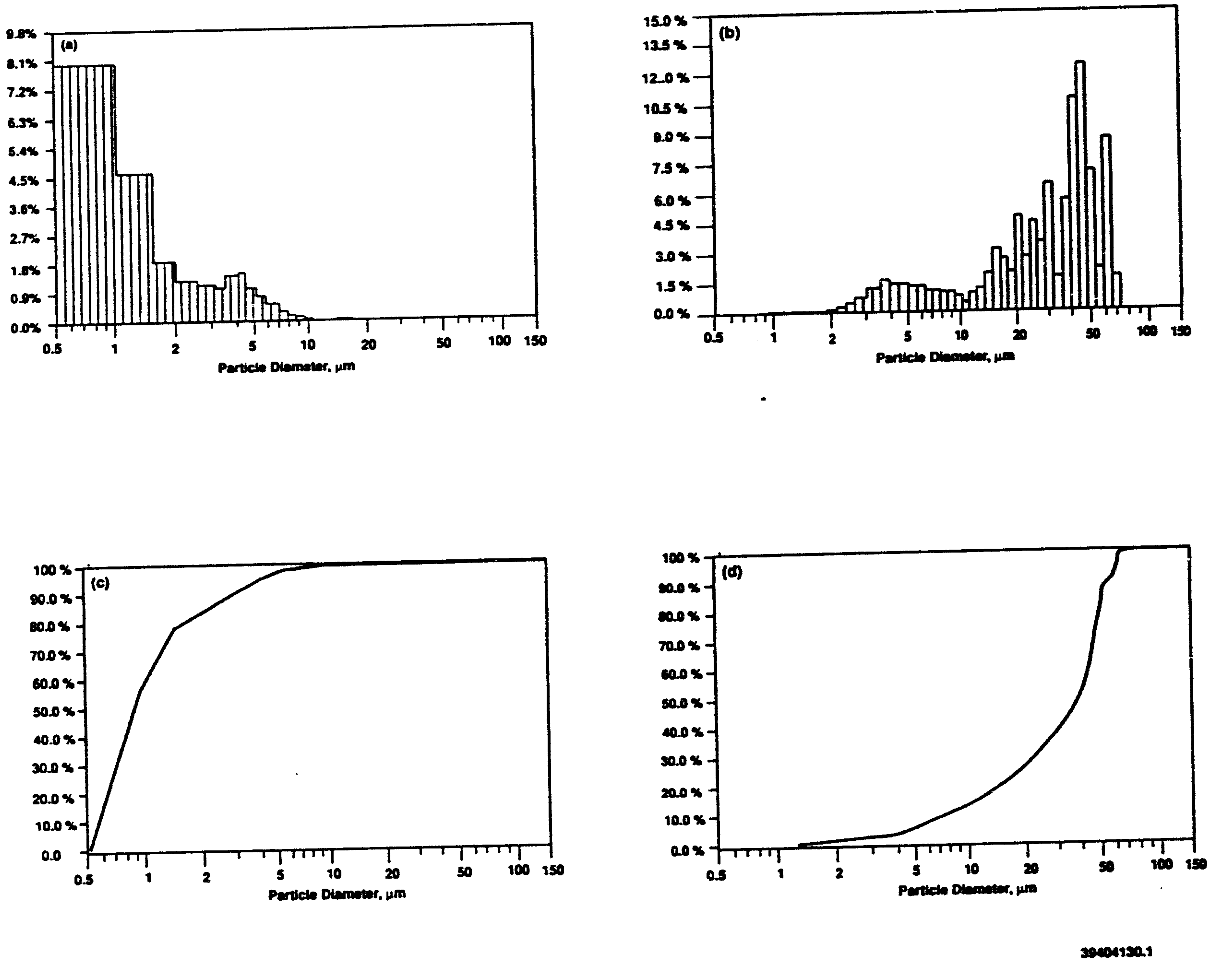

Figure 3.2. Particle Size Data for Untreated U-110 Sludge: a) Probability Number Density Graph, b) Probability Volume Density Graph, c) Probability Number Distribution Graph, and d) Probability Volume Distribution Graph

