PNNL-11278 Rev. 1
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G. J. Lumetta
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Prepared for the U.S. Department of Energy
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Pacific Northwest National Laboratory
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DISCLAIMER

Abstract

Sludge washing and caustic leaching tests supporting the developing baseline Hanford tank sludge pretreatment flowsheet were conducted at Pacific Northwest National Laboratory in FY-1996. Five tanks (BY-104, BY-110, C-107, S-107, and SX-108) were investigated. The sludges contained from 2 to 20 weight % of aluminum, and the aluminum removed by washing with dilute sodium hydroxide varied from virtually no removal (Tank C-107) to nearly complete removal (Tank BY-110). Caustic leaching, however, removed > 70% of aluminum in all cases except SX-108 from which little aluminum was removed. Overall, 24 Hanford tank sludges have now been investigated, and the data indicate that caustic leaching will remove 57% of the water-insoluble aluminum fraction, which is the same value previously assumed for flowsheet development.

Microscopy studies confirmed that aluminosilicate species resist attack by caustic. However, other aluminum-containing species were also observed in leached residents, suggesting that slow kinetics might hinder the process. Boehmite appeared to be the major aluminum-containing phase in the leached S-107 and SX-108 sludges, but some aluminosilicates were also present. A large fraction of the aluminum oxide material in C-107 and SX-108 sludges was removed, but some remained after leaching. The major aluminum-containing species in the leached C-107 solids was an amorphous aluminum/silicate/clay agglomerate.

The tank sludges contain < 1 weight % of chromium. Washing with dilute sodium hydroxide removed 24 to 70% of the chromium. Caustic leaching did not significantly improve chromium removal from BY-104 and BY-110, but some improvement was made with C-107, S-107, and SX-108 sludges. Experimental data from the 24 tank sludges that have now been investigated indicate that caustic leaching will remove 46% of the chromium. Flowsheet development previously assumed that 64% would be removed.

The tank sludges contain from 0.02 to 1.4 weight % of phosphorus. Washing with dilute sodium hydroxide removed most of the phosphorus from BY-104 and S-107 sludges, and caustic leaching did little to improve this removal. Simple washing only removed approximately 70% of the phosphorus from C-107, but caustic leaching increased this to 94%. On the other hand, little phosphorus was removed from BY-110 sludge even with caustic leaching. Experimental data from the 24 tank sludges that have now been investigated indicate that caustic leaching will remove 75% of the water-insoluble phosphorus fraction. Flowsheet development previously assumed that 74% would be removed.

Summary

This report describes the sludge washing and caustic leaching tests conducted at Pacific Northwest National Laboratory in FY-1996. These tests supported the development of the baseline Hanford tank sludge pretreatment flowsheet. The work was funded by the U.S. Department of Energy through the Tank Waste Remediation System (TWRS; EM-30) and the Tank Focus Area (TFA; EM-50). The results of this work can be summarized as follows.

- Table S.1 summarizes the Al behavior for the five tanks investigated. The amount of Al in the sludges varied from about 2 to 20 wt%. The Al removed by washing with dilute NaOH (simple wash) varied from virtually no removal (Tank C-107) to nearly complete removal (Tank BY-110). When caustic leaching (enhanced sludge washing) was applied, >70% of the Al was removed in all cases, except SX-108, for which very poor Al removal was observed. Based on the projected mass of Al in each tank and the measured Al removal efficiencies, the experimental data generated for the 24 Hanford tank sludges investigated to date indicate that 57% of the water-insoluble Al fraction will be removed from these 24 tanks by caustic leaching.

- Table S.2 summarizes the Cr behavior for the five tanks investigated. In all cases, the amount of Cr in the sludges was <1 wt%. The Cr removed by washing with dilute NaOH varied from 24 to 70%. In the cases of BY-104 and BY-110, caustic leaching did little to improve the Cr removal. On the other hand, slightly more Cr was removed by caustic leaching of C-107 and S-107 sludges. Spectrophotometric measurements indicated that the dissolved Cr existed primarily as chromate in both the wash and leach solutions, with no evidence of dissolved Cr(III). Based on the projected mass of Cr in each tank and the measured Cr removal efficiencies, the experimental data generated for the 24 Hanford tank sludges investigated to date indicate that 46% of the water-insoluble Cr fraction will be removed from these 24 tanks by caustic leaching.

Table S.1. Summary of Aluminum Removal

		Aluminum Removed, %	
Tank	Al, wt%	Simple Wash	Enhanced Sludge Washing[(a)]
BY-104	1.9	65	98
BY-110	3.4	94	96
C-107	9.5	1	78
S-107	20.5	8	73
SX-108	9.0	6	29

(a) The term "Enhanced Sludge Washing" refers to the process of leaching the sludge with aqueous NaOH (2 to 3 M), then washing with dilute NaOH solution to remove dissolved components and added NaOH. The values reported represent the cumulative removal achieved by leaching twice with caustic, then washing three successive times with 0.01 M NaOH/0.01 M $NaNO_2$.

Table S.2. Summary of Chromium Removal

Tank	Cr, wt%	Chromium Removed, %	
		Simple Wash	Enhanced Sludge Washing
BY-104	0.5	69	71
BY-110	0.4	47	48
C-107	0.1	34	48
S-107	0.6	24	53
SX-108	0.8	71	78

- Table S.3 summarizes the P behavior for the five tanks investigated. The amount of P present in these sludges varied from 0.2 to 1.4 wt%. In the cases of BY-104 and S-107, simply washing with dilute NaOH removed most of the P; caustic leaching did little to improve the P removal from these two tank sludges. Simple washing of C-107 sludge removed only ~70% of the P, but when caustic leaching was employed, the P removal increased to 94%. On the other hand, poor P removal was seen for the BY-110 sludge, even when leached with caustic. Based on the projected mass of P in each tank and the measured P removal efficiencies, the experimental data generated for the 24 Hanford tank sludges investigated to date indicate that 75% of the water-insoluble P fraction will be removed from these 24 tanks by caustic leaching.

Table S.3. Summary of Phosphorus Removal

Tank	P, wt%	Phosphorus Removed, %	
		Simple Wash	Enhanced Sludge Washing
BY-104	0.3	93	95
BY-110	0.6	19	23
C-107	1.4	69	94
S-107	0.2	100	98
SX-108	0.1	9	37

- The mass-weighted removals of water-insoluble Al, Cr, and P by caustic leaching are projected to be 57%, 46%, and 75%, respectively for the 24 tanks investigated to date. Extrapolation of the experimental data to the entire tank inventory, which was recently performed by others, suggested caustic leaching would remove an overall 60% of the water-insoluble Al, 10% of the water-insoluble Cr, and 70% if the water-insoluble P.

- Microscopy studies confirmed the refractory nature of aluminosilicate species towards attack by caustic. However, incomplete removal of other Al-containing species was also observed, suggesting that slow kinetics might hinder Al removal in some cases even when the Al is not present as aluminosilicates. Indeed, boehmite appeared to be the predominant Al-containing phase in the leached S-107 and SX-108 sludges, but some aluminosilicates were also present. Microscopy studies indicated that a large fraction of the aluminum oxide material contained in C-107 and SX-108 sludges was removed, but some did remain after leaching. The predominant Al-containing species in the leached C-107 solids was an amorphous Al/Si clay agglomerate. Some previously unseen phases were found for the tanks investigated in this work. These included $Ni_3O_2(OH)_4$ (BY-104 and BY-110 sludges), grimalidite, CrO(OH) (BY-110 sludge), and $Ca_3Al_2O_6$ (SX-108 sludge). Some mixed-metal phases were observed. For example, Sr was found to be associated with hydroxyapitite in BY-104 and BY-110 sludges, and SX-108 contained a mixed Mn/Fe oxide phase. Uranium was commonly found as β-U_3O_8.

- Radiochemical analyses of the washing and caustic leaching solutions indicated very low concentrations of transuranic elements and ^{90}Sr. Only ^{137}Cs and ^{99}Tc showed any appreciable solubility under these alkaline conditions for the five tank sludges investigated in this work. In general, the amount of ^{137}Cs dissolved was increased by caustic leaching, compared to simple washing with dilute NaOH. No significant differences could be discerned in the behavior of ^{99}Tc in the simple washing versus caustic leaching steps.

- Solids settling behavior was varied, but was generally good. Except in the case of BY-110 sludge, settling velocities tended to be greater in the wash steps than in the leach steps. This was likely because the viscosity of the wash solutions was less than that of the leach solution. There appeared to be some correlation of maximum settling velocity with the volume of the centrifuged solids layer, but an analogous correlation of the maximum settling velocity to the volume of the settled solids layer was tenuous. The parameters influencing sludge settling behavior are complex and not completely understood. Further work is needed in this area so that reliable predictions of settling behavior can be made.

Acknowledgments

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Contents

Figures

Tables

1.0 Introduction

During the past few years, the primary mission at the U.S. Department of Energy's Hanford Site has changed from producing plutonium to restoring the environment. Large volumes of high-level radioactive wastes (HLW), generated during past Pu production and other operations, are stored in underground tanks on site. The current plan for remediating the Hanford tank farms consists of waste retrieval, pretreatment, treatment (immobilization), and disposal. The HLW will be immobilized in a borosilicate glass matrix; the resulting glass canisters will then be disposed of in a geologic repository. Because of the expected high cost of HLW vitrification and geologic disposal, pretreatment processes will be implemented to reduce the volume of borosilicate glass produced in disposing of the tank wastes.

The baseline sludge pretreatment flowsheet involves retrieving the sludge by sluicing and pumping with inhibited water (0.01 M NaOH/0.01 M $NaNO_2$), leaching the sludge with hot caustic (3 M NaOH), then washing the sludge with inhibited water to remove the added NaOH and the components dissolved during the caustic leaching step. The retrieval, leachate, and wash solutions will be combined and processed to remove ^{137}Cs (and possibly other radionuclides). The decontaminated solution will then be routed to the low-level waste (LLW) stream, where it will be immobilized in a glass matrix. The leached solids, which will contain a large fraction of the transuranic (TRU) elements and ^{90}Sr, will be immobilized for deep geologic disposal along with the radionuclides removed from the wash and leach solutions (Orme 1995).

The key process in the baseline sludge pretreatment flowsheet is caustic leaching of the sludge. Caustic leaching is expected to remove a large fraction of the Al, which is present in large quantities in Hanford tank sludges. The Al will be removed by converting aluminum oxides/hydroxides to sodium aluminate. For example, boehmite and gibbsite are dissolved according to the following equations (Weber 1982).

$$AlOOH(s) + NaOH(aq) \rightarrow NaAlO_2(aq) + H_2O \tag{1.1}$$

$$Al(OH)_3(s) + NaOH(aq) \rightarrow NaAlO_2(aq) + 2H_2O \tag{1.2}$$

A significant portion of the P is also expected to be removed from the sludge by metathesis of water-insoluble metal phosphates to insoluble hydroxides and soluble Na_3PO_4. An example of this is shown for iron(III) phosphate in the following equation.

$$FePO_4(s) + 3NaOH(aq) \rightarrow Fe(OH)_3(s) + Na_3PO_4(aq) \tag{1.3}$$

Similar metathesis reactions can occur for insoluble sulfate salts, allowing the removal of sulfate from the HLW stream.

Caustic leaching of Hanford tank sludges has resulted in enhanced Cr dissolution when compared to simply washing the sludges with dilute hydroxide solution. This might be due to the increased solubility of

Cr(III) at high hydroxide concentrations (Rai, Sass, and Moore 1987). The increased solubility of Cr(III) at high hydroxide concentration is due to the formation of the tetrahydroxochromium(III) anion.

$$Cr(OH)_3(s) + NaOH(aq) \rightarrow Na[Cr(OH)_4](aq) \qquad (1.4)$$

Results of previous studies of the baseline Hanford sludge washing and caustic leaching process have been reported (Lumetta and Rapko 1994; Rapko, Lumetta, and Wagner 1995, Temer and Villareal 1995a and 1995b). This report describes the sludge washing and caustic leaching tests performed at the Pacific Northwest National Laboratory in FY 1996. The sludges used in this study were taken from Hanford single-shell tanks C-107, S-107, BY-104, BY-110, and SX-108. Table 1.1 lists the primary and secondary waste types stored in these tanks.

Table 1.1. Primary and Secondary Waste Types Stored in the Tanks Investigated[(a)]

Tank	Primary Waste	Secondary Waste
BY-104	TBP-F	EB-ITS
BY-110	TBP-F	EB-ITS
C-107	1C	CW
S-107	R	EB
SX-108	R	None

(a) The waste types are defined as follows (Hill, Anderson, and Simpson 1995).

CW	Cladding waste
EB	Evaporator bottoms
F	Ferrocyanide-scavanged waste
ITS	In-tank solidification
R	High-level REDOX process waste
TBP	Waste from tributyl phosphate extraction process
1C	Waste from first decontamination cycle of the bismuth phosphate process

2.0 Experimental

The materials and methods used in the sludge washing and caustic leaching screening tests are discussed in this section.

2.1 Materials

Sludge washing and caustic leaching screening tests were performed on sludges from five Hanford tanks. The five tanks are listed in Table 2.1 along with the details of the individual samples investigated.

Leach and wash solutions were prepared using reagent grade NaOH and $NaNO_2$. The concentrations of the NaOH solutions were confirmed by titration with standard HCl.

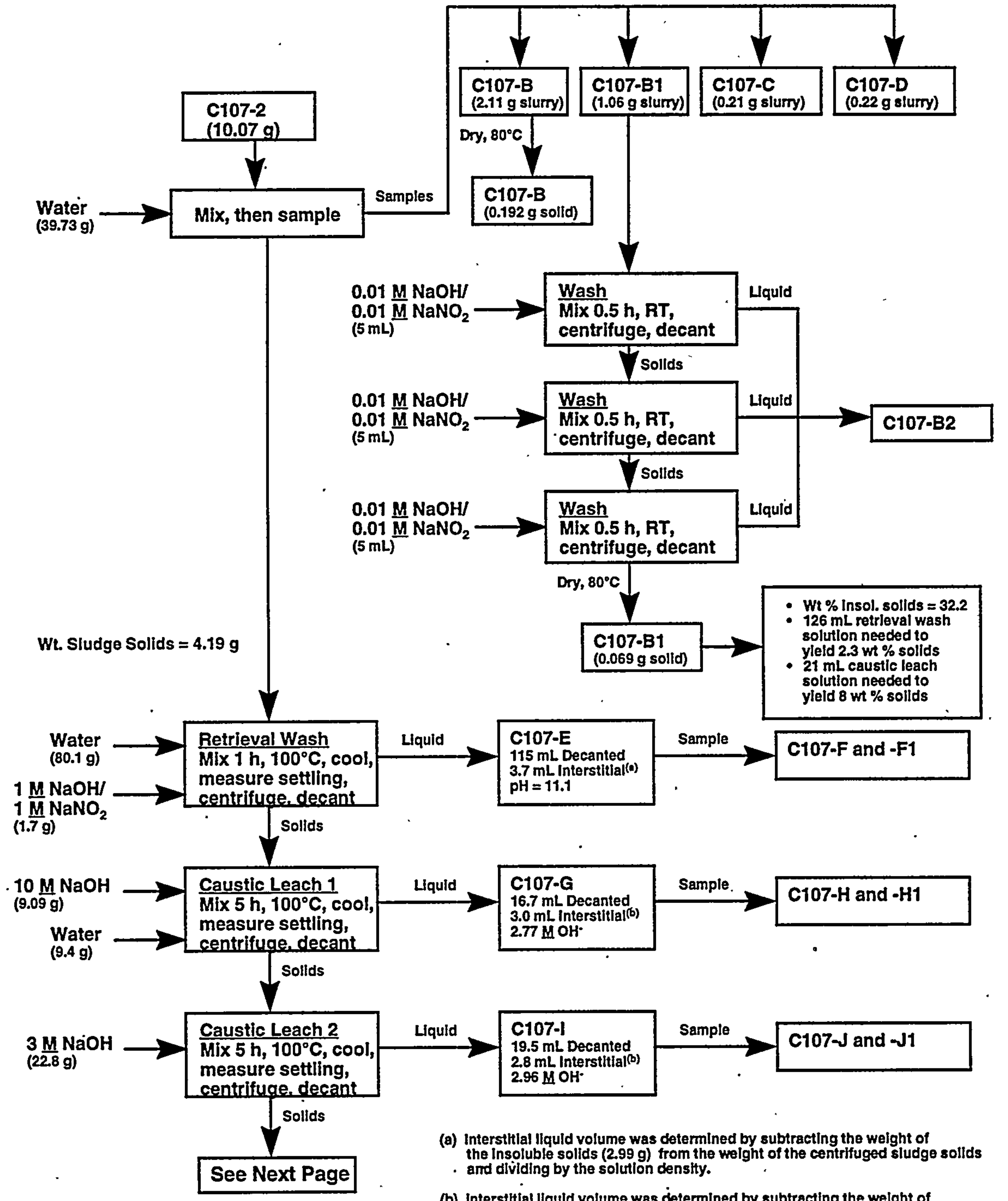
2.2 Standard Testing Procedure

The C-107 test was performed in the last quarter of FY-1995 using the standard testing procedure that was approved at that time. This procedure was described previously (Rapko, Lumetta, and Wagner 1995). Figure 2.1 provides the details of the C-107 test in schematic form.

Table 2.1. Description of Tank Sludge Samples Used

Tank	Core Number	Description
BY-104	116	Core composite (222-S LABCORE sample number S96T000371)(a)
BY-110	113	Core composite (222-S LABCORE sample number S96T000497)
C-107	71	Core composite was prepared at PNNL
S-107	105, 110, 111	Composite of three core composites (222-S LABCORE sample numbers S95T003158, S95T003159, and S95T003164)
SX-108	Auger Sample	Upper half of auger sample (222-S LABCORE sample number S95T002574)

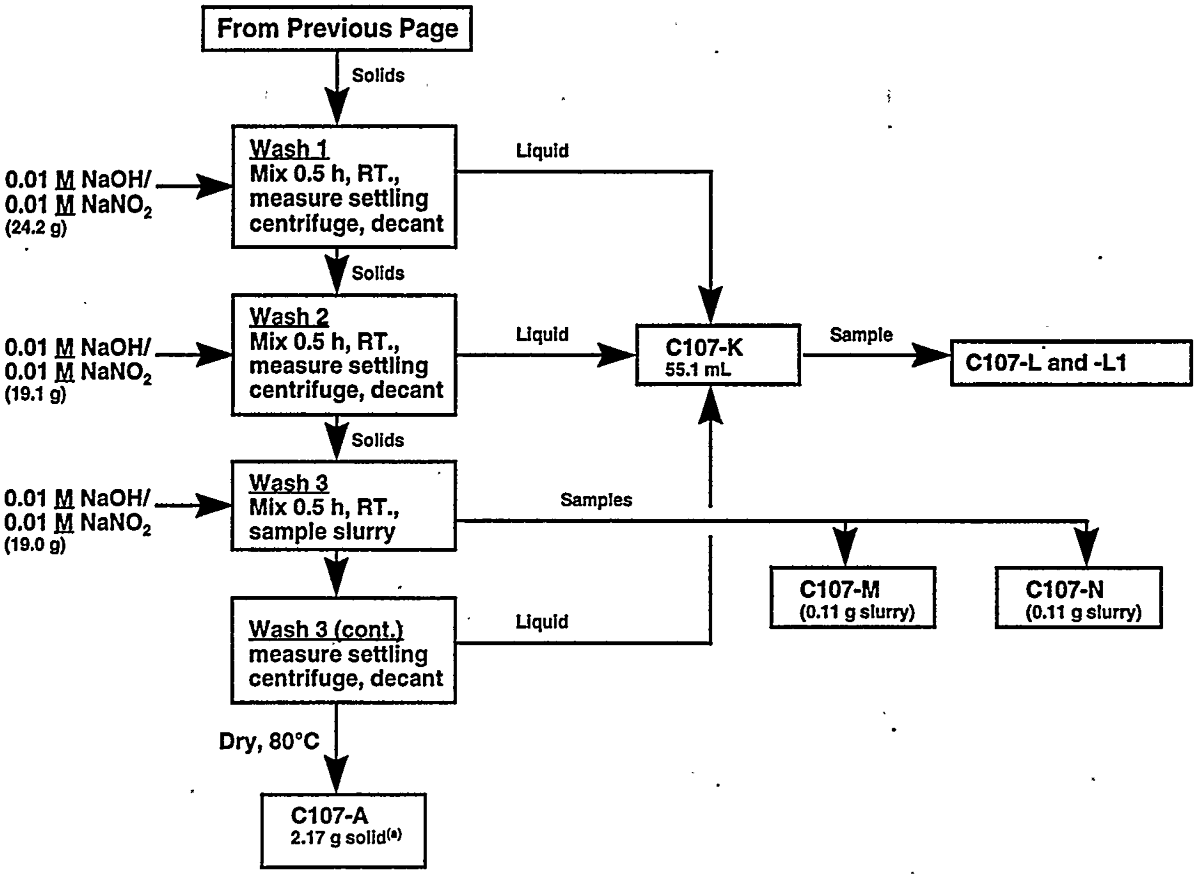
(a) Identifying number used at the Westinghouse Hanford Company (WHC) 222-S laboratory for tracking samples.



(a) Interstitial liquid volume was determined by subtracting the weight of the insoluble solids (2.99 g) from the weight of the centrifuged sludge solids and dividing by the solution density.

(b) Interstitial liquid volume was determined by subtracting the weight of the dried leached solids (2.17 g) from the weight of the centrifuged sludge solids and dividing by the solution density.

Figure 2.1. Schematic of C-107 Sludge Washing and Caustic Leaching Test



(a) Final weight of dried solids was adjusted for that removed in samples M and N.

C107-2.PPT

Figure 2.1. (contd)

For the BY-110 and S-107 tests, the same general sludge washing and caustic leaching procedure was used; specific details for each test are given in the schemes depicted in Figures 2.2 and 2.3. The procedure consisted of the following steps.

1. A portion of the as-received sludge was placed in a high-density polyethylene (HDPE) bottle.[a]

2. The sludge was slurried in water (2 g water/g sludge); then four aliquots of the slurry were removed.

3. One of the aliquots was dried to a constant weight at 105°C; this dried aliquot was submitted for analysis.

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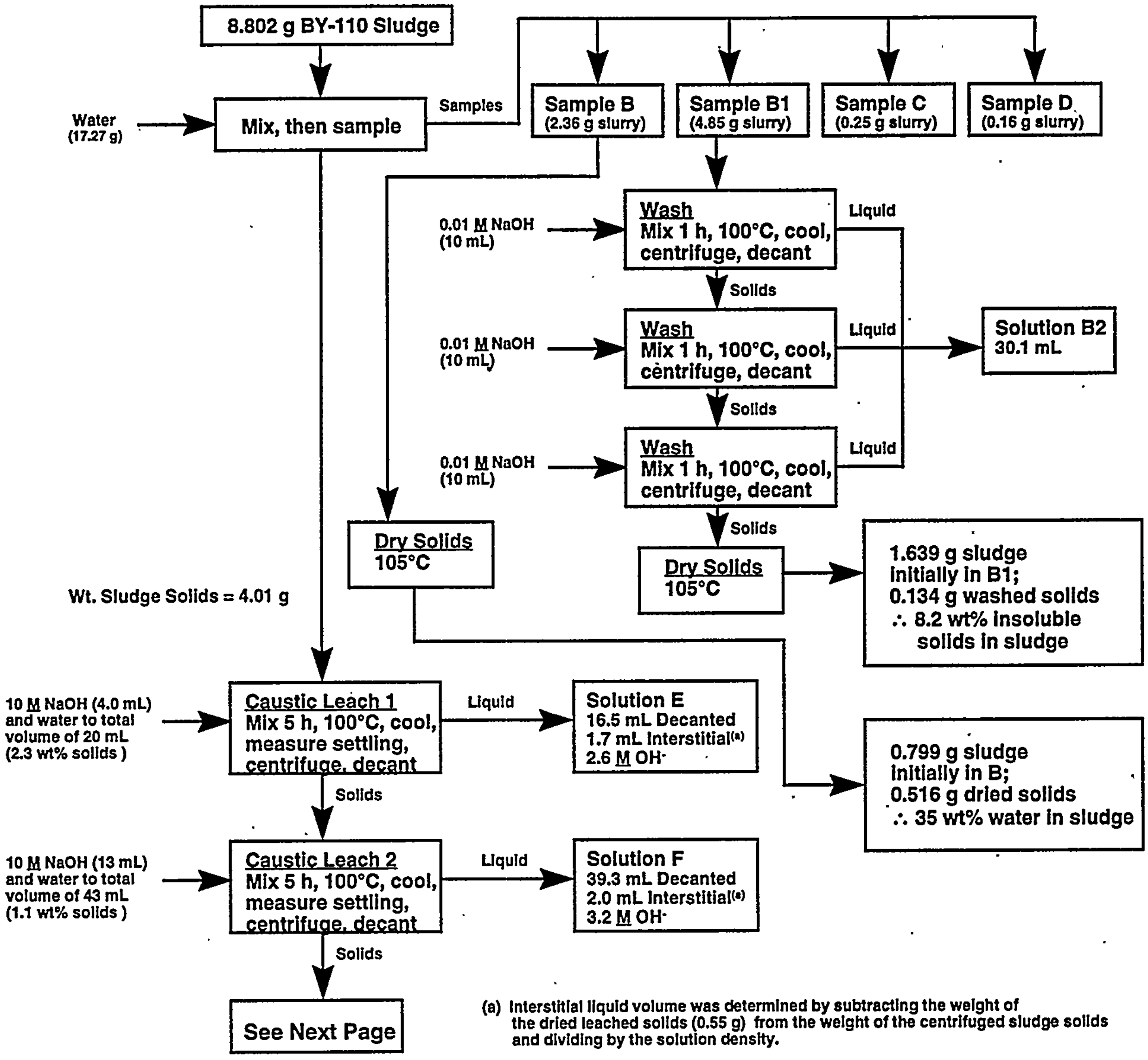
[a] Before using, the HDPE bottle was heated at least 1 week at 105°C to remove volatile materials.



(a) Interstitial liquid volume was determined by subtracting the weight of the dried leached solids (0.55 g) from the weight of the centrifuged sludge solids and dividing by the solution density.

Figure 2.2. Schematic of BY-110 Sludge Washing and Caustic Leaching Test

4. Two of the aliquots were saved. One was used for particle-size measurements; the second was used for microscopy studies.

5. The fourth aliquot was washed with three 10-mL portions of 0.01 M NaOH at 100°C[a] and was then dried to a constant weight at 105°C. This weight was assumed to represent the water-insoluble solids

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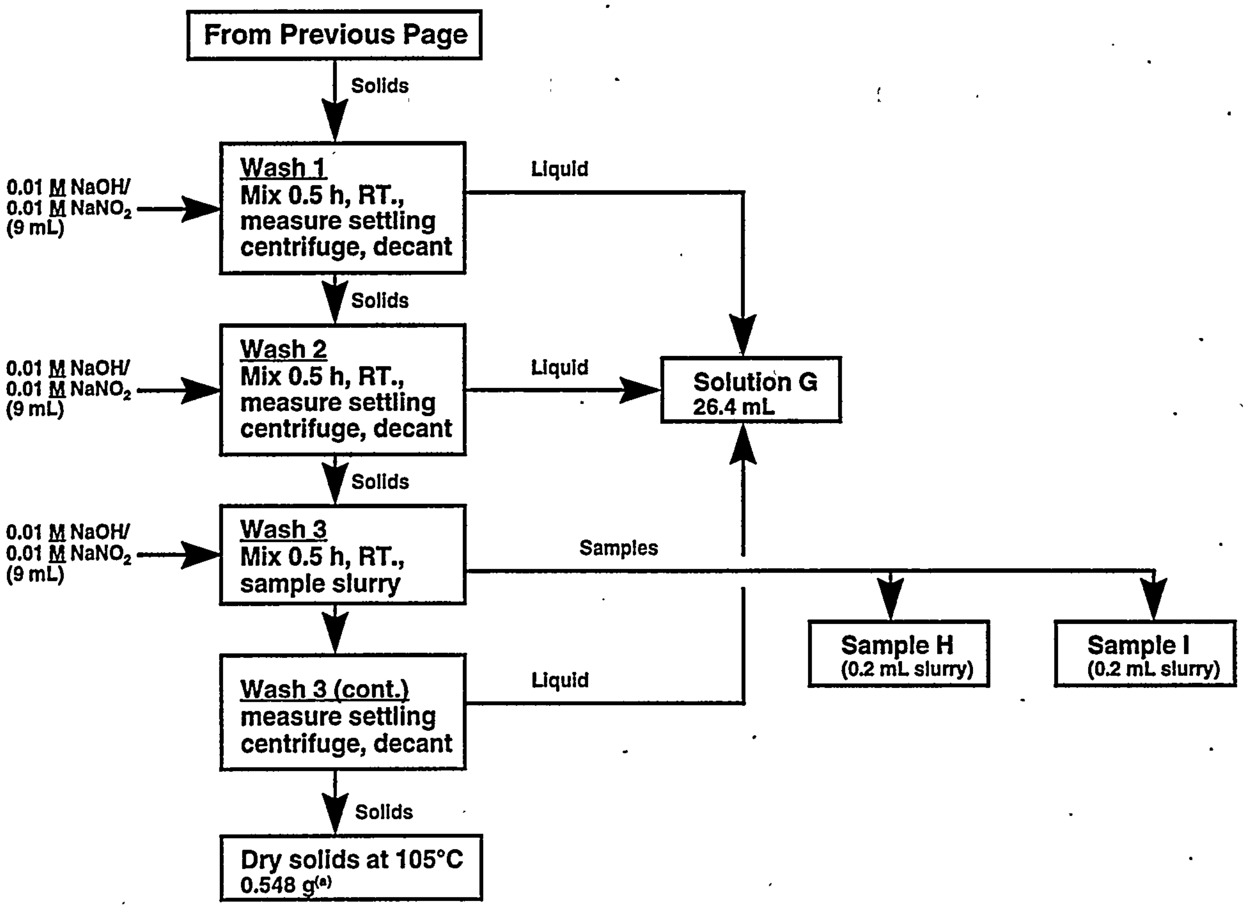
[a] All heating steps performed at 100°C were done by immersing the bottle containing the washing or leaching mixture in a boiling water bath.



(a) Final weight of dried solids was adjusted for that removed in samples H and I.

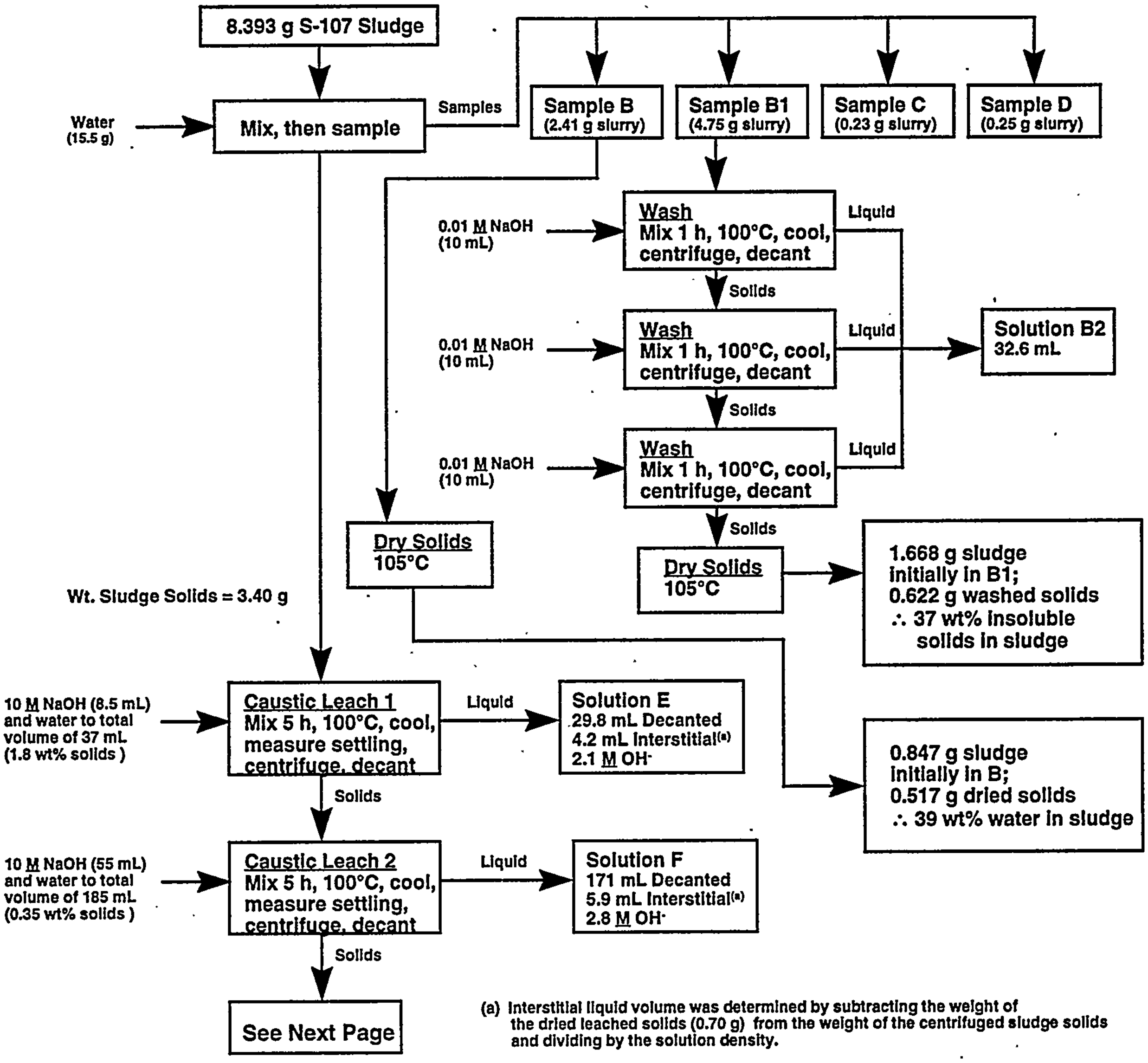
B110-1.PPT

Figure 2.2. (contd)

in the sludge and was used to determine the weight percent of such solids in the original sludge sample. The wash solution and washed solids were analyzed to determine the behavior of each sludge component during washing with 0.01 M NaOH.

6. The weight percent of water-insoluble solids determined in Step 5 was used to determine the total volume of leaching solution needed to yield a slurry containing 5 wt% solids. Water and 10 M NaOH were added to the sludge slurry to give the appropriate volume of leaching solution, with a targeted final free hydroxide concentration of 2 M NaOH.[a] The resulting mixture was stirred and heated at 100°C for 5 h.

(a) In determining the amount of NaOH required, it was assumed that each mole of Al and Cr would consume one mole of hydroxide, and that each mole of Bi would consume three moles of hydroxide during the leaching process. The best available information regarding the sludge composition was used in this determination.



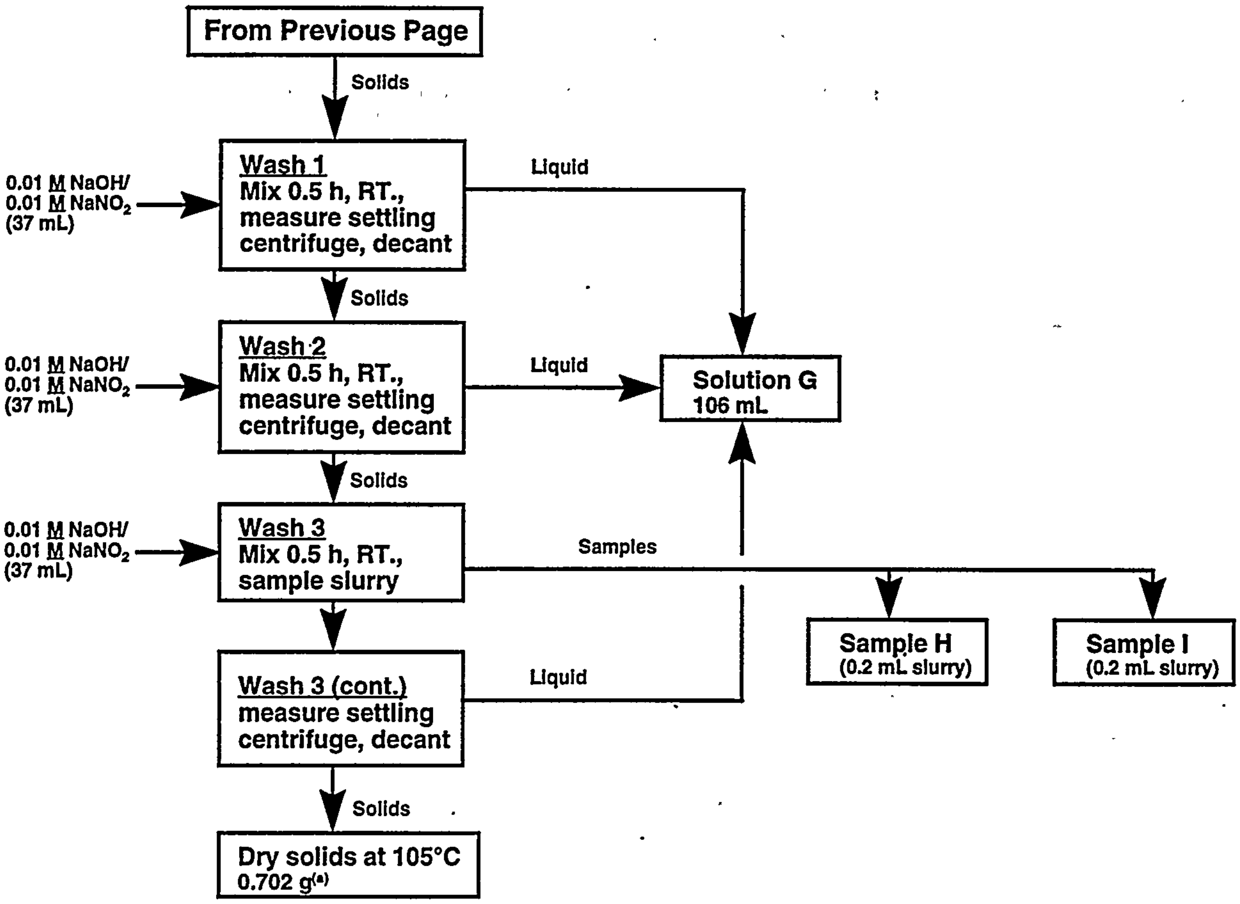
(a) Interstitial liquid volume was determined by subtracting the weight of the dried leached solids (0.70 g) from the weight of the centrifuged sludge solids and dividing by the solution density.

Figure 2.3. Schematic of S-107 Sludge Washing and Caustic Leaching Test

7. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity. The height of the sludge solids was monitored as a function of time.

8. Once the sludge had stopped settling, the mixture was centrifuged, and the solution was decanted. Hereafter, this solution will be referred to as the "first leach" solution.

9. The weight percent of water-insoluble solids determined in Step 5 was used to determine the total volume of leaching solution needed to yield a slurry containing 1 wt% solids.



(a) Final weight of dried solids was adjusted for that removed in samples H and I.

S107-1.PPT

Figure 2.3. (contd)

10. At this point, the sludge was typically transferred to a larger container that was more consistent with the volume of the leaching solution to be used. The sludge was transferred using several portions of water.

11. Water and 10 M NaOH were added to the sludge to give a caustic-leaching mixture with the volume determined in Step 9, with a targeted final free hydroxide concentration of 3 M NaOH. The resulting mixture was stirred and heated at 100°C for 5 h.

12. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity. The height of the sludge solids was monitored as a function of time.

13. Once the sludge had stopped settling, the mixture was centrifuged, and the solution was decanted. Hereafter, this solution will be referred to as the "second leach" solution.