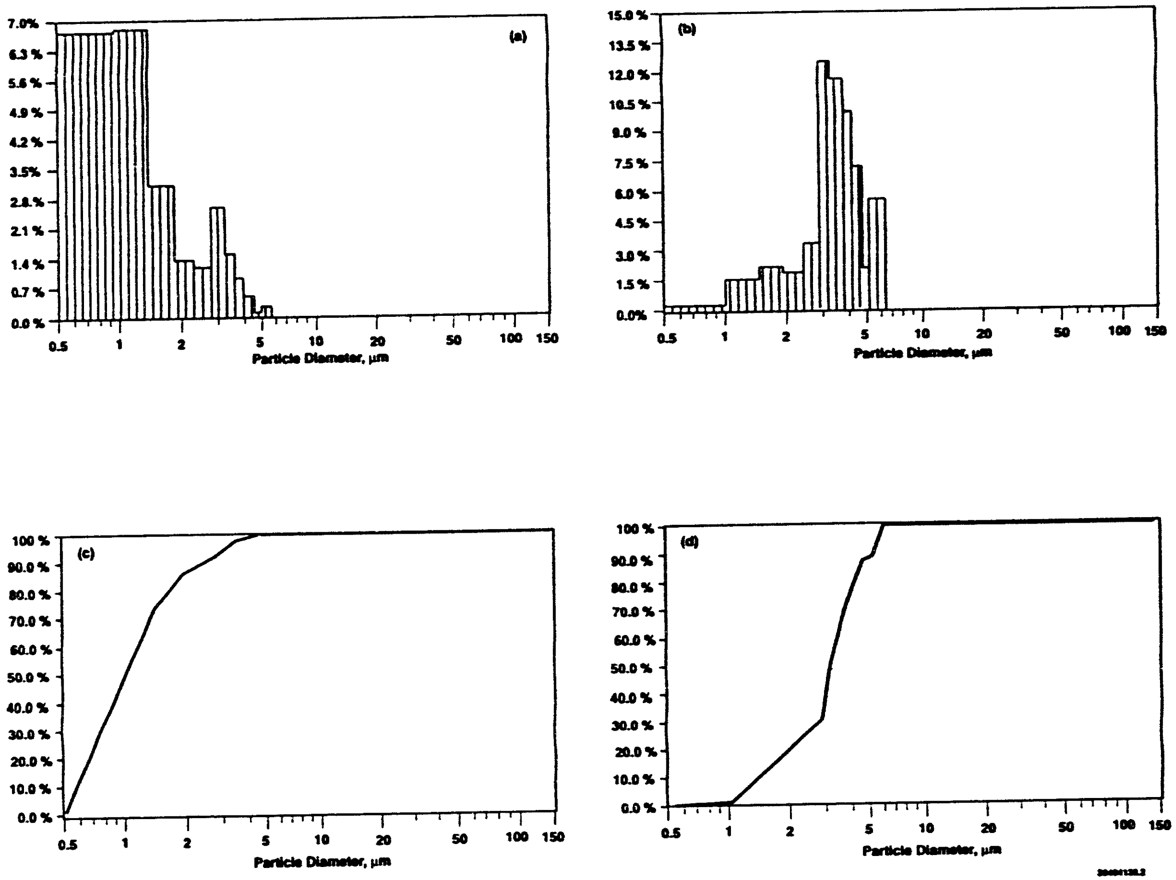

Figure 3.3. Particle Size Data for Alkaline-Leached U-110 Sludge Before Sonication Step: a) Probability Number Density Graph, b) Probability Volume Density Graph, c) Probability Number Distribution Graph, and d) Probability Volume Distribution Graph

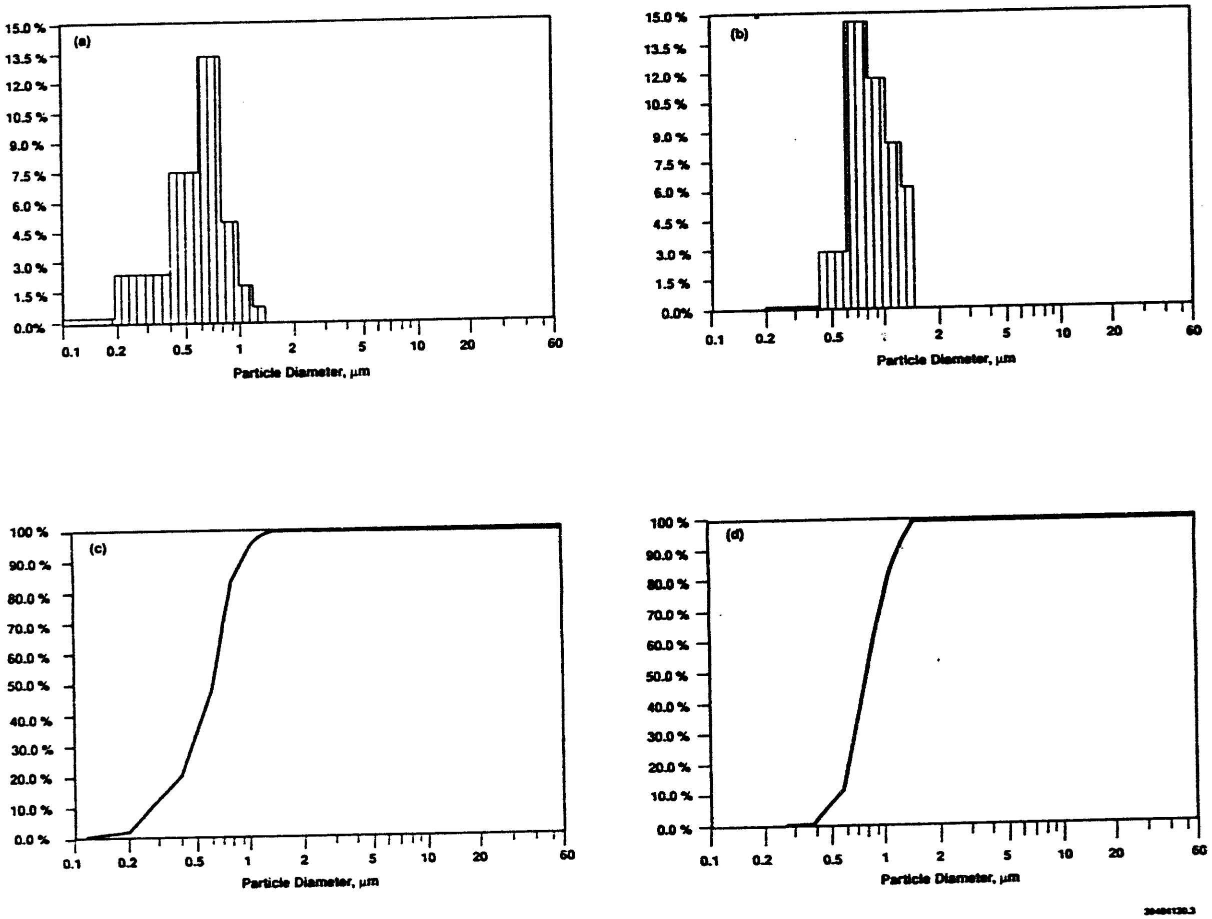

Figure 3.4. Particle Size Data for Alkaline-Leached U-110 Sludge After Sonication Step: a) Probability Number Density Graph, b) Probability Volume Density Graph, c) Probability Number Distribution Graph, and d) Probability Volume Distribution Graph

Table 3.3. Behavior of Radionuclides During Washing, Alkaline Leaching, and Dissolution of Tank U-110 Sludge

		Amount of Component Found, %				
	µCi/g Dry Sludge	Wash	First Leach Soln.	Second Leach Soln.	2 M HNO_3	2 M HNO_3/1 M HF
TRU	0.372	0.2	<0.6	<1.5, >0.1	<96.7, >94.8	2.8
$^{239+240}Pu^{(a)}$	0.254	0.3	0.0	0.0	96.6	3.1
$^{239+240}Pu^{(b)}$	0.226	0.4	0.0	0.0	95.3	4.3
$^{238}Pu + ^{241}Am^{(a)}$	0.104	0.2	0.0	0.0	97.8	2.0
$^{238}Pu^{(b)}$	0.007	3.8	0.0	0.0	87.6	8.6
$^{241}Am^{(c)}$	0.096	0.0	0.0	0.0	98.5	1.5
$^{241}Am^{(d)}$	0.093	0.0	0.0	0.0	100	0.0
$^{243+244}Cm$	0.002	0.0	0.0	0.0	100	0.0
^{90}Sr	370	0.0	0.6	0.9	94.8	3.7
^{137}Cs	22.1	5.1	1.7	3.0	89.2	0.9
^{60}Co	0.005	0.0	0.0	0.0	100	0.0
^{40}K	0.079	0.0	0.0	0.7	99.3	0.0
^{154}Eu	0.145	0.0	0.0	0.0	100	0.0
^{155}Eu	0.093	0.0	0.0	0.0	100	0.0

(a) Determined from the alpha energy spectra without separating Pu from the other alpha emitters.
(b) Determined from the alpha energy spectra after separating Pu from the other alpha emitters.
(c) Obtained by subtracting ^{238}Pu, determined by alpha energy analysis after separating Pu from the other alpha emitters, from $^{238}Pu + ^{241}Am$, which was determined by alpha energy analysis without separating Pu from the other alpha emitters.
(d) Determined from the gamma spectra.

4.0 Summary of Sludge Washing and Alkaline Leaching Studies

Sludge washing and alkaline leaching tests have been performed on five different SST wastes (B-110, B-201, C-109, C-112, and U-110). The results of these studies are summarized in this appendix. The results are divided into three parts: 1) sludge compositions, 2) results of sludge washing tests, and 3) results of caustic leaching tests.

During the course of the tank waste pretreatment studies, compositions were determinimumed for the various tank sludges. These compositions are presented in Tables 4.1 through 4.5 along with those determinimumed by the Tank Waste Characterization Program. In general, the compositions determinimumed in the course of the pretreatment studies agree with those obtained by the Characterization Program, especially for the major sludge components.

The results of the sludge washing tests are given in Tables 4.6 through 4.10. The results are presented in terms of the percent of each component removed by washing. For each test, a reference is provided where the experimental details can be found.

The results of sludge washing and alkaline leaching tests are given in Tables 4.11 through 4.14. The results are presented in terms of the cumulative removal of each component achieved by sludge washing and alkaline leaching. Again, appropriate references are provided for the experimental details.

The P:Ca mole ratios in the leached residues are of special interest. In each case, the P:Ca value is near the value of 0.67 expected for $Ca_3(PO_4)_2$, suggesting that this material may be the controlling one regarding phosphate leaching. Base on thermodynamic considerations, calcium phosphate would not be expected to be metathesized by caustic solutions, and these results support the hypothesis that $Ca_3(PO_4)_2$ is the primary phosphate material remaining after alkaline leaching.