14. The leached sludge was successively washed with three portions of 0.01 M NaOH/0.01 M $NaNO_2$; the volume of each portion of wash solution was equal to the volume of the first caustic-leach solution determined in Step 6. For the first two portions, mixing was stopped after mixing for at least 0.5 h at room temperature, and the solids were allowed to settle under the force of gravity. Again, the height of the sludge solids was monitored as a function of time. In the case of the third wash, two aliquots of the suspension were removed before the solids were allowed to settle. One aliquot was saved for a particle-size measurement; the second was used for microscopy studies. In each case, after gravity settling, the mixture was centrifuged, and then the wash liquor was decanted.

15. Finally, the remaining residue was dried to a constant weight at 105°C.

16. The wash and leach solutions were analyzed as were portions of the untreated sludge solids, the solids after washing with dilute NaOH, and the caustic-leached solids.

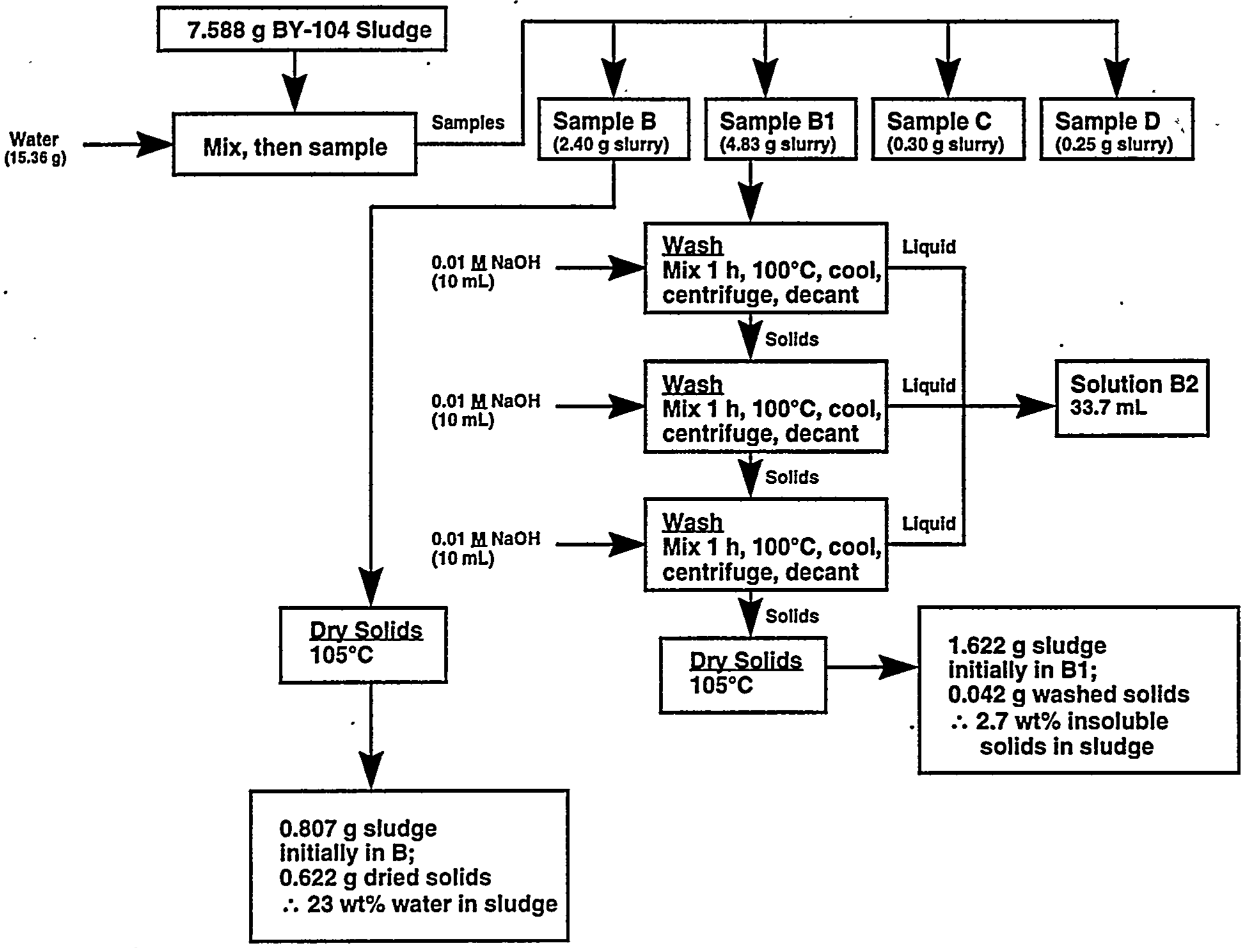
A slight deviation from the above described procedure was necessary for the BY-104 test. In that case, the weight percent of insoluble solids was found to be unusually low (2.7 wt%). Because of this, it was necessary to use a much larger sludge sample than originally planned so that an adequate amount of leached sludge solids would be available for analysis. It was decided that a ~50-g sample of BY-104 sludge would be used. But this presented a problem because the volume of the leach mixture needed to be 27 mL to obtain a leach slurry containing 5 wt% solids. Clearly, it was impossible to have a leach mixture of 27 mL when starting with 50 g of sludge. Thus, the 50-g portion of sludge was washed with 0.01 M NaOH before performing the first caustic leaching step. Figure 2.4 provides the details of this experimental procedure for the BY-104 test.

The procedure for the SX-108 test also deviated slightly from that described above in that the leaching and washing mixtures were not centrifuged before decanting the solution (Figure 2.5). Because of the high radioactivity of the SX-108 sludge, it was necessary to perform this test in the hot cells. A suitable centrifuge was not available in the hot cell facility.

2.3 Analytical Methods

Portions of the sludges were analyzed before and after the sludge washing/caustic leaching treatment. The solid samples were solubilized for analysis by a well established KOH fusion method.[a] In the case of the BY-104, BY-110, and SX-108 sludge solids, a sodium peroxide fusion was also conducted; this allowed for the determination of K and Ni, and also gave a duplicate analytical result for other sludge components. The mean values are reported for those components determined through both fusion methods. Samples of the retrieval wash, the first and second caustic leach, and the final wash solutions were analyzed after acidification with HNO_3. Typically, acidification was performed within two or three days after the washing or leaching step was performed. The major metallic elements (Al, Bi, Cr, Fe, Na, etc.) as well as P and Si were determined by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). Anions were determined by ion chromatography. Alpha spectroscopy was used to determine the TRU elements, and gamma spectroscopy was used to measure the gamma-emitting radionuclides, such as ^{137}Cs. Uranium concentrations were determined by laser fluorimetry. A proportional beta counter was used to determine ^{90}Sr and ^{99}Tc after chemical separation of these isotopes from the other radionuclides.

(a) Method used was from the *Analytical Chemistry Laboratory (ACL) Procedure Compendium*. PNL-MA-599. Analytical Chemistry Laboratory Department. Pacific Northwest National Laboratory, Richland, Washington.



See Next Page

Figure 2.4. Schematic of BY-104 Sludge Washing and Caustic Leaching Test

Established procedures were used for all these analyses (see footnote [a] on page 2.8). It has recently been reported that the procedure for ^{99}Tc does not always give satisfactory results for Hanford tank wastes containing complexing agents,(a) but because none of the tank sludges investigated in this work contain significant quantities of complexing agents, the method should be reliable for these wastes.

In most cases, particle-size measurements were made using a Microtrac® X100 particle- size analyzer (Leeds & Northrup, North Wales, PA) with the particles being slurried in water for the measurement. In

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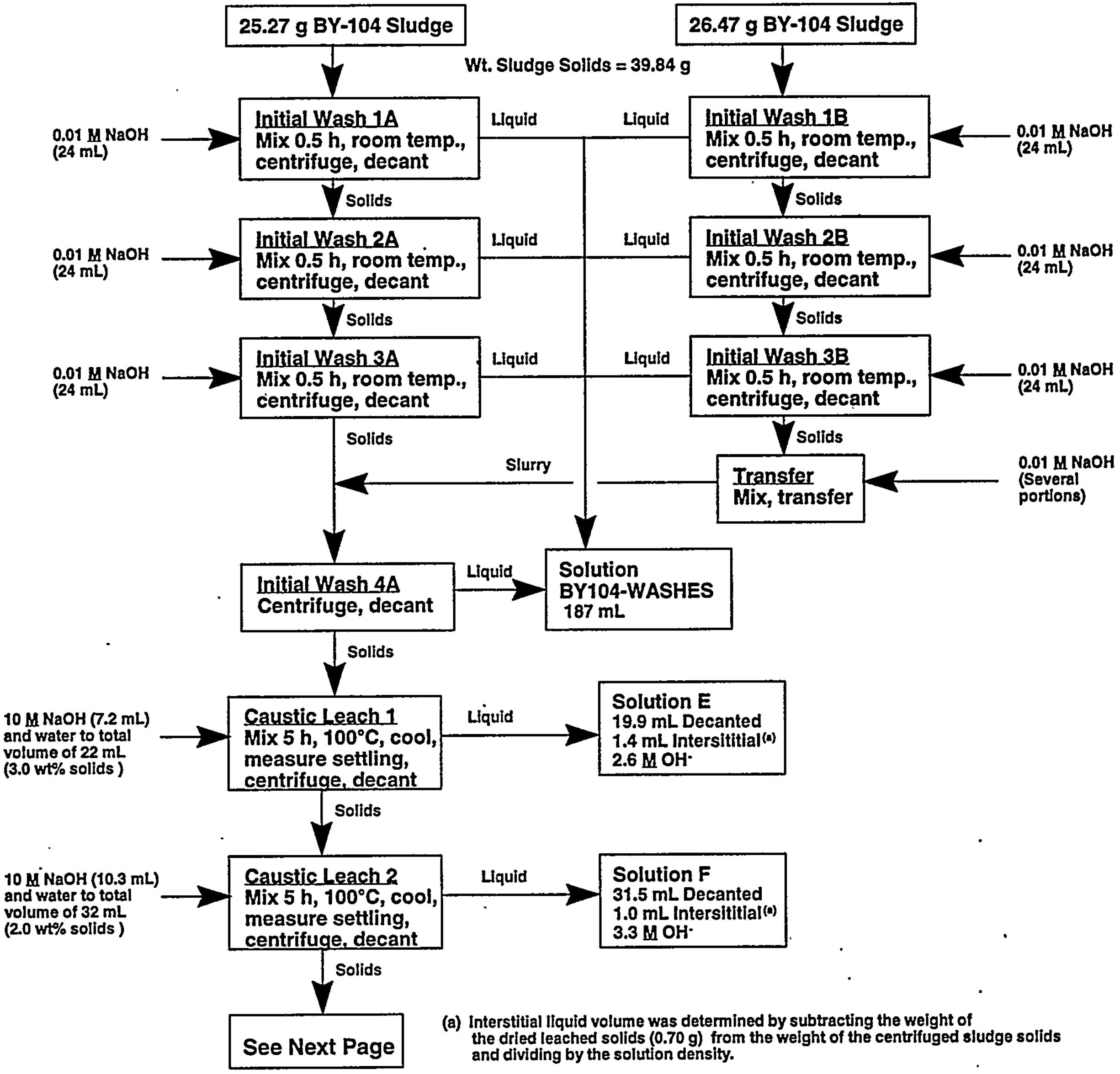
(a) *Technetium Removal and Speciation: A Progress Report*, by D. L. Blanchard et al., Pacific Northwest National Laboratory, Richland, Washington (1996).



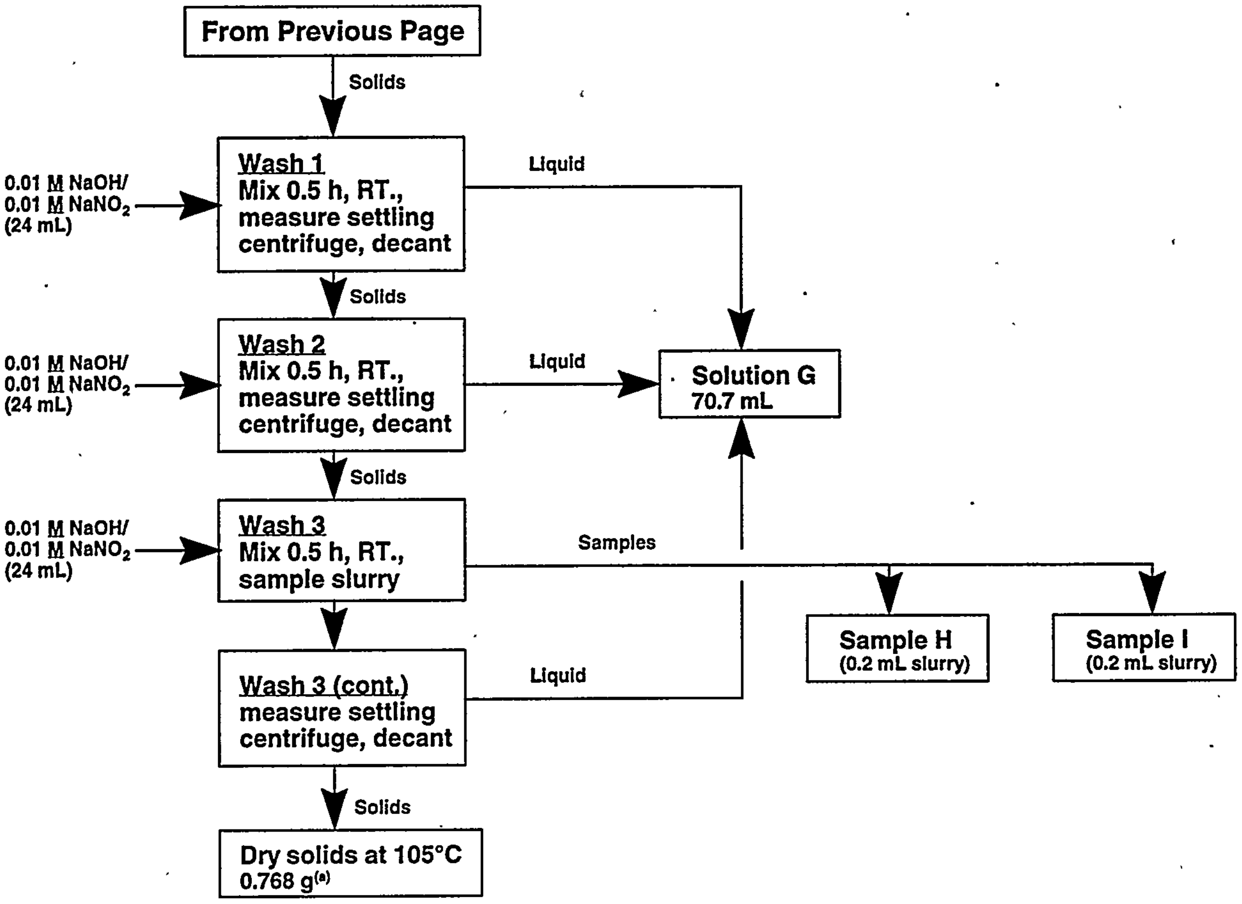
(a) Interstitial liquid volume was determined by subtracting the weight of the dried leached solids (0.70 g) from the weight of the centrifuged sludge solids and dividing by the solution density.

Figure 2.4. (contd)

the case of the C-107 test, a Brinkmann Instruments Model PSA 2010 was used to measure the particle-size distributions. For the C-107 measurements, the solids were suspended in a 1:1 mixture of water and glycerine.

Free hydroxide concentrations in the caustic leach solutions were determined by titration with standard HCl, as described previously (Rapko, Lumetta, and Wagner 1995).

The transmission electron microscopy (TEM) samples were prepared by dispersing a drop of the solids slurry on TEM copper grids covered with carbon films. This work was performed on a JEOL 1200

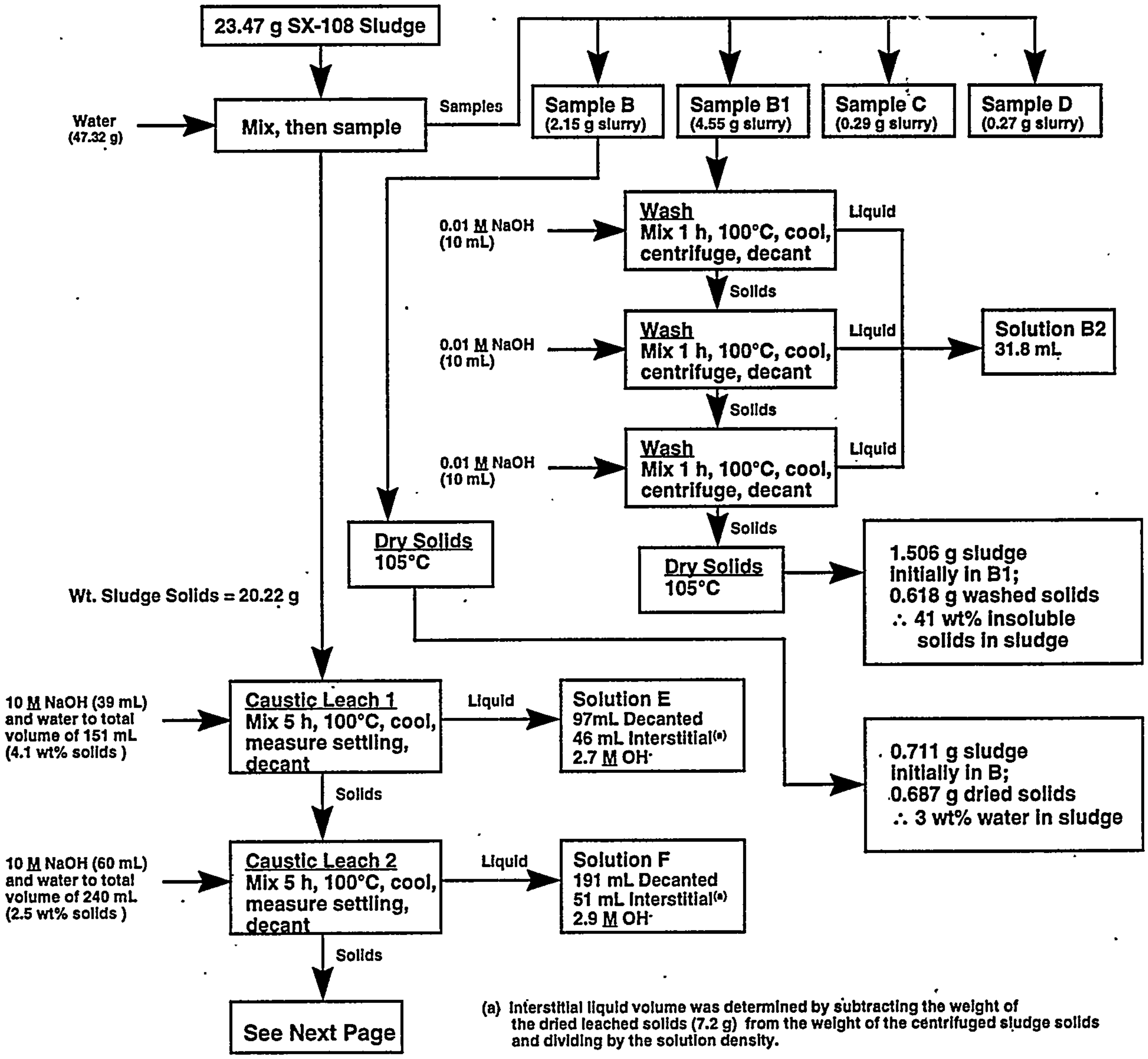


(a) Final weight of dried solids was adjusted for that removed in samples H and I.

BY-104.PPT

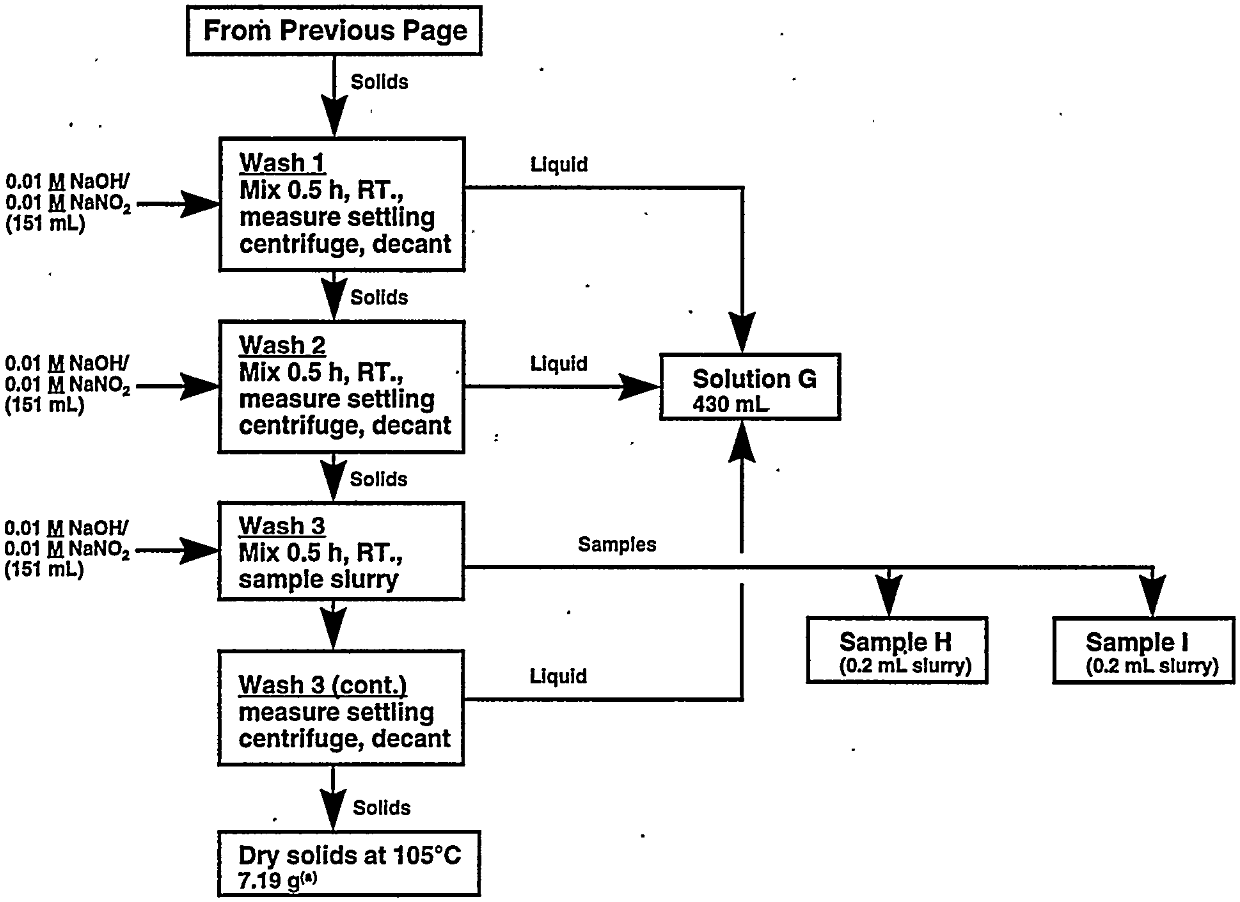
Figure 2.4. (contd)

analytical TEM operating at 120 kV. The analyses proceeded as follows: 1) the morphology, distribution, and sizes of particles were evaluated by electron imaging; 2) the chemical compositions of the particles were identified by electron dispersive X-ray (EDS); 3) the crystal structures of the particles were studied by electron diffraction; and 4) the diffraction patterns were compared with the JCPS-EDD Data Base published by the International Center for Diffraction Data.



(a) Interstitial liquid volume was determined by subtracting the weight of the dried leached solids (7.2 g) from the weight of the centrifuged sludge solids and dividing by the solution density.

Figure 2.5. Schematic of SX-108 Sludge Washing and Caustic Leaching Test



(a) Final weight of dried solids was adjusted for that removed in samples H and I.

SX108-2.PPT

Figure 2.5. (contd)

3.0 Results

Data obtained from the sludge washing and caustic leaching screening tests are presented in this section. The presentation is organized on a tank-by-tank basis.

3.1 Results of S-107 Test

3.1.1 Simple Sludge Washing with 0.01 M NaOH

Tables 3.1 and 3.2 show the results of the simple washing portion of the S-107 experiment (washing of portion B.1). Analysis of the untreated sludge solids (portion B) revealed the major components of the sludge to be Al (20.5 wt%), Na (16.0 wt%), U (1.4 wt%), Zr (0.97 wt%), Si (0.71 wt%), Cr (0.60 wt%), Fe (0.49 wt%), P (0.20 wt%), Ca (0.18 wt%), and Mn (0.13 wt%). For Al, Cr, Fe, Mn, and U, the mass recoveries during the simple washing portion of the test were within 20%. For the other nonradioactive components, the mass recoveries were high, especially for P for which three times as much was found in the wash solution and the washed solids as was found in the untreated sludge. Table 3.1 reports the P concentrations determined by ICP/AES. The phosphate ion concentration in the wash solution (B2) was determined to be 520 µg/mL by ion chromatography, which corresponds to 170 µg/mL of P. This value is only 9% lower than that obtained by ICP/AES; thus the discrepancy in the P mass recovery is likely due to an error in analyzing the untreated solids (no P was detected in the washed solids). This error arises again in analyzing the data from the caustic-leaching portion of the test (*vide infra*).

Simple washing only removed a small fraction (8%) of the Al from the S-107 sludge. Chromium and Si were removed somewhat better with 24% and 44% being removed, respectively. Phosphorus appeared to be completely removed, but as mentioned above, this result should be viewed with caution because of the poor reconciliation of mass. The P detection limit in the analysis of the washed solids was 943 µg/g; with 0.622 g of washed solids, up to 587 µg of undetected P could have been present in the washed solids. Based on this, it can be concluded that >91% of the P was removed. As expected, Na was efficiently removed, with only 7% remaining in the washed solids.

Table 3.2 summarizes the behavior of the radionuclides during simple washing of S-107 sludge. Washing removed ^{137}Cs and ^{99}Tc appreciably, but none of the other radionuclides. The 98% removal of Tc indicates that this element is likely present primarily in a soluble form such as pertechnetate. Mass recoveries for all the radionuclides were within 25%.

3.1.2 Caustic Leaching

Tables 3.3 through 3.9 summarize the results of the S-107 caustic leaching test. Table 3.3 shows the concentrations for the nonradioactive waste components in each process stream and the mass of each component dissolved in each process step. Mass recoveries (Table 3.4) for most of the important sludge constituents (Al, Cr, Fe, U) were acceptable. Mass recovery for Na was somewhat low, but this is to be expected because of the corrections needed to account for the large amount of Na added in the caustic leaching steps. As was the case with the simple washing portion of the test, the P recovery is high with four times as much P being detected in the leach and wash solutions and the treated residue as was

Table 3.1. Results of Tank S-107 Sludge Washing: Nonradioactive Components

	Wash Solution (B2)		Washed Solids (B1)			Component Distribution, %		Concentration in Initial Solids µg/g	
Component	Conc., µg/mL	Mass, µg	Conc., µg/g	Mass, µg	Total Mass, µg	Wash Solution	Washed Solids	Summation Method	Direct Analysis
Al	522	17017	303000	188466	205483	8	92	2.02E+05	2.05E+05
B	62.1	2024	843	524	2549	79	21	2.51E+03	7.03E+02
Ba	<0.01	<0.3	76.8	48	48	<1	>99	4.70E+01	3.96E+01
Bi	<0.11	<3	377	<234	<237	<2	>98	<2.3E+02	<3.4E+02
Ca	11.6	378	3830	2382	2760	14	86	2.72E+03	1.77E+03
Cr	52.2	1702	8790	5467	7169	24	76	7.06E+03	6.03E+03
Fe	0.6	20	9310	5791	5810	0	100	5.72E+03	4.89E+03
K	52.5	1712	(a)	(a)	(a)	(a)	(a)	(a)	(a)
La	<0.08	<3	<283	<176	<179	<1	>99	<1.8E+02	<2.6E+02
Li	0.9	29	<113	<70	<99	>29	<71	<9.7E+01	<1.7E+02
Mg	1	33	413	257	289	11	89	2.85E+02	<3.4E+02
Mn	<0.05	<2	2340	1455	1455	0	100	1.43E+03	1.26E+03
Mo	1.3	42	<189	<118	<160	>26	<74	<1.57E+02	<1.7E+02
Na	6320	199132 [b]	24500	15239	214371	93	7	2.11E+05	1.60E+05
Ni	0.5	16	(c)	(c)	(c)	(c)	(c)	(c)	(c)
P	186	6064	<943	<587	<6650	>91	<9	<6.55E+03	2.04E+03
Pb	<0.26	<8	1080	672	672	<1	>99	6.61E+02	<8.5E+02
Si	165	5379	11000	6842	12221	44	56	1.20E+04	7.10E+03
Sr	<0.02	<1	994	618	618	<1	>99	6.09E+02	4.80E+02
Ti	<0.03	<1	152	95	95	<1	>99	9.31E+01	9.00E+01
U	6.33E-04	0	24400	15177	15177	0	100	1.49E+04	1.40E+04
Zn	0.6	20	1060	659	679	3	97	6.68E+02	6.41E+02
Zr	<0.6	<20	33400	20775	20775	<1	>99	2.04E+04	9.72E+03

(a) Potassium values for sludge solids not reported because sample preparation involved KOH fusion.

(b) Value adjusted for the Na added as 0.01 M NaOH.

(c) Nickel values for sludge solids not reported because Ni crucible used in KOH fusion preparation.

Table 3.2. Results of Tank S-107 Sludge Washing: Radioactive Components

	Wash Solution (B2)		Washed Solids (B1)			Component Distribution, %		Concentration in Initial Solids, μCi/g		
Component	Conc., μCi/mL	Activity, μCi	Conc., μCi/g	Activity, μCi	Total Activity, μCi	Wash	Washed Solids	Summation Method	Direct Analysis	Recovery, %
Total Alpha	< 1E-05	< 3.3E-04	3.36	2.09E+00	2.09E+00	0	100	2.06E+00	1.73E+00	119
^{239,240}Pu	Not Determined		1.69	1.05E+00	1.05E+00	0	100	1.03E+00	8.95E-01	116
^{241}Am+^{238}Pu	Not Determined		1.62	1.01E+00	1.01E+00	0	100	9.92E-01	7.92E-01	125
^{241}Am(g)	Not Detected		1.28	7.96E-01	7.96E-01	0	100	7.84E-01	6.35E-01	123
^{243,244}Cm	Not Determined		0.046	2.86E-02	2.86E-02	0	100	2.82E-02	4.20E-02	67
^{137}Cs	3.62	118	56.6	3.52E+01	1.53E+02	77	23	1.51E+02	1.41E+02	107
^{60}Co	Not Detected		0.279	1.74E-01	1.74E-01	0	100	1.71E-01	1.50E-01	114
^{154}Eu	Not Detected		0.344	2.14E-01	2.14E-01	0	100	2.11E-01	1.85E-01	114
^{155}Eu	Not Detected		0.277	1.72E-01	1.72E-01	0	100	1.70E-01	< 0.3	--
^{90}Sr	< 5E-04	< 1.6E-02	437	2.72E+02	2.72E+02	0	100	2.68E+02	2.29E+02	117
^{99}Tc	4.32E-03	0.14	3.90E-03	2.43E-03	1.43E-01	98	2	1.41E-01	1.40E-01	101

Table 3.3. Concentrations of the Nonradioactive S-107 Sludge Components in the Various Process Solutions

	First Leach Solution (E)		Second Leach Solution (F)		Final Wash Solution (G)		Leached Solids (A)		
Component	Conc., µg/mL	Mass, µg[a]	Conc., µg/mL	Mass, µg[a]	Conc., µg/mL	Mass, µg[a]	Conc., µg/g	Mass, µg[a]	Total Mass, µg
Al	11725	398650	949	118728	83.2	3220	272000	190944	711542
B	57.3	1948	63.4	10981	77.9	7883	505	355	21167
Ba	<0.01	0	<0.01	<2	<0.01	<1	197	138	138
Bi	1.3	44	<0.13	<18	<0.11	<11	468	329	<402
Ca	10	340	9.9	1710	9.5	949	6600	4633	7632
Ce	0.13	<4	1.4	247	0.11	<4	518	364	611
Cr	200	6800	24.4	3479	2.6	132	13100	9196	19607
Fe	1.6	54	3.1	542	0.5	35	21850	15339	15970
K	130	4420	48.1	7968	28.7	2758	(b)	--	--
La	<0.1	<3	<0.1	<17	<0.08	<8	<276	<194	<223
Li	2.6	88	0.5	78	<0.03	0	<110	<77	<244
Mg	<0.13	<4	1.4	248	1.3	130	1005	706	1083
Mn	<0.07	<2	<0.07	<12	<0.06	<6	5370	3770	3770
Mo	4	136	<0.07	0	<0.06	<6	<184	<129	<265
Na	72020	2448680	68380	11800776	4620	86278	20550	14426	354954 [c]
Nd	<0.13	<4	<0.13	<22	<0.11	<11	441	310	<348
Ni	0.9	31	<0.04	<3	<0.03	<3	(d)	--	--
P	765	26010	28.2	1778	<0.28	0	840	590	28378
Pb	29	986	3.9	569	<0.25	<4	1530	1074	2629
Se	36.7	1248	<0.78	0	<0.66	<72	<2209	<1551	<2870
Si	52.4	1782	139	24383	64.5	6017	6015	4223	36404
Sr	<0.02	<1	<0.02	<3	<0.02	<2	2380	1671	1671
Ti	<0.03	<1	<0.03	<5	<0.03	<3	387	272	272
U	6.92	235	6.18	1065	0.46	12	53200	37346	38659
Zn	4.1	139	1.3	213	0.8	77	1815	1274	1704
Zr	0.4	14	0.4	69	<0.03	<1	81550	57248	57331

(a) Mass values represent the mass of material dissolved in a given step, these values are corrected for interstitial solution carried over from the previous step.

(b) Potassium values for sludge solids not reported because sample preparation involved KOH fusion.

(c) Value adjusted for the Na added as NaOH.

(d) Nickel values for sludge solids not reported because Ni crucible used in KOH fusion preparation.

determined in the untreated sludge solids. Indeed, more P was found in the solutions alone (0.028 g P) than would be expected based upon direct analysis of the sludge (0.007 g P). The values determined by IC as phosphate ion (see Table 3.5) corroborated the solution P concentrations determined by ICP/AES. Again, this appears to be due to an erroneously low value for the P concentration in the untreated solids.

Table 3.5 shows the concentrations of the anionic components in the various process solutions. As expected, significant amounts of NO_3^-, NO_2^-, and PO_4^{3-} were detected in solution. Additionally, a fair amount of SO_4^{2-} was detected. The amount of SO_4^{2-} found in the first caustic leach solution was approximately (within 4%) the same as that found in the simple wash solution when normalized to the initial amount of sludge solids used. Thus, caustic leaching removed little or no additional SO_4^{2-}. Total extent of SO_4^{2-} removal could not be determined because the sludge solids were not analyzed for this component.[a]

(a) Methods are currently being investigated for reliably determining sulfate in tank sludges so that sulfate removal can be quantified in future tests.

Table 3.4. Concentrations of the Nonradioactive S-107 Sludge Components in the Initial Sludge Solids

Component	Concentration in Initial Solids, µg/g Summation Method	 Direct Analysis	Mass Recovery, %
Al	2.09E+05	2.05E+05	102
B	6.22E+03	7.03E+02	885
Ba	4.06E+01	3.96E+01	103
Bi	< 1.2E+02	< 3.4E+02	--
Ca	2.24E+03	1.77E+03	127
Ce	1.79E+02	< 3.4E+02	--
Cr	5.76E+03	6.03E+03	96
Fe	4.69E+03	4.89E+03	96
K	(a)	(a)	--
La	< 6.5E+01	< 2.6E+02	--
Li	< 7.2E+01	<1.7E+02	--
Mg	3.18E+02	< 3.4E+02	--
Mn	1.11E+03	1.26E+03	88
Mo	< 7.8E+01	< 1.7E+02	--
Na	1.04E+05	1.60E+05	65
Nd	< 1.0E+02	< 3.4E+02	--
Ni	(b)	(b)	--
P	8.34E+03	2.04E+03	409
Pb	7.72E+02	< 8.5E+02	--
Se	< 8.4E+02	<2.0E+03	--
Si	1.07E+04	7.10E+03	151
Sr	4.91E+02	4.80E+02	102
Ti	7.98E+01	9.00E+01	89
U	1.14E+04	1.40E+04	81
Zn	5.00E+02	6.41E+02	78
Zr	1.68E+04	9.72E+03	173

(a) Potassium values for sludge solids not reported because sample preparation involved KOH fusion.

(b) Nickel values for sludge solids not reported because Ni crucible was used in KOH fusion preparation.

Table 3.5. Anion Concentrations in the Various S-107 Process Solutions

Component	Wash Solution (B2)		First Leach Solution (E)		Second Leach Solution (F)		Final Wash Solution (G)	
	Conc., µg/mL	Dissolved, µg/g sludge solids(a)	Conc., µg/mL	Dissolved, µg/g sludge solids(a)	Conc., µg/mL	Dissolved, µg/g sludge solids(a)	Conc., µg/mL	Dissolved, µg/g sludge solids(a)
OH^-	Not Determined		35,700	N/A(b)	47,600	N/A(b)	Not Determined	
NO_3^-	3,000	96,260	9,400	93,890	270	2441	18	93
NO_2^-	1,570	50,376	4,900	48,942	120	194	470	N/A(c)
PO_4^{3-}	520	16,685	1,800	17,979	110	3499	6	0
SO_4^{2-}	90	2,888	300	2,996	<5	<260	<5	<160
F	454	14,567	800	7,991	<25	<1,300	<25	<780
Cl	102	3,273	280	2,797	<25	<1,300	<25	<780
Br^-	<25	<802	<50	<500	<25	<1,300	<25	<780

(a) Amount of component dissolved in a given process step.

(b) Hydroxide added as NaOH.

(c) Nitrite was added in this step as part of the washing solution (0.01 M NaOH/0.01 M $NaNO_2$).

Table 3.6. Distribution of Nonradioactive S-107 Sludge Components Between the Various Process Streams

	Component Distribution, %(a)			
Component	First Leach Solution (E)	Second Leach Solution (F)	Final Wash Solution (G)	Leached Solids
Al	56	17	0	27
B	9	52	37	2
Ba	0	<2	<1	>97
Bi	~12	0	0	~88
Ca	4	22	12	61
Ce	0	40	0	60
Cr	35	18	1	47
Fe	0	3	0	96
K	Not determined	Not determined	Not determined	Not determined
La	(c)	(c)	(c)	(c)
Li	(c)	(c)	(c)	(c)
Mg	0	23	12	65
Mn	0	0	0	100
Mo	>51	0	0	<49
Na	Not determined	Not determined	Not determined	3(b)
Nd	<2	<6	<3	>89
Ni	Not determined	Not determined	Not determined	Not determined
P	92	6	0	2
Pb	38	22	0	41
Se	>43	0	<2	<55
Si	5	67	17	12
Sr	0	0	0	100
Ti	0	<2	<1	>97
U	1	3	0	97
Zn	8	12	5	75
Zr	0	0	0	100

(a) Amounts reported are adjusted for carry over of interstitial liquid; that is, the values reported for the solutions represent the amount of material actually dissolved during that step.

(b) Amount of Na in residue determined by comparing the amount of Na in the untreated solid to that in the leached solid.

(c) Analyte was below detection limit for all process streams

Table 3.7. Concentrations of the Radioactive S-107 Sludge Components in the Various Process Solutions

	First Leach Solution (E)		Second Leach Solution (F)		Final Wash Solution (G)		Leached Solids		
Component	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/g	Activity, µCi[(a)]	Total Activity, µCi
Total Alpha	< 1.3E-04	< 4.3E-03	< 3E-05	< 4.9E-03	< 2E-05	< 2.0E-03	8.05E+00	5.65E+00	5.65E+00
^{239,240}Pu	Not Determined		Not Determined		Not Determined		4.04E+00	2.84E+00	2.84E+00
^{241}Am+^{238}Pu	Not Determined		Not Determined		Not Determined		3.87E+00	2.72E+00	2.72E+00
^{241}Am(g)	Not Detected		Not Detected		Not Detected		3.01E+00	2.11E+00	2.11E+00
^{243,244}Cm	Not Determined		Not Determined		Not Determined		1.40E-01	9.83E-02	9.83E-02
^{137}Cs	1.12E+01	3.66E+02	8.16E-01	9.66E+01	4.80E-02	4.18E-01	2.70E+00	1.90E+00	4.65E+02
^{60}Co	4.76E-04	1.56E-02	< 6.5E-05	< 1.0E-02	< 4.4E-05	< 4.5E-03	6.57E-01	4.61E-01	4.77E-01
^{154}Eu	Not Detected		Not Detected		Not Detected		8.91E-01	6.25E-01	6.25E-01
^{155}Eu	Not Detected		Not Detected		Not Detected		5.77E-01	4.05E-01	4.05E-01
^{90}Sr	1.39E-03	4.55E-02	7.35E-04	1.24E-01	4.36E-04	4.32E-02	1.06E+03	7.44E+02	7.44E+02
^{99}Tc	1.13E-02	3.70E-01	7.33E-05	0	2.42E-04	2.59E-02	6.26E-03	4.39E-03	4.00E-01

(a) Activity values represent the activity of material dissolved in a given step, these values are corrected for interstitial solution carried over from the previous step.

Table 3.8. Concentrations of the Radioactive Components in the Initial S-107 Sludge Solids

Component	Concentration in Initial Solids, µCi/g Summation Method	Direct Analysis	Recovery, %
Total Alpha	1.66E+00	1.73E+00	96
^{239,240}Pu	8.33E-01	8.95E-01	93
^{241}Am+^{238}Pu	7.98E-01	7.92E-01	101
^{241}Am(g)	6.21E-01	6.35E-01	98
^{243,244}Cm	2.89E-02	4.20E-02	69
^{137}Cs	1.37E+02	1.41E+02	97
^{60}Co	1.40E-01	1.50E-01	93
^{154}Eu	1.84E-01	1.85E-01	99
^{155}Eu	1.19E-01	< 0.3	--
^{90}Sr	2.19E+02	2.29E+02	95
^{99}Tc	1.17E-01	1.40E-01	84

Table 3.9. Distribution of Radioactive S-107 Sludge Components Between the Various Process Streams

	Component Distribution, %[(a)]			
Component	First Leach Solution (E)	Second Leach Solution (F)	Final Wash Solution (G)	Leached Solids
Total Alpha	0	0	0	100
^{239,240}Pu	0	0	0	100
^{241}Am+^{238}Pu	0	0	0	100
^{241}Am(g)	0	0	0	100
^{243,244}Cm	0	0	0	100
^{137}Cs	79	21	0	0
^{60}Co	3	0	0	97
^{154}Eu	0	0	0	100
^{155}Eu	0	0	0	100
^{90}Sr	0	0	0	100
^{99}Tc	92	0	6	1

(a) Amounts reported are adjusted for carry over of interstitial liquid; that is, the values reported for the solutions represent the amount of material actually dissolved during that step.

In contrast, the amount of F⁻ ion in solution during the caustic leaching was only half that in the simple wash solution, indicating that leaching with caustic might have a detrimental effect on F⁻ removal.

The data in Table 3.6 indicate a dramatic increase in the amount of Al removed by caustic leaching compared to dilute NaOH washing. Only 8% of the Al was removed by simple washing, whereas a total of 73% was removed by caustic leaching. Most of the Al dissolution occurred during the first leaching step, but an additional ~20% was dissolved in the second leaching step. The amount of Cr removed was also improved by caustic leaching, with a total of 53% removed by caustic leaching compared to 24% by simple washing. The amounts of Al and Cr dissolved in the first leaching step were greater than in the second leaching step. Given the much lower concentrations of Al and Cr in the second leach solution compared to the first, it is unlikely that removal of these components was limited by solubility. As was the case with simple washing, P appeared to be efficiently removed from the S-107 sludge. The amount of Na in the leached solids was only 3% of that originally in the sludge solids.

Tables 3.7 through 3.9 summarize the radionuclide behavior during the caustic leaching test. Good mass recoveries (Table 3.8) were obtained for all detected radionuclides except ^{243,244}Cm, which is a relatively minor component in the S-107 sludge. As was observed with the simple washing case, ^{137}Cs and ^{99}Tc were the only radioactive materials significantly solubilized during the caustic leaching test. These two radionuclides were virtually quantitatively removed from the sludge solids by caustic leaching. In addition, a small amount of ^{60}Co was detected in the first leach solution.

3.1.3 Settling and Particle Size Data

Table 3.10 and Figures 3.1 and 3.2 present the settling data from the first caustic leaching step and the final three washing steps. Settling data for the second caustic leaching step are not presented because the solids in that step settled differently than in the other steps. In the first leach and the washing steps, sludge solids were clearly separated from the supernatant liquid. Thus in these cases, the height of the sludge layer could easily be followed as a function of time. In contrast, for the second caustic leaching step, the mixture remained cloudy for a period and no clear demarkation existed between the solids and the liquid. In this case, the solids layer built up from the bottom of the container until the supernatant liquid became clear. This occurred within ~4 h. Such behavior has been observed before (Rector and Bunker 1995) for very dilute slurries. At high solids concentrations (e.g., the first leach and the wash steps), the solid particles interact with one another to form a three-dimensional web structure that collapses upon itself during the settling process. On the other hand, for dilute slurries, (e.g., the second leach step), the second particles are far enough apart that interactions between them are weak, and the solids essentially fall freely through the liquid. This leads to a situation where the heavier particles fall faster while the lighter particles fall more slowly (yielding a solution that remains cloudy for a longer period of time).

Generally, the solids settled at reasonable rates; the slowest settling was observed in the first caustic leaching step in which the maximum observed settling velocity (v_{max}) was ~0.2 mm/min. The settling data were normalized according to a formula recommended by personnel at WHC.(a) The normalized settling data (Figure 3.2) indicated that the settling behavior was very similar for the first leaching step and the three washing steps.

(a) G. T. MacLean, Westinghouse Hanford Company, personal communication, 1996.

Table 3.10. Settling Data From the S-107 Caustic Leaching Test[a]

First Caustic Leach

t, min	h, mm	T	H
0	36	0.00	1.00
5	35	0.03	0.97
17	33	0.09	0.92
23	31	0.12	0.86
37	29	0.20	0.81
48	27	0.25	0.75
75	22	0.40	0.61
105	18	0.55	0.50
137	16	0.72	0.44
163	15	0.86	0.42
237	14	1.25	0.39
268	13	1.41	0.36
1231	9	6.50	0.25

First Wash

t, min	h, mm	T	H
0	40	0.00	1.00
3	31	0.19	0.78
5	24	0.32	0.60
9	17	0.58	0.43
21	13	1.35	0.33
54	10	3.47	0.25
134	8	8.61	0.20
4204	7.5	270	0.19

Second Wash

t, min	h, mm	T	H
0	44	0.00	1.00
4	40	0.21	0.91
7	27	0.37	0.61
11	21	0.59	0.48
16	18	0.85	0.41
32	14	1.71	0.32
100	11	5.34	0.25
254	10	13.6	0.23
1279	9	68.3	0.20

Third Wash

t, min	h, mm	T	H
0	43	0.00	1.00
5	40	0.19	0.93
8	32	0.30	0.74
12	26	0.45	0.60
16	22	0.60	0.51
35	17.5	1.30	0.41
104	14.5	3.87	0.34
255	11.5	9.49	0.27
390	11	14.5	0.26
1420	10	52.8	0.23

(a) t = time, h = sludge height, T = normalized time value = t^*v_{max}/h_0, $H = h/h_0$.

Figures 3.3 and 3.4, respectively, present particle-size data for the untreated and treated S-107 sludge solids. Leaching the sludge with caustic greatly reduced the size of the particles and greatly narrowed the particle-size distribution. The volume distribution for the untreated S-107 sludge indicated a mean particle size of 12.8 µm, while that for the treated material was 0.35 µm. Based on the number distribution, the mean particle size decreased from 0.52 µm for the untreated S-107 sludge to 0.13 µm for the treated material. The largest particle observed for the untreated material was 100 µm, but for the treated material, no particles greater than 1.5 µm were observed. A particle-size measurement was also made with the untreated material after an ultrasonic field was applied. This had very little effect, except to break up some of the largest particles (>80 µm).

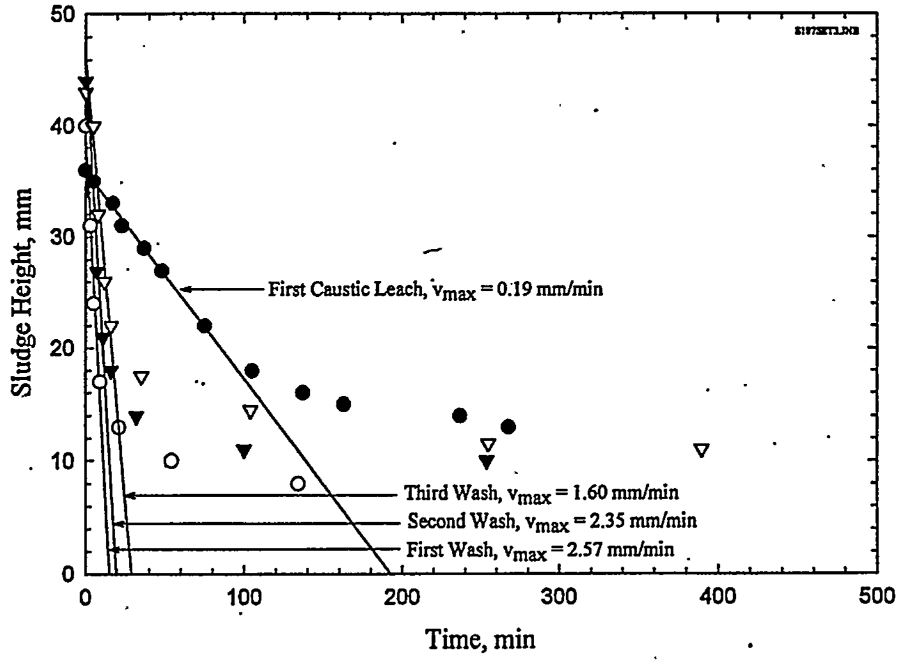


Figure 3.1. Settling Data From the S-107 Caustic Leaching Test

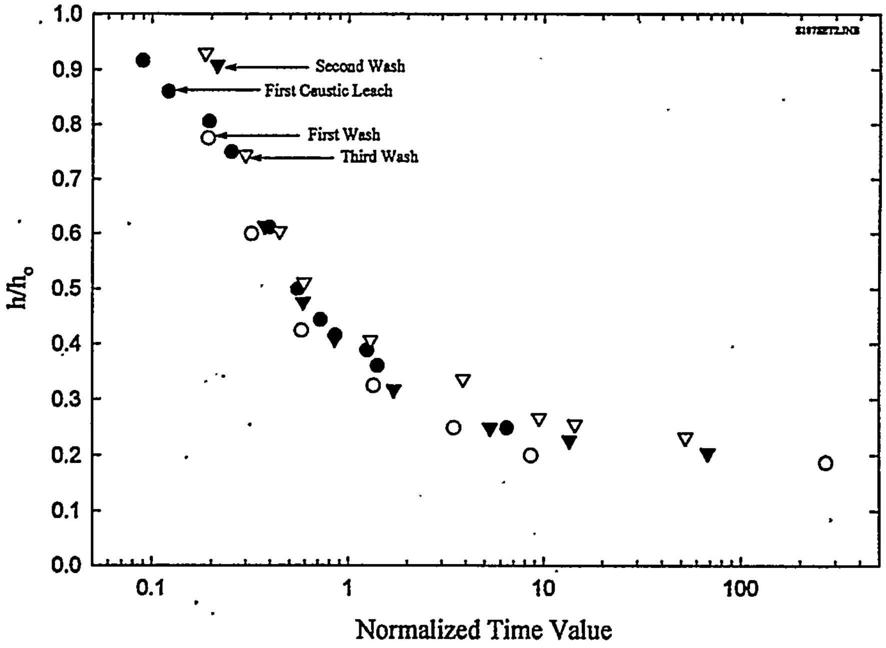


Figure 3.2. Normalized Settling Data From the S-107 Caustic Leaching Test

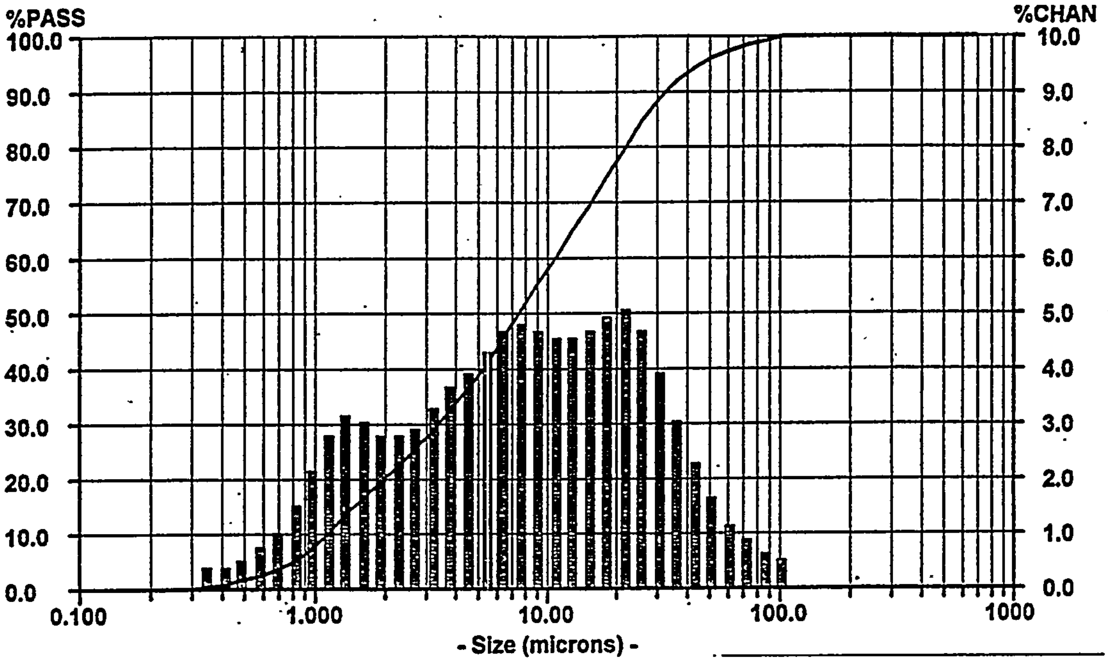


Figure 3.3. Particle-Size Volume Distribution for the Untreated S-107 Solids

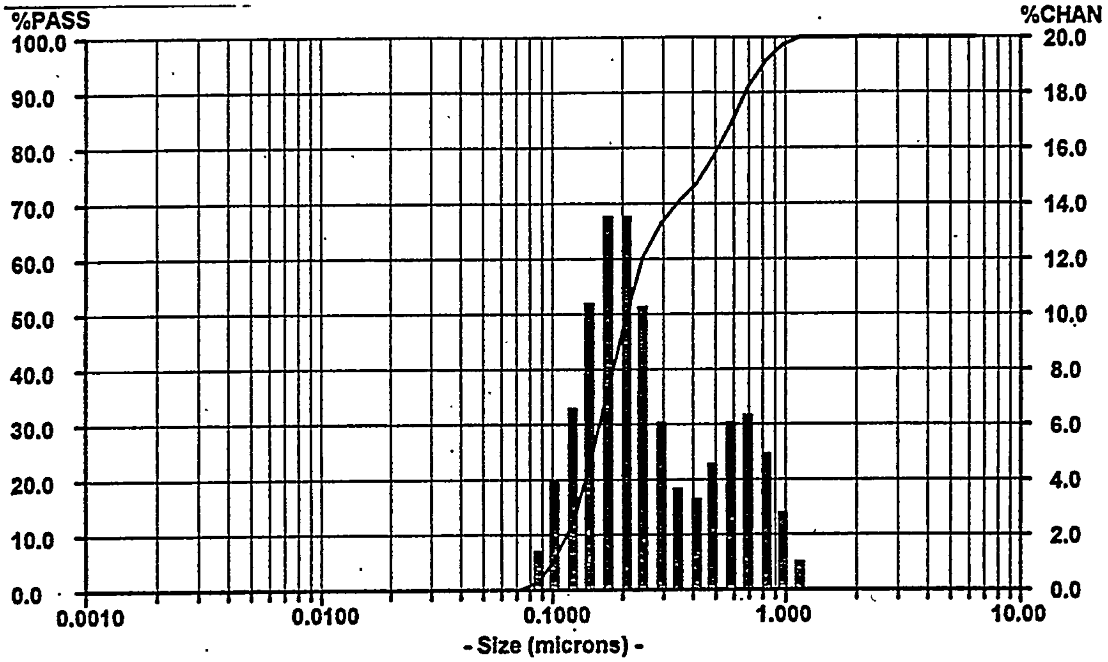


Figure 3.4. Particle-Size Volume Distribution for the Leached S-107 Solids

3.1.4 Microscopy Studies

As expected from the ICP/AES analysis, Al, Na, Si, Zr, Fe, and U were predominant elements indicated in a large area EDS spectrum of the untreated S-107 solids. X-ray diffraction (XRD) analysis indicated that Al primarily existed as boehmite, with a plate-like shape of ~0.1 μm. Aluminum was also associated with Si in clay, an amorphous phase with rod-like shape more than 0.5 μm long. The Zr-rich cubic particles of about 0.2 μm were in both multicrystalline and single crystalline phases and were apparently different types of ZrO_2. The Fe-rich particles were a multicrystalline phase of FeOOH, and exist as large agglomorates (Figure 3.5). A single crystalline uranium-containing particle was identified as either UO_3 or $UO_3{\cdot}H_2O$ by XRD. The latter particles are on the order of 0.1 μm (Figure 3.6).

The microscopy studies of the untreated S-107 sludge solids indicate that the primary particles were on the order of 0.1 to 0.5 μm. These values were much different than the particle-size distribution, which ranged from 0.3 to 100 μm. This suggests that under the conditions of the particle-size measurement (suspension in water), the particles are agglomorated.

As with the untreated S-107 material, a combination of XRD and EDS analysis indicated boehmite as the major Al-containing phase in the leached solids. Amorphous Si/Al clay material was also observed. Both of these species can be seen in Figure 3.7. Again, the FeOOH, ZrO_2, and UO_3 (or $UO_3{\cdot}H_2O$) were also evident. The main difference seen between the treated and untreated material is the loss of most of the Na-containing material.

3.2 Results of C-107 Test

The C-107 test was performed somewhat differently than the other tests described in this report. The C-107 test was performed in FY-1995 using the procedure that was approved for testing at that time (Rapko, Lumetta, and Wagner 1995). Subsequently, modifications to the test procedure occurred. In the older version of the test procedure, the sludge was contacted with 0.01 M NaOH/0.01 M $NaNO_2$ at nominally 2 wt% solids to mimic the retrieval of the waste. Subsequent to this "retrieval wash" step, the solids were leached with caustic at nominally 8 wt% solids. The leach steps were then followed by washing with 0.01 M NaOH/0.01 M $NaNO_2$. This section presents the results of the test using sludge from C-107. Tables 3.11 through 3.14 summarize the behavior of the nonradioactive components; Tables 3.15 through 3.17 summarize the radionuclide behavior.

3.2.1 Retrieval Wash

Very little (1%) Al was dissolved upon washing the C-107 sludge with 0.01 M NaOH/0.01 M $NaNO_2$ at 2 wt% solids (Table 3.12). A significant fraction (34%) of the Cr dissolved during this wash step, which was likely chromate ion as indicated by the yellow color of the retrieval wash solution. Most of the P (~70%) dissolved in this step. The only other nonradioactive components that showed appreciable dissolution in the 0.01 M NaOH/0.01 M $NaNO_2$ solution were B, Li, and Mo. A small amount of U was also dissolved. Because of the large amount of Na added in subsequent steps, it was impossible to determine precisely how much Na was removed from the sludge by simple washing.

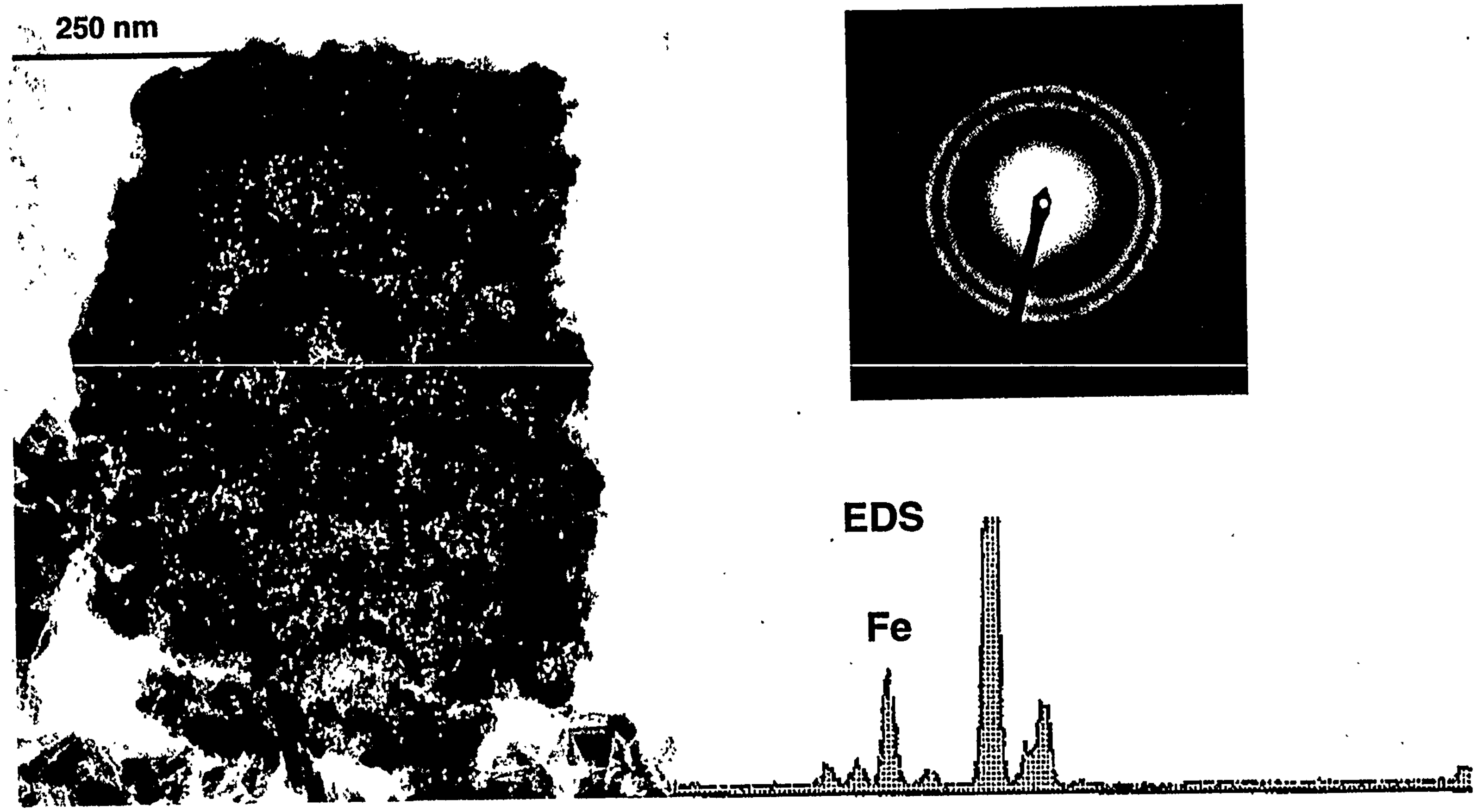


Figure 3.5. FeOOH Particles in the Untreated S-107 Sludge

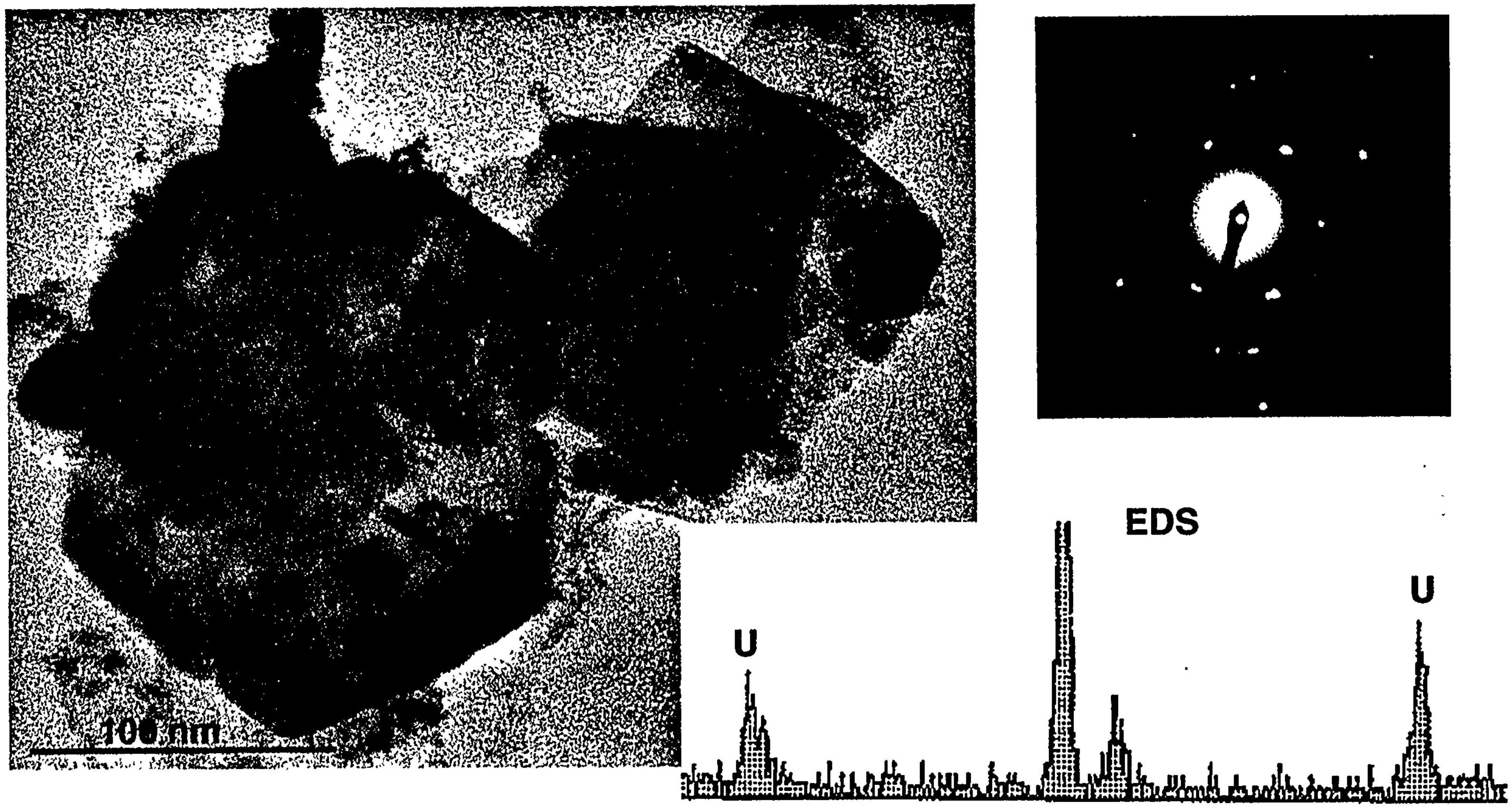


Figure 3.6. Uranium Oxide Particles in the Untreated S-107 Sludge

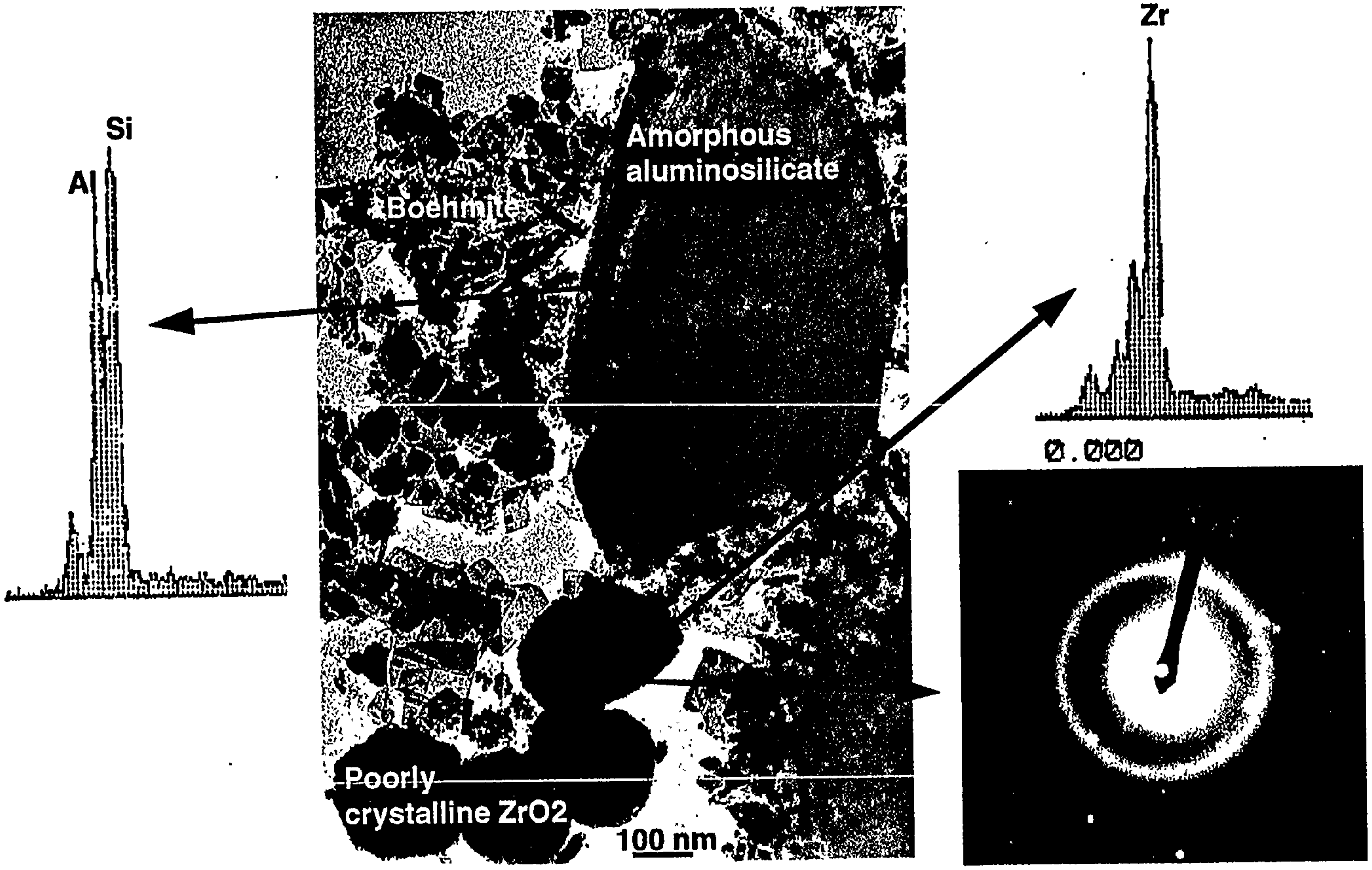


Figure 3.7. Boehmite, Amorphous Aluminosilicate, and Poorly Crystalline ZrO_2 in the Leached S-107 Sludge

Table 3.11. Concentrations of the Nonradioactive C-107 Sludge Components in the Various Process Streams

	Retrieval Solution (E)		First Caustic Leach (G)		Second Caustic Leach (I)		Final Wash (K)		Leached Solids (A)		
Component	Conc., μg/mL	Mass, μg[a]	Conc., μg/mL	Mass, μg[a]	Conc., μg/mL	Mass, μg[a]	Conc., μg/mL	Mass, μg[a]	Conc., μg/g	Mass, μg	Total Mass, μg
Ag	<0.13	<15	1.70	33	<0.26	<6	0.68	37	1139	2472	2542
Al	44.0	5240	12852	253000	2997	28271	550	21930	41061	89102	397543
As	<0.85	<101	9.78	193	<1.7	<38	<0.85	<47	249	540	<919, >733
B	0.34	40	1.36	25	<0.34	<8	0.94	52	38	83	<208, >200
Ba	<0.09	<11	<0.18	<4	<0.18	<4	<0.09	<5	2718	5899	5899
Bi	<0.85	<101	4.42	87	<1.7	<38	<0.85	<47	387	840	<1113, >927
Ca	2.89	344	4.17	70	<0.86	<19	<0.43	<24	4110	8919	9333
Cd	<0.13	<15	<0.26	<5	<0.26	<6	<0.13	<7	459	996	<1029, >996
Ce	<0.85	<101	7.31	144	<1.7	<38	4.42	244	1310	2842	<3369, >3230
Co	<0.09	<11	1.02	20	0.43	6	0.51	27	139	301	<365, >354
Cr	15.7	1871	34.3	614	12.1	166	1.2	32	1320	2864	5546
Cu	<0.09	<11	2.72	54	1.96	35	1.53	79	792	1718	1886
Fe	0.17	20	6.21	122	4.17	74	6.72	358	318312	690737	691311
K	19.6	2337	299	5819	134	2082	1.36	0	(b)	(b)	(b)
La	<0.64	<76	<1.2	<24	<1.2	<27	<0.64	<35	922	2002	<2164, >2002
Li	11.0	1305	4.51	45	2.30	38	<0.26	<14	79	172	1559
Mg	<0.85	<101	<1.7	<33	<1.7	<38	<0.85	<47	1538	3338	<3557, >3338
Mn	<0.09	<11	<0.18	<4	<0.18	<4	<0.09	<5	16925	36727	36727
Mo	0.94	111	1.79	31	<0.52	<12	<0.26	<14	156	339	<507, >481
Na	3327	395881	75262	1469351	74301	1431119	81109	4261085	50121	108763	7666198
Nd	<0.64	<76	7.65	151	4.08	68	4.85	256	2129	4620	5095
Ni	<0.26	<31	<0.52	<10	<0.52	<12	<0.26	<14	(d)	(d)	(d)
P	351	41775	750	13362	142	928	22.0	814	1594	3459	60338
Pb	<0.51	<61	88.6	1745	73.3	1368	90.6	4787	16548	35908	43809
Se	<0.85	<101	<1.7	<33	<1.7	<38	<0.85	<47	431	935	<1154, >935
Si	4.68	556	61.4	1190	172	3647	367	19766	35987	78091	103250
Sr	<0.09	<11	<0.18	<4	<0.18	<4	<0.09	<5	438	950	<974, >950
Ti	<0.13	<15	<0.26	<5	<0.26	<6	<0.13	<7	1086	2358	2358
U	21.5	2559	2.52	0	373	8314	17.3	0	18100	39277	50150
Y	<0.17	<20	<0.34	<7	<0.34	<8	<0.17	<9	233	505	<549, >505
Zn	<0.21	<25	12.2	239	3.66	45	<0.21	<12	352	763	<1084, >1047
Zr	<0.17	<20	3.23	64	<0.34	<8	2.47	136	17637	38272	38472

(a) Mass values represent the mass of material dissolved in a given step, these values are corrected for interstitial solution carried over from the previous step.

(b) Potassium values are not reported because the sample was dissolved for analysis using a KOH fusion technique.

(c) Adjusted for the 3.07 g of Na added as NaOH.

(d) Nickel values are not reported because a Ni crucible was used during the KOH fusion procedure.

Table 3.12. Distribution of Nonradioactive C-107 Sludge Components Between the Various Process Streams

	Component Distribution, %[(a)]				
Component	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Ag	<1	1	0	1	>97
Al	1	64	7	6	22
As	<11	23	0	<5	<77, >61
B	20	12	0	26	42
Ba	0	0	0	0	100
Bi	<9	8	0	<4	<92, >77
Ca	4	1	0	0	95
Cd	<1	0	0	<1	>98
Ce	0	3	0	8	89
Co	0	6	2	8	85
Cr	34	11	3	0	52
Cu	0	3	2	4	91
Fe	0	0	0	0	100
K	Not Determined	Not Determined	Not Determined	Not Determined	Not Determined
La	<4	<1	<1	<1	>93
Li	84	3	2	0	11
Mg	<3	<1	<1	<1	>94
Mn	0	0	0	0	100
Mo	23	6	0	0	71
Na	Not Determined	Not Determined	Not Determined	Not Determined	28(b)
Nd	0	3	1	5	>91
Ni	Not Determined	Not Determined	Not Determined	Not Determined	Not Determined
P	69	22	2	1	6
Pb	0	4	3	11	82
Se	<9	<3	<3	<4	>82
Si	1	1	4	19	76
Sr	0	0	0	0	100
Ti	0	0	0	0	100
U	5	0	17	0	78
Y	<4	<1	<1	<2	>98
Zn	0	23	3	0	74
Zr	0	0	0	0	100

(a) Amounts reported are adjusted for carry over of interstitial liquid; that is, the values reported for the solutions represent the amount of material actually dissolved during that step.

(b) Amount of Na in residue determined by comparing the amount of Na in the untreated solid to that in the leached solid.

Table 3.13. Mass Recoveries for the Nonradioactive C-107 Sludge Components

	Concentration in Dried Sludge, g/g Sludge		
Component	Direct Analysis	Summation Method[(a)]	Recovery, %
Ag	8.53E-04	6.04E-04	71
Al	8.68E-02	9.48E-02	109
As	1.86E-04	1.67E-04	90
B	4.39E-04	4.67E-05	11
Ba	1.45E-03	1.40E-03	97
Bi	2.73E-04	2.17E-04	80
Ca	2.73E-03	2.22E-03	81
Cd	2.62E-04	2.37E-04	91
Ce	7.97E-04	7.64E-04	96
Co	9.19E-05	8.44E-05	92
Cr	1.25E-03	1.32E-03	106
Cu	5.48E-04	4.49E-04	82
Fe	1.79E-01	1.65E-01	92
K	(b)	(b)	(b)
La	4.93E-04	4.76E-04	97
Li	2.89E-04	3.68E-04	128
Mg	7.78E-04	7.95E-04	102
Mn	9.36E-03	8.74E-03	93
Mo	1.14E-04	1.13E-04	100
Na	9.14E-02	(c)	(c)
Nd	1.08E-03	1.21E-03	112
Ni	(d)	(d)	(d)
P	9.50E-03	1.43E-02	151
Pb	1.06E-02	1.04E-02	98
Se	2.57E-04	2.23E-04	87
Si	2.58E-02	2.46E-02	95
Sr	2.41E-04	2.26E-04	94
Ti	5.99E-04	5.61E-04	94
U	1.11E-02	1.19E-02	107
Y	1.14E-04	1.20E-04	105
Zn	3.62E-04	2.47E-04	68
Zr	5.70E-03	9.16E-03	161

(a) In determining concentrations by the summation method, solution concentrations were assumed to be zero if below the detection limit.

(b) Potassium values for sludge solids not reported because sample preparation involved KOH fusion.

(c) Na mass balance could not be resolved due to the relatively large out of Na added during leaching.

(d) Nickel values for sludge solids not reported because Ni crucible used in KOH fusion preparation.