Table 4.1. Summary of B-110 Sludge Composition

Core No.	1		1		1,2,3,4		
Ref.	(a)		(a)		(b)		(c)
Test No.	B110-4		B110-4		B110-6		N/A
	g/g Wet Sludge						
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	
Al	1.5E-03	7.0E-04	1.5E-03	1.1E-03	2.2E-03	2.1E-03	1.2E-03
Bi	2.5E-02	2.4E-02	2.2E-02	2.1E-02	2.5E-02	2.2E-02	2.0E-02
Ca	9.0E-04	9.0E-04	8.7E-04	8.7E-04	1.8E-03	1.5E-03	9.7E-04
Cr	8.9E-04	8.9E-04	9.0E-04	8.9E-04	9.7E-04	9.6E-04	9.7E-04
Fe	2.1E-02	2.1E-02	2.0E-02	2.0E-02	2.3E-02	2.3E-02	1.9E-02
Mg	1.6E-04	1.5E-04	1.8E-04	1.8E-04			1.9E-04
Mn	7.7E-05	7.3E-05	7.4E-05	7.2E-05	1.3E-04	1.0E-04	9.0E-05
Na	1.4E-01	1.4E-01	1.1E-01	1.1E-01	9.9E-02	9.9E-02	1.0E-01
P	1.9E-02	1.8E-02	1.8E-02	1.8E-02	2.0E-02	2.0E-02	5.2E-02
Pb	1.3E-03	9.7E-04	1.2E-03	9.9E-04	1.3E-03	9.6E-04	6.6E-04
Si	1.3E-02	1.3E-02	7.0E-03	7.0E-03	1.4E-02	1.4E-02	9.9E-03
Sr	2.2E-04	2.2E-04	2.4E-04	2.4E-04	2.7E-04	2.4E-04	2.2E-04
U			1.9E-03	6.1E-04			4.0E-04
Zn	9.4E-05	8.5E-05	1.2E-04	1.1E-04	1.8E-04	6.4E-06	5.0E-04
	µCi/g Wet Sludge						
TRU	0.20		0.29		0.34		0.20
^{90}Sr	220		218		250		169
^{137}Cs	14.9		14.6		16		15.1
^{99}Tc	Not Determined		Not Determined		0.026		0.02

(a) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.

(b) Lumetta, G. J., B. M. Rapko, C. D. Carlson, M. J. Wagner, and R. J. Barrington. 1994. *Sludge Treatment and Extraction Technology Development: Radionuclide Separations. Report for the Third Quarter FY 1994.* TWRSPP-94-051. Pacific Northwest Laboratory, Richland, Washington.

(c) Colton, N. G. 1994. *Sludge Pretreatment Chemistry Evaluation: Enhanced Sludge Washing Separation Factors.* TWRSPP-94-053. Pacific Northwest Laboratory, Richland, Washington.

Table 4.2. Summary of B-201 Sludge Composition

Core No.	26	26	27	27	
Ref.	(a)	(b)	(a)	(b)	(c)
Test No.	B201-1	B201-2	B201-3	B201-4	N/A
	g/g Dry Sludge				g/g Wet Sludge
Al	8.2E-03	7.8E-03	6.5E-03	9.8E-03	4.9E-03
Ba	4.0E-04	5.0E-04		2.6E-04	4.0E-04
Bi	1.8E-01	2.4E-01	1.9E-01	2.2E-01	1.0E-01
Ca	2.7E-02	2.4E-02	2.4E-02	3.0E-02	1.4E-02
Cr	6.3E-03	7.9E-03	7.0E-03	7.9E-03	3.3E-03
Fe	3.0E-02	3.0E-02	3.4E-02	3.3E-02	1.5E-02
La	3.1E-02	4.1E-02	3.0E-02	3.2E-02	1.5E-02
Mg	3.5E-03	3.9E-03		3.3E-03	3.4E-03
Mn	4.5E-02	5.6E-02	5.4E-02	5.5E-02	2.3E-02
Na	8.3E-02	8.1E-02	8.0E-02	1.0E-01	4.2E-02
P	1.1E-02	1.4E-02	1.1E-02	1.4E-02	1.8E-02
Pb	1.6E-03	3.1E-03		1.3E-03	1.5E-03
Si	4.3E-02	4.3E-02	3.0E-02	5.0E-02	2.4E-02
Sr	1.5E-03	1.9E-03	1.9E-03	2.1E-03	9.3E-04
Ti	1.1E-03	1.1E-03	7.0E-04	9.7E-04	
Zr		3.0E-04		5.1E-04	6.2E-05
	μCi/g Wet Sludge				
TRU	2.3	3	2.4	3	0.83
^{90}Sr	4.22	3.2	6.26	6.8	2.3
^{137}Cs	1.23	0.61	0.16	0.2	13.7
^{99}Tc	Not Detected	0.0031	0.0035	<0.0002	0.002

(a) This work.

(b) Lumetta, G. J., R. J. Barrington, and M. J. Wagner. 1994. *Sludge Treatment and Extraction Technology Development: Sludge Dissolution Laboratory Studies. Report for the Third Quarter FY 1994.* TWRSPP-94-50. Pacific Northwest Laboratory, Richland, Washington.