Table 3.14. Anion Concentrations in the Various C-107 Process Solutions

	Retrieval Wash Solution		First Leach Solution		Second Leach Solution		Final Wash Solution	
Component	Conc., µg/mL	Dissolved, µg/g sludge solids[a]	Conc., µg/mL	Dissolved, µg/g sludge solids[a]	Conc., µg/mL	Dissolved, µg/g sludge solids[a]	Conc., µg/mL	Dissolved, µg/g sludge solids[a]
OH^-	Not Determined		47,800	N/A[b]	51,900	N/A[b]	Not Determined	
NO_3^-	1225	34,441	110	0	<50	<270	<50	<660
NO_2^-	2210	61345[c]	390	0	60	41	280	N/A[d]
PO_4^{3-}	770	21,649	1930	8,380	400	755	70	652
SO_4^{2-}	240	6,748	<50	<235	<50	<270	<50	<660
F^-	40	1,125	(f)	--	(f)	--	(f)	--
Cl^-	40	1,125	(f)	--	(f)	--	(f)	--
Br^-	80	<1,175	60	211	<25	<135	<25	<330

(a) Amount of component dissolved in a given process step.

(b) Hydroxide added as NaOH.

(c) Corrected for nitrite was added in this step as part of the washing solution (0.01 M NaOH/0.01 M $NaNO_2$).

(d) Nitrite was added in this step as part of the washing solution (0.01 M NaOH/0.01 M $NaNO_2$).

(f) Analyte could not be accurately determined due to matrix interference.

Table 3.15. Concentrations of the Radioactive C-107 Sludge Components in the Various Process Solutions

	Concentration, µCi/mL				Concentration, µCi/g	
Component	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue	Total µCi
Total Alpha	1.89E-03	4.42E-03	1.36E-03	5.95E-03	2.78E+01	60.9381882
^{239,240}Pu	1.61E-03	3.68E-03	1.17E-03	2.17E-03	9.56E+00	21.11358735
^{241}Am + ^{238}Pu	2.80E-04	7.38E-04	1.90E-04	3.78E-03	1.75E+01	38.19643285
^{241}Am(g)	< 5.1E-04	< 5.1 E-03	< 1.7E-03	< 6.0E-04	1.91E+01	41.4088
^{137}Cs	5.71E-01	1.22E+01	2.96E+00	6.43E-01	7.32E+01	521.77782
^{90}Sr	1.06E-02	1.67E-01	1.76E-01	2.69E-01	1.37E+04	29723.85933
^{99}Tc	2.18E-03	4.22E-04	8.02E-05	< 2.6E-5	2.87E-03	0.264746702
^{243,244}Cm	< 1.7E-05	< 1.7 E-05	< 1.7E-05	< 1.7E-05	7.51E-01	1.628168
^{154}Eu	< 2.6E-04	< 1.7 E-03	< 2.6E-04	< 2.6E-04	2.27E+01	49.2136
^{155}Eu	< 8.5E-04	< 7.6 E-03	< 2.6E-03	< 1.7E-03	2.02E+01	43.7936
^{125}Sb	4.46E-03	< 1.7 E-02	< 4.2E-03	1.85E-03	8.08E+00	17.51744
^{60}Co	< 8.5E-05	< 2.6 E-04	< 1.7E-04	< 1.7E-04	3.86E+00	8.36848

Table 3.16. Distribution of the Radioactive C-107 Sludge Components Between the Various Process Streams

Component	Component Distribution, %				
	Retrieval Solution (E)	First Caustic Leach (G)	Second Caustic Leach (I)	Wash (K)	Residue (A)
Total Alpha	0	0	0	1	99
^{239,240}Pu	1	0	0	1	98
^{241}Am+^{238}Pu	0	0	0	1	99
^{241}Am(g)	0	0	0	0	100
^{137}Cs	13	46	6	7	30
^{90}Sr	0	0	0	0	100
^{99}Tc	97	0	0	0	2
^{243,244}Cm	0	0	0	0	100
^{154}Eu	0	0	0	0	100
^{155}Eu	0	0	0	0	100
^{125}Sb	3	0	0	1	100
^{60}Co	0	0	0	0	100

Table 3.17. Mass Recoveries for the Radioactive C-107 Sludge Components

Component	Concentration, µCi/g		Recovery, %
	Direct Analysis	Summation Method	
Total Alpha	1.51E+01	1.45E+01	96
^{239,240}Pu	5.77E+00	5.03E+00	87
^{241}Am+^{238}Pu	9.31E+00	9.10E+00	98
^{241}Am(g)	9.83E+00	9.87E+00	100
^{137}Cs	1.27E+02	1.24E+02	98
^{90}Sr	5.58E+03	7.08E+03	127
^{99}Tc	4.44E-02	6.31E-02	142
^{243,244}Cm	4.99E-01	3.88E-01	78
^{154}Eu	1.03E+01	1.17E+01	114
^{155}Eu	9.15E+00	1.04E+01	114
^{125}Sb	4.41E+00	4.17E+00	95
^{60}Co	2.09E+00	1.99E+00	95

3.2.2 Caustic Leaching

The data in Table 3.12 indicate a dramatic increase in the amount of Al removed from C-107 sludge by caustic leaching compared to simple washing. As was the case with S-107, most of the Al dissolution occurred during the first leaching step; 64% of the Al dissolved during the first caustic leaching step, with an additional 7% dissolved in the second leaching step. The data indicated an additional 6% Al dissolution in the final washing steps, but this quantity might have been carried over in the interstitial liquid remaining after the second leaching step. Nevertheless, a total of 78% of the Al was removed from the C-107 sludge. Given the similar conditions of the first and second leaching steps, it is doubtful that solubility limits constrained the removal of Al. Caustic leaching only slightly increased Cr removal. The total Cr removal was 48%, which is very similar to the value obtained with S-107 sludge. Again, the lack of Cr removal in the second leach step suggests that Cr removal was not limited by solubility. A total of 94% of the P was removed from the C-107 sludge, indicating that this treatment was quite effective at removing P from the HLW stream. The amount of Na in the leached solids was 28% of that originally in the untreated sludge solids. It is unclear whether this significant Na residue was due to inefficient washing of NaOH from the solids or from the presence of some unleachable Na-containing species. But given the fact that the Na residues were generally much lower for the other tank sludges investigated, it is unlikely that the high relative amount of Na in the C-107 residue was due to inefficient removal of NaOH.

Mass recoveries for the nonradioactive C-107 sludge components were generally good (Table 3.13). As was the case with the S-107 test, P was an exception with a high mass recovery. This suggests a systematic problem with the KOH fusion method for preparing samples from sludge solids. This hypothesis is supported by comparing the P data generated in this work to that generated on a parallel test performed at Los Alamos National Laboratory (Temer and Villarreal 1995b). In the Los Alamos work, sludges were dissolved for analysis using acid digestion rather than caustic fusion. For the untreated sludge solids, the Los Alamos workers reported a value of 0.0365 g P/g sludge solids, which is nearly four times the value of 0.0095 g P/g sludge solids obtained in this work. In the future, alternate analytical preparation methods will be used to attempt to alleviate this problem.

Table 3.14 presents the concentrations of the anionic components in the various process solutions. As expected, significant amounts of NO_3^-, NO_2^-, and PO_4^{3-} were detected in solution, especially in the retrieval wash solution. Sulfate was only detected in the retrieval wash solution; caustic leaching did not appear to solubilize more SO_4^{2-}. But again, because the solids were not analyzed for anions, the extent of SO_4^{2-} removal from the sludge could not be assessed. A small amount of F^- was detected in the retrieval wash solution, but quantitation of F^- in subsequent solutions was vitiated by matrix interferences.

Tables 3.15 through 3.17 summarize the radionuclide behavior during the C-107 caustic leaching test. Generally, good mass recoveries (Table 3.17) were obtained for all detected radionuclides in the C-107 sludge. As expected, ^{137}Cs and ^{99}Tc were the only radioactive materials significantly solubilized during washing and caustic leaching. Technetium was nearly quantitatively removed from the sludge solids. On the other hand, a considerable fraction (30%) of the ^{137}Cs remained in the sludge solids after leaching and washing.

3.2.3 Settling and Particle-Size Data

The settling behavior during the C-107 retrieval wash step was similar to that observed for the second S-107 leaching step; that is, the supernatant mixture slowly cleared, with the sludge layer building up from the bottom of the vessel. The supernatant liquid cleared and the sludge layer stabilized within 7 h. Very poor settling behavior was observed for the two caustic leaching steps. Essentially the sludge solids did not settle after ~24 h; instead, stable suspensions were formed. Similar behavior was observed for the three final wash steps as well. This behavior can be explained based on the high solids concentrations (~9 wt%) in the leaching and final washing step. At this concentration of solids, the interactions between the particles are great enough that a three-dimensional network of solids particles is generated that is capable of supporting its own weight, which hinders settling.

Figures 3.8 and 3.9, respectively, present particle-size data for the untreated and treated C-107 sludge solids. The mean particle size changed relatively little upon leaching the C-107 sludge. The number

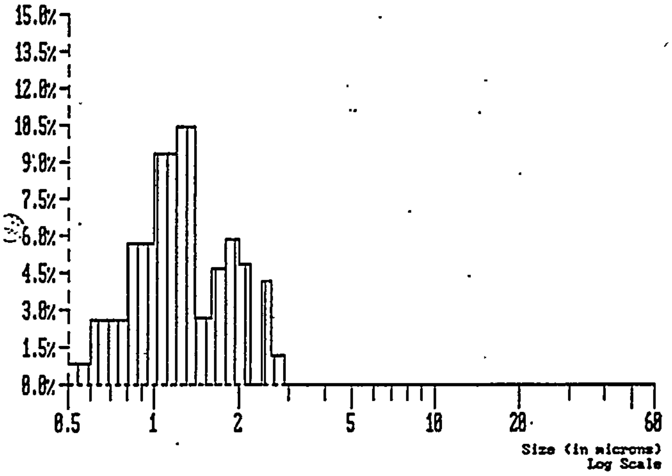


Figure 3.8. Particle-Size Volume Distribution for the Untreated C-107 Solids

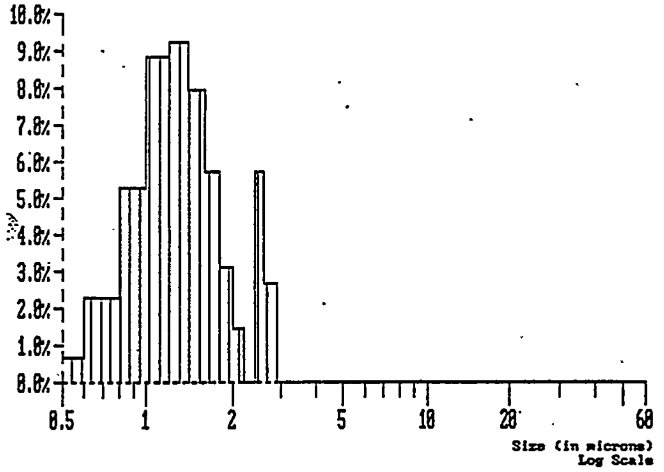


Figure 3.9. Particle-Size Volume Distribution for the Leached C-107 Solids

distributions indicated the mean particle sizes to be 0.89 µm for the untreated C-107 sludge and 0.92 µm for the treated material. The volume distributions indicated the mean particle sizes to be 1.32 µm for the untreated C-107 solids and 1.36 µm after caustic leaching. This contrasts greatly to what was observed for the S-107 sludge in which a large reduction in particle size occurred upon leaching, but was consistent with the changes observed for other sludge leaching tests (Rapko, Lumetta, and Wagner 1995).

3.2.4 Microscopy Studies

The overall EDS revealed that the untreated C-107 sludge is rich in Fe, Na, Si, Al, and Zr. In this case, the Al is not only associated with Si in clay materials, but is also present in sharp-edged grains of ~0.2 µm. The EDS and the X-ray diffraction pattern suggest that this material is one of the aluminum oxides, $(Al_2O_3)_x \cdot (H_2O)_y$, where x=5 and y=1, or x=11 and y=1.79, or x=1 and y=0. The Fe-rich particles appear to be primarily an iron(III) oxy/hydroxide species, while the Zr-rich materials are different types of ZrO_2. In addition, $Pb_5(OH)(PO_4)_3$ particles have a distinctive rod-like shape (Figure 3.10).

The leaching/washing process removed most of the Na salts and apparently a large fraction of the aluminum oxides, although some $(Al_2O_3)_x \cdot (H_2O)_y$, remained in the residue. The primary Al-containing material in the leached residue was an amorphous Al/Si clay agglomerate of ~0.3 µm (Figure 3.11).

The iron (III) oxy/hydroxide species was by far the most abundant material identified in the leached solids. This agrees well with the ICP/AES results, which indicated that the residual solids were 32 wt% Fe (Table 3.11).

3.3 Results of BY-104 Test

3.3.1 Simple Sludge Washing With 0.01 M NaOH

Table 3.18 lists the concentrations of the nonradioactive BY-104 sludge components in the initial wash solution, and Table 3.19 presents the percentages of each component dissolved in the simple washing process. Large fractions of Al (65%), Cr (69%), and P (93%) were removed by washing with dilute hydroxide solution. Silicon was also significantly removed (46%). Because the washed solids were not directly analyzed, the Na removal by simple washing could not assessed. However, based on the very low percentage (2.7 wt%) of water-insoluble solids in this waste, it can be assumed that Na is easily removed.

3.3.2 Caustic Leaching

Tables 3.18 and 3.19, respectively, also list the concentrations of the nonradioactive BY-104 sludge components in the caustic leach solutions and the percentages of each component dissolved in the leaching and final washing steps. Caustic leaching resulted in an additional 33% removal of Al; the first leaching step dissolved most of this additional Al. Leaching with caustic removed little additional Cr or P from the BY-104 sludge.

Table 3.20 gives the mass recoveries for the nonradioactive sludge components. Mass recoveries were reasonable for major components such as Al and Na, but poor for many of the minor BY-104 sludge components. The poor recovery for the minor components can be attributed to the large analytical uncertainties in determining these components at levels near the detection limits coupled with the relatively large volume of the initial wash solution.

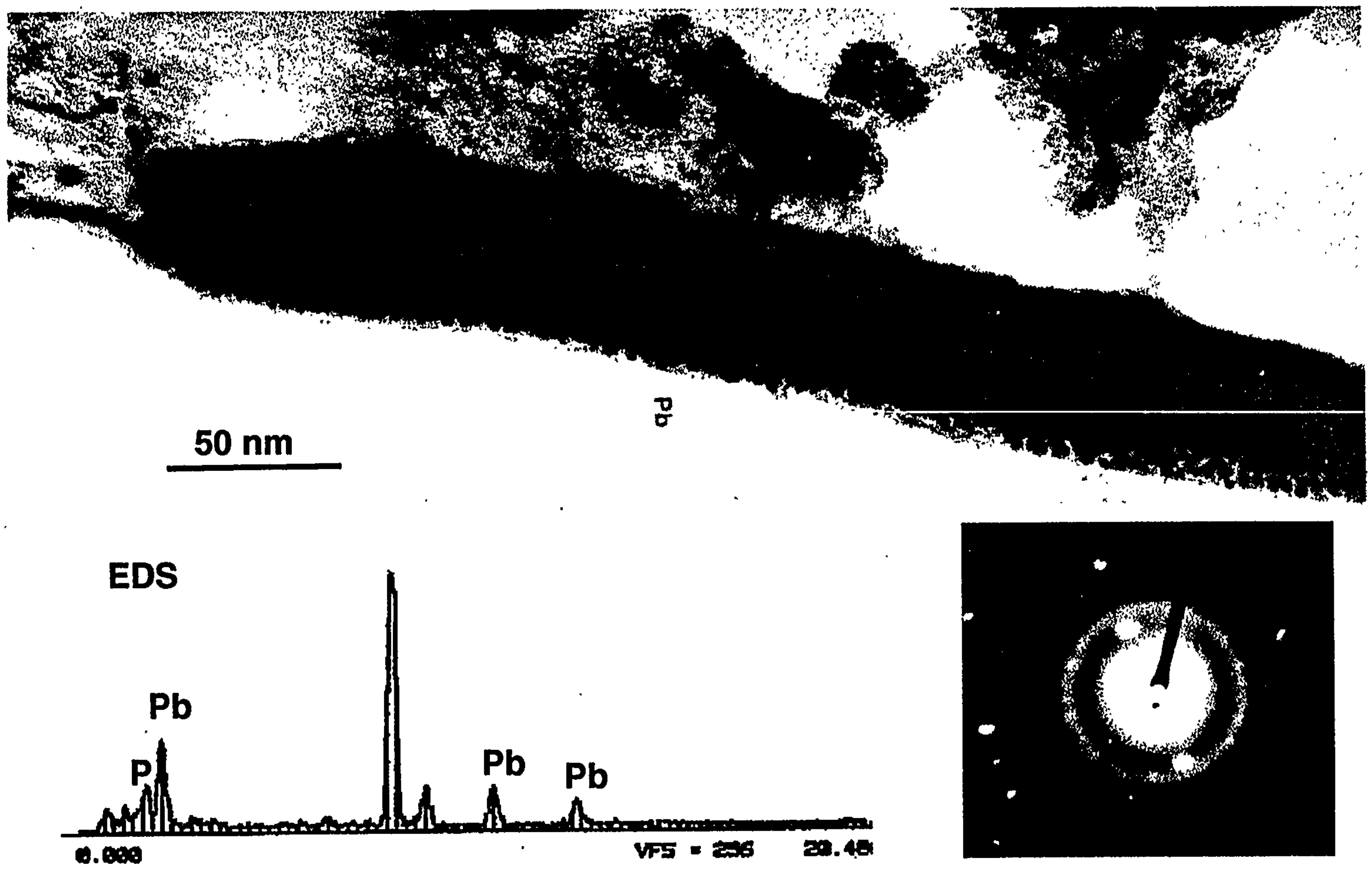


Figure 3.10. Rod-like $Pb_5(OH)(PO_4)_3$ Particle in Untreated C-107 Sludge

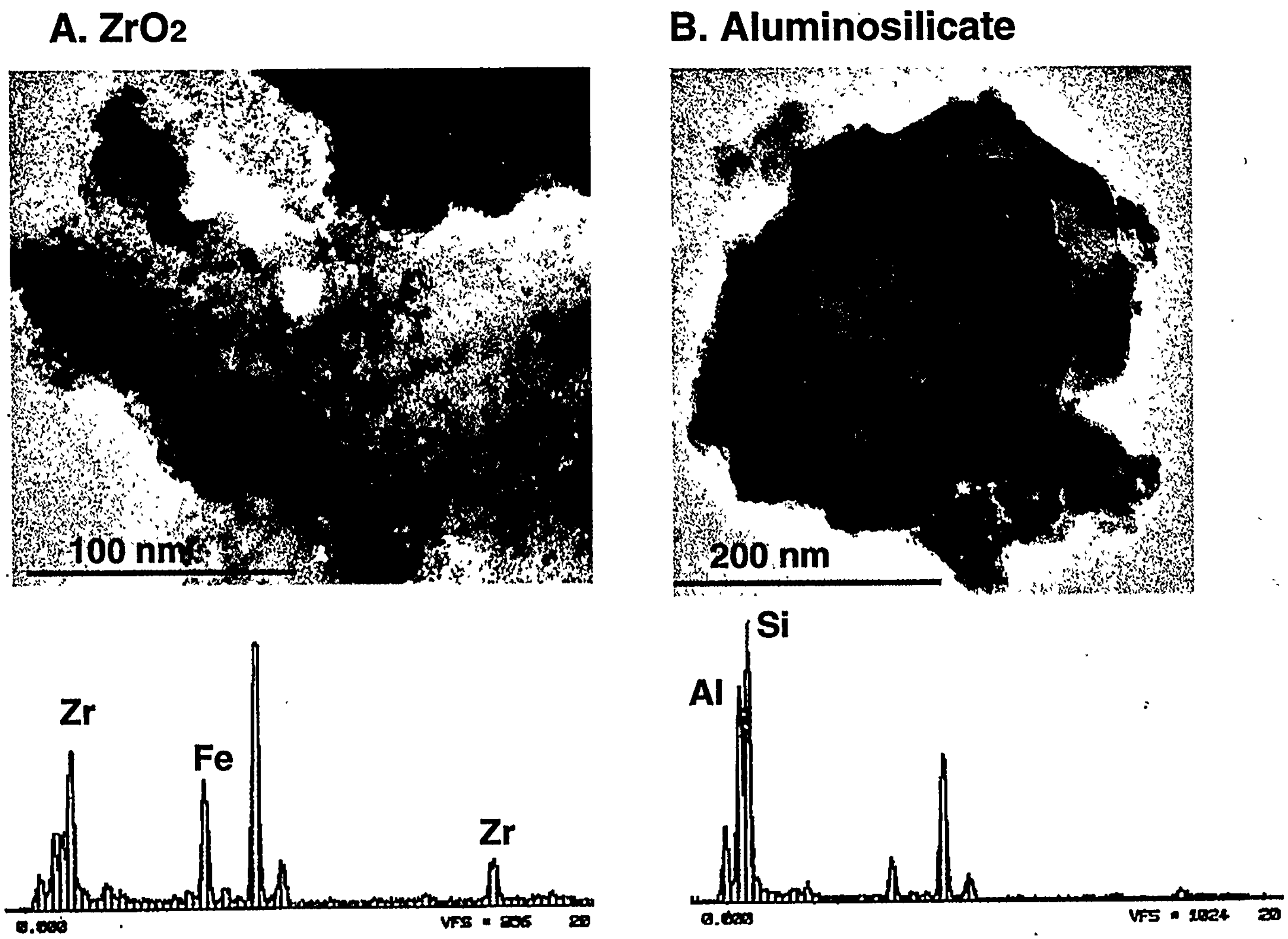


Figure 3.11. Amorphous Zirconia and Aluminosilicate Materials in the Leached C-107 Sludge

Table 3.18. Concentrations of the Nonradioactive BY-104 Sludge Components in the Various Process Solutions

	Initial Wash Solution		First Leach Solution		Second Leach Solution		Final Wash Solution		Leached Solids		
Component	Conc., µg/mL	Mass, µg[(a)]	Conc., µg/mL	Mass, µg[(a)]	Conc., µg/mL	Mass, µg[(a)]	Conc., µg/mL	Mass, µg[(a)]	Conc., µg/g	Mass, µg	Total Mass, µg
Al	2425	453475	10595	225674	606	4862	14.6	426	14900	11443	695880
B	2.24	419	<0.07	<1	<0.07	<2	<0.06	<4	<145	<111	<538, >419
Ba	<0.01	<2	<0.01	0	<0.01	0	<0.01	<1	787	604	604
Bi	<0.11	<21	<0.13	<3	<0.13	<4	<0.11	<8	4115	3160	3160
Ca	<0.26	<49	<0.33	<7	<0.33	<10	2.17	153	23400	17971	18125
Cd	<0.02	<4	<0.03	<1	<0.03	<1	<0.03	<2	1845	1417	1417
Co	<0.05	<9	<0.07	<1	<0.07	<2	<0.06	<4	1120	860	860
Cr	1081	202147	113	2407	89	2734	5.82	322	112000	86016	293627
Cu	<0.05	<9	<0.07	<1	<0.07	<2	<0.06	<4	278	214	<231, >214
Fe	<0.05	<9	4	85	1.79	53	1.11	77	114500	87936	88150
K	796	148852	<2.6	<55	<2.6	<81	<2.2	<153	10500	8064	156916
La	<0.05	<9	<0.1	<2	<0.1	<3	<0.08	<6	<2180	<1674	<1694
Mn	<0.05	<9	<0.07	<1	<0.07	<2	<0.06	<4	6015	4620	4620
Mo	5.69	1064	<0.07	<1	<0.07	<2	<0.06	<4	<85	<65	<1137, >1065
Na	70140	13116180	75270	1603251	72150	2239497	2200	83390	16300	12518	12958836
Ni	<0.03	<6	2.35	50	2.24	70	0.73	49	25400	19507	19676
P	843	157641	166	3536	18.1	356	1.12	61	11200	8602	170195
Pb	6.91	1292	45.1	961	27.2	821	<0.28	0	8040	6175	9248
Se	<0.11	<21	33	703	<0.78	0	<0.66	<46	<2905	<1609	<2378, >703
Si	76.8	14362	36.3	773	162	5214	7.33	356	14100	10829	31534
Sr	<0.02	<4	<0.02	0	<0.02	<1	0.02	1	25600	19661	19662
Ti	<0.03	<6	<0.03	<1	<0.03	<1	<0.03	<2	305	234	<244, >234
U	0.1	17	16.9	360	23.0	724	1.6	90	77100	59213	60404
V	0.95	178	1.3	28	<0.02	0	<0.02	<1	<145	<111	<318, >206
Zn	<0.02	<4	6.75	144	4.4	134	0.7	45	959	737	1059
Zr	<0.03	<6	<0.03	<1	<0.03	<1	<0.03	<2	947	727	727

(a) Mass values represent the mass of material dissolved in a given step, these values are corrected for interstitial solution carried over from the previous step.

(b) Value adjusted for the Na added as NaOH.

Table 3.19. Distribution of Nonradioactive BY-104 Sludge Components Between the Various Process Streams

Component	Component Distribution, %[a]				
	Initial Wash Solution	First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids
Al	65	32	1	0	2
B	> 78	0	0	0	< 22
Ba	0	0	0	0	100
Bi	< 1	0	0	0	> 99
Ca	0	0	0	< 1	> 99
Cd	0	0	0	0	100
Co	< 2	0	0	0	> 98
Cr	69	1	1	0	29
Cu	< 4	< 1	< 1	< 2	> 93
Fe	0	0	0	0	100
K	95	0	0	0	5
La	< 1	0	0	0	> 99
Mn	0	0	0	0	100
Mo	> 94	0	0	0	< 6
Na	Not Determined	Not Determined	Not Determined	Not Determined	0.1
Ni	0	0	0	0	100
P	93	2	0	0	5
Pb	14	10	9	0	67
Se	< 1	> 23	0	< 2	< 75
Si	46	2	17	1	34
Sr	0	0	0	0	100
Ti	< 2	0	0	< 1	> 97
U	0	1	1	0	98
V	< 87, > 57	< 13, > 8	0	0	< 35
Zn	0	14	13	4	69
Zr	< 1	0	0	0	> 99

(a) Amounts reported are adjusted for carry over of interstitial liquid; that is, the values reported for the solutions represent the amount of material actually dissolved during that step.

(b) Amount of Na in residue determined by comparing the amount of Na in the untreated solid to that in the leached solid.

Table 3.20. Concentrations of the Nonradioactive BY-104 Sludge Components in the Initial Sludge Solids

	Concentration in Initial Solids, μg/g		
Component	Summation Method	Direct Analysis[(a)]	Mass Recovery, %
Al	1.75E+04	1.88E+04	93
B	1.06E+01	$\boxed{\text{3.06E+02}}$	3
Ba	1.52E+01	< 4.1E+01	–
Bi	7.93E+01	< 1.0E+03	–
Ca	4.55E+02	$\boxed{\text{4.70E+03}}$	10
Cd	3.56E+01	< 6.1E+01	–
Co	2.16E+01	< 2.0E+02	–
Cr	7.37E+03	5.08E+03	145
Cu	5.36E+00	< 2.0E+02	–
Fe	2.21E+03	$\boxed{\text{1.16E+03}}$	192
K	3.98E+03	$\boxed{\text{1.25E+04}}$	32
La		< 3.1E+03	–
Mn	1.16E+02	$\boxed{\text{3.39E+02}}$	34
Mo	2.70E+01	< 1.2E+02	–
Na	3.25E+05	3.04E+05	107
Ni	4.92E+02	$\boxed{\text{7.99E+02}}$	62
P	4.27E+03	$\boxed{\text{3.10E+03}}$	138
Pb	2.32E+02	< 8.2E+02	–
Se	1.76E+01	< 4.1E+03	–
Si	7.92E+02	$\boxed{\text{2.13E+03}}$	37
Sr	4.94E+02	$\boxed{\text{4.36E+02}}$	113
Ti	5.88E+00	< 1.0E+02	–
U	1.52E+03	3.29E+02	461
V	5.15E+00	< 2.0E+02	–
Zn	2.66E+01	< 2.0E+02	–
Zr	1.83E+01	< 2.0E+02	–

(a) Values in boxes are near the analytical detection limits.

Table 3.21 presents the anion concentrations in the various BY-104 process solutions. The initial wash solution contained a large amount of NO_3^- (~ 1 M); little NO_3^- was in solution in subsequent steps. The PO_4^{3-} concentrations determined by IC are consistent with the concentrations of P determined by ICP/AES, and the results confirm that caustic leaching removed little or no additional P. The low concentration of SO_4^{2-} in the first leach solution compared to the initial wash solution indicates that caustic leaching removed no more SO_4^{2-}. This result is consistent with that seen for S-107 and C-107, indicating that either the SO_4^{2-} in these wastes is water-soluble and thus completely removed by dilute hydroxide washing, or the water-insoluble fraction of the SO_4^{2-} is not easily metathesized with hydroxide. Similar behavior was seen for fluoride and chloride ions.

Table 3.21. Anion Concentrations in the Various BY-104 Process Solutions

	Initial Wash Solution		First Leach Solution		Second Leach Solution		Final Wash Solution	
Component	Conc., µg/mL	Dissolved, µg/g sludge solids[a]	Conc., µg/mL	Dissolved, µg/g sludge solids[a]	Conc., µg/mL	Dissolved, µg/g sludge solids[a]	Conc., µg/mL	Dissolved, µg/g sludge solids[a]
OH^-	Not Determined		43,700	N/A[b]	55,400	N/A[b]	Not Determined	
NO_3^-	63,000	295,708	190	102	120	91	10	15
NO_2^-	8,700	40,836	<15	<8	<15	<13	430	N/A[c]
PO_4^{3-}	2,380	11,171	450	241	50	25	3	4
SO_4^{2-}	6,900	32,387	90	48	<15	<13	<1.5	<3
F^-	1,700	7,979	<25	<14	<25	<20	<25	<45
Cl^-	500	2,347	<25	<14	<25	<20	<7.5	<14
Br^-	<250	<1,175	<7.5	<4	<7.5	<6	<0.75	<2

(a) Amount of component dissolved in a given process step.

(b) Hydroxide added as NaOH.

(c) Nitrite was added in this step as part of the washing solution (0.01 M NaOH/0.01 M $NaNO_2$).

Tables 3.22 and 3.23 summarize the behavior of the radionuclides in the BY-104 sludge washing and caustic leaching test. No unusual trends were observed. Virtually all of the ^{137}Cs and ^{99}Tc was dissolved the initial wash step, indicating that these radionuclides are in soluble forms. The TRUs and ^{90}Sr remained predominantly in the solids.

3.3.3 Settling and Particle-Size Data

Table 3.24 and Figures 3.12 and 3.13 present the BY-104 settling data from the caustic leaching steps and the first washing step. Settling data for the second and third washing steps could not be obtained due to poor visibility through solids stuck to the side walls of the vessel. Generally, the solids settled at reasonable rates; the maximum settling velocities were greater than those observed for the S-107 sludge solids. The normalized settling data (Figure 3.13) indicated a wider spread of behavior than observed for the S-107 test (Figure 3.2), but the overall shape and slopes of the normalized settling curves for BY-104 were similar to those for S-107.

Figures 3.14 and 3.15, respectively, present particle-size data for the untreated and treated BY-104 sludge solids. Similar to what was observed in the case of S-107 sludge, the mean particle size, based on the volume distribution, was greatly reduced during caustic leaching. The volume distribution for the untreated BY-104 sludge indicated that the mean particle size was 10.51 μm, while that for the treated sludge was 1.96 μm. Based on the number distribution, the mean particle size remained essentially constant—0.68 μm before treatment and 0.83 μm after treatment. For the untreated material, virtually all of the particles were less than 75 μm, while for the treated material, the maximum particle diameter observed was 8 μm. Sonicating the samples decreased the measured particle sizes. After sonicating for 5 min, the mean particle size for the untreated material was 6.98 μm according to the volume distribution, while that for the treated material was 1.54 μm.

3.3.4 Microscopy Studies

The overall EDS revealed the untreated BY-104 solids were rich in Na, Fe, Al, Cr, S, and P. Sodium nitrate and sulfate appeared to be the predominant Na salts present. Similar to what was observed for the C-107 solids, a large fraction of the Al was present in sharp-edged grains of 0.2 to 1.0 μm which, based on the EDS and the X-ray diffraction pattern, was likely one of the aluminum oxides, $(Al_2O_3)_x\cdot(H_2O)_y$, where x=5 and y=1, or x=11 and y=1.79, or x=1 and y=0. Also like C-107, amorphous Al/Si clays were also evident. Chromium and Fe were found in the single crystalline phase of donathite, $Fe(Cr,Fe)_2O_4$.

As might be expected from the ICP/AES results, the microscopy investigation revealed that the leaching/washing process removed most of the Na salts and the aluminum oxides. The overall EDS of the treated BY-104 solids indicated the material was rich in Fe, Ca, P, Ni, U, and Sr. A single-crystalline Fe-containing phase was identified as a FeOOH species, but this material has a different unit cell than goethite (Figure 3.16). The Ca in the sample existed as hydroxyapatite, $Ca_5(PO_4)_3(OH)$, but this phase also had some Sr associated with it (Figure 3.17). Uranium was present as β-U_3O_8 (Figure 3.17), while Ni was present as $Ni_3O_2(OH)_4$ (Figure 3.18). Some Al oxide was observed in the treated solids indicating incomplete removal of this material (Figure 3.18), but this was not a major component of the leached solids.

Table 3.22. Concentrations of the Radioactive BY-104 Sludge Components in the Various Process Solutions

Component	Initial Wash Solution		First Leach Solution		Second Leach Solution		Final Wash Solution		Leached Solids		Total Activity, µCi
	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/g	Activity, µCi	
Total Alpha	<8.4E-05	<1.6E-02	<2.6E-04	<5.4E-03	4.29E-04	1.37E-02	<3.3E-05	<2.3E-03	5.81E+00	4	4
^{239,240}Pu	Not Determined		Not Determined		Not Determined		Not Determined		2.49E+00	2	2
^{241}Am+^{238}Pu	Not Determined		Not Determined		Not Determined		Not Determined		2.87E+00	2	2
^{241}Am(g)	Not Detected		Not Detected		Not Detected		Not Detected		2.59E+00	2	2
^{243,244}Cm	Not Determined		Not Determined		Not Determined		Not Determined		1.98E-02	0.02	0.02
^{137}Cs	258	4.82E+04	1.26E+00	0	5.23E-01	1.50E+01	1.34E-02	4.24E-01	4.91E+00	4	48265
^{60}Co	Not Detected		Not Detected		Not Detected		Not Detected		9.56E-01	1	1
^{154}Eu	Not Detected		Not Detected		Not Detected		Not Detected		2.41E+00	2	2
^{155}Eu	Not Detected		Not Detected		Not Detected		Not Detected		2.11E+00	2	2
^{90}Sr	<3.2E-02	<5.9E+00	7.29E-03	1.52E-01	1.04E-02	3.23E-01	1.10E-02	7.67E-01	2.08E+03	1597	1599
^{99}Tc	9.36E-02	1.75E+01	2.69E-04	0	8.67E-04	2.74E-02	4.17E-05	2.08E-03	<1.2E-01	<9.2E-02	18

(a) Activity values represent the activity of material dissolved in a given step, these values are corrected for interstitial solution carried over from the previous step.

Table 3.23. Distribution of the Radioactive BY-104 Sludge Components Between the Various Process Streams

	Component Distribution, %[a]					Concentration in Initial Solids, µCi/g		
Component	Initial Wash Solution	First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids	Summation Method	Direct Analysis	Mass Recovery, %
Total Alpha	0	0	0	0	100	1.12E-01	5.90E-02	190
^{239,240}Pu	(b)	(b)	(b)	(b)	(b)	4.80E-02	3.80E-02	126
^{241}Am+^{238}Pu	(b)	(b)	(b)	(b)	(b)	5.53E-02	1.62E-02	342
^{241}Am(g)	0	0	0	0	100	4.99E-02	< 3E-01	--
^{243,244}Cm	(b)	(b)	(b)	(b)	(b)	3.82E-04	6.37E-04	60
^{137}Cs	100	0	0	0	0	1.21E+03	8.38E+01	1446
^{60}Co	0	0	0	0	100	1.84E-02	< 2E-02	--
^{154}Eu	0	0	0	0	100	4.65E-02	< 3E-02	--
^{155}Eu	0	0	0	0	100	4.07E-02	< 3E-01	--
^{90}Sr	0	0	0	0	100	4.01E+01	1.13E+01	355
^{99}Tc	100	0	0	0	0	4.40E-01	< 1.8E-01	--

(a) Amounts reported are adjusted for carry over of interstitial liquid; that is, the values reported for the solutions represent the amount of material actually dissolved during that step.

(b) Analyses of the solutions were not done for these particular isotopes, but component distributions should be the same as for the total alpha activity.

Table 3.24. Settling Data From the BY-104 Caustic Leaching Test[(a)]

First Caustic Leach				Second Caustic Leach				First Wash			
t, min	h, mm	T	H	t, min	h, mm	T	H	t, min	h, mm	T	H
0	53	0.00	1.00	0	76	0.00	1.00	0	58	0.00	1.00
7	49	0.23	0.92	1	75	0.04	0.99	2	58	0.24	1:00
11	42	0.36	0.79	2	75	0.08	0.99	4	38	0.48	0.66
15	39	0.50	0.74	5	62	0.20	0.82	6	30	0.72	0.52
19	36	0.63	0.68	10	50	0.39	0.66	8	25	0.97	0.43
23	33	0.76	0.62	15	35	0.59	0.46	10	23	1.21	0.40
28	30	0.92	0.57	20	29	0.78	0.38	12	22	1.45	0.38
32	27.5	1.06	0.52	30	24	1.17	0.32	14	21	1.69	0.36
36	25	1.19	0.47	40	21.5	1.56	0.28	16	20	1.93	0.34
40	24	1.32	0.45	50	20.5	1.95	0.27	18	20	2.17	0.34
45	23	1.49	0.43	60	19	2.34	0.25	23	19	2.78	0.33
55	21	1.82	0.40	75	18	2.93	0.24	28	18	3.38	0.31
65	20	2.15	0.38	90	18	3.52	0.24	33	17	3.98	0.29
80	19	2.64	0.36	145	16	5.67	0.21	48	16	5.79	0.28
110	18	3.63	0.34	275	15	10.7	0.20	78	15	9.41	0.26
150	16.5	4.95	0.31	480	15	18.8	0.20	113	14	13.6	0.24
210	16	6.93	0.30	3015	14.5	118	0.19	213	14	25.7	0.24
300	16	9.91	0.30	4275	14.5	167	0.19	293	14	35.4	0.24
460	15	15.2	0.28					1243	13	150	0.22
4500	15	149	0.28								

(a) t = time, h = sludge height, T = normalized time value = t^*v_{max}/h_0, $H = h/h_0$.