(c) Colton, N. G. 1994. *Sludge Pretreatment Chemistry Evaluation: Enhanced Sludge Washing Separation Factors.* TWRSPP-94-053. Pacific Northwest Laboratory, Richland, Washington.

Table 4.3. Summary of C-109 Sludge Composition

Core No.	47		47		
Ref.	(a)		(a)		(b)
Test No.	C109-1		C109-1		N/A
	g/g Wet Sludge				
	Maximum	Minimum	Maximum	Minimum	
Al	5.4E-02	5.4E-02	1.4E-01	1.4E-01	1.2E-01
As	2.8E-04	1.2E-05	5.1E-04	3.1E-04	
B	1.0E-04	1.4E-05	3.5E-04	3.0E-04	9.1E-05
Ba	1.7E-04	1.2E-04	2.5E-04	2.4E-04	6.4E-05
Bi	4.1E-03	1.9E-03	4.6E-03	2.7E-03	1.2E-02
Ca	8.2E-03	8.0E-03	1.3E-02	1.2E-02	2.0E-02
Ce	5.4E-04	9.6E-05	5.3E-04	1.0E-04	
Cr	3.8E-04	3.4E-04	4.5E-04	4.3E-04	2.4E-04
Fe	9.1E-03	9.1E-03	1.6E-02	1.5E-02	1.9E-02
La	1.0E-03	7.7E-04	1.3E-03	1.2E-03	
Mg	6.9E-04	2.4E-04	9.7E-04	7.0E-04	4.9E-04
Mn	8.6E-04	8.1E-04	1.4E-03	1.4E-03	1.2E-04
Na	N.D.(c)	N.D.(c)	5.7E-02	5.7E-02	8.4E-02
Nd	9.8E-04	9.8E-04	1.9E-03	1.9E-03	
P	7.4E-03	7.4E-03	9.6E-03	9.5E-03	5.9E-02
Pb	3.5E-03	3.4E-03	5.0E-03	4.9E-03	4.7E-03
Sb	2.5E-04	3.1E-05	3.5E-04	1.9E-04	
Se	4.6E-04	1.6E-05	4.0E-04	8.2E-05	
Si	5.4E-03	5.4E-03	4.9E-02	4.9E-03	9.0E-03
Sr	1.8E-04	1.4E-04	2.9E-04	2.7E-04	1.9E-04
Ti	1.9E-04	1.5E-04	1.2E-03	1.2E-03	
U	1.6E-02	7.3E-03	1.9E-02	1.0E-02	8.5E-03
Zn	1.5E-04	6.2E-05	1.8E-04	1.3E-04	3.7E-04
Zr	1.6E-04	1.2E-04	4.0E-04	3.8E-04	
	μCi/g Wet Sludge				
TRU	0.85		1.17		0.67
^{90}Sr	610		1640		1055
^{137}Cs	405		4170		715
^{99}Tc	0.04		0.044		0.101

(a) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.

(b) Colton, N. G. 1994. *Sludge Pretreatment Chemistry Evaluation: Enhanced Sludge Washing Separation Factors.* TWRSPP-94-053. Pacific Northwest Laboratory, Richland, Washington.

(c) N.D. = not determined.

Table 4.4. Summary of C-112 Sludge Composition

Core No.	36		36		
Ref.	(a)		(a)		(b)
Test No.	C112-1		C112-2		N/A
	g/g Wet Sludge				
	Maximum	Minimum	Maximum	Minimum	
Al	4.5E-03	4.5E-03	1.1E-02	1.1E-02	1.8E-02
As	2.6E-04	1.7E-05	2.9E-03	1.1E-04	
B	9.2E-04	8.4E-04	2.9E-03	2.8E-03	1.3E-04
Ba	7.7E-05	3.6E-05	2.9E-04	6.8E-05	8.7E-05
Bi	2.8E-03	7.6E-04	1.2E-02	1.3E-03	
Ca	1.1E-02	1.1E-02	2.6E-02	2.6E-02	2.5E-02
Ce	4.8E-04	6.6E-05			
Co	8.6E-05	4.5E-05	3.4E-03	3.4E-03	
Cr	2.7E-04	2.7E-04	1.4E-03	3.3E-04	2.5E-04
Cu	1.0E-04	5.9E-05	3.7E-04	8.0E-05	5.7E-05
Fe	1.8E-02	1.8E-02	6.8E-02	6.8E-02	2.5E-02
La	2.4E-04	3.3E-05			
Mg	5.9E-04	1.7E-04	5.4E-03	7.5E-04	5.6E-04
Mn	2.0E-04	1.6E-04	7.7E-04	3.3E-04	2.4E-04
Na	N.D.[c]	N.D.[c]	1.6E-01	1.6E-01	1.2E-01
Nd	2.8E-03	2.8E-03	1.2E-03	9.1E-05	
P	4.2E-02	4.2E-02	5.9E-02	5.6E-02	8.8E-02
Pb	1.0E-03	7.7E-04	2.6E-03	1.3E-03	2.2E-03
Si	1.0E-02	9.8E-03	2.8E-02	2.8E-02	2.5E-03
Sn	4.7E-03	5.9E-04			
Sr	4.2E-04	3.7E-04	9.2E-04	7.6E-04	3.2E-04
Ti	8.7E-05	4.6E-05	6.5E-04	6.1E-04	
U	1.1E-01	9.9E-02	2.4E-01	1.9E-01	6.0E-02
Zn	2.1E-04	1.7E-04	7.0E-04	2.7E-04	3.6E-04
Zr	1.0E-04	6.0E-05	1.8E-03	1.8E-03	2.6E-05
	μCi/g Wet Sludge				
TRU	0.16		0.19		0.45
^{90}Sr	68		250		2004
^{137}Cs	870		27,000		795
^{99}Tc	0.073		Not Detected		0.124