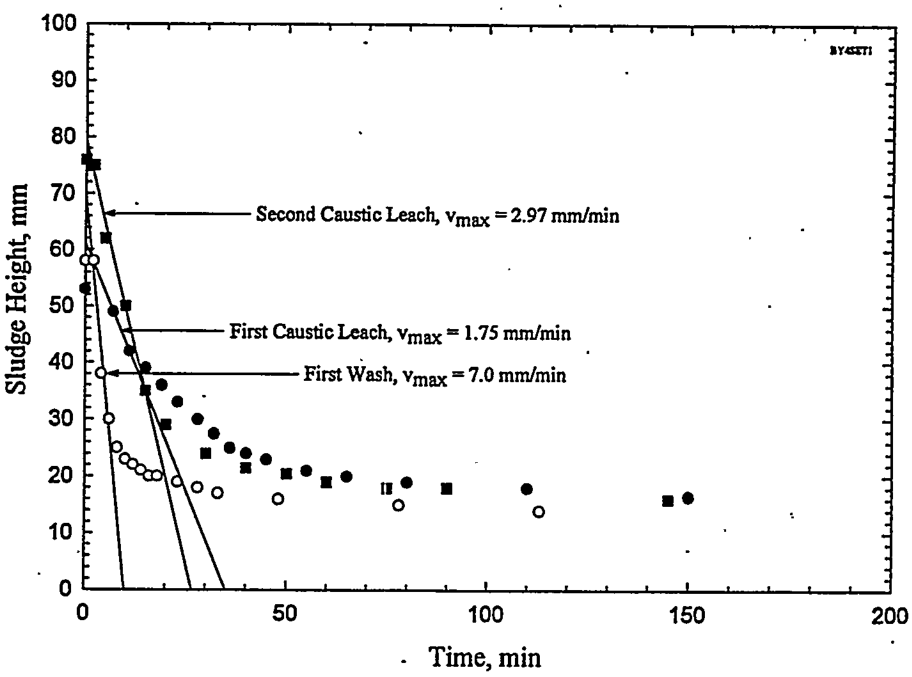


Figure 3.12. Settling Data From the BY-104 Caustic Leaching Test

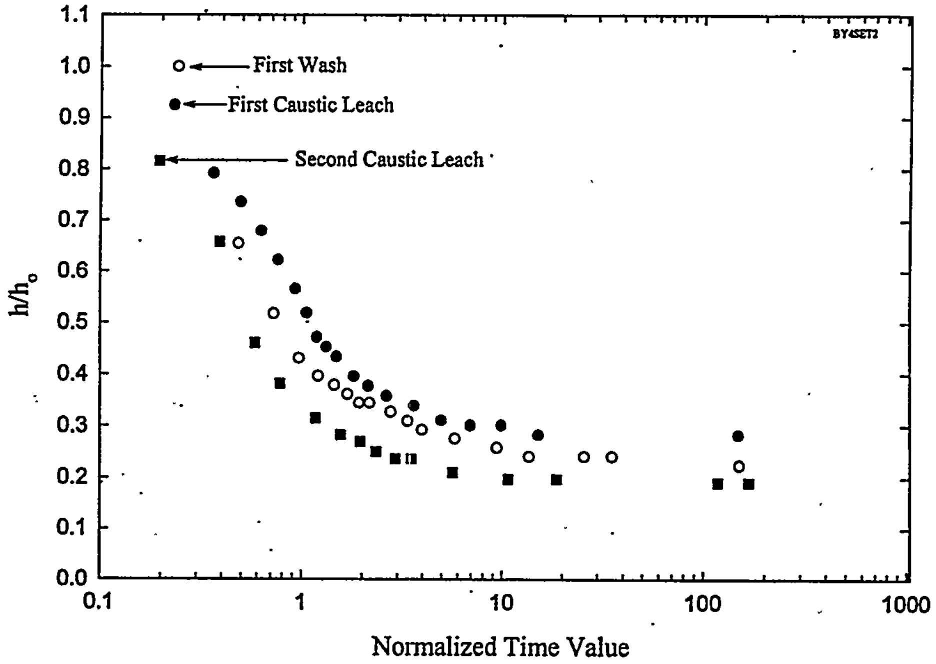


Figure 3.13. Normalized Settling Data From the BY-104 Caustic Leaching Test

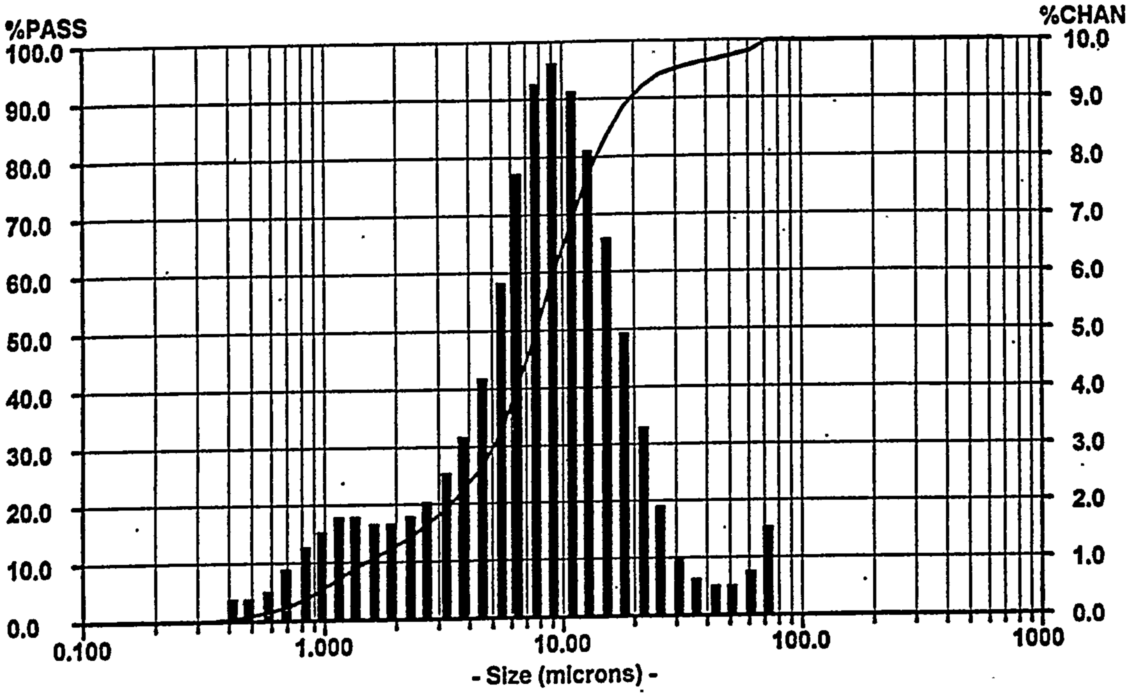


Figure 3.14. Particle-Size Volume Distribution for the Untreated BY-104 Solids

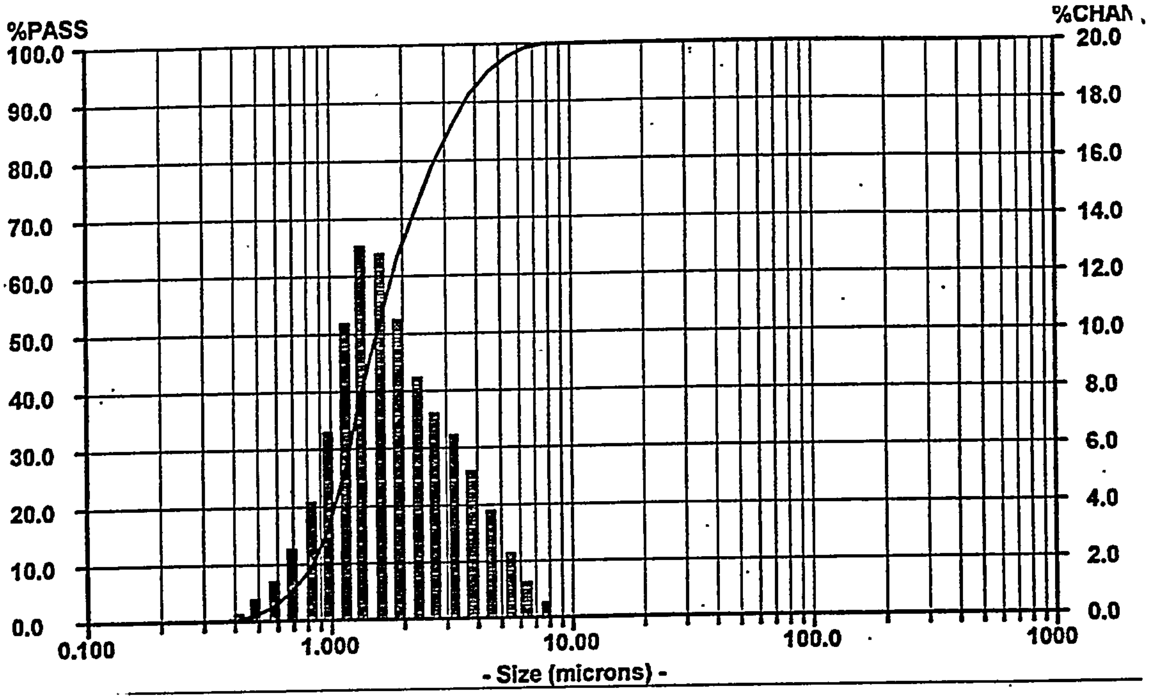


Figure 3.15. Particle-Size Volume Distribution for the Leached BY-104 Solids

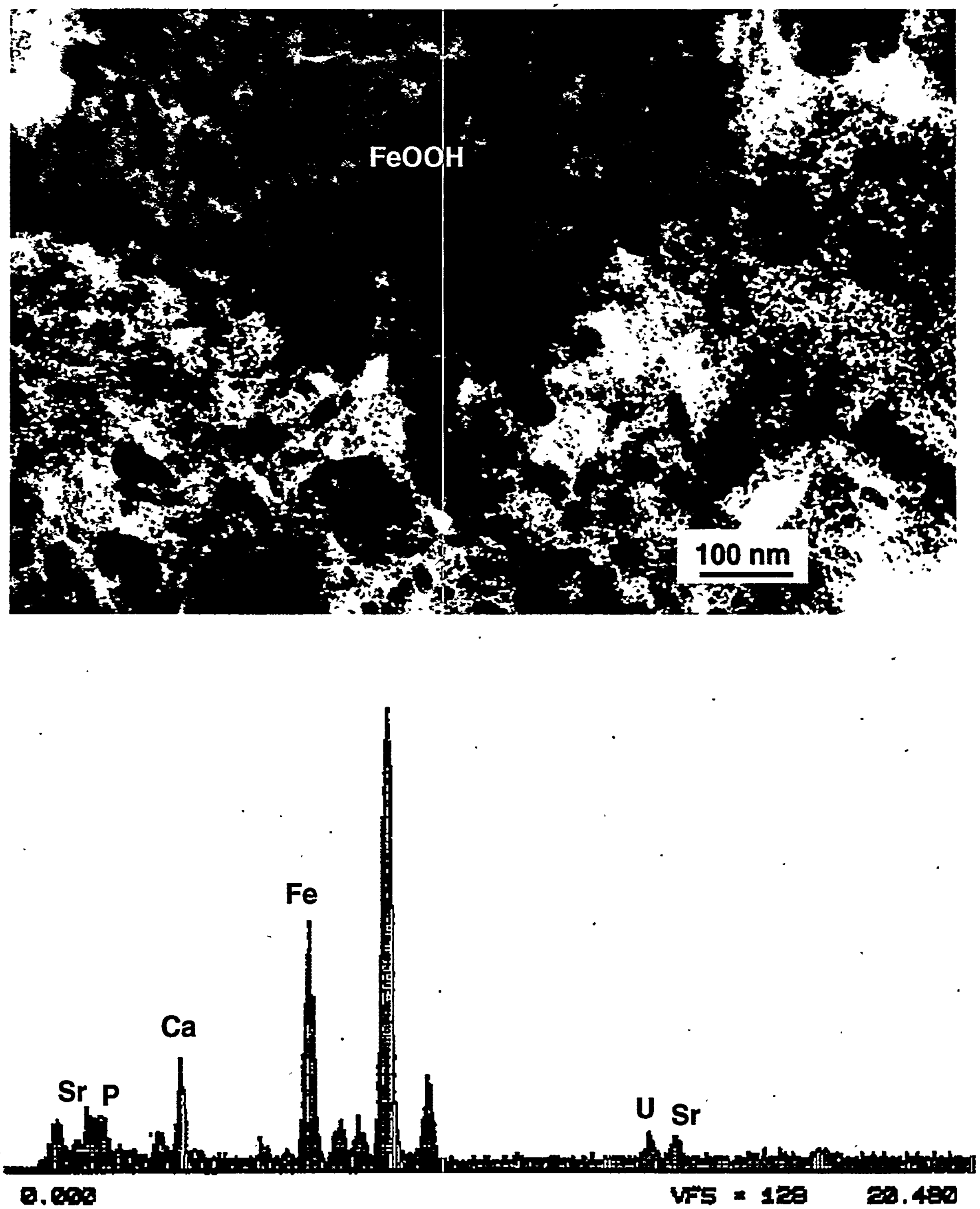


Figure 3.16. FeOOH Particles in the Leached BY-104 Sludge

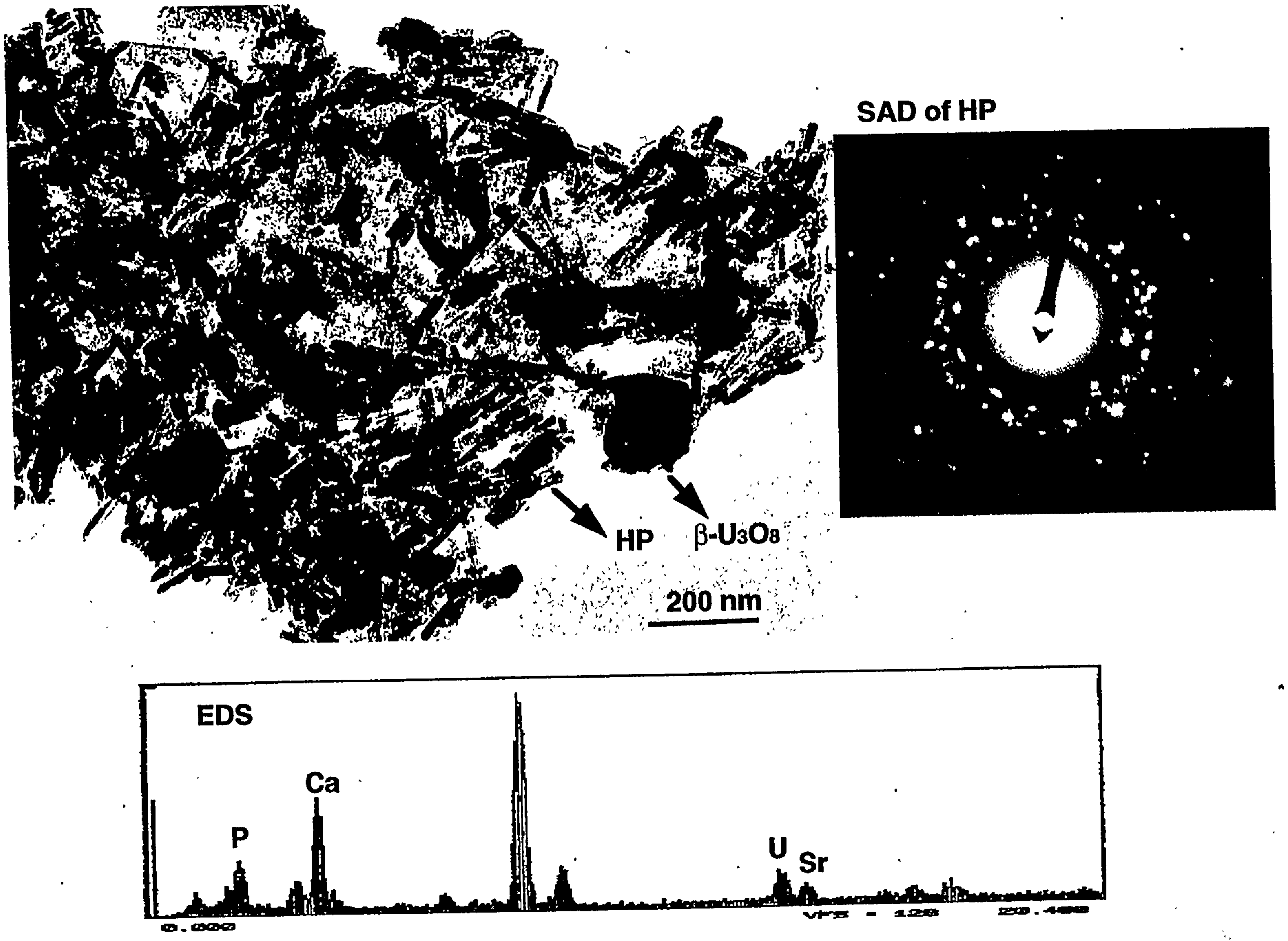


Figure 3.17. Hydroxyapatite (HP) and β-U_3O_8 in the Leached BY-104 Solids

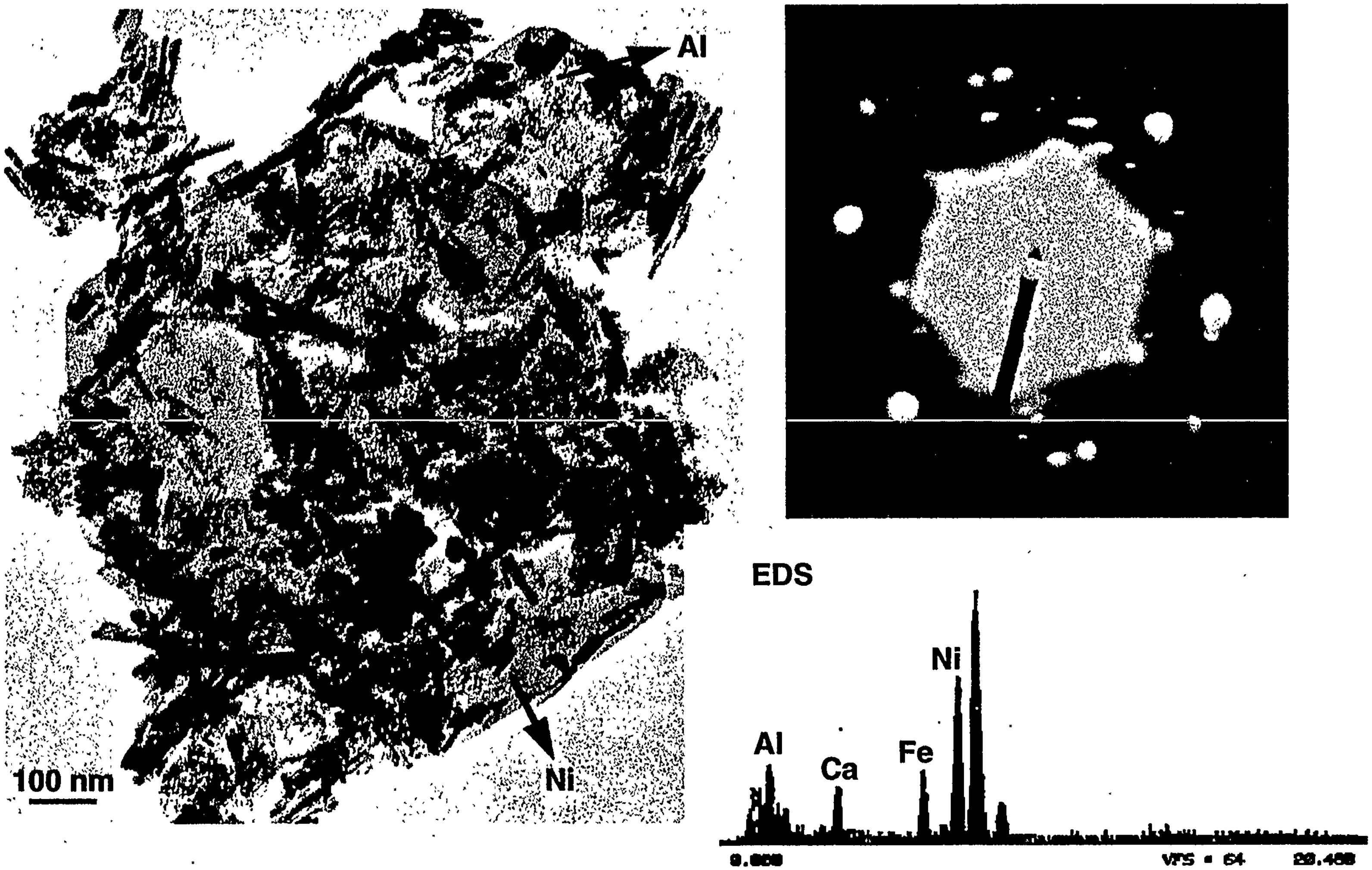


Figure 3.18. $Ni_3O_2(OH)_4$ and $(Al_2O_3)_x \cdot (H_2O)_y$ in the Leached BY-104 Solids

3.4 Results of BY-110 Test

3.4.1 Simple Sludge Washing With 0.01 M NaOH

Table 3.25 lists the behaviors of the nonradioactive BY-110 sludge components during simple sludge washing. Similar to BY-104, washing the BY-110 sludge with dilute hydroxide solution removed a large fraction of Al (94%). However, unlike BY-104, dilute hydroxide washing only removed 19% of the P from the BY-110 sludge. Dilute hydroxide washing removed nearly all (98%) of the Na. Again, mass recoveries for minor sludge components were fairly poor; mass recoveries for most of the major BY-110 sludge components tended to be somewhat high.

Table 3.26 lists the behaviors of the radioactive BY-110 sludge components during simple sludge washing. As usual, only ^{137}Cs and ^{99}Tc showed any appreciable dissolution in the dilute NaOH wash solution. Cesium was very soluble; 98% was removed. Although ^{99}Tc was below the detection limit in the washed solids, it could be concluded that >81% of the ^{99}Tc was removed by simple washing.

3.4.2 Caustic Leaching

Tables 3.27, 3.28, and 3.29 summarize the results of the BY-110 caustic leaching test for the nonradioactive waste components. The amount of Al solubilized in the first leaching step (94%) was virtually identical to that obtained by washing with dilute hydroxide. The second leaching step dissolved an additional 2% of the Al. Caustic leaching had little effect on the amount of Cr removed from the sludge. The caustic leaching procedure removed a total of 48% of the Cr, but washing with dilute hydroxide removed 47% (Table 3.25). Caustic leaching appeared to modestly increase the amount of P dissolved over that removed by dilute hydroxide washing.

Table 3.30 presents the anion concentration in the various BY-110 process solutions. The PO_4^{3-} concentrations determined by IC agree well with the concentrations of P determined by ICP/AES. In this case, the first caustic leaching solution contained 29,500 µg of SO_4^{2-} ion per gram of sludge solids processed, whereas the simple washing solution contained 27,000 µg of SO_4^{2-} per gram of sludge solids processed. The ~10% increase in the amount of SO_4^{2-} in leach solution compared to the wash solution cannot be considered to be significant, given the uncertainties in the measurement. The amount of F ion in solution increased ~20% in going from the dilute hydroxide wash (4840 µg F dissolved/g sludge solids) to the first caustic leach (5900 µg F dissolved/g sludge solids).

Tables 3.31, 3.32, and 3.33 summarize the behavior of the radioactive BY-110 waste components. As observed with dilute hydroxide washing, ^{137}Cs was readily dissolved with virtually 100% being dissolved. Although the ^{99}Tc detection limit was somewhat high for the leached solids, it could be concluded that >86% of the ^{99}Tc was removed—mostly in the first leaching step. All other radionuclides remained in the solid phase. Mass recoveries for the radioactive components were somewhat low for the alpha emitters and somewhat high for ^{90}Sr.

3.4.3 Settling and Particle-Size Data

Table 3.34 and Figures 3.16 and 3.17 present the BY-110 settling data from the caustic leaching steps and the three washing steps. Wide variability in the settling behavior was observed, with most rapid settling occurring in the second leaching step and the slowest during the second wash. The normalized

Table 3.25. Results of Tank BY-110 Sludge Washing: Nonradioactive Components

Component	Wash Solution (B2)		Washed Solids (B1)		Total Mass, μg	Component Distribution, %		Concentration in Initial Solids, μg/g		Recovery, %
	Conc., μg/mL	Mass, μg	Conc., μg/g	Mass, μg		Wash Solution	Washed Solids	Summation Method	Direct Analysis[(a)]	
Al	1407	42351	21750	2915	45265	94	6	4.28E+04	3.37E+04	127
B	0.5	15	<265	<36	<51	>30	<70	<4.8E+01	8.15E+02	--
Ba	<0.01	0	928	124	124	0	100	1.18E+02	1.00E+02	118
Bi	<0.11	<3	7585	1016	<1020	0	100	<9.6E+02	<1.25E+03	--
Ca	1.9	57	96600	12944	13002	0	100	1.23E+04	1.13E+04	109
Cd	<0.02	<1	145	19	<20	<3	>97	<1.9E+01	<7.48E+01	--
Cr	80.1	2411	20300	2720	5131	47	53	4.85E+03	3.70E+03	131
Fe	16.9	509	115000	15410	15919	3	97	1.50E+04	1.23E+04	122
K	185	5569	18800	2519	8088	69	31	7.64E+03	1.96E+04	39
La	<0.08	<2	<3980	<533	<536	--	--	<5.1E+02	<3.74E+03	--
Mg	<0.11	<3	6110	819	<822	0	100	<7.8E+02	<5.00E+03	--
Mn	<0.05	<2	1855	249	<250	<1	>99	<2.4E+02	5.49E+02	--
Mo	1.4	42	<160	<21	<64	>66	<34	<6.0E+01	<1.50E+02	--
Na	10300	303130 [(b)]	36900	4945	308075	98	2	2.91E+05	2.95E+05	99
Ni	0.24	7	46000	6164	6171	0	100	5.83E+03	4.74E+03	123
P	52.9	1592	50300	6740	8332	19	81	7.88E+03	5.57E+03	141
Pb	3.5	105	4650	623	728	14	86	6.89E+02	<1.00E+03	--
Se	4.8	144	<5315	<712	<857	>17	<83	<8.1E+02	<5.00E+03	--
Si	7.35	221	9000	1206	1427	16	84	1.35E+03	4.47E+03	30
Sr	<0.02	<1	34250	4590	4590	0	100	4.34E+03	3.02E+03	144
Ti	<0.03	<1	445	60	<61	<1	>99	<5.7E+01	<1.25E+02	--
U	10.8	325	142000	19028	19353	2	98	1.83E+04	9.66E+03	189
Zn	0.24	7	640	86	93	8	92	8.79E+01	<2.50E+02	--
Zr	<0.03	<1	317	42	<43	<2	>98	<4.1E+01	<2.50E+02	--

(a) Values in boxes are near the analytical detection limits.

(b) Value adjusted for the Na added as 0.01 M NaOH.

Table 3.26. Results of Tank BY-110 Sludge Washing: Radioactive Components

	Wash Solution (B2)		Washed Solids (B1)			Component Distribution, %		Concentration in Initial Solids, μCi/g		
Component	Conc., μCi/mL	Activity, μCi	Conc., μCi/g	Activity, μCi	Total Activity, μCi	Wash	Washed Solids	Summation Method	Direct Analysis	Recovery, %
Total Alpha	< 2.1E-04	< 6.3E-03	1.33E+00	0.18	1.78E-01	0	100	1.68E-01	1.93E-01	87
^{239,240}Pu	Not Determined		8.47E-01	0.11	1.13E-01	0	100	1.07E-01	1.41E-01	76
^{241}Am+^{238}Pu	Not Determined		3.64E-01	0.05	4.88E-02	0	100	4.61E-02	5.22E-02	88
^{241}Am(g)	Not Detected		<8E-01	<1.1E-01	<1.1E-01	--	--	< 1E-01	< 5E-01	--
^{238}U	Not Determined		4.07E-02	0.01	5.45E-03	0	100	5.20E-03	Not Detected	--
^{234}U	Not Determined		7.89E-02	0.01	1.06E-02	0	100	1.00E-02	Not Detected	--
^{137}Cs	6.86E+00	206	3.28E+01	4.40	2.11E+02	98	2	1.99E+02	1.81E+02	110
^{60}Co	Not Detected		6.54E-02	0.01	8.76E-03	0	100	8.28E-03	< 4E-02	--
^{154}Eu	Not Detected		6.35E-01	0.09	8.51E-02	0	100	8.04E-02	< 8E-02	--
^{155}Eu	Not Detected		<7E-01	<9.4E-02	<9.4E-02	--	--	< 8.9E-02	< 5E-01	--
^{90}Sr	< 2E-02	< 6.0E-01	2.35E+03	315	3.15E+02	0	100	2.98E+02	1.68E+02	177
^{99}Tc	4.79E-03	1.44E-01	< 2.4E-01	< 3.2E-02	< 1.8E-01, > 1.4E-01	> 81	< 19	< 1.7E-01, > 1.3E-01	< 2.3E-01	--

Table 3.27. Concentrations of the Nonradioactive BY-110 Sludge Components in the Various Process Solutions

	First Leach Solution (E)		Second Leach Solution (F)		Final Wash Solution (G)		Leached Solids		
Component	Conc., μg/mL	Mass, μg[(a)]	Conc., μg/mL	Mass, μg[(a)]	Conc., μg/mL	Mass, μg[(a)]	Conc., μg/g	Mass, μg	Total Mass, μg
Al	9048	164674	454	3414	38.6	177	13850	7590	175854
B	2.94	54	<0.07	0	<0.06	<2	<225	<123	<178
Ba	<0.01	0	<0.01	0	<0.01	0	965	529	529
Bi	<0.12	<2	<0.13	<5	<0.11	<3	7655	4195	<4205
Ca	<0.30	<5	1.8	75	<0.28	<4	90000	49320	<49399
Cd	<0.02	0	<0.02	<1	<0.02	<1	150	82	82
Cr	481	8754	42.8	954	6.3	91	19250	10549	20349
Fe	17.5	319	15.9	629	5.7	128	122500	67130	68205
K	1140	20748	48	49	<2.2	0	9830	5387	26184
La	<0.06	<1	<0.10	<4	<0.08	<2	<3355	<1839	<1846
Mg	<0.12	<2	<0.13	<5	<0.11	<3	5930	3250	3250
Mn	<0.06	<1	<0.07	<3	<0.06	<2	1865	1022	1022
Mo	8.7	158	0.3	0	<0.06	<1	<135	<74	<232
Na	108840	1980888	71630	2780454	5940	23654	36800	20166	889900 [(b)]
Ni	<0.04	<1	0.25	10	<0.03	0	44400	24331	24331
P	422	7680	29.6	508	2.1	0	49600	27181	35369
Pb	27	491	7	244	<0.28	0	3655	2003	2738
Se	30.2	550	1.8	23	<0.66	<15	<4470	<2450	<3022
Si	33.5	610	92.7	3781	9.4	79	4780	2619	7089
Sr	<0.02	0	0.2	8	<0.02	0	36150	19810	19818
Ti	<0.03	<1	<0.03	<1	<0.03	<1	460	252	252
U	4.45	81	18.5	758	7.63	177	136500	74802	75819
Zn	<0.02	0	1	41	0.4	9	510	279	330
Zr	<0.03	<1	<0.03	<1	<0.03	<1	247	135	135

(a) Mass values represent the mass of material dissolved in a given step, these values are corrected for interstitial solution carried over from the previous step.

(b) Value adjusted for the Na added as NaOH.

Table 3.28. Distribution of Nonradioactive BY-110 Sludge Components Between the Various Process Streams

Component	Component Distribution, %(a)			
	First Leach Solution (E)	Second Leach Solution (F)	Final Wash Solution (G)	Leached Solids
Al	94	2	0	4
B	>30	0	<1	<69
Ba	0	0	0	100
Bi	0	0	0	100
Ca	0	0	0	100
Cd	0	<1	<1	>99
Cr	43	5	0	52
Fe	<1	1	0	>98
K	79	0	0	21
La	--	--	--	--
Mg	0	0	0	100
Mn	0	0	0	>99
Mo	>68	0	0	<32
Na	Not determined	Not determined	Not determined	2(b)
Ni	0	0	0	100
P	22	1	0	77
Pb	18	9	0	73
Se	>18	<1	0	<81
Si	9	53	1	37
Sr	0	0	0	100
Ti	0	0	0	>99
U	0	1	0	99
Zn	0	13	3	85
Zr	0	<1	0	>99

(a) Amounts reported are adjusted for carry over of interstitial liquid; that is, the values reported for the solutions represent the amount of material actually dissolved during that step.

(b) Amount of Na in residue determined by comparing the amount of Na in the untreated solid to that in the leached solid.

Table 3.29. Concentrations of the Nonradioactive BY-110 Sludge Components in the Initial Sludge Solids

	Concentration in Initial Solids, µg/g		
Component	Summation Method	Direct Analysis[(a)]	Mass Recovery, %
Al	4.39E+04	3.37E+04	130
B	<4.5E-01, >1.3E+01	$\boxed{\text{8.15E+02}}$	--
Ba	1.32E+02	$\boxed{\text{1.00E+02}}$	132
Bi	1.05E+03	<1.2E+03	--
Ca	1.23E+04	1.13E+04	109
Cd	2.1E+01	<7.5E+01	--
Cr	5.07E+03	3.70E+03	137
Fe	1.70E+04	1.23E+04	138
K	6.53E+03	$\boxed{\text{1.96E+04}}$	33
La	<4.6E+02	<3.7E+03	--
Mg	8.1E+02	<5.0E+03	--
Mn	2.5E+02	$\boxed{\text{5.49E+02}}$	47
Mo	<5.8E+01, >4.0E+01	<1.5E+02	--
Na	2.22E+05	2.95E+05	75
Ni	6.07E+03	4.74E+03	128
P	8.82E+03	$\boxed{\text{5.57E+03}}$	158
Pb	6.83E+02	<1.0E+03	--
Se	<7.6E+02, >1.4E+02	<5.0E+03	--
Si	1.77E+03	$\boxed{\text{4.47E+03}}$	40
Sr	4.94E+03	3.02E+03	164
Ti	6.3E+01	<1.2E+02	--
U	1.87E+04	1.99E+04	94
Zn	8.2E+01	<2.5E+02	--
Zr	3.4E+01	<2.5E+02	--

(a) Values in boxes are near the analytical detection limits.

Table 3.30. Anion Concentrations in the Various BY-110 Process Solutions

	Wash Solution (B2)		First Leach Solution (E)		Second Leach Solution (F)		Final Wash Solution (G)	
Component	Conc., µg/mL	Dissolved, µg/g sludge solids[a]	Conc., µg/mL	Dissolved, µg/g sludge solids[a]	Conc., µg/mL	Dissolved, µg/g sludge solids[a]	Conc., µg/mL	Dissolved, µg/g sludge solids[a]
OH^-	Not Determined		43,900	N/A[b]	55,100	N/A[b]	Not Determined	
NO_3^-	6,600	187,769	41,000	186,085	1,820	1408	140	73
NO_2^-	2,400	68,280	15,600	70,803	650	97	470	N/A[c]
PO_4^{3-}	150	4,267	1,300	5,900	110	585	7	0
SO_4^{2-}	950	27,027	6,500	29,501	270	32	30	< 530
F^-	170	4,836	1,300	5,900	< 25	< 260	< 25	< 175
Cl^-	120	3,414	900	4,085	< 25	< 260	< 25	< 175
Br^-	< 25	< 710	< 250	< 1,135	< 13	< 135	< 5	< 35

(a) Amount of component dissolved in a given process step.

(b) Hydroxide added as NaOH.

(c) Nitrite was added in this step as part of the washing solution (0.01 M NaOH/0.01 M $NaNO_2$).

Table 3.31. Concentrations of the Radioactive BY-110 Sludge Components in the Various Process Solutions

	First Leach Solution (E)		Second Leach Solution (F)		Final Wash Solution (G)		Leached Solids		
Component	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/g	Activity, µCi	Total Activity, µCi
Total Alpha	<2.4E-04	<4.4E-03	<2.6E-04	< 1.1E-02	<3E-05	< 9E-04	1.12E+00	6.14E-01	6.14E-01
^{239,240}Pu	Not Determined		Not Determined		Not Determined		6.82E-01	3.74E-01	3.74E-01
^{241}Am+^{238}Pu	Not Determined		Not Determined		Not Determined		3.37E-01	1.85E-01	1.85E-01
^{241}Am(g)	Not Detected		Not Detected		Not Detected		<7E-01	<3.8E-01	<3.8E-01
^{238}U	Not Detected		Not Detected		Not Detected		5.33E-02	2.92E-02	2.92E-02
^{234}U	Not Detected		Not Detected		Not Detected		4.77E-02	2.61E-02	2.61E-02
^{137}Cs	4.32E+01	7.86E+02	2.34E+00	2.34E+01	1.85E-01	5.19E-01	2.16E+00	1.18E+00	8.11E+02
^{60}Co	Not Detected		Not Detected		Not Detected		6.94E-02	3.80E-02	3.80E-02
^{154}Eu	Not Detected		Not Detected		Not Detected		6.71E-01	3.68E-01	3.68E-01
^{155}Eu	Not Detected		Not Detected		Not Detected		6.40E-01	3.51E-01	3.51E-01
^{90}Sr	1.48E-02	2.69E-01	4.99E-01	2.06E+01	4.25E-03		2.33E+03	1.28E+03	1.30E+03
^{99}Tc	3.56E-02	6.48E-01	4.29E-04	~0	7.60E-05	1.28E-03	< 1.9E-01	< 1.0E-01	<7.5E-01, > 6.5E-01

(a) Activity values represent the activity of material dissolved in a given step, these values are corrected for interstitial solution carried over from the previous step.

Table 3.32. Distribution of Radioactive BY-110 Sludge Components Between the Various Process Streams

	Component Distribution, %[(a)]			
Component	First Leach Solution (E)	Second Leach Solution (F)	Final Wash Solution (G)	Leached Solids
Total Alpha	0	0	0	100
$^{239,240}Pu$	0	0	0	100
$^{241}Am+^{238}Pu$	0	0	0	100
$^{241}Am(g)$	0	0	0	100
^{238}U	--	--	--	--
^{234}U	--	--	--	--
^{137}Cs	97	3	0	0
^{60}Co	0	0	0	100
^{154}Eu	0	0	0	100
^{155}Eu	0	0	0	100
^{90}Sr	0	2	0	98
^{99}Tc	> 86	0	< 1	< 13

(a) Amounts reported are adjusted for carry over of interstitial liquid; that is, the values reported for the solutions represent the amount of material actually dissolved during that step.

Table 3.33. Concentrations of the Radioactive Components in the Initial BY-110 Sludge Solids

	Concentration in Initial Solids, µCi/g		
Component	Summation Method	Direct Analysis	Recovery, %
Total Alpha	1.53E-01	1.93E-01	79
$^{239,240}Pu$	9.32E-02	1.41E-01	66
$^{241}Am+^{238}Pu$	4.61E-02	5.22E-02	88
$^{241}Am(g)$	<9.5E-05	<5E-01	--
^{238}U	7.28E-03	Not Detected	--
^{234}U	6.52E-03	Not Detected	--
^{137}Cs	2.02E+02	1.81E+02	112
^{60}Co	9.48E-03	<4E-02	--
^{154}Eu	9.17E-02	<8E-02	--
^{155}Eu	8.75E-02	<5E-01	--
^{90}Sr	3.24E+02	1.68E+02	193
^{99}Tc	< 1.9E-01, > 1.6E-01	< 2.3E-01	--

Table 3.34. Settling Data From the BY-110 Caustic Leaching Test[(a)]

First Caustic Leach

t, min	h, mm	T	H
0	20	0.00	1.00
5	20	0.07	1.00
10	19	0.14	0.95
15	18.5	0.20	0.93
20	18	0.27	0.90
25	16	0.34	0.80
30	15	0.41	0.75
35	14	0.47	0.70
40	12	0.54	0.60
45	11	0.61	0.55
50	11	0.68	0.55
55	10	0.74	0.50
60	9	0.81	0.45
65	9	0.88	0.45
70	9	0.95	0.45
80	9	1.08	0.45
120	8	1.62	0.40

Second Caustic Leach

t, min	h, mm	T	H
0	41	0.000	1.00
2	40	0.005	0.98
3	39	0.007	0.95
5	38	0.012	0.93
8	36	0.019	0.88
13	33	0.031	0.80
18	29	0.043	0.71
23	26.5	0.056	0.65
28	23	0.068	0.56
33	20	0.080	0.49
38	18	0.092	0.44
43	17	0.10	0.41
48	15	0.12	0.37
53	13.5	0.13	0.33
58	13.5	0.14	0.33
73	12	0.18	0.29
82	11	0.20	0.27
93	11	0.22	0.27
118	10	0.28	0.24
168	9	0.41	0.22
228	9	0.55	0.22
313	8	0.76	0.20
418	8	1.01	0.20
1138	8	2.75	0.20
3795	8	9.16	0.20

First Wash

t, min	h, mm	T	H
0	14	0.00	1.00
6	13	0.04	0.93
12	12.5	0.08	0.89
29	11	0.21	0.79
49	10.5	0.35	0.75
66	9.5	0.47	0.68
100	9	0.71	0.64
160	9	1.13	0.64
220	9	1.56	0.64
405	8	2.86	0.57
1270	8	8.98	0.57

Second Wash

t, min	h, mm	T	H
0	12	0.00	1.00
10	11.5	0.05	0.96
18	11	0.08	0.92
36	11	0.17	0.92
66	9	0.30	0.75
96	9	0.44	0.75
126	8.5	0.58	0.71
156	8.5	0.72	0.71
216	8.5	0.99	0.71
1206	8	5.53	0.67
2766	8	12.7	0.67

Third Wash

t, min	h, mm	T	H
0	13	0.00	1.00
5	13	0.05	1.00
30	13	0.28	1.00
47	11	0.43	0.85
65	10	0.60	0.77
85	9	0.78	0.69
100	8	0.92	0.62
125	7	1.15	0.54
1153	7	10.6	0.54

(a) t = time, h = sludge height, T = normalized time value = t^*v_{max}/h_0, $H = h/h_0$.

settling data (Figure 3.12) indicated a wider spread of behavior than observed for either the S-107 test or the BY-104 test. The settling behavior during the second caustic leaching step is significantly different than that observed for the other steps. This is likely a reflection of the lower solids concentration in the second caustic leaching slurry compared to the first leaching slurry and the washing steps.

Figures 3.18 and 3.19, respectively, present particle-size data for the untreated and treated BY-110 sludge solids. Unfortunately, due to a combination of a computer error and limited sample size, only the volume distributions after sonicating for 5 min are available. These indicate an overall increase in the mean particle size from 4.8 μm before leaching to approximately 7.8 μm after leaching.

3.4.4 Microscopy Studies

Due to insufficient sample, it was not possible to analyze the untreated BY-110 solids by microscopy. For the leached BY-110 solids, the overall EDS revealed the solids were rich in Fe, Ca, P, Ni, Cr, U, and Sr. Two Fe-containing phases were identified, maghemite (γ-Fe_2O_3) and an amorphous Fe/Si phase (Figure 3.23). One Cr-containing phase was identified as grimaldite, CrO(OH) (Figure 3.24). Nickel was found to be present as $Ni_3O_2(OH)_4$ (Figure 3.25) and U as β-U_3O_8 (Figure 3.23). These latter two minerals were also found in the leached BY-104 solids. The Ca in the leached BY-110 solids existed as hydroxyapatite, $Ca_5(PO_4)_3(OH)$, but this phase also had some Sr associated with it (Figure 3.26); this was also very similar to what was observed for BY-104.

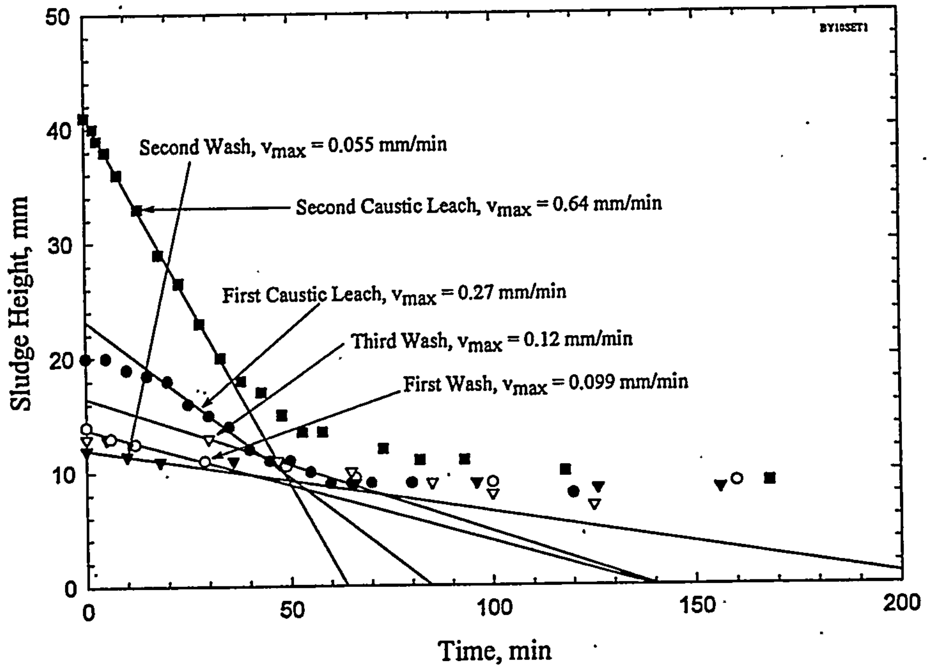


Figure 3.19. Settling Data From the BY-110 Caustic Leaching Test

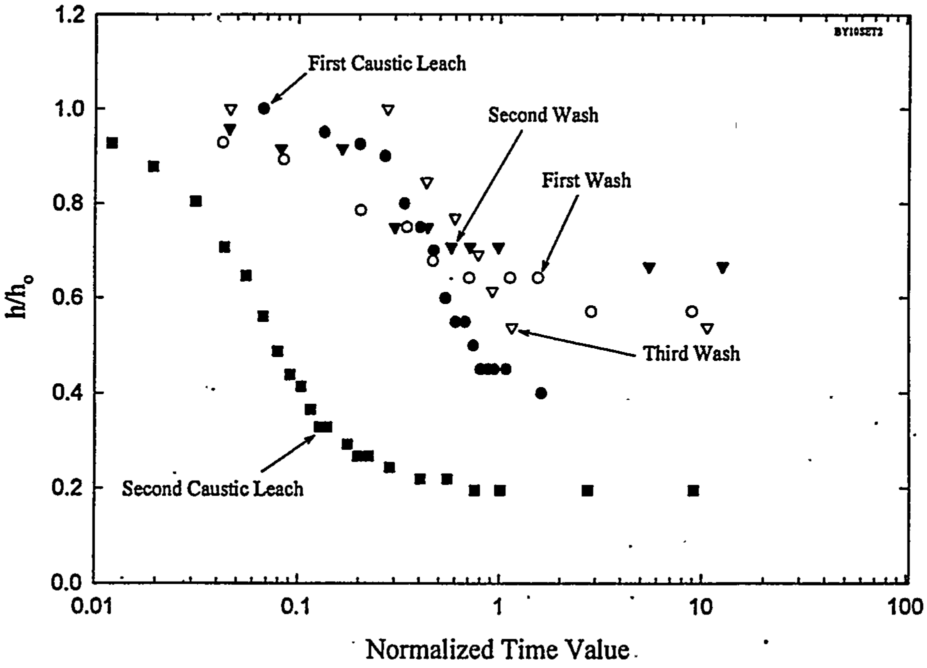


Figure 3.20. Normalized Settling Data From the BY-110 Caustic Leaching Test

3.5 Results of SX-108 Test

3.5.1 Simple Sludge Washing With 0.01 M NaOH

Table 3.35 summarizes the behaviors of the nonradioactive SX-108 sludge components during simple sludge washing. The Al behavior of the SX-108 sludge was very similar to that for the other REDOX sludges investigated to date (i.e., S-104 and S-107). Namely, only a small fraction (6%) of the Al was removed by simple water washing (compared to 3% for S-104 and 8% for S-107). Interestingly, the Cr behavior for SX-108 sludge (71% removed) fell between that observed for S-104 (90% removed by simple wash; Rapko, Lumetta, and Wagner 1995) and S-107 (24% removed); indicating variable Cr speciation in the REDOX sludges. Phosphorus appeared to be poorly removed by dilute hydroxide washing, but this is a relatively minor component of the SX-108 sludge. Nearly all (96%) of the Na was removed by dilute hydroxide washing.

Mass recoveries for some of the key elements (e.g., Al, Cr, Fe) were somewhat high. The reason for this is unknown. A very low mass recovery (35%) was obtained for P, but this analyte was present in quantities near the analytical detection limit, so considerable uncertainty was associated with its determination.

Table 3.36 summarizes the behaviors of the radioactive SX-108 sludge components during simple sludge washing. Only ^{137}Cs, ^{99}Tc, and ^{90}Sr were detected in the wash solution. The amount of ^{90}Sr dissolved was insignificant with respect to the amount of ^{90}Sr in the solids. A significant fraction (37%) of the ^{137}Cs remained in the washed solids. No significant conclusions could be drawn concerning the ^{99}Tc behavior because of the high detection limit for this radionuclide in the analysis of the washed solids.

Table 3.35. Results of SX-108 Sludge Washing: Nonradioactive Components

	Wash Solution (B2)		Washed Solids (B1)			Component Distribution, %		Concentration in Initial Solids, µg/g		
Component	Conc., µg/mL	Mass, µg	Conc., µg/g	Mass, µg	Total Mass, µg	Wash Solution	Washed Solids	Summation Method	Direct Analysis	Recovery, %
Ag	<0.03	<1	<47	<29	<30	<3	>97	<2.0E+01	1.90E+02	<10
Al	372	11830	287000	177366	189196	6	94	1.30E+05	9.02E+04	144
As	0.95	30	517	320	350	9	91	2.41E+02	3.50E+02	69
B	1	32	174	108	139	23	77	9.58E+01	2.92E+02	33
Ba	<0.01	0	435	269	269	0	100	1.85E+02	1.40E+02	132
Bi	<0.11	<3	<470	<290	<294	--	--	<2.0E+02	<4.2E+02	--
Ca	2.5	80	10160	6279	6358	1	99	4.37E+03	8.72E+03	50
Cd	<0.02	<1	89	55	<56	<1	>99	3.80E+01	4.20E+01	90
Ce	<0.11	<3	1040	643	<646	<1	>99	4.42E+02	2.94E+03	15
Cr	302	9604	6410	3961	13565	71	29	9.33E+03	7.94E+03	118
Cu	<0.05	<2	154	95	<97	<2	>98	6.70E+01	1.27E+02	53
Fe	<0.03	<1	52800	32630	32630	0	100	2.24E+04	1.64E+04	137
K	39	1240	5050	3121	4361	28	72	3.00E+03	8.33E+03	36
La	<0.08	<3	398	246	246	<1	>99	1.69E+02	1.96E+02	86
Li	<0.03	<1	120	74	<75	<1	>99	5.10E+01	1.07E+02	48
Mg	1.3	41	1055	652	693	6	94	4.77E+02	5.04E+02	95
Mn	<0.05	<2	17550	10846	10846	0	100	7.46E+03	5.25E+03	142
Mo	0.7	22	<56	<35	<57	>39	<61	<3.9E+01, >1.5E+01	<5.0E+01	--
Na	8641	267884 [(a)]	16500	10197	278081	96	4	1.91E+05	2.28E+05	84
Nd	<0.11	<3	1220	754	754	0	100	5.19E+02	<5.9E+02	--
Ni	0.5	16	4060	2509	2525	1	99	1.74E+03	1.89E+03	92
P	1.6	51	859	531	582	9	91	4.00E+02	1.15E+03	35
Pb	1	32	1485	918	950	3	97	6.53E+02	6.16E+02	106
Si	<0.53	<17	8405	5194	<5211	0	100	3.57E+03	4.26E+03	84
Sr	<0.02	<1	1790	1106	1106	0	100	7.61E+02	5.54E+02	137
Ti	<0.03	<1	237	146	146	<1	>99	1.00E+02	8.30E+01	121
U	0.35	11	5460	3374	3385	0	100	2.33E+03	1.51E+04	15
V	0.3	10	65	40	50	19	81	3.42E+01	6.00E+01	57
Y	<0.04	<1	157	97	<98	<1	>99	6.70E+01	5.20E+01	129
Zn	0.5	16	300	185	201	8	92	1.38E+02	1.21E+02	114
Zr	<0.03	<1	811	501	501	0	100	3.45E+02	7.90E+01	436

(a) Value adjusted for the Na added as 0.01 M NaOH.

Table 3.36. Results of SX-108 Sludge Washing: Radioactive Components

	Wash Solution (B2)		Washed Solids (B1)			Component Distribution, %	
Component	Conc., µCi/mL	Activity, µCi	Conc., µCi/g	Activity, µCi	Total Activity, µCi	Wash	Washed Solids
Total Alpha	< 7E-05	< 2E-03	3.29E+00	2.03E+00	2.03E+00	0	100
^{239,240}Pu	Not Determined		1.47E+00	9.08E-01	9.08E-01	0	100
^{241}Am+^{238}Pu	Not Determined		1.82E+00	1.12E+00	1.12E+00	0	100
^{241}Am(g)	< 5E-03	< 2E-01	2.11E+00	1.30E+00	< 1.5E+00	< 30	> 70
^{137}Cs	6.61E+00	2.10E+02	1.99E+02	1.23E+02	3.33E+02	63	37
^{60}Co	< 8E-05	< 3E-03	1.18E-01	7.29E-02	< 7.59E-02	< 4	> 96
^{154}Eu	< 5E-04	< 2E-02	1.90E+00	1.17E+00	1.17E+00	0	100
^{155}Eu	< 5E-03	< 2E-01	1.18E+00	7.29E-01	< 9.3E-01	< 22	> 78
^{90}Sr	5.39E-02	1.71E+00	3.12E+03	1.93E+03	1.93E+03	0	100
^{99}Tc	5.50E-03	1.75E-01	< 3.0E-01	< 1.9E-01	< 0.36, > 0.17	> 49	< 51

3.5.2 Caustic Leaching

Tables 3.37, 3.38, and 3.39 summarize the results of the SX-108 caustic leaching test for the nonradioactive waste components. The most striking result from this test was the very poor removal of Al. Only ~30% of the Al was removed by the caustic leaching method, and most of that removed (28%) was solubilized in the first leaching step. This result is similar to what was observed for Tank S-104 sludge in which only a total of 38% of the Al was removed (Rapko, Lumetta, and Wagner 1995). Because of the larger solution volume used in the second leach step, and the lower Al concentration in the second leach solution compared to the first leach solution (see Table 3.37), it can be concluded that the Al removal was not likely limited by solubility (as was given as a possible explanation for the poor removal of Al from S-104 sludge; Rapko et al. 1996). Indeed, it has been shown that much higher Al concentrations can be achieved under analogous conditions (see Section 4.2).

The Cr removal appeared slightly better than achieved by simple water washing (78% versus 71%), but this increase is not significant. Phosphorus removal was improved over the simple washing case, but it was still poor. Sodium was efficiently removed from the SX-108 sludge material, with the concentration in the leached sludge being only 3% of that in the untreated material.

The mass recoveries (Table 3.39) for certain components were high, but consistently so. For example, the recovery for Al in the caustic leaching part of the test was 48% high, but the Al recovery was similar (44% high, see Table 3.37) in the simple washing portion of the test. Indeed, the Al concentration in the SX-108 sludge solids determined by summing the Al found in all the process solutions was virtually the same for the simple washing portion of the test and the caustic leaching portion of the test. The Al concentration determined by the summation method was 13 wt%, compared to 9 wt% determined by direct analysis. It should be noted that two different fusion methods were used in the direct analysis of the sludge solid, both giving similar results—8.9 wt% in the peroxide fusion and 9.1 wt% in the KOH fusion.

A similar situation occurred with the Cr mass recovery as well. In the simple washing portion of the experiment, the Cr recovery was 18% high, while in the caustic leaching portion of the test, the Cr recovery was 17% high. Again, the Cr concentrations determined by the summation method in the two different portions of the test were the same—0.93 wt%. Although the spread in the Cr concentration value determined by direct analysis using the two different sample preparation methods was greater than that seen for Al, the Cr values were within 15% (0.73 versus 0.85 wt% Cr), and they were consistently lower than the summation method values.

The reasons for the discrepancies between the Al and Cr (and other components) values determined by direct analysis of the sludge solids and those determined by the summation method are not known.

Table 3.40 presents the anion concentration in the various SX-108 process solutions. The PO_4^{3-} concentrations determined by IC agree reasonably well with the concentrations of P determined by ICP/AES, considering the low concentrations of P in these solutions. The first caustic leaching solution contained 3,610 μg of SO_4^{2-} ion per gram of sludge solids processed, whereas the simple washing solution contained 4,050 μg of SO_4^{2-} per gram of sludge solids processed. Thus, either all the SO_4^{2-} in the sludge is water-soluble and easily removed, or no significant improvement in SO_4^{2-} ion removal occurs upon leaching with caustic. On the other hand, an approximately 50% increase in the amount of F ion in solution occurred in going from the dilute hydroxide wash (1,100 μg F dissolved/g sludge solids) to the first caustic leach (1,630 μg F dissolved/g sludge solids).

Table 3.37. Concentrations of the Nonradioactive SX-108 Sludge Components in the Various Process Solutions

	First Leach Solution (E)		Second Leach Solution (F)		Final Wash Solution (G)		Leached Solids		
Component	Conc., µg/mL	Mass, µg(a)	Conc., µg/mL	Mass, µg(a)	Conc., µg/mL	Mass, µg(a)	Conc., µg/g	Mass, µg	Total Mass, µg
Ag	<0.03	<4	<0.03	<6	<0.03	<13	56	403	<424
Al	5369	767767	1080	14386	104	0	270000	1941300	2723453
As	8.6	1230	<0.10	0	<0.09	<40	478	3437	<4679
B	3.8	543	<0.10	0	<0.08	<35	148	1064	<1632
Ba	<0.01	<1	<0.01	<2	<0.01	<4	545	3919	<3905
Bi	<0.33	<47	<0.33	<64	<0.28	<122	410	2948	<3165
Ca	<0.33	<47	<0.33	<64	3	1488	11200	80528	<81663
Cd	<0.02	<3	<0.02	<4	<0.02	<9	118	848	<859
Ce	<0.46	<65	<0.46	<90	<0.39	<170	1080	7765	<8047
Cr	992	141856	208	4704	21	-192	5760	41414	187782
Cu	<0.07	<10	<0.07	<14	<0.06	<26	166	1194	<1237
Fe	<0.07	<10	<0.07	<14	<0.06	<26	71700	515523	512655
K	178	25454	71	8994	<2.2	0	5230	37604	72052
La	<0.07	<10	<0.07	<14	<0.06	<26	515	3703	<3732
Li	<0.04	<6	<0.04	<8	<0.03	<13	140	1007	<1027
Mg	<0.13	<18	<0.13	<25	<0.11	<48	1275	9167	<9208
Mn	<0.07	<10	<0.07	<14	<0.06	<26	21200	152428	151580
Mo	2.5	358	<0.04	0	<0.03	<13	68	489	<854
Na	86060	8347820	67990	12986090	6292	3120832	21800	156742	1631484 (b)
Nd	<0.46	<65	<0.46	<90	<0.39	<170	1410	10138	<10407
Ni	<0.04	<6	<0.04	<8	<0.03	<13	4750	34153	33963
P	22	3146	<0.33	0	<0.28	<122	734	5277	<8494
Pb	16	2288	5	474	<0.11	0	1705	12259	15021
Si	16	2288	21	4346	3.4	615	10670	76717	83967
Sr	<0.02	<3	<0.02	<5	<0.02	<9	2205	15854	15766
Ti	<0.05	<7	<0.05	<12	<0.04	<17	262	1884	<1910
U	0.83	119	0.42	63	0.08	18	21200	152428	152628
V	1	143	<0.02	<5	<0.02	<9	70	503	<656
Y	<0.01	<1	<0.01	<2	<0.01	<4	190	1366	1359
Zn	1.7	243	<0.07	<17	<0.06	<26	316	2272	<2544
Zr	<0.03	<4	<0.03	<7	<0.03	<13	1100	7909	7865

(a) Mass values represent the mass of material dissolved in a given step, these values are corrected for interstitial solution carried over from the previous step.

(b) Value adjusted for the Na added as NaOH.

Table 3.38. Distribution of Nonradioactive SX-108 Sludge Components Between the Various Process Solutions

	Component Distribution, %(a)			
Component	First Leach Solution (E)	Second Leach Solution (F)	Final Wash Solution (G)	Leached Solids
Ag	< 1	< 1	< 3	> 94
Al	28	1	0	71
As	26	0	0	74
B	33	0	2	65
Ba	0	0	0	100
Bi	< 1	< 2	< 4	> 93
Ca	0	0	2	98
Cd	0	0	< 2	> 98
Ce	< 1	< 1	< 2	> 96
Cr	75	3	0	22
Cu	< 1	< 1	< 2	> 96
Fe	0	0	0	100
K	35	13	0	52.
La	0	0	< 1	> 99
Li	< 1	< 1	< 1	> 97
Mg	0	0	< 1	> 99
Mn	0	0	0	100
Mo	42	0	0	58
Na	Not determined	Not determined	Not determined	3(b)
Nd	< 1	< 1	< 2	> 96
Ni	0	0	0	100
P	37	0	0	63
Pb	15	3	0	82
Si	3	5	1	91
Sr	0	0	0	100
Ti	0	< 1	< 1	> 98
U	0	0	0	100
V	22	0	0	78
Y	0	0	0	100
Zn	10	0	0	90
Zr	0	0	0	100

(a) Amounts reported are adjusted for carry over of interstitial liquid; that is, the values reported for the solutions represent the amount of material actually dissolved during that step.

(b) Amount of Na in residue determined by comparing the amount of Na in the untreated solid to that in the leached solid.

Table 3.39. Concentrations of the Nonradioactive Components in the Initial SX-108 Sludge Solids

	Concentration in Initial Solids, µg/g		
Component	Summation Method	Direct Analysis	Mass Recovery, %
Ag	2.00E+01	1.88E+02	11
Al	1.34E+05	9.02E+04	149
As	2.30E+02	3.50E+02	61
B	8.00E+01	2.92E+02	28
Ba	1.93E+02	1.40E+02	138
Bi	1.45E+02	< 420	--
Ca	4.03E+03	8.72E+03	46
Cd	4.17E+02	4.20E+01	101
Ce	3.82E+02	2.94E+03	14
Cr	9.29E+03	7.94E+03	117
Cu	5.90E+01	1.27E+02	48
Fe	2.54E+04	1.64E+04	155
K	3.55E+03	8.33E+03	43
La	1.82E+02	1.96E+02	94
Li	5.00E+01	1.07E+02	47
Mg	4.51E+02	5.04E+02	90
Mn	7.50E+03	5.25E+03	143
Mo	4.16E+02	< 50	--
Na	8.06E+04	2.28E+05	35
Nd	5.00E+02	< 590	--
Ni	1.68E+03	1.89E+03	89
P	4.15E+02	1.15E+03	37
Pb	7.39E+02	6.16E+02	120
Si	4.13E+03	4.26E+03	97
Sr	7.80E+02	5.54E+02	141
Ti	9.30E+01	8.30E+01	114
U	7.55E+03	1.51E+04	50
V	3.20E+01	6.00E+01	54
Y	6.70E+01	5.20E+01	130
Zn	1.24E+02	1.21E+02	104
Zr	3.90E+02	7.90E+01	494

Table 3.40. Anion Concentrations in the Various SX-108 Process Solutions

	Wash Solution (B2)		First Leach Solution (E)		Second Leach Solution (F)		Final Wash Solution (G)	
Component	Conc., µg/mL	Dissolved, µg/g sludge solids[(a)]	Conc., µg/mL	Dissolved, µg/g sludge solids[(a)]	Conc., µg/mL	Dissolved, µg/g sludge solids[(a)]	Conc., µg/mL	Dissolved, µg/g sludge solids[(a)]
OH^-	Not Determined		46,750	N/A[(b)]	49,300	N/A[(b)]	Not Determined	
NO_3^-	11,700	255,887	37,000	261,672	6,200	0	490	0
NO_2^-	575	12,576	2,000	14,144	390	118	430	N/A[(c)]
PO_4^{3-}	3	66	45	318	12	41	<2.5	0
SO_4^{2-}	185	4,046	510	3,607	110	156	9	0
F^-	50	1,094	230	1,627	40	0	3	0
Cl^-	90	1,968	290	2,051	70	178	9	44
Br^-	< 12.5	<273	< 12.5	<88	< 12.5	< 150	< 1.3	<35

(a) Amount of component dissolved in a given process step.

(b) Hydroxide added as NaOH.

(c) Nitrite was added in this step as part of the washing solution (0.01 M NaOH/0.01 M $NaNO_2$).

Tables 3.41 through 3.43 present the radiochemical data from the SX-108 caustic leaching test. The data indicated that only ^{137}Cs, and possibly ^{99}Tc, are dissolved to any extent during the caustic leaching process. The amount of ^{137}Cs dissolved (87%) was greater than seen with simple washing (63%). Again, because of high ^{99}Tc detection limits, no significant conclusions could be made regarding ^{99}Tc behavior.

3.5.3 Settling and Particle-Size Data

Table 3.44 and Figures 3.20 and 3.21 present the SX-108 settling data from the caustic leaching steps and the three washing steps. Wide variability in the settling behavior was observed, with most rapid settling occurring in the washing steps. The normalized settling data (Figure 3.21) indicated a wider spread of behavior than observed for either the S-107 test or the BY-104 test, but less of a spread than the BY-110 test.

Figures 3.22 and 3.23, respectively, present particle size data for the untreated and treated SX-108 sludge solids. On average, the particle size decreased upon leaching with caustic. Based on the volume occupied by the particles, the mean size for the untreated material was 25.7 μm, while that for the treated material was 4.1 μm. There was some uncertainty in the measurement for the untreated material in that a duplicate run indicated the mean particle size to be 12.8 μm (volume distribution). This illustrates the difficulty in taking homogeneous samples from tank sludges. On the other hand, duplicate runs for the treated material were consistent with one another. As was seen with the other sludges investigated in this work, sonication resulted in only slight decreases in the mean particle sizes—25.7 to 23.5 μm for the untreated material and 4.1 to 3.1 for the treated sludge solids.

3.5.4 Microscopy Studies[(a)]

The overall EDS revealed that the untreated SX-108 solids were rich in Al and Na, and Si, Fe, Mn, and U were also evident; this is consistent with the ICP/AES results (Table 3.39). Figure 3.31 presents a comparison of the main solid phases present before and after treatment. Aluminum was present in several phases, including 1) boehmite (Figure 3.32); 2) sharp-edged grains of 0.2 to 1.0 μm which, based on the EDS and the X-ray diffraction pattern, was likely one of the aluminum oxides, $(Al_2O_3)_x \cdot (H_2O)_y$, where x=5 and y=1, or x=11 and y=1.79, or x=1 and y=0; and 3) amorphous Al/Si clay (Figure 3.33). A single-crystalline Fe-containing phase was identified as an FeOOH species, which was also associated with some Cr (Figure 3.34). Like BY-104 and BY-110, U was present as β-U_3O_8 (Figure 3.32).

The overall EDS of the treated SX-108 solids indicated that the material was rich in Al, Si, Fe, Mn, Na, and U. Boehmite was a major Al-containing phase in the treated material. Aluminum oxide and amorphous aluminosilicates were also evident in the treated SX-108 material. Another Al-containing species identified was $Ca_3Al_2O_6$. Separate Fe-, Mn and Fe-, and U-containing large agglomerates of several microns were observed. Based on the EDS and X-ray patterns, these were identified as single-crystalline FeOOH, single-crystalline $(Mn,Fe)_3O_4$ (Figure 3.35), and multi-crystalline β-U_3O_8, respectively.

(a) The microscopy analysis for treated and untreated SX-108 solids was performed on samples taken from a different test than that reported here. The overall results of this previous test are not reported here because of problems reconciling the mass balance for major sludge components. However, because the microscopy studies are qualitative in nature, the microscopic examination of the sludge solids from this previous test were deemed adequate.

Table 3.41. Concentrations of the Radioactive SX-108 Sludge Components in the Various Process Streams

	First Leach Solution (E)		Second Leach Solution (F)		Final Wash Solution (G)		Leached Solids		
Component	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/g	Activity, µCi	Total Activity, µCi
Total Alpha	< 1.0E-04	< 1.4E-02	< 1.2E-04	< 2.9E-02	< 8.8E-05	< 3.8E-02	1.32E+01	9.49E+01	9.49E+01
^{239,240}Pu	Not Determined		Not Determined		Not Determined		6.32E+00	4.54E+01	4.54E+01
^{241}Am+^{238}Pu	Not Determined		Not Determined		Not Determined		6.88E+00	4.95E+01	4.95E+01
^{241}Am(g)	Not Detected		Not Detected		Not Detected		7.97E+00	5.73E+01	5.73E+01
^{137}Cs	1.66E+01	2.37E+03	3.33E+00	3.56E+01	3.58E-01	0	4.81E+01	3.46E+02	2.76E+03
^{60}Co	Not Detected		Not Detected		Not Detected		4.88E-01	3.51E+00	3.51E+00
^{154}Eu	< 5E-03	< 7E-01	< 4E-04	< 1E-01	< 2E-04	< 9E-02	6.41E+00	4.61E+01	< 47, > 46
^{155}Eu	< 7E-02	< 1E+01	< 4E-03	< 1E-01	< 1E-03	< 4E-01	5.04E+00	3.62E+01	< 47, > 36
^{90}Sr	2.66E-01	3.80E+01	2.90E-01	5.74E+01	3.38E-02	0	1.13E+04	8.12E+04	8.13E+04
^{99}Tc	1.85E-02	2.65E+00	2.86E-03	0	< 3.3E-04	0	< 3E-01	< 2.2E+00	< 4.80, > 2.65

(a) Activity values represent the activity of material dissolved in a given step, these values are corrected for interstitial solution carried over from the previous step.

Table 3.42. Distribution of Radioactive SX-108 Sludge Components Between the Various Process Solutions

Component	Amount of Component, %			
	First Leach Solution (E)	Second Leach Solution (F)	Final Wash Solution (G)	Leached Solids
Total Alpha	0	0	0	100
^{239,240}Pu	0	0	0	100
^{241}Am+^{238}Pu	0	0	0	100
^{241}Am(g)	0	0	0	100
^{137}Cs	86	1	0	13
^{60}Co	0	0	0	100
^{154}Eu	<2	0	0	>98
^{155}Eu	<21	0	0	>79
^{90}Sr	0	0	0	100
^{99}Tc	>55	>3	0	<45

Table 3.43. Concentrations of the Radioactive Components in the Initial SX-108 Sludge Solids

Component	Concentration in Initial Solids, μCi/g		
	Summation Method	Direct Analysis	Recovery, %
Total Alpha	4.69E+00	8.89E+00	53
^{239,240}Pu	2.25E+00	4.06E+00	55
^{241}Am+^{238}Pu	2.45E+00	4.83E+00	51
^{241}Am(g)	2.83E+00	5.70E+00	50
^{137}Cs	1.36E+02	4.52E+01	301
^{60}Co	1.74E-01	3.58E-01	48
^{154}Eu	2.32E+00	4.94E+00	47
^{155}Eu	< 2.3, > 1.8	3.90E+00	--
^{90}Sr	4.02E+03	9.38E+03	43
^{99}Tc	< 0.24, > 0.13	< 0.2	--

Table 3.44. Settling Data From the SX-108 Caustic Leaching Test[(a)]

First Caustic Leach

t, min	h, mm	T	H
0	60	0.00	1.00
10	58	0.05	0.97
20	56	0.09	0.93
30	53	0.14	0.88
40	50	0.18	0.83
50	46	0.23	0.77
80	36	0.36	0.60
110	30	0.50	0.50
140	28	0.63	0.47
170	27	0.76	0.45
200	27	0.90	0.45
230	26	1.04	0.43
290	25	1.31	0.42
350	25	1.57	0.42
410	24	1.85	0.40
470	23	2.12	0.38
530	22	2.38	0.37
5780	18	26.01	0.30

Second Caustic Leach

t, min	h, mm	T	H
0	97	0.00	1.00
10	90	0.08	0.93
20	82	0.16	0.85
30	75	0.24	0.77
40	67	0.31	0.69
50	60	0.39	0.62
60	52	0.47	0.54
70	44	0.55	0.45
80	40	0.63	0.41
90	38	0.71	0.39
100	37	0.78	0.38
110	36	0.86	0.37
120	36	0.94	0.37
150	34	1.18	0.35
210	31	1.65	0.32
270	30	2.12	0.31
330	28	2.59	0.29
390	27	3.06	0.28
450	26	3.53	0.27
510	25	4.00	0.26
1410	21	11.05	0.22

First Wash

t, min	h, mm	T	H
0	74	0.00	1.00
5	72	0.31	0.97
10	68	0.62	0.92
15	45	0.93	0.61
25	40	1.55	0.54
35	38	2.18	0.51
45	37	2.80	0.50
75	33	4.66	0.45
105	31	6.53	0.42
135	29	8.39	0.39
165	27	10.26	0.36
225	27	13.99	0.36
285	26	17.72	0.35
345	26	21.45	0.35
405	25	25.18	0.34
1305	24	81.12	0.32

Second Wash

t, min	h, mm	T	H
0	81	0.00	1.00
5	79	0.30	0.98
10	76	0.59	0.94
15	52	0.89	0.64
20	45	1.19	0.56
25	42	1.48	0.52
30	40	1.78	0.49
40	39	2.37	0.48
50	37	2.96	0.46
60	35	3.56	0.43
90	33	5.33	0.41
120	32	7.11	0.40
180	28	10.67	0.35
240	27	14.22	0.33
300	26	17.78	0.32
360	26	21.33	0.32
420	25	24.89	0.31
480	25	28.44	0.31
1380	25	81.78	0.31

Third Wash

t, min	h, mm	T	H
0	80	0.00	1.00
5	76	0.19	0.95
10	60	0.39	0.75
15	45	0.58	0.56
20	40	0.78	0.50
30	38	1.16	0.48
40	36	1.55	0.45
50	35	1.94	0.44
80	32	3.10	0.40
110	30	4.26	0.38
140	29	5.43	0.36
200	27	7.75	0.34
260	25	10.07	0.31
320	25	12.40	0.31
1370	24	53.09	0.30

(a) t = time, h = sludge height, T = normalized time value = t^*v_{max}/h_0, $H = h/h_0$.

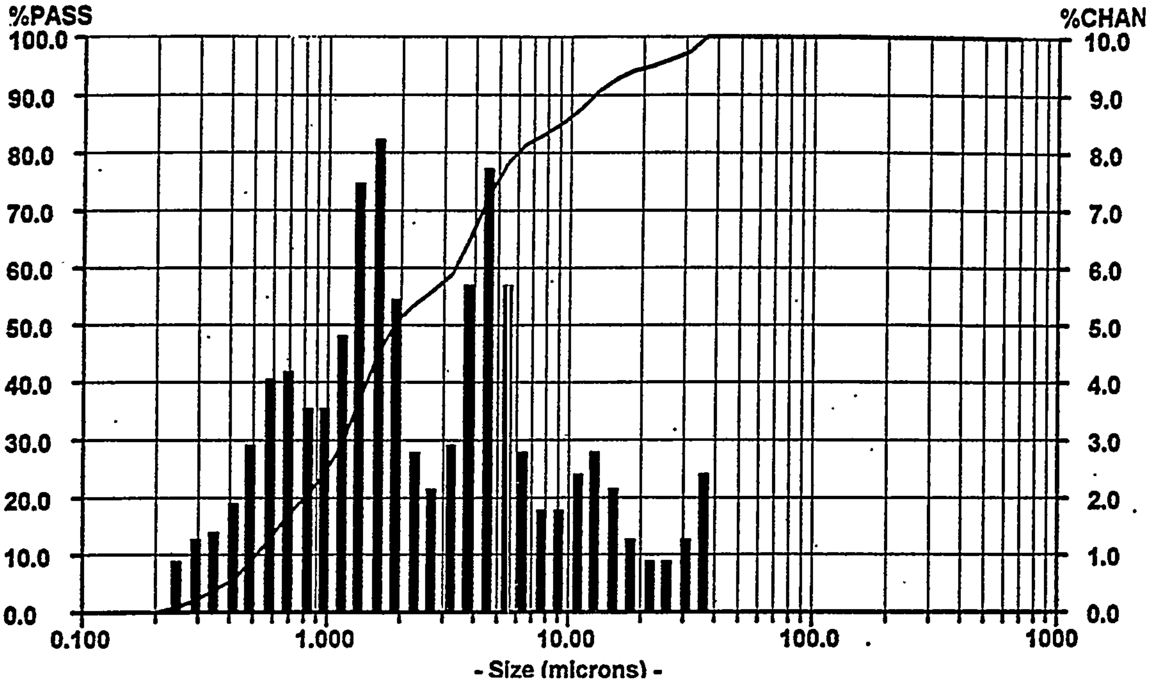


Figure 3.21. Particle-Size Volume Distribution for the Untreated BY-110 Solids

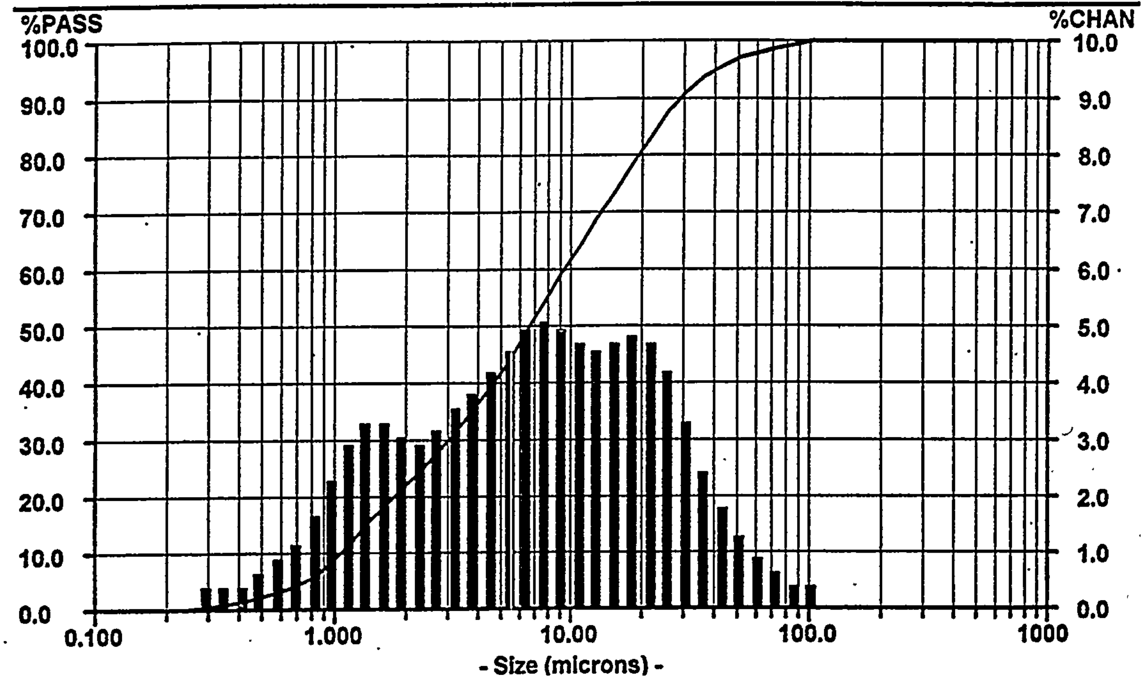


Figure 3.22. Particle-Size Volume Distribution for the Leached BY-110 Solids

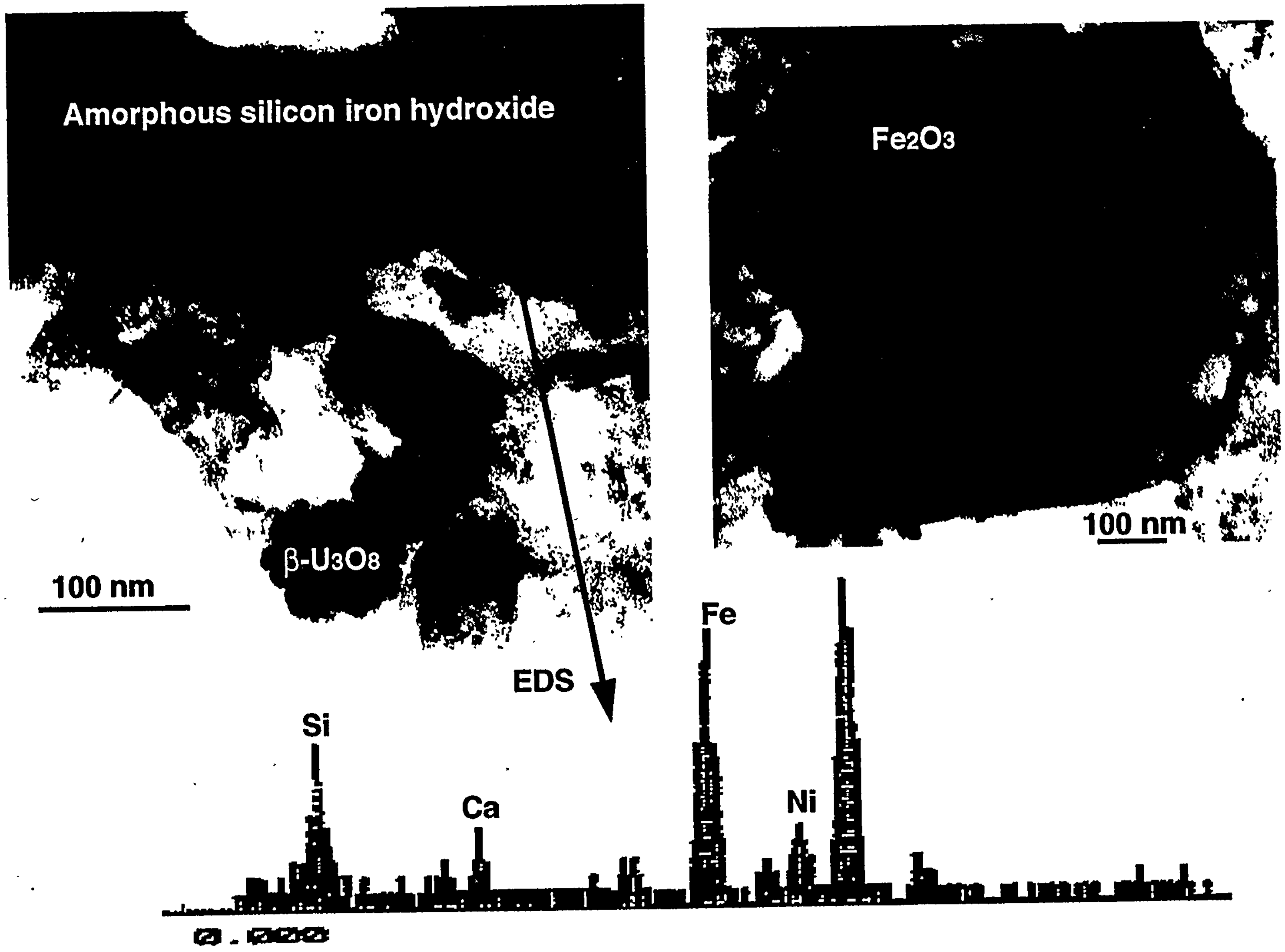


Figure 3.23. Amorphous Si/Fe Hydroxide and Fe_2O_3 Phases in the Leached BY-110 Solids. Also shown is the β-U_3O_8 phase.