(a) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.
(b) Colton, N. G. 1994. *Sludge Pretreatment Chemistry Evaluation: Enhanced Sludge Washing Separation Factors.* TWRSPP-94-053. Pacific Northwest Laboratory, Richland, Washington.
(c) N.D. = not determined.

Table 4.5. Summary of U-110 Sludge Composition

Core No.	12		14		14		
Ref.	(a)		(b)		(c)		(d)
Test No.	U110-1A		U110-2B		U110-2C		N/A
	g/g Dry Sludge						g/g Wet Sludge
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	
Al	1.5E-01	1.5E-01	1.8E-01	1.8E-01	2.1E-01	2.1E-01	1.7E-01
B	3.6E-03	3.6E-03			8.6E-04	7.1E-04	2.9E-04
Ba	7.9E-05	7.9E-05	1.8E-03	1.7E-03	1.3E-04	7.4E-05	5.2E-05
Bi	N.D.[a]	N.D.[a]	N.D.[a]	N.D.[a]	1.0E-02	8.0E-03	1.4E-02
Ca	1.0E-03	1.0E-03	7.1E-03	7.1E-03	1.4E-03	1.2E-03	2.8E-03
Co	2.0E-03	1.4E-03					1.2E-04
Cr	1.3E-03	1.3E-03	3.2E-04	2.1E-04	7.3E-04	6.4E-04	3.9E-04
Cu	1.2E-04	1.2E-04					2.9E-04
Fe	2.0E-02	2.0E-02	7.8E-03	7.8E-03	1.0E-02	1.0E-02	1.0E-02
Mg	5.9E-04	5.9E-04	5.4E-04	5.4E-04	7.1E-04	2.1E-05	1.4E-03
Mn	5.1E-03	5.1E-03	2.7E-03	2.7E-03	3.7E-03	3.6E-03	2.4E-03
Na	1.1E-01	1.1E-01			5.0E-01	5.0E-01	1.1E-01
P	1.4E-02	7.8E-03	1.3E-02	7.0E-03	1.9E-02	1.8E-02	4.4E-02
Pb	9.9E-04	9.1E-04					4.9E-04
Se	9.3E-04	9.3E-04					
Si	4.0E-02	4.0E-02	7.4E-03	7.1E-03	1.1E-02	1.1E-02	1.1E-02
Sr	6.5E-04	6.5E-04	3.4E-04	3.4E-04	4.3E-04	4.1E-04	4.0E-04
Ti	1.0E-04	8.3E-05			3.3E-03	3.3E-03	
U	1.8E-02	1.3E-02			1.4E-02	4.2E-04	8.5E-03
Zn	1.8E-04	1.8E-04	1.2E-03	1.2E-03			1.8E-04
Zr	8.9E-04	2.6E-04			2.1E-04	1.4E-04	2.2E-04

	μCi/g Dry SludgeμCi/g Wet Sludge			
TRU	0.60	0.29	0.37	0.24
^{90}Sr	555	300	370	261
^{137}Cs	52.1	18.8	22.1	17.8
^{99}Tc	Not Determined	Not Determined	Not Determined	0.005

(a) Lumetta, Wagner, Colton, and Jones. 1993.
(b) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.
(c) This work.
(d) Colton, N. G. 1994. *Sludge Pretreatment Chemistry Evaluation: Enhanced Sludge Washing Separation Factors.* TWRSPP-94-053. Pacific Northwest Laboratory, Richland, Washington.

Table 4.6. Summary of Sludge Washing Results for Tank B-110 Sludge

Core No. Ref. Expt. No.	1 (a) B110-4[c]	1 (a) B110-4[c]	1,2,3,4 (b) B110-6[d]
	Amount Removed, %		
Al	≤27	≤18	≤6
Bi	≤2	≤1	≤4
Ca	10	10	≤6
Cr	10	10	10
Cu	≤30	≤26	
Fe	0	0	0
Mg	0	9	
Mn	≤30	≤2	≤8
Na	Not Determined	93	~100
P	≤87, ≥84	≤82, ≥81	42
Pb	≤14	≤11	≤10
Si	25	31	1
Sr	0	0	≤4
U		≤42	14
Zn	≤10	≤5	≤24
TRU	0	0	0
^{90}Sr	0	0	0
^{137}Cs	82	72	48
^{99}Tc	Not Determined	Not Determined	94

(a) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.
(b) Lumetta, G. J., B. M. Rapko, C. D. Carlson, M. J. Wagner, and R. J. Barrington. 1994. *Sludge Treatment and Extraction Technology Development: Radionuclide Separations. Report for the Third Quarter FY 1994.* TWRSPP-94-051. Pacific Northwest Laboratory, Richland, Washington.
(c) Washed with 0.1 M NaOH at 100°C.
(d) Washed with water at room temperature.