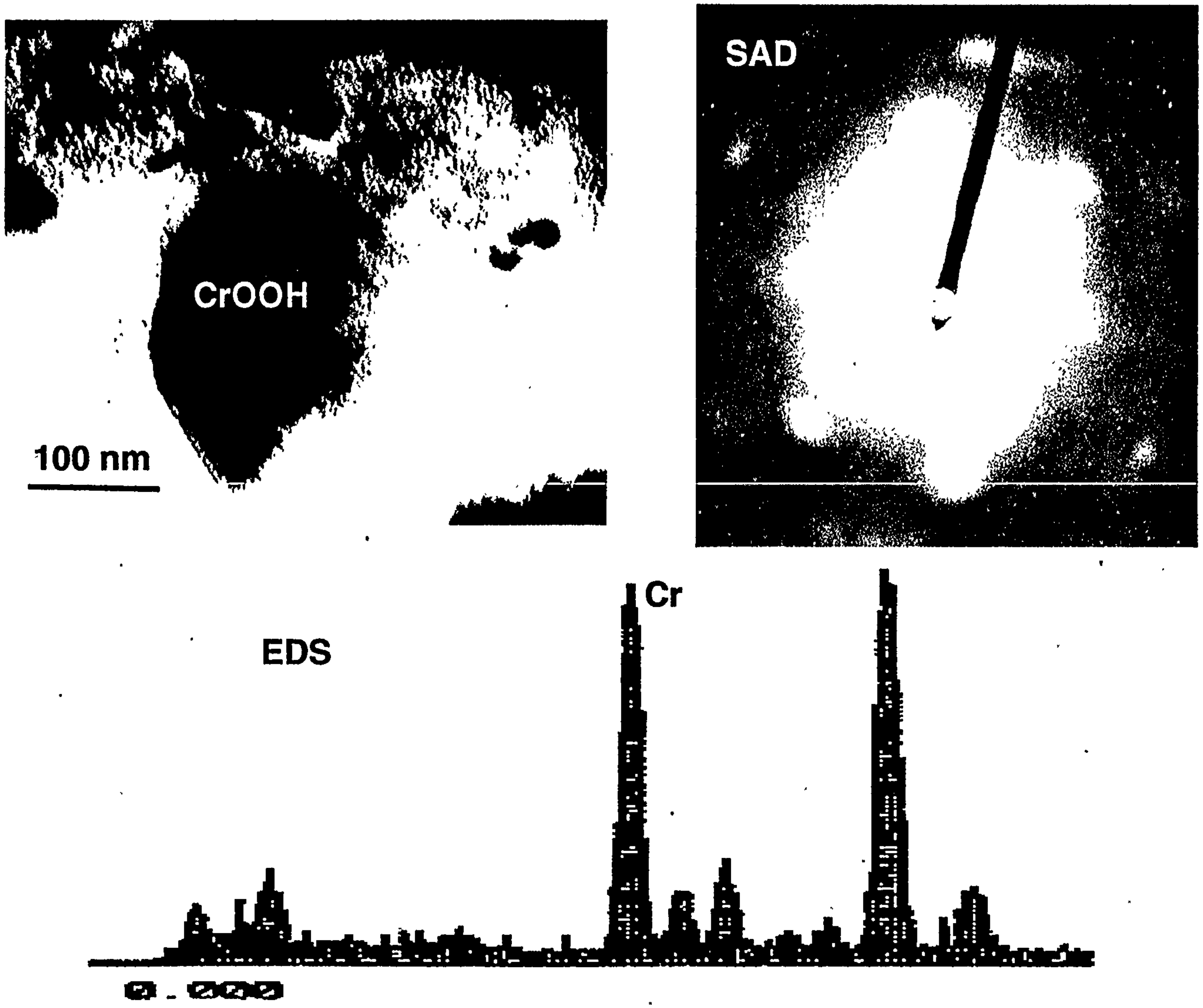


Figure 3.24. Grimaldite in the Leached BY-110 Solids

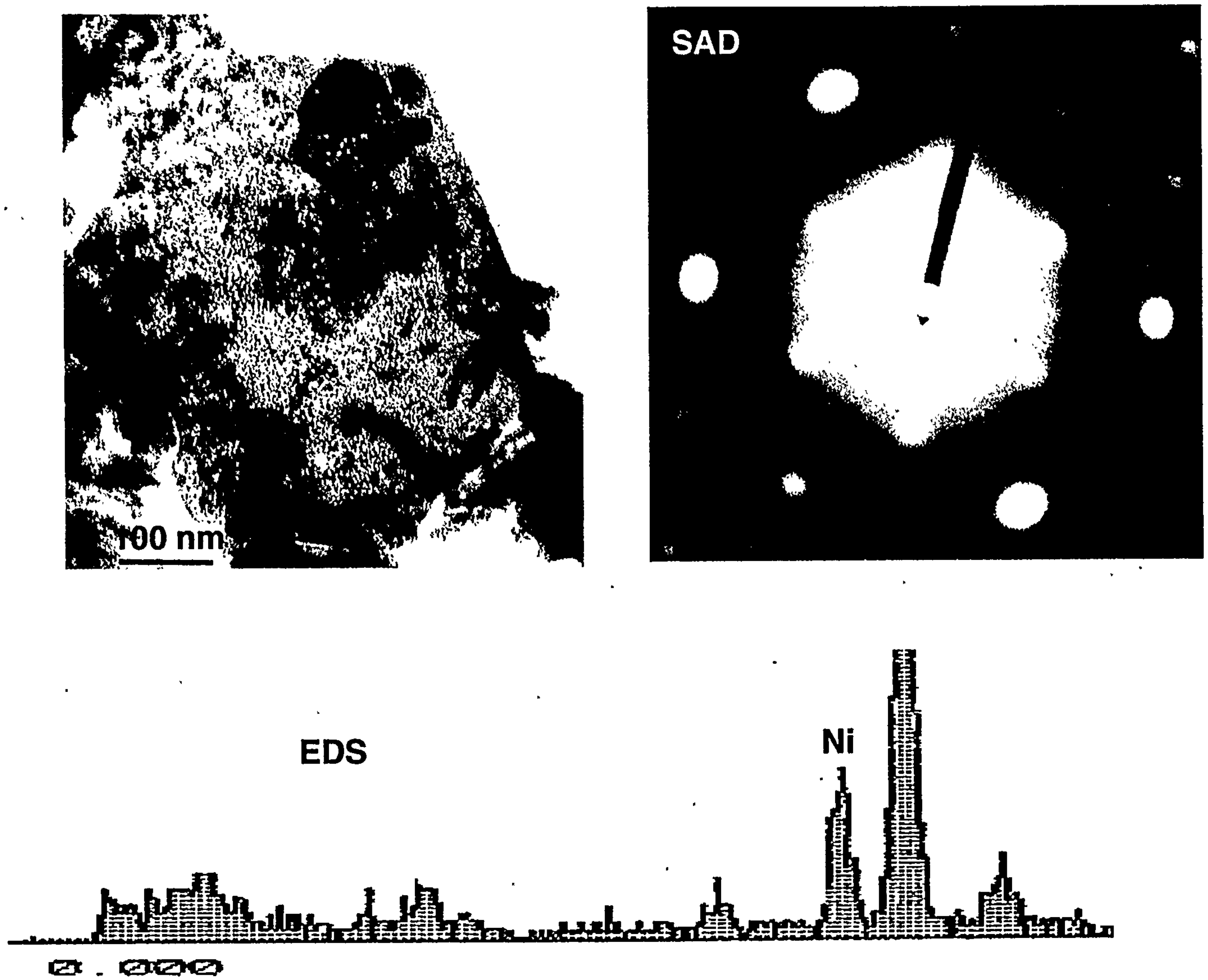


Figure 3.25. $Ni_3O_2(OH)_4$ in the Leached BY-110 Solids

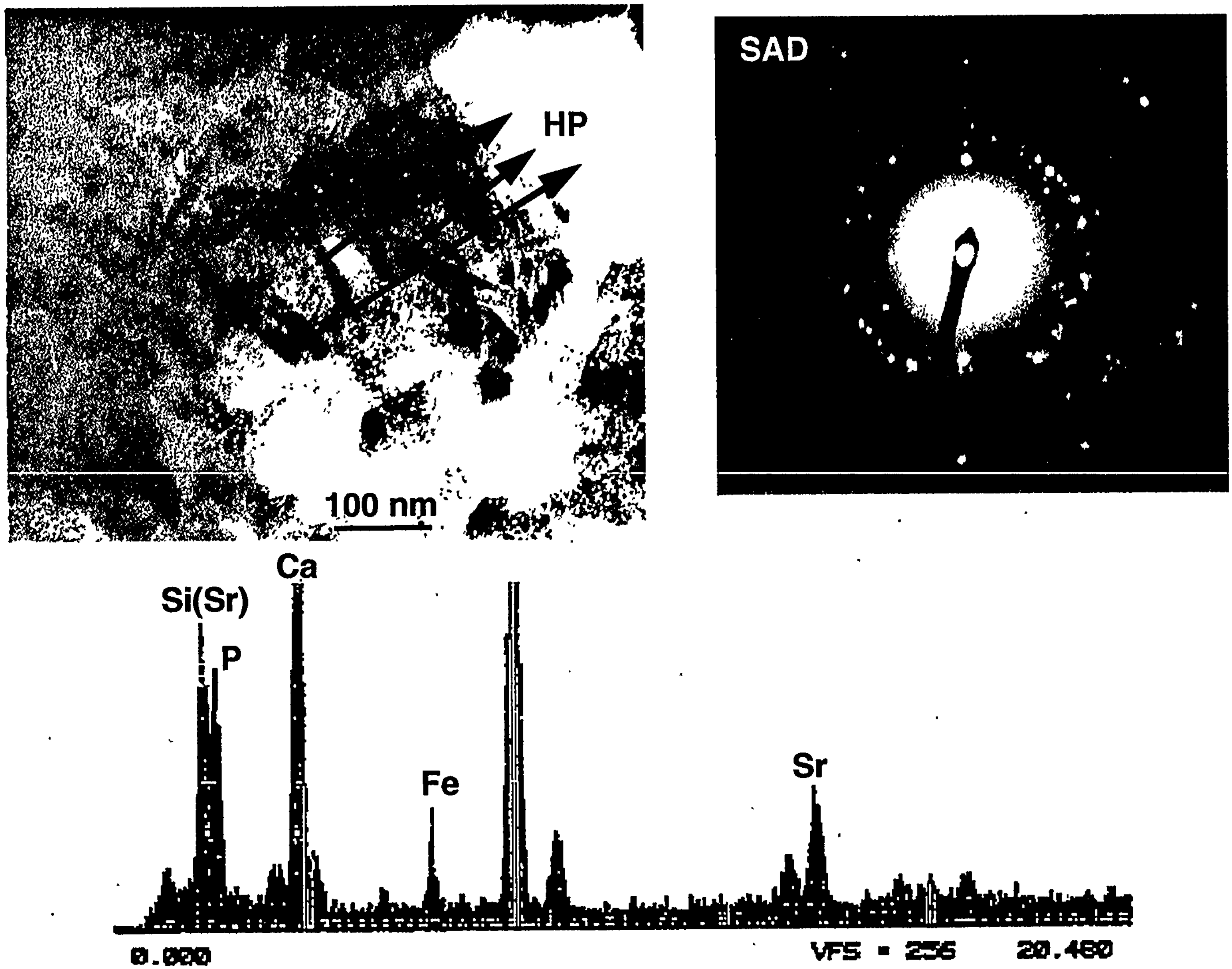


Figure 3.26. Hydroxyapitite (HP) Particles Imbedded in Amorphous Si/Fe Hydroxide. The EDS spectrum indicates Sr is associated with the HP.

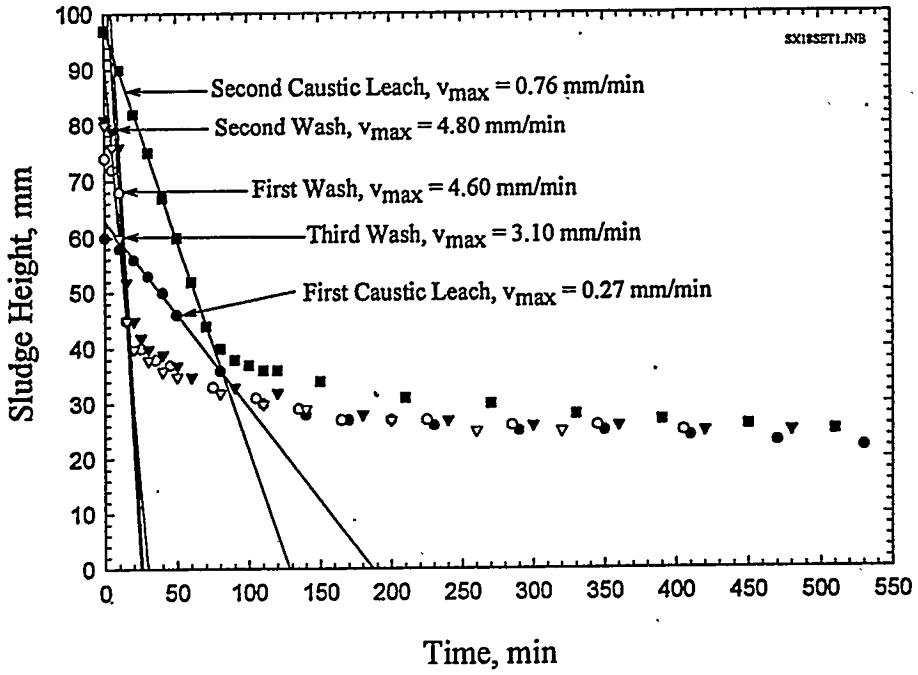


Figure 3.27. Settling Data From the SX-108 Caustic Leaching Test

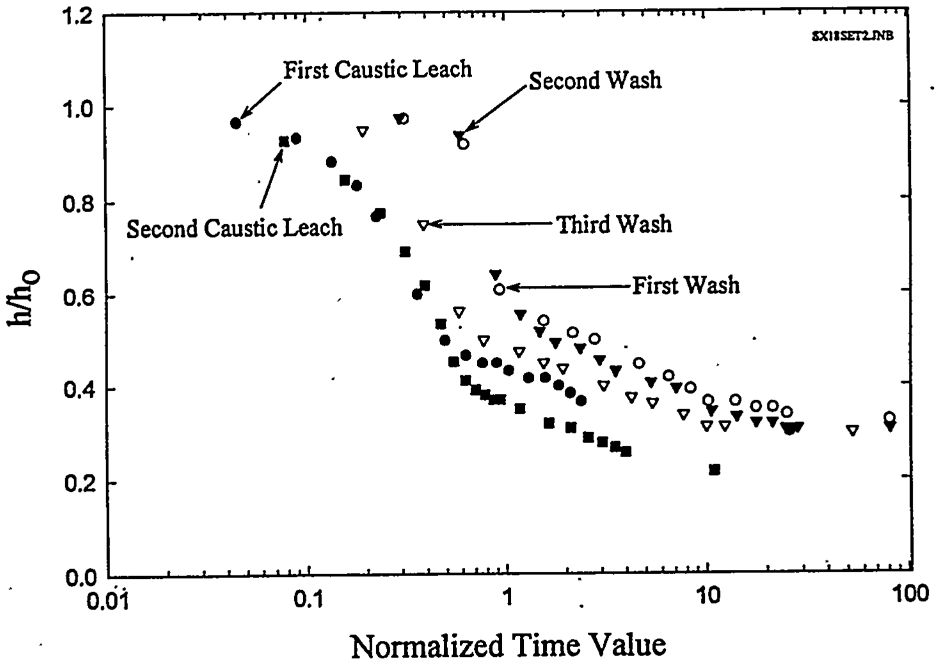


Figure 3.28. Normalized Settling Data From the SX-108 Caustic Leaching Test

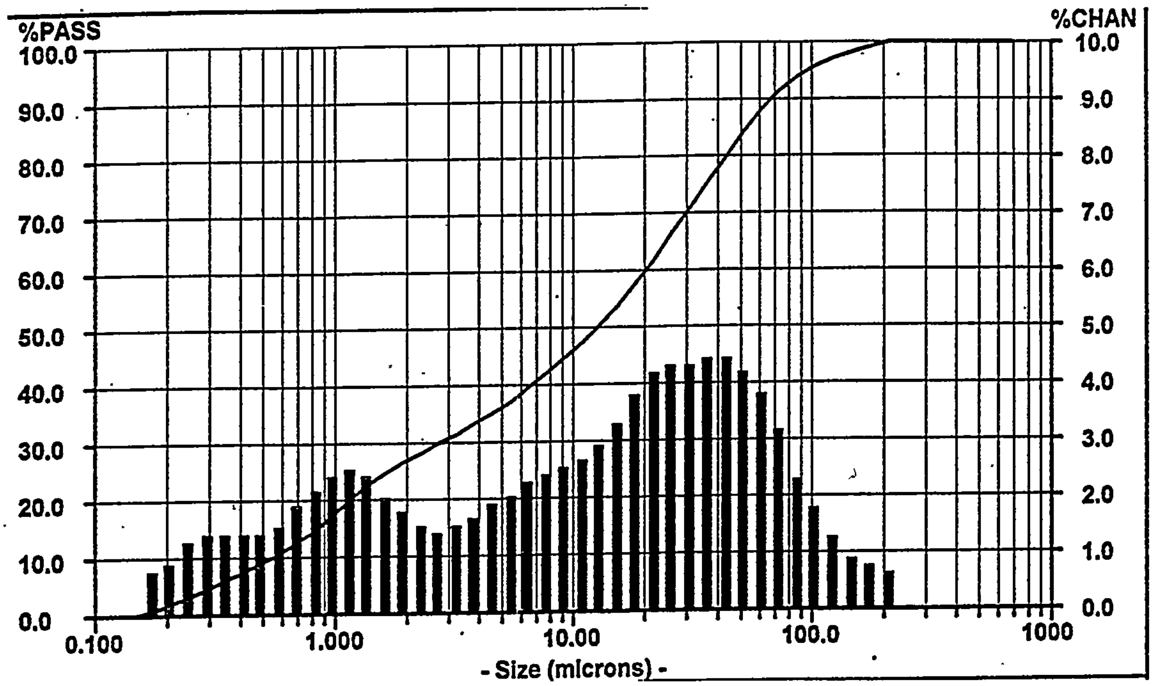


Figure 3.29. Particle-Size Volume Distribution for the Untreated SX-108 Solids

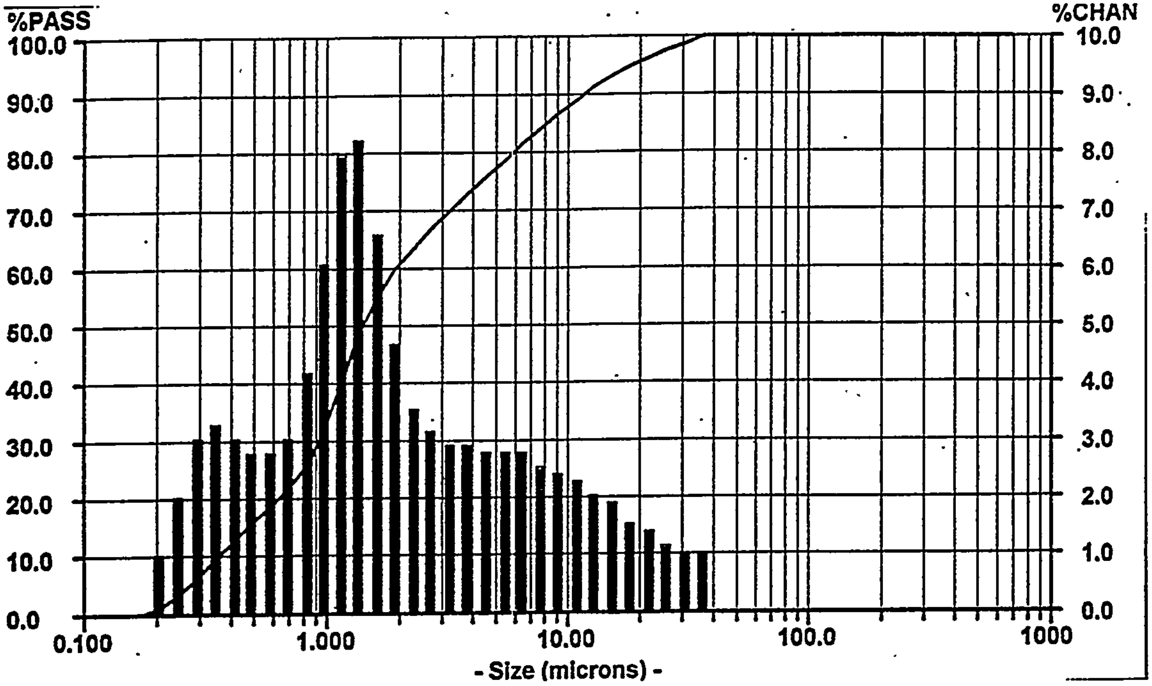


Figure 3.30. Particle-Size Volume Distribution for the Leached SX-108 Solids

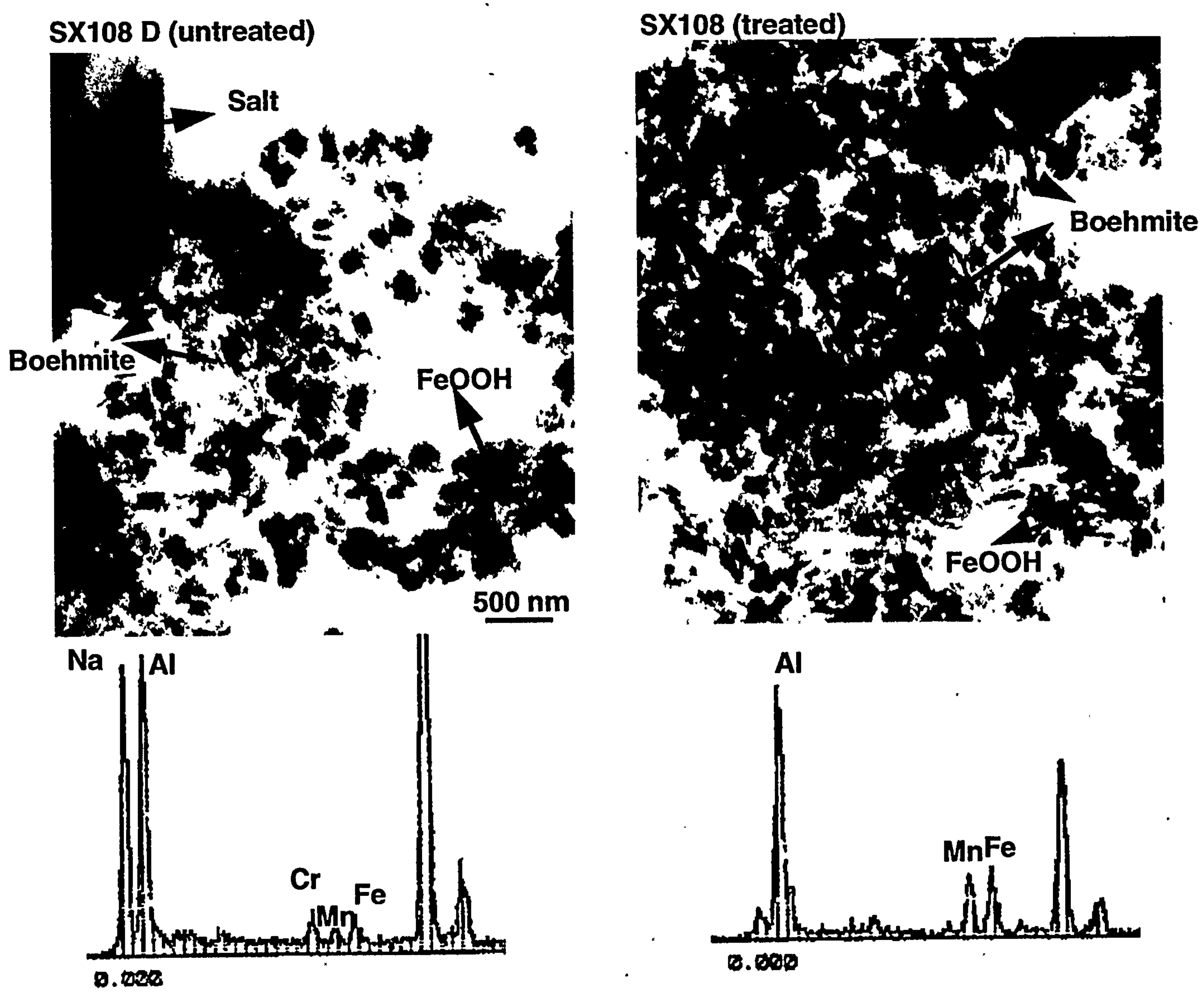


Figure 3.31. Comparison of the Main Solid Phases in SX-108 Sludge Before and After Treatment

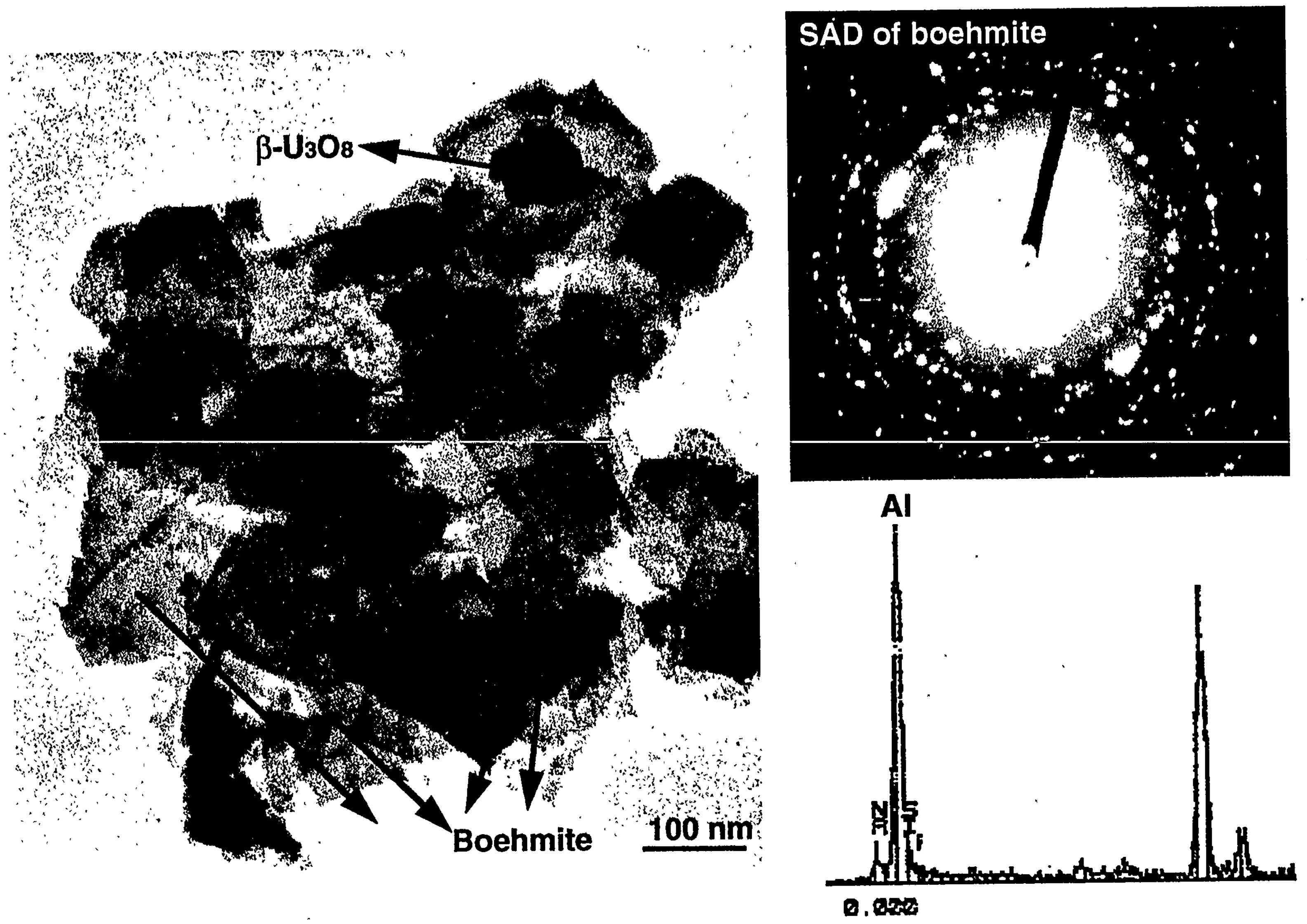


Figure 3.32. Boehmite Particles in the Untreated SX-108 Sludge; a β-U_3O_8 Particle is Also Evident in this Micrograph

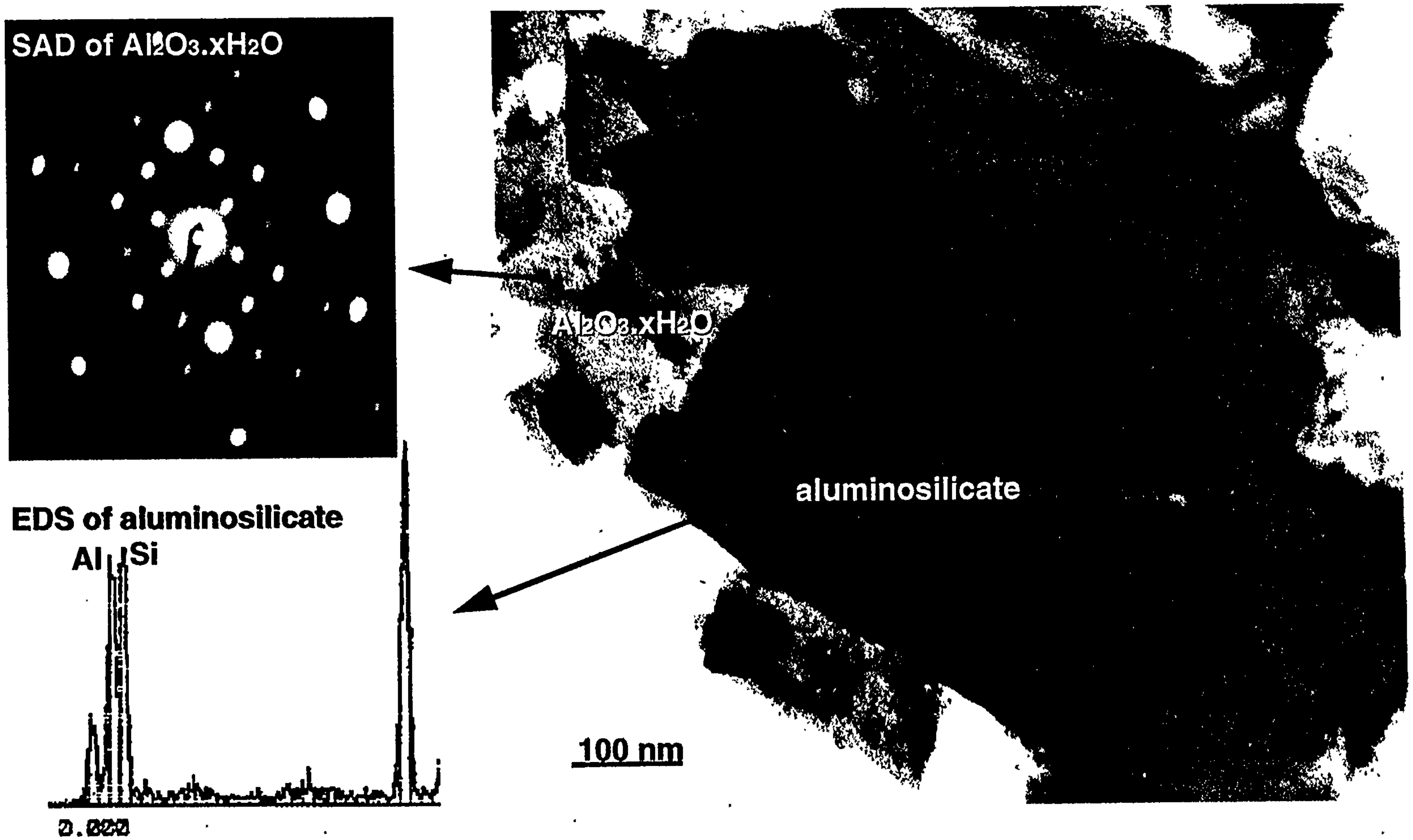


Figure 3.33. Aluminum Oxide and Aluminosilicate Phases in the Untreated SX-108 Sludge

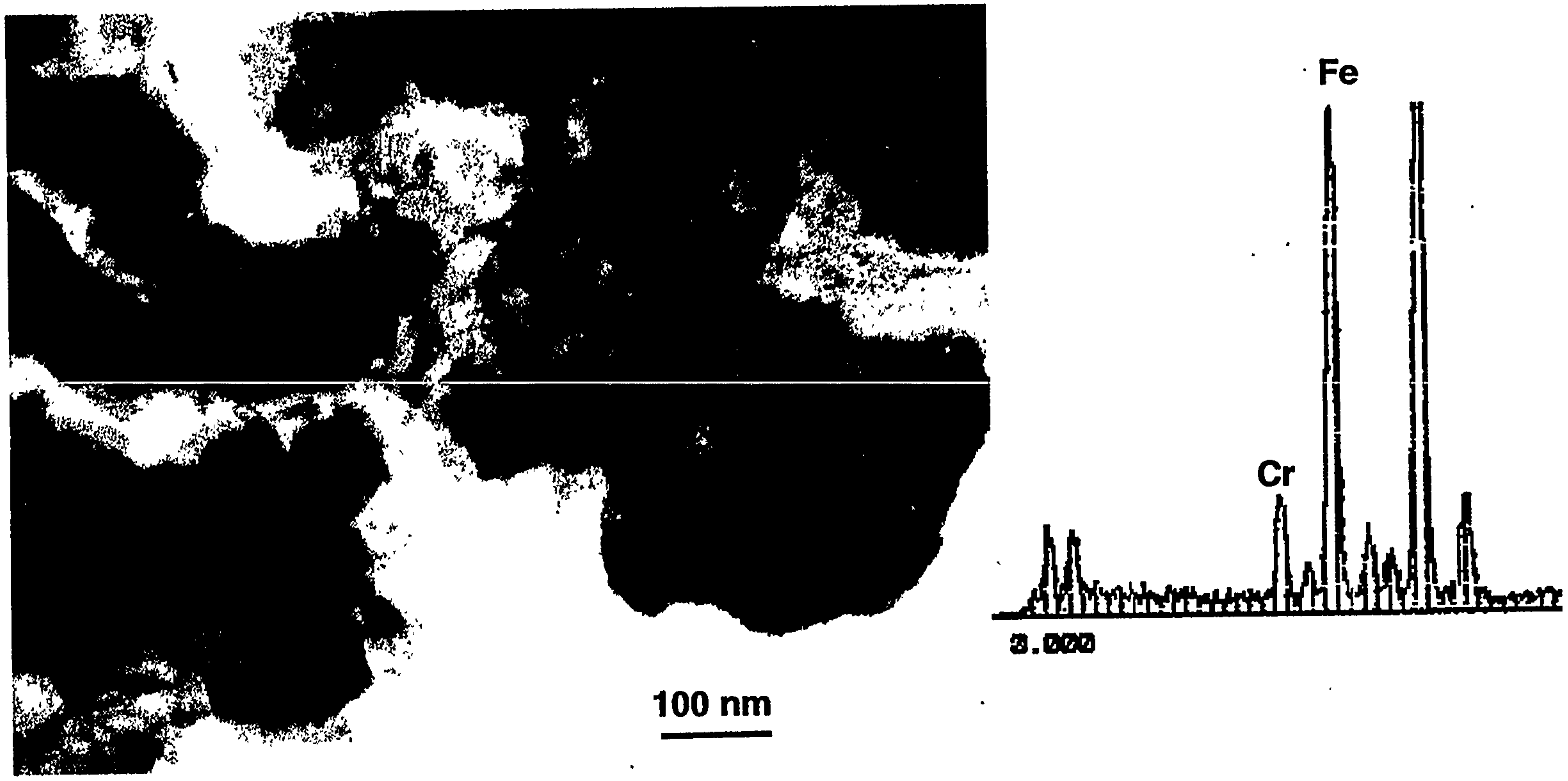


Figure 3.34. FeOOH Particles in the Untreated SX-108 Sludge Solids; the EDS Spectrum Indicates Some Cr Associated With This Phase

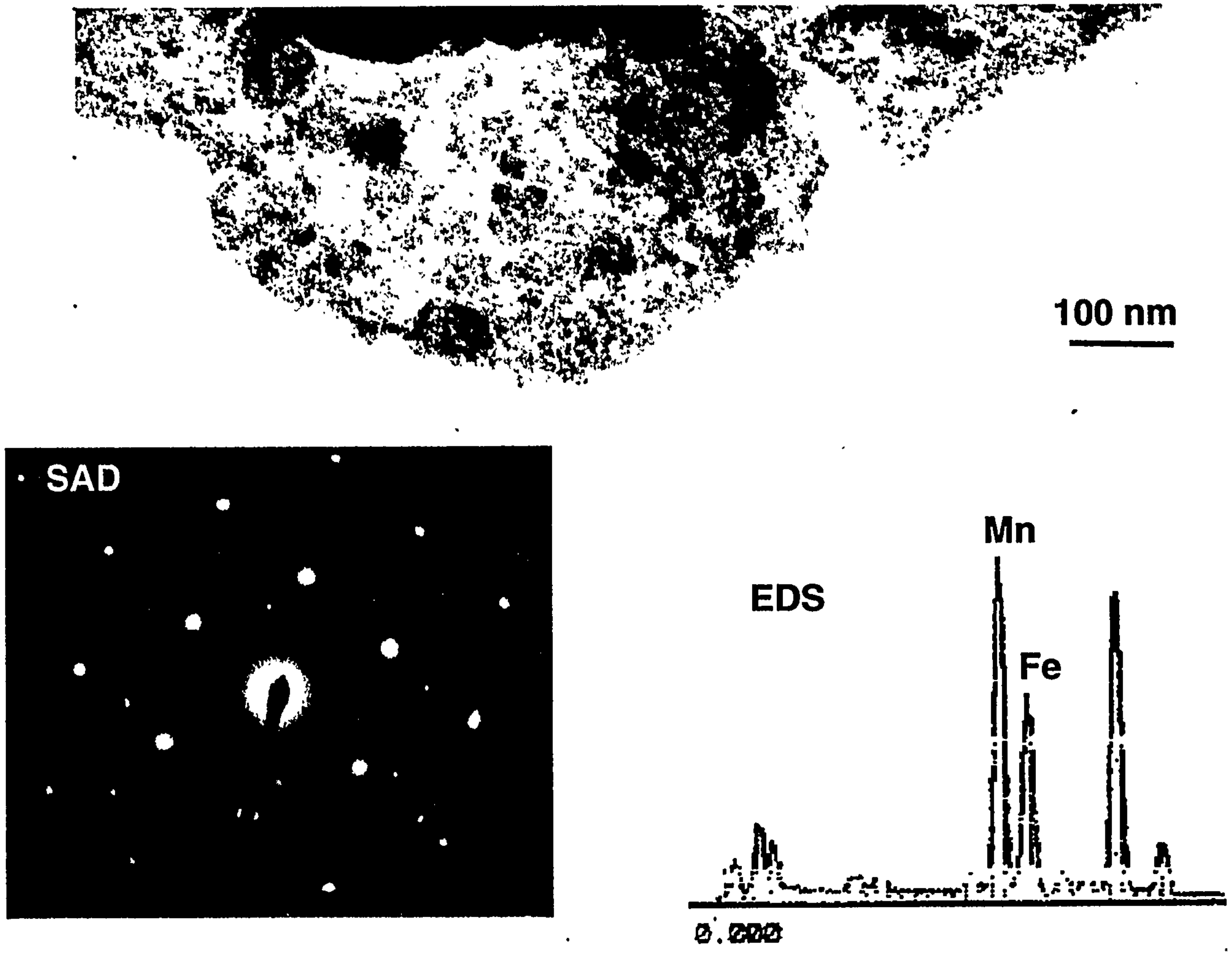


Figure 3.35. Mixed Mn and Fe Oxide, (Mn, Fe)$_3$O$_4$, in the Treated SX-108 Sludge Solids

4.0 Discussion

The implications of the experimental results presented in Section 3.0 to the processing of Hanford tank sludge are discussed in this section. In addition, the stability of aluminate solutions under conditions similar to the process tests is discussed.

4.1 Waste Component Removal as a Function of Waste Type

Caustic leaching and washing studies have now been performed on a total of 24 different Hanford tank sludges. The tank sludges investigated can be organized into several groups, based on the waste types stored. The primary means of organizing the single-shell tanks into groups is the Sort on Radioactive Waste Type (SORWT) model (Hill, Anderson, and Simpson 1995). For SORWT groups 3, 5, 7, 10, 13, and 16, more than one tank has been investigated. The comparative behavior of the major tank constituents between tanks in the same SORWT group is of interest because it is an indication of the validity of extrapolating results from a few tanks (or even one) to the entire set within a group.

Table 4.1 compares the behaviors of Al, Cr, and P between tanks in the same SORWT group. The cumulative Al removal is reasonably consistent within SORWT groups 3, 5, 7, 10, and 13. In contrast, Al removal significantly varied from tank-to-tank within SORWT group 16, with only 2% removed from B-111 compared to 18% for B-110. Because the SORWT group 16 tanks have a relatively low Al content, these differences are not expected to have a large impact on the prediction of HLW volumes. Only for SORWT group 13 was Cr removal consistent from one tank to another. Wide variability in Cr removal was observed for SORWT groups 3, 7, 10, and to a lesser extent 5 and 16. Reasonably consistent P removals were observed for tanks from SORWT groups 5, 10, and 16. Two of the three tanks investigated from SORWT group 13 (C-108 and C-112) displayed very similar P behavior, but only about half as much P was removed from the third group 13 tank investigated (C-109). A significant spread in P removal was observed for the SORWT group 7 tanks, and a very wide variability in P removal was observed for SORWT group 3.

Behavior of the SORWT group 4 tanks is of special interest due to the large inventory of Al and Cr expected to be in these wastes. Tanks S-104 and SX-108 fall in this SORWT group; although Tank S-107 falls in SORWT group 1, it is compared to S-104 and SX-108 here because the primary waste type in all of these tanks is REDOX HLW. The estimated water-insoluble Al inventory for the SORWT groups 1 and 4 tanks is ~50% of the total for all of the single-shell and double-shell Hanford storage tanks, and the estimated water-insoluble Cr inventory for these tanks is ~70% of the total tank inventory. Thus, uncertainties in the projected Al and Cr removals from the tanks containing primarily REDOX sludge could have a large impact on the uncertainty in the amount of HLW glass projected to be produced. The S-104 caustic leaching and washing test conducted at Pacific Northwest in FY-1995 indicated that only 38% of the Al was removed; this result was substantiated by a duplicate test run at Los Alamos, which revealed a 33% Al removal (Temer and Villarreal 1995a). The behavior of the SX-108 sludge was similar with only ~30% Al removal. In contrast, 73% of the Al was removed from the S-107 sludge. The greater Al removal for S-107 might be a reflection of the fact that S-104 and SX-108 experienced some boiling at one point, whereas S-107 did not. The boiling process might have converted Al to a form more difficult to dissolve.

Table 4.1. Aluminum, Chromium, and Phosphorus Removals As a Function of Waste Type

	SORWT	Waste Types[b]		Aluminum		Chromium		Phosphorus		References	
Tank	Group[a]	Primary	Secondary	Initial, wt %[c]	Removed, %[d]	Initial, wt %[c]	Removed, %[d]	Initial, wt %[c]	Removed, %[d]	Initial, wt %	Removed, %
BY-104	3	TBP-F	EB-ITS	1.88	98	0.51	71	0.31	95	(k)	(k)
BY-110	3	TBP-F	EB-ITS	3.37	96	0.37	48	0.56	23	(k)	(k)
BX-105	5	TBP	CW	7.91	100	2.01	96	4.53	100	(e)	(h)
BX-109	5	TBP	CW	0.14	97	0.03	81	4.50	96	(l)	(l)
B-201	7	224	N/A	1.23	25	0.85	56	1.50	26	(e)	(f)
B-202	7	224	N/A	0.26	19	1.12	29	1.00	44	(h)	(h)
C-107	10	1C	CW	8.70	78	0.12	48	0.95	94	(k)	(k)
T-107	10	1C	CW	3.26	78	0.07	61	6.26	99	(e)	(h)
U-110	10	1C	CW	22.7	82	0.05	82	1.93	99	(e)	(j)
C-108	13	TBP-F	1C	15.1	94	0.06	80	5.95	80	(h)	(h)
C-109	13	TBP-F	1C	16.1	81	0.03	85	2.54	42	(e)	(f)
C112	13	TBP-F	1C	3.09	85	0.04	88	4.91	84	(e)	(f)
B-110	16	2C	5-6	0.29	18	0.23	52	3.93	98	(e)	(f)
B-111	16	2C	5-6	0.38	2	0.32	40	4.10	91	(e)	(g)
S-104	4	R	N/A	18.1	38	0.66	97	0.01	N/A	(e)	(g)
SX-108	4	R	N/A	9.02	29	0.79	78	0.12	37	(k)	(k)
S-107	1	R	EB	20.5	73	0.60	53	0.20	98	(k)	(k)
BX-107	12	1C	TBP	3.31	68	0.22	29	5.31	93	(e)	(g)
T-104	Ungrouped	1C	N/A	5.52	64	0.31	50	8.22	97	(e)	(h)
T-111	15	2C	224	0.24	13	0.82	63	4.25	72	(e)	(g)
B-104	Ungrouped	2C	EB	0.25	63	0.12	72	3.46	99	(l)	(l)
C-103	20	SRS	SR-WASH	3.73	48	0.16	11	1.05	66	(e)	(g)
TY-104	22	TBP	1C-F	2.11	63	0.54	86	5.96	98	(e)	(i)
SY-103	N/A	CC		4.70	90	1.30	12	0.78	98	(g)	(g)

(a) Based on a statistical method of grouping single-shell tanks (Hill, Anderson, and Simpson 1995)

(b) 5-6 = High-level B Plant waste from bottom of Section 5
224 = Lanthanum fluoride decontamination waste
1C = First bismuth phosphate decontamination cycle waste
2C = Second bismuth phosphate decontamination cycle waste
CC = Complex concentrate
CW = Cladding waste
EB = Evaporator bottoms
ITS = In-tank solidification
F = Ferrocyanide-scavenged waste
R = High-level REDOX waste
SRS = Strontium leached sludge
SR-WASH = Particulates from Sr wash of PUREX wastes in the AR vault
TBP = Tributyl phosphate waste

(c) Based on dry weight of sludge solids

(d) Cumulative removal achieved by high caustic leaching followed by washing with dilute caustic

(e) Colton 1995

(f) Lumetta and Rapko 1994

(g) Rapko, Lumetta, Wagner 1995

(h) Temer and Villarreal 1995a

(i) Temer and Villarreal 1995b

(j) Based on results reported to Westinghouse Hanford Company a letter report (Lumetta 1995. *Caustic Leaching of Chemically Reconstituted Hanford Tank Sludges: Results of FY 1995 Studies*. TWRSPP-95-047, Pacific Northwest National Laboratory, Richland, Washington) in combination with results reported in Lumetta and Rapko 1994.

(k) This work

(l) Temer and Villarreal 1996

Thermodynamic modeling conducted in FY-1995 suggested that the Al removal from the S-104 sludge might have been limited by the solubility of Al under the test conditions (Rapko et al. 1996). However, this has not been verified experimentally. Indeed, a study of the stability of aluminate solutions under conditions similar to those used in the caustic leaching tests indicated that the S-104 Al removal was probably not solubility limited (see Section 4.2). Furthermore, the procedure followed in the SX-108 test was the same as that followed in the S-107 test. Based on the Al concentrations listed in Table 3.38 for the SX-108 leach solutions, it is unlikely that the SX-108 Al removal was limited by solubility.

The behavior of Cr was also markedly different between S-104, S-107, and SX-108 sludges, again making projections about overall Cr removal uncertain. Similarly, wide variability in the P removal was observed for the S-107 sludge compared to SX-108. The S-104 sludge did not contain a significant amount of P.

For no other SORWT group has more than one tank been investigated. However, several pairs of tanks have been investigated that contain the same primary waste types. These include BX-107 and T-104, for which the primary waste type is first-cycle decontamination waste from the bismuth phosphate process, and T-111 and B-104, for which the primary waste type is second-cycle decontamination waste from the bismuth phosphate process. The behaviors of Al and P are quite similar for tanks BX-107 and T-104 sludges, but 20% more Cr was removed from T-104 compared to BX-107. Aluminum and P removal varies significantly between T-111 and B-104, but the Cr behavior is reasonably similar.

Two of the other tank sludges investigated to date (C-103 and SY-103) cannot be directly compared to any other tank investigated. The remaining tank, TY-104, has the same primary waste type as BX-105 and BX-109. The Cr and P behaviors for TY-104 are similar to those seen for BX-105 and BX-109, but the Al removal was significantly less in the TY-104 case.

4.2 Stability of Aluminate Solutions

As mentioned in the previous section, caustic leaching tests performed in FY-1995 indicated relatively poor removal of Al from Tank S-104 sludge. Results of thermodynamic modeling suggested that the Al removal achieved during the test might have been limited by the solubility of $Al(OH)_3$ (gibbsite) at the temperature at which analytical samples were taken (~25°C). This raised serious concerns about whether leach solutions should be sampled while still hot. To address these concerns, two experiments were performed to determine if Al precipitation is rapid over the time frame usually involved in the baseline tests.

In the first of these tests, an ~2-g portion of boehmite (0.03 mole Al) was digested with 10 mL of 5.6 M NaOH at 90°C for ~1 day. While maintaining temperature, the solids were allowed to settle for 3 h, then an aliquot of the hot solution was filtered through a syringe filter that had been preheated in a boiling water bath. An aliquot of the filtered solution was immediately acidified to prevent precipitation before analysis (Sample 1). The heater was turned off, and the boehmite/hydroxide mixture was allowed to stand overnight at room temperature (much like what is done during our tests with actual waste). The cooled solution was sampled then (Sample 2) and again after standing at room temperature for another 4 days (Sample 3).

The samples were analyzed for Al by ICP/AES. There was considerable scatter between multiple analyses of the same sample, but the overall trends were consistent. The Al concentrations (in µg/mL) found for each sample were as follows; the reported uncertainties are standard deviations.

Sample 1: 27530±1610
Sample 2: 24630±2580
Sample 3: 31230±5475

These values are the same, within experimental error, indicating that the solution was stable over the ~5-day period after heating was stopped, at an Al concentration of ~1 M (representing ~30% of the total Al present in the system).

The measured free-hydroxide concentrations were as follows.

Sample 1: 1.9 M OH
Sample 2: not measured
Sample 3: 2.8 M OH

The reason for this variation is not known. One might expect that the free-hydroxide concentration would increase upon precipitation of Al as gibbsite or aluminum oxide (as was observed in going from Sample 1 to Sample 3), but such a precipitation was not corroborated by the ICP data.

The starting boehmite material and the solids left after leaching were studied by microscopy (Figure 4.1). The starting material was indeed boehmite with needle or plate-like particles. The leached sample had a different morphology (more or less spherical and smaller in size). Electron dispersion spectroscopy indicated some Na in the leached sample, and the X-ray diffraction pattern was slightly different from boehmite. The diffraction pattern suggested that the material was sodium aluminate hydrate.

In the second test, 3 g of a single-shell tank simulant and 1 g of boehmite were mixed with 4 M NaOH (25 mL) for 5 h at 100°C. The stirrer was turned off, and the solids were allowed to settle overnight while maintaining the temperature at 100°C. The hot supernatant solution was sampled without filtering (Sample 4). The heater was turned off, and the system was allowed to stand overnight at room temperature. The supernatant solution was again sampled without filtering (Sample 5) and with filtering through a 0.2-µm membrane (Sample 6). The free hydroxide concentration after standing at room temperature overnight was 2.8 M.

The Al concentrations (in µg/mL) found for each sample were as follows.

Sample 4: 29800
Sample 5: 21100
Sample 6: 24150

The values obtained before and after filtering do not appear to differ significantly. In this case, the Al concentration might have decreased slightly upon standing at room temperature overnight.

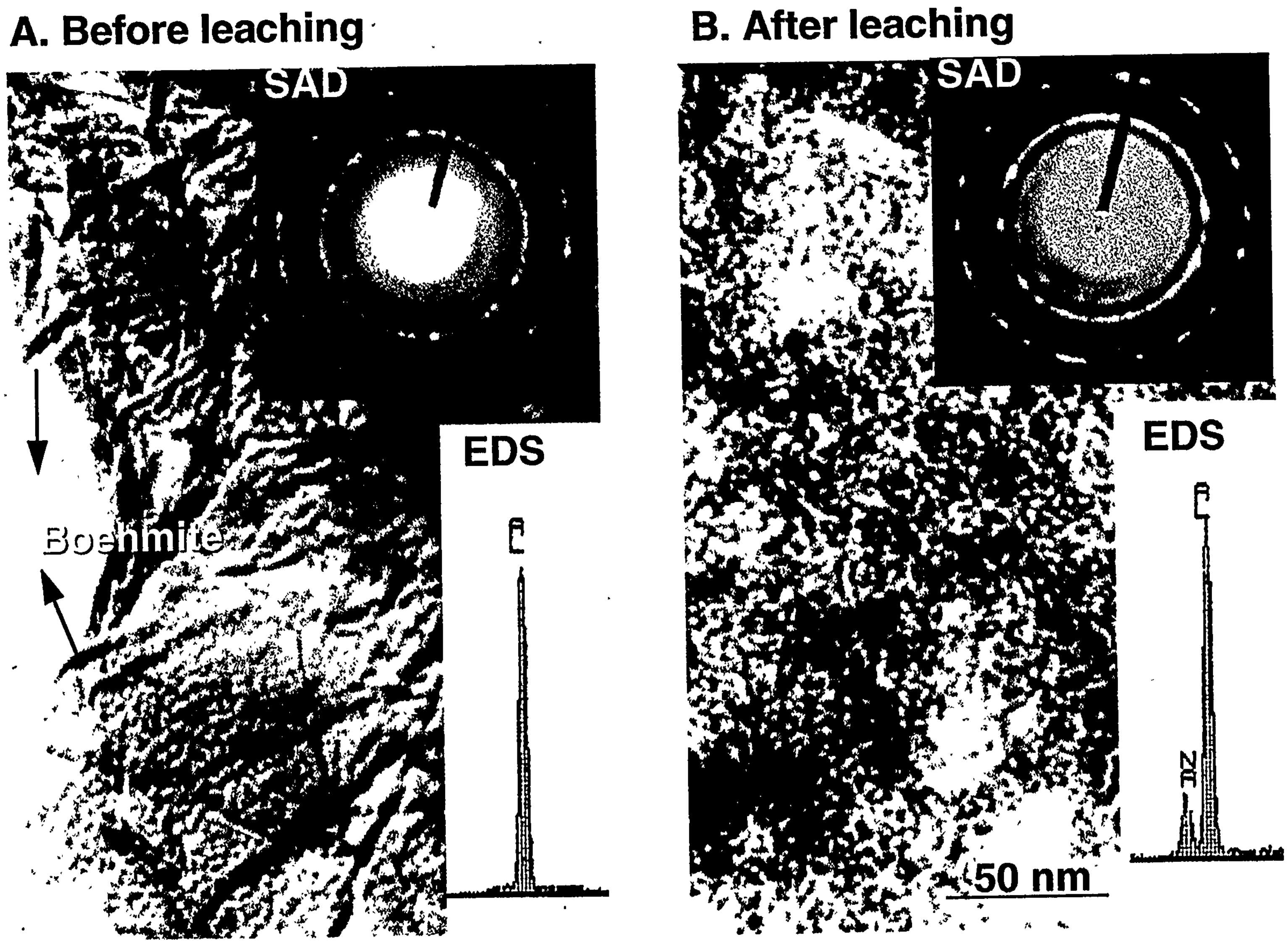


Figure 4.1. Solid Phases Before (a) and After (b) Leaching of Boehmite in NaOH Solution

The room temperature Al concentrations from these two tests can be compared to those observed in the test with S-104 sludge.

	Al, μg/mL	$[OH^-]$, M
S-104 First Leach	19,000	3.7
S-104 Second Leach	14,000	2.9
Sample 2	24,630	2.8[(a)]
Sample 6	24,150	2.8

(a) Measured for Sample 3

These data clearly show that comparable conditions can produce Al concentrations higher than those observed during the S-104 test; this casts serious doubt on the supposition that the S-104 Al leaching data were limited by solubility considerations (as was accepted in the treatment of the data for flowsheet development purposes [Orme 1995]).

The identification of sodium aluminate as the solid phase present after digesting boehmite in aqueous caustic solution, along with the apparent stability of dissolved boehmite solutions, seems to lend credence to the supposition that the poor Al removal from S-104 was due to kinetics of the leaching/dissolution process rather than limited solubility. If Al had reprecipitated on cooling before sampling, one would not expect to find boehmite as the only Al-containing species in the solid phase, which is what was observed when the S-104 residue was analyzed by microscopy (Rapko et al. 1996).

The revised baseline testing procedure (see Section 2.2) allows for the use of higher solution-to-solids ratios, which should reduce the concern regarding solubility limits.

4.3 Comparing the Experimental Results to Planning Assumptions

4.3.1 Aluminum

Table 4.2 presents a summary of the Al removals from the 24 tank sludges investigated to date. In this table, the inventories of water-insoluble Al (as taken from Orme 1995) for each tank investigated are listed along with the amount of "water-insoluble" Al removed from these sludges (as determined experimentally). The amount of water-insoluble Al was determined by subtracting the contribution of dilute hydroxide washing to the overall Al removals reported in the referenced documents. The projected amounts of Al remaining in the sludges after processing were obtained by multiplying the fraction of insoluble Al removed by the inventory of insoluble Al in each tank, then subtracting that value from the tank inventory of water-insoluble Al. The mass-weighted average Al removal was then be obtained by summing the total amounts remaining in the sludges and comparing that value to the total amounts originally in the tank sludges.

Table 4.2. Mass-Weighted Removal of Aluminum From Tank Sludges Investigated

Tank	Initial Mass, kg[(a)]	Removed, %[(b)]	Final Mass, kg	Reference for Removal %
B-104	1.99E+04	61	7.83E+03	(i)
B-110	7.40E+02	18	6.07E+02	(c)
B-111	1.11E+03	2	1.09E+03	(d)
B-201	4.50E+02	25	3.38E+02	(c)
B-202	1.60E+02	19	1.30E+02	(e)
BX-105	4.04E+03	100	0.00E+00	(e)
BX-107	5.43E+04	68	1.76E+04	(d)
BX-109	2.52E+04	92	1.94E+03	(i)
BY-104	1.35E+04	94	7.95E+02	(f)
BY-110	1.64E+04	33	1.10E+04	(f)
C-103	2.56E+04	48	1.33E+04	(d)
C-107	3.95E+04	78	8.78E+03	(f)
C-108	2.84E+03	94	1.76E+02	(e)
C-109	1.58E+03	79	3.26E+02	(c)
C-112	1.28E+04	77	2.91E+03	(c)
S-104	1.57E+05	36	1.00E+05	(d)
S-107	1.01E+05	71	2.96E+04	(f)
SX-108	5.78E+04	24	4.37E+04	(f)
SY-103	7.45E+03	89	8.19E+02	(d)
T-104	5.70E+04	62	2.19E+04	(d)
T-107	2.06E+04	77	4.72E+03	(e)
T-111	9.65E+02	13	8.40E+02	(d)
TY-104	1.48E+03	59	6.02E+02	(g)
U-110	1.73E+04	82	3.14E+03	(h)
Total:	6.39E+05		2.72E+05	

Total Removal For Tanks Investigated: 57

(a) The component inventories were taken from Orme 1995. The total Al and Si inventories include that which is listed as cancrinite in the reference. There were cases where the Al and Si inventories were listed as zero, even though these components have been identified in analyses of these sludges. To estimate the Al and Si inventories in those cases, the experimentally determined concentration was normalized to the experimentally determined Fe concentration. Then, using the Fe inventory reported in Orme 1995, the inventory of the component was estimated.

(b) Amount of water-insoluble Al removed from the sludge by caustic leaching.

(c) Lumetta and Rapko 1994

(d) Rapko, Lumetta, and Wagner 1995

(e) Temer and Villarreal 1995a

(f) This work

(g) Temer and Villarreal 1995b

(h) Taken from data reported to WHC in a letter report (Lumetta 1995, *Caustic Leaching of Chemically Reconstituted Hanford Tank Sludges: Results of FY 1995 Studies*, TWRSPP-95-047, Pacific Northwest National Laboratory, Richland Washington) in combination with the simple sludge washing removal data given by Lumetta and Rapko (1994).

(i) Temer and Villarreal 1996

The mass-weighted average Al removal is projected to be 57% for the 24 tank sludges investigated to date, which is the same value previously assumed for flowsheet development (Orme 1995). Colton has recently estimated the removal of water-insoluble Al to be 60%, based on the entire single-shell tank inventory.[a]

4.3.2 Phosphorus

For the purposes of flowsheet development, it has been assumed that 74% of the water-insoluble P fraction of the tank sludges will be removed by caustic leaching (Orme 1995). Table 4.3 indicates that the mass-weighted average removal of the water-insoluble P is 75% for the tanks investigated to date, which agrees very well with the planning assumption. Colton's recent evaluation for the entire single-shell tank inventory yielded a value (70% P removal).

4.3.3 Chromium

For planning purposes, it has been assumed that 64% of the water-insoluble Cr will be removed from the tank sludges by enhanced sludge washing (Orme 1995). Table 4.4 indicates the mass-weighted average removal of insoluble Cr removal to be 46% for the tank sludges investigated to date. The experimental results indicate a lower removal efficiency than that assumed for flowsheet development. Colton's evaluation indicated even lower (10%) removal of the water-insoluble Cr.

The mechanism of Cr removal is uncertain. It is generally assumed that the Cr removed by washing with dilute hydroxide solution is present as Cr(VI) and that the remainder of the Cr in the sludge solids is Cr(III). It has been suggested that the removal of Cr(III) from the sludge proceeds according to Equation 1.4. However, the caustic-leach solutions often have a yellow color distinctive of Cr(VI). To try to address the oxidation state of Cr removed at the higher hydroxide concentrations of the caustic leach, a spectrophotometric study was performed to quantitate the amount of Cr(VI) in the wash and leach solutions. Table 4.5 presents the results. For the dilute hydroxide wash solutions and the caustic-leach solutions, the chromate concentrations were within 10% of the total Cr concentrations determined by ICP/AES, indicating that Cr(VI) is the dominant form of Cr in solution. The final-wash solutions also appeared to be all chromate, although the amount of chromate found spectrophotometrically was generally greater than the amount of Cr found by ICP/AES. These high chromate values were likely due to interferences from other absorbing species at the very low Cr concentration involved for those wash solutions. The dominance of CrO_4^{2-} in the caustic-leach solutions suggests that Cr(III) is oxidized to Cr(VI) under the caustic-leaching conditions, and that Equation 1.4 provides an incomplete mechanism for Cr removal from the sludges by caustic leaching.

(a) N. G. Colton. 1996. Status Report: Pretreatment Chemistry Evaluation—Wash and Leach Factors for the Single-Shell Tank Waste Inventory. Draft. Pacific Northwest National Laboratory, Richland, Washington.

Table 4.3. Mass-Weighted Removal of Phosphorus From Tank Sludges Investigated

Tank	Initial Mass, kg[(a)]	Removed, %[(b)]	Final Mass, kg	Reference for Removal %
B-104	2.43E+04	98	4.42E+02	(i)
B-110	2.37E+04	97	8.17E+02	(c)
B-111	2.18E+04	84	3.44E+03	(d)
B-201	3.80E+02	20	3.06E+02	(c)
B-202	3.65E+02	22	2.84E+02	(e)
BX-105	1.85E+03	100	0.00E+00	(e)
BX-107	4.11E+04	91	3.60E+03	(d)
BX-109	2.51E+04	83	4.18E+03	(i)
BY-104	2.53E+03	17	2.11E+03	(f)
BY-110	4.52E+03	5	4.29E+03	(f)
C-103	3.60E+01	53	1.68E+01	(d)
C-107	2.94E+04	82	5.35E+03	(f)
C-108	2.55E+03	20	2.04E+03	(e)
C-109	1.67E+03	17	1.38E+03	(c)
C-112	2.53E+03	71	7.23E+02	(c)
S-104	0.00E+00	38	0.00E+00	(d)
S-107	1.10E+01	0	1.10E+01	(f)
SX-108	3.75E+02	31	2.60E+02	(f)
SY-103	5.20E+01	92	4.00E+00	(d)
T-104	4.41E+04	39	2.68E+04	(d)
T-107	1.57E+04	93	1.05E+03	(e)
T-111	2.17E+04	44	1.22E+04	(d)
TY-104	3.43E+02	88	4.29E+01	(g)
U-110	1.42E+04	90	1.42E+03	(h)
Total:	2.78E+05		7.07E+04	

Total Removal For Tanks Investigated: 75

(a) Orme 1995
(b) Amount of water-insoluble Al removed from the sludge by caustic leaching.
(c) Lumetta and Rapko 1994
(d) Rapko, Lumetta, and Wagner 1995
(e) Temer and Villarreal 1995a
(f) This work
(g) Temer and Villarreal 1995b
(h) Taken from data reported to WHC in a letter report (Lumetta 1995, *Caustic Leaching of Chemically Reconstituted Hanford Tank Sludges: Results of FY 1995 Studies*, TWRSPP-95-047, Pacific Northwest National Laboratory, Richland Washington) in combination with the simple sludge washing removal data given by Lumetta and Rapko (1994).
(i) Temer and Villarreal 1996

Table 4.4. Mass-Weighted Removal of Chromium From Tank Sludges Investigated

Tank	Initial Mass, kg(a)	Removed, %(b)	Final Mass, kg	Reference for Removal %
B-104	8.52E+01	71	2.46E+01	(i)
B-110	9.32E+01	47	4.97E+01	(c)
B-111	8.62E+01	18	7.08E+01	(d)
B-201	1.22E+01	30	8.52E+00	(c)
B-202	1.18E+01	10	1.06E+01	(e)
BX-105	1.10E+01	92	9.17E-01	(e)
BX-107	1.33E+02	10	1.20E+02	(d)
BX-109	3.10E+02	46	1.68E+02	(i)
BY-104	4.49E+01	3	4.34E+01	(f)
BY-110	6.13E+01	.2	6.01E+01	(f)
C-103	2.35E+01	9	2.13E+01	(d)
C-107	9.50E+01	21	7.48E+01	(f)
C-108	2.20E+01	17	1.83E+01	(e)
C-109	6.60E+00	25	4.95E+00	(c)
C-112	1.27E+01	77	2.93E+00	(c)
S-104	1.14E+04	70	3.42E+03	(d)
S-107	4.77E+03	38	2.95E+03	(f)
SX-108	8.01E+03	24	6.08E+03	(f)
SY-103	8.12E+02	7	7.52E+02	(d)
T-104	1.90E+02	12	1.67E+02	(d)
T-107	5.06E+01	33	3.40E+01	(e)
T-111	2.82E+02	51	1.37E+02	(d)
TY-104	1.43E+01	50	7.15E+00	(g)
U-110	8.64E+01	55	3.89E+01	(h)
Total:	2.66E+04		1.43E+04	

Total Removal For Tanks Investigated: 46

(a) Orme 1995

(b) Amount of water-insoluble Al removed from the sludge by caustic leaching.

(c) Lumetta and Rapko 1994

(d) Rapko, Lumetta, and Wagner 1995

(e) Temer and Villarreal 1995a

(f) This work

(g) Temer and Villarreal 1995b

(h) Taken from data reported to WHC in a letter report (Lumetta 1995, *Caustic Leaching of Chemically Reconstituted Hanford Tank Sludges: Results of FY 1995 Studies*, TWRSPP-95-047, Pacific Northwest National Laboratory, Richland Washington) in combination with the simple sludge washing removal data given by Lumetta and Rapko (1994).

(i) Temer and Villarreal 1996

Table 4.5. Amount of Cr Present in Solution as Cr(VI)

		Concentration, µg/mL		
Solution	Description	Total Cr[a]	CrO_4^{2-}[b]	Chromate, %
BY104-B2	Dilute hydroxide wash of BY-104	1080	1000	93
BY104-E	First caustic leach of BY-104	113	115	102
BY104-F	Second caustic leach of BY-104	89	87	98
BY104-G	Final wash of leached BY-104	6	9	150
BY110-B2	Dilute hydroxide wash of BY-110	80	83	104
BY110-E	First caustic leach of BY-110	480	495	103
BY110-F	Second caustic leach of BY-110	43	48	112
BY110-G	Final wash of leached BY-110	6	9	150
S107-B2	Dilute hydroxide wash of S-107	52	57	110
S107-E	First caustic leach of S-107	200	200	100
S107-F	Second caustic leach of S-107	24	23	96
S107-G	Final wash of leached S-107	3	4	133

(a) Total Cr concentration determined by ICP/AES.
(b) Spectrophotometrically determined Cr concentration as CrO_4^{2-}.

4.4 Sludge Settling Behavior

Table 4.6 summarizes information on sludge settling behavior for the BY-104, BY-110, S-107, and SX-108 tests. The only statistically significant correlation that can be drawn for these data is that between the maximum settling velocity (v_{max}) and the volume fraction of the centrifuged solids. Figure 4.2a presents a plot of these two parameters. Essentially, the volume fraction of the centrifuged solids tended to be less for cases with higher maximum settling velocities. One would expect a corresponding correlation between the v_{max} and the volume fraction of the settled solids, but this correlation is tenuous at best. Figure 4.2b is a plot of the latter two parameters. As can be seen, the volume fraction of the settled solids drops off rapidly as v_{max} increases, but changes in the volume fraction of the settled solids are not statistically significant above a v_{max} of ~0.5 mm/min.

Except for the BY-110 case, the settling velocities tended to be greater in the wash steps than in the leach steps. This is likely because the viscosity of the wash solution should be significantly less than that of the leach solution.

Table 4.6. Summary of Sludge Settling Behavior

		Volume Fraction, %[(a)]		Solids Concentration, wt%	
Description	v_{max}, mm/min	Settled	Centrifuged	Total Slurry	Centrifuged Solids
BY-104 First Leach	1.75	18	5	3.0	33
BY-104 Second Leach	2.97	12	3	2.0	39
BY-104 First Wash	7.00	16	(b)	3.0	(b)
BY-110 First Leach	0.27	18	17	2.3	21
BY-110 Second Leach	0.64	14	8	1.1	20
BY-110 First Wash	0.099	52	(b)	2.3	(b)
BY-110 Second Wash	0.055	67	(b)	2.3	(b)
BY-110 Third Wash	0.12	35	17	2.3	25
S-107 First Leach	0.19	19	12	1.8	13
S-107 Second Leach	(c)	7	6	0.35	9
S-107 First Wash	2.57	14	(b)	1.8	(b)
S-107 Second Wash	2.35	15	(b)	1.8	(b)
S-107 Third Wash	1.60	19	5	1.8	12
SX-108 First Leach	0.27	25	(d)	4.1	12(e)
SX-108 Second Leach	0.76	20	(d)	2.5	11(e)
SX-108 First Wash	4.60	28	(d)	4.1	(b)
SX-108 Second Wash	4.80	27	(d)	4.1	(b)
SX-108 Third Wash	3.10	38	(d)	4.1	9(e)

(a) Percent of the total slurry volume occupied by the solids layer.

(b) Not determined.

(c) Maximum settling velocity could not be determined because there was no clear demarkation between the liquid and solid phases during settling; see Section 3.1 for details.

(d) Not centrifuged.

(e) The mixtures were not centrifuged, so these values represent the concentration of the solids in the gravity-settled layer.

It can be concluded that the parameters influencing sludge settling behavior are complex and not completely understood. Further work is needed in this area so that reliable predictions of settling behavior can be made.

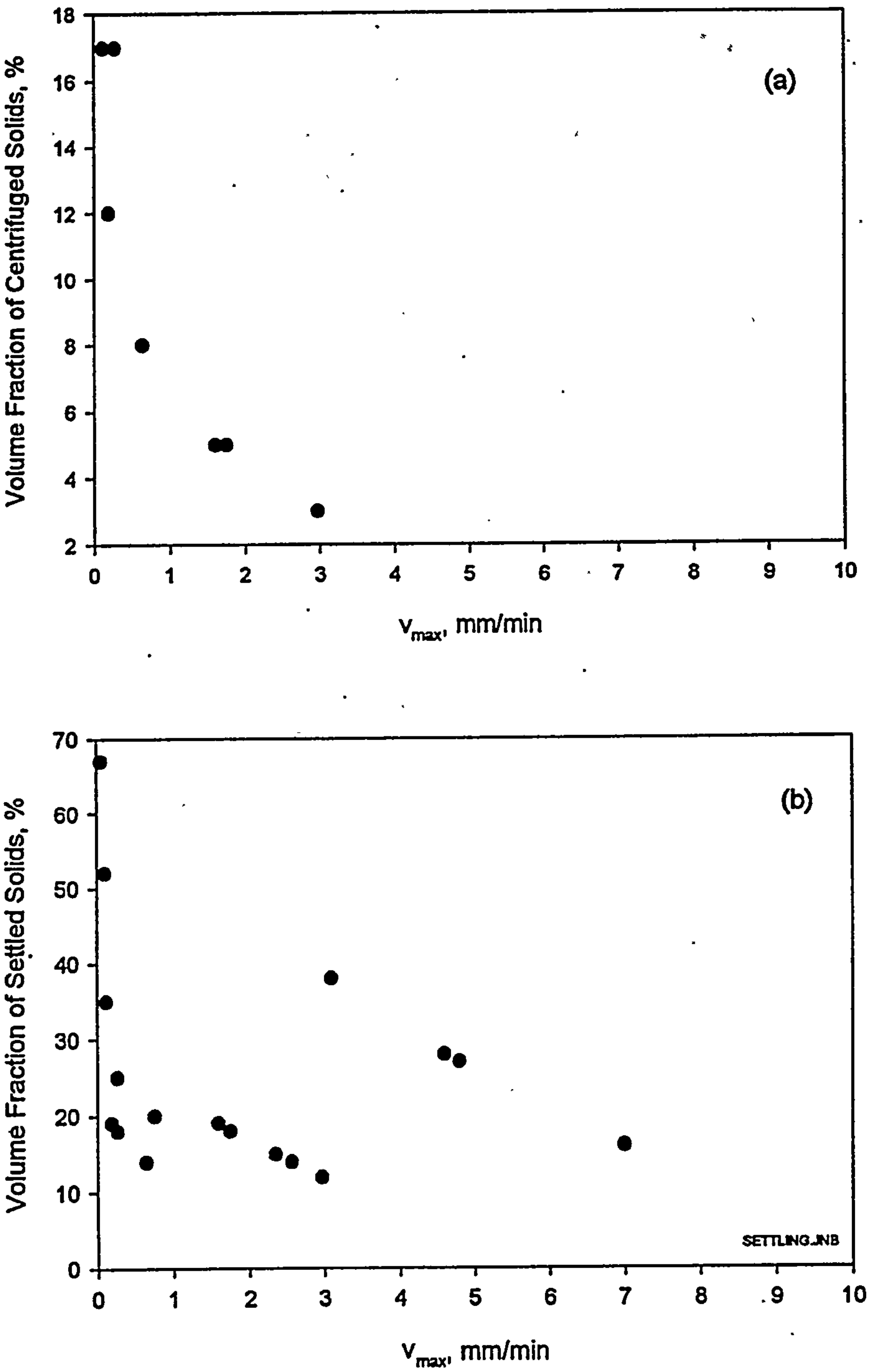


Figure 4.2. a) Plot of the Volume Fraction of the Centrifuged Solids Versus the Maximum Settling Velocity; b) Plot of the Volume Fraction of Gravity-Settled Solids Versus the Maximum Settling Velocity.

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