Table 4.7. Summary of Sludge Washing Results for Tank B-201 Sludge

Core No. Ref. Expt. No.	26 (a) B201-1[(c)]	27 (a) B201-3[(c)]	27 (b) B201-4[(c)]
	Amount Removed, %		
Al	≤1	≤2	≤1
Ba	≤2	≤11	≤6
Bi	0	≤1	0
Ca	0	1	0
Cr	33	41	27
Fe	1	0	0
La	0	≤1	0
Mg	≤2	≤10	≤5
Mn	0	0	0
Na	Not Determined	Not Determined	73
P	3	14	6
Pb	3	≤9	≤5
Si	5	8	10
Sr	≤1	≤1	≤2
Ti	≤1	≤1	≤2
TRU	0	0	0
^{90}Sr	0	0	0
^{137}Cs	22	11	17
^{99}Tc	Not Detected	Not Detected	74

(a) This work.
(b) Lumetta, G. J., R. J. Barrington, and M. J. Wagner. 1994. *Sludge Treatment and Extraction Technology Development: Sludge Dissolution Laboratory Studies. Report for the Third Quarter FY 1994.* TWRSPP-94-50. Pacific Northwest Laboratory, Richland, Washington.
(c) Washed with 0.1 M NaOH at 100°C.

Table 4.8. Summary of Sludge Washing Results for Tank C-109 Sludge

Core No.	47	47
Ref.	(a)	(a)
Expt. No.	C109-1[b]	C109-1[b]
	Amount Removed, %	
Al	8	2
As	≤51	≤18
B	≤46	≤9
Ba	≤14	≤6
Bi	≤29	≤17
Ca	≤2, ≥1	≤1
Ce	≤44	≤29
Cr	≤84, ≥75	≤69, ≥66
Fe	5	3
La	≤14	≤6
Mg	≤35	≤16
Mn	≤3	≤1
Na	Not Determined	76
Nd		7
P	33	27
Pb	≤4	≤2
Sb		≤22
Se		≤38
Si	4	1
Sr	≤13	≤5
Ti	≤13	≤1
U	≤29	≤16
Zn	≤32	≤17
Zr	≤15	≤4
TRU	0	0
^{90}Sr	0.5	0
^{137}Cs	8	1
^{99}Tc	~96	~95

(a) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.
(b) Washed with 0.1 M NaOH at 100°C.

Table 4.9. Summary of Sludge Washing Results for Tank C-112 Sludge

Core No.	36	36
Ref.	(a)	(a)
Expt. No.	C112-1[b]	C112-2[b]
	Amount Removed, %	
Al	34	17
As	≤50	≤4
B	≤5	≤1
Ba	≤28	≤7
Bi	≤39	≤9
Ca	1	0
Ce	≤46	
Co	≤25	≤1
Cr	48	≤46, ≥10
Cu	≤22	≤6
Fe	3	1
La	≤46	
Mg	≤37	≤4
Mn	≤11	≤3
Na	81	64
Nd	14	<9
P	48	≤43, ≥41
Pb	≤13	≤5
Si	8	0
Sn	≤46	
Sr	<5	≤3
Ti	≤25	≤3
U	≤4	≤2
Zn	≤21	≤6
Zr	≤22	≤1
TRU	<1.4	<1.1
^{90}Sr	0	0
^{137}Cs	9	0.1
^{99}Tc	~97	Not Detected

(a) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.
(b) Washed with 0.1 M NaOH at 100°C.

Table 4.10. Summary of Sludge Washing Results for Tank U-110 Sludge

Core No.	12	14
Ref.	(a)	(b)
Expt. No.	U110-1A(c)	U110-2C(d)
	Amount Removed, %	
Al	1	1
B	4	≥82
Ba	5	≤1
Bi	Not Determined	≤1
Ca	23	≤1
Co	≤12	
Cr	60	≤73, ≥64
Cu	≤4	
Fe	0	0
Mg	2	≤2
Mn	0	0
Na	69	Not Determined
P	≥56	≤92, ≥89
Pb	≤7	
Pd	Not Determined	
Se	15	
Si	0	≤6, ≥5
Sr	0	0
Ti	≤9	0
U	≤7	≤2
Zn	1	
Zr	≤11	≤1
TRU	0	0
^{90}Sr	0	0
^{137}Cs	10	5

(a) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.
(b) This work.
(c) Washed with 0.01 M NaOH at 100°C.
(d) Washed with 0.1 M NaOH at 100°C.

Table 4.11. Summary of Sludge Washing and Caustic Leaching Results for Tank B-110 Sludge

Core No.	1	1,2,3,4
Ref.	(a)	(b)
Expt. No.	B110-4[c]	B110-6[d]
	Cumulative Removal, Wash + Caustic Leach, %	
Al	≤43	≤25, ≥18
Bi	≤4	≤9
Ca	19	≤13
Cr	64	52
Cu	≤58	
Fe	0	0
Mg	0	
Mn	≤6	≤18
Na	Not Determined	Not Determined
P	≥97	98
Pb	≤27	≤22
Si	74	58
Sr	0	≤9
U		43
Zn	≤32, ≥25	≥31
TRU	0	0
^{90}Sr	0.1	0
^{137}Cs	97	92
^{99}Tc	Not Determined	100
	Selected Components in Leached Sludge:	
g Na/g Fe	0.16	0.4
mol P/mol Ca	<0.97	0.37

(a) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.

(b) Lumetta, G. J., B. M. Rapko, C. D. Carlson, M. J. Wagner, and R. J. Barrington. 1994. *Sludge Treatment and Extraction Technology Development: Radionuclide Separations. Report for the Third Quarter FY 1994.* TWRSPP-94-051. Pacific Northwest Laboratory, Richland, Washington.

(c) Washed with 0.1 M NaOH at 100°C, then leached with 3 M NaOH at 100°C.

(c) Washed with water at room temperature, then leached with 3 M NaOH at 100°C.

Table 4.12. Summary of Sludge Washing and Caustic Leaching Results for Tank B-201 Sludge

Core No. Ref. Expt. No.	26 (a) B201-1[b]	27 (a) B201-3[b]
	Cumulative Removal, Wash + Caustic Leach, %	
Al	16	39
Ba	≤13	≤26
Bi	≤3	≤3
Ca	≤2	≤2, ≥1
Cr	48	65
Fe	1	0
La	≤1	≤2
Mg	≤16	≤22
Mn	0	0
Na	Not Determined	Not Determined
P	13	39
Pb	≤15, ≥3	≤27, ≥17
Si	36	65
Sr	≤4	≤5
Ti	≤5	≤5
TRU	0	0
^{90}Sr	0	0
^{137}Cs	34	15
^{99}Tc	Not Detected	Not Detected
	Selected Components in Leached Sludge:	
g Na/g Fe	1.5	1.2
mol P/mol Ca	0.6	0.58

(a) This work.
(b) Washed with 0.1 M NaOH at 100°C, then leached with 3 M NaOH at 100°C.

Table 4.13. Summary of Sludge Washing and Caustic Leaching Results for Tanks C-109 and C-112 Sludges

Tank:	C-109	C-112
Core No.	47	47
Ref.	(a)	(a)
Expt. No.	C109-1[b]	C112-1[b]
	Component Dissolved in Wash, %	
Al	81	85
As	≤95	≤94
B	≤86	≤9
Ba	≤26	≤53
Bi	≤54	≤73
Ca	≤3, ≥1	≤2, ≥1
Ce	≤82	≤91
Co	≤77	≤48
Cr	85	88
Cu	≤50	≤41
Fe	5	6
La	≤26	≤87
Mg	≤65	≤70
Mn	≤5	≤5
Na	Not Determined	85
Nd		22
P	42	84
Pb	≤44, ≥41	≤24
Sb		≤80
Se		≤89
Si	16	17
Sr	≤24	≤10
Ti	≤24	≤47
U	≤55	≤8
Zn	≤59	≤46
Zr	≤28	≤41
TRU	0	<2
^{90}Sr	1	0
^{137}Cs	98	98
^{99}Tc	96	~97
	Selected Components in Leached Sludge:	
g Na/g Fe	0.6	0.87
mol P/mol Ca	0.7	0.83

(a) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.
(b) Washed with 0.1 M NaOH at 100°C, then leached with 3 M NaOH at 100°C.

Table 4.14. Summary of Sludge Washing and Alkaline Leaching Results for Tank U-110 Sludge

Core No.	14	14
Ref.	(a)	(b)
Expt. No.	U110-2B[c]	U110-2C[d]
	Cumulative Removal, Wash + Caustic Leach, %	
Al	79	84
B		≥94
Ba	≤1	≤31
Bi	Not Determined	≤20
Ca	52	≤15
Cr	≤74, ≥47	≤76, ≥71
Fe	1	0
Mg	26	≤56
Mn	0	≤1
Na	Not Determined	Not Determined
P	≤49, ≥35	≥98
Si	8	≤17, ≥9
Sr	0	≤4
Ti		0
U		≤56
Zn	64	
Zr		≤19
TRU	2	<2.4
^{90}Sr	0	1.5
^{137}Cs	31	10
	Selected Components in Leached Sludge:	
g Na/g Fe	(e)	1.7
mol P/mol Ca	(e)	<0.45

(a) Lumetta, Rapko, Wagner, Carlson, and Barrington. 1994.
(b) This work.
(c) Leached directly with 5 M NaOH, without prior sludge washing. Percent removal values should be considered to be minimum values because determination was not made of constituents contained in the interstitial liquid after the 5 M NaOH leaching step.
(d) Washed with 0.1 M NaOH at room temperature, then leached with 3 M NaOH/2 M Na2CO3 at 100°C, followed by sonication.
(e) Data not available to determine these values following the 5 M NaOH leach step.

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