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Washing and Caustic Leaching of Hanford Tank Sludge: Results of FY 1997 Studies

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Summary

This report describes the sludge washing and caustic leaching tests conducted at Pacific Northwest National Laboratory in FY 1997. These tests supported the development of the baseline Hanford tank sludge pretreatment flowsheet. The U.S. Department of Energy funded the work through the Tanks 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 in FY 1997. The Al concentrations in the sludges varied from about 1 to 16 wt%. The Al removed by washing with dilute NaOH (simple wash) varied from very little (Tank S-104[a]) to over half of the Al removed (Tank BY-108) for the single-shell tanks investigated. Caustic leaching (enhanced sludge washing) led to little improvement in Al removal from BY-108 sludge, but it dramatically improved removal from the other single-shell tank sludges investigated in FY 1997. Dilute hydroxide washing alone resulted in nearly complete Al removal for the double-shell tank waste (AN-104) investigated; caustic leaching essentially removed the water-insoluble fraction of the AN-104 Al. Taking into account all the testing data to date, caustic leaching was generally effective at removing Al. Only three groups of sludges displayed consistently low (< 50%) Al removal—sort on radioactive waste type (SORWT) groups 7, 16, and 20. Extended caustic leaching (several days at 100°C) significantly improves Al removal (and in some cases, Cr removal) from REDOX process sludge (SORWT groups 1 and 4) when compared to previous testing methods in which samples were only leached for 5 h. This can be attributed to slow dissolution of boehmite. The longer leaching times led to nearly complete removal of Al from the three REDOX sludges examined (S-101, S-104, and S-111). The Al removal data generally indicate good agreement for tanks within a given SORWT group.

- Table S.1 summarizes the Cr behavior for the five tanks investigated in FY 1997. In all cases, the Cr concentration in the sludge was <1 wt%. The Cr removed by washing with dilute NaOH varied from 18 to 94%. In the case of BY-108, caustic leaching did little to improve the Cr removal. On the other hand, significantly more Cr was removed from the AN-104, S-101, and S-111 sludges by caustic leaching. Caustic leaching also improved Cr removal from the S-104 sludge. Spectrophotometric measurements detected Cr(VI) in both the wash and leach solutions. Spectrophotometric determination of the Cr(VI) concentrations generally agreed with the inductively coupled plasma/atomic emission spectroscopy (ICP/AES) analyses of total Cr concentrations. No spectral evidence for Cr(III) was observed, but due to the relatively high detection limits for Cr(III) by visible spectrophotometry, its existence in the washing and leaching solutions could not be entirely ruled out.

- Chromium(III) hydroxide can dissolve in high caustic solutions at room temperature, but heating such solution causes precipitation of guyanaite, syn (CrOOH), which does not readily redissolve in aqueous caustic media. Thus, caustic leaching in and of itself (i.e., in the absence of oxidants) is not likely to remove much Cr(III) from the Hanford tank sludges.

(a) The common 241- prefix is omitted from waste tank designations.

- Table S.1 summarizes the P behavior for the five tanks investigated in FY 1997. The amount of P present in these sludges varied from 0.002 to 2.35 wt%. In all cases, simply washing with dilute NaOH removed > 70% of the P. Caustic leaching led to improved P removal from S-101 sludge, but had little impact on the other sludges. Taking into account all the testing data to date, P removal by caustic leaching exceeds 90% for most tank sludges. Only for BY-110, SX-108, B-201, B-202, and C-109, did P removal fall below 50%.

Table S.1. Summary of Al, Cr, and P Removal

		Aluminum Removed, %	
Tank	Al, wt%[(a)]	Simple Wash[(b)]	ESW[(c)]
AN-104	2.61	99	100
BY-108	1.26	63	71
S-101	14.7	12	96
S-104	15.3	2	99
S-111	16.0	10	100

		Chromium Removed, %	
Tank	Cr, wt%[(a)]	Simple Wash[(b)]	ESW
AN-104	0.25	34	63
BY-108	0.04	49	43
S-101	0.71	44	89
S-104	0.45	94	99
S-111	0.4	18	98

		Phosphorus Removed, %	
Tank	P, wt%[(a)]	Simple Wash[(b)]	ESW[(c)]
AN-104	0.12	98	100
BY-108	2.35	73	70
S-101	0.23	87	97
S-104	0.002	> 44	> 58
S-111	0.2	100	100

(a) Concentration based on dry weight of sludge, except for S-111 which is on a wet sludge basis.
(b) Washing with dilute NaOH
(c) Enhanced Sludge Washing (ESW) refers to the process of leaching the sludge with NaOH (2 to 3 M), then washing with dilute NaOH.

- Cesium-137 will likely need to be removed from the sludge washing and leaching solutions before these solutions are immobilized as low-level waste. The behavior of ^{137}Cs in sludges from ferrocyanide-scavenged tanks suggests that the ^{137}Cs might still be present as the cesium nickel ferrocyanide salt. The quantities of transuranics, ^{90}Sr, and ^{99}Tc in the washing and leaching solutions are generally low, and removal of these isotopes from the low-level waste stream probably will not be necessary.

Glossary

CC	complex concentrate waste
CW	cladding waste
DIA	diatomaceous earth
DSSF	double-shell slurry feed
EB	evaporator bottoms
EDS	electrode dispersion spectroscopy
ESW	enhanced sludge washing
F	ferrocyanide-scavenged waste
HLW	high-level waste
ICP/AES	inductively coupled plasma/atomic emission spectroscopy
ITS	in-tank solidification
LANL	Los Alamos National Laboratory
LLW	low-level waste
NRC	U.S. Nuclear Regulatory Commission
OWW	organic solvent wash from PUREX
PNNL	Pacific Northwest National Laboratory
PUREX	plutonium uranium extraction process
R	high-level REDOX process waste
REDOX	REDOX process for Pu recovery
SAD	selected area diffraction
SORWT	sort on radioactive waste type
SRS	strontium leached sludge
TBP	tributyl phosphate
TEM	transmission electron microscopy
TRU	transuranic elements

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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 tank wastes will be partitioned into high-level and low-level fractions. The low-level waste (LLW) will be processed to remove ^{137}Cs (and possibly other radionuclides), and then it will be immobilized in a glass matrix and disposed of by shallow burial on site. The HLW will be immobilized in a borosilicate glass matrix; the resulting glass canisters will then be disposed of in a geologic repository (Orme et al. 1996). Because of the expected high cost of HLW vitrification and geologic disposal, pretreatment processes will be implemented to reduce the volume of immobilized high-level waste (IHLW).

Dilute hydroxide washing is the minimum pretreatment that would be performed on Hanford tank sludges. This method simply involves mixing the sludge with dilute (0.1 $\underline{M}$ or less) NaOH, then performing some sort of solid/liquid separation. This is meant to remove water-soluble sludge components (mainly sodium salts) from the HLW stream. Dilute hydroxide is used rather than water to maintain the ionic strength high enough that colloidal suspensions are avoided.

Caustic leaching (sometimes referred to as enhanced sludge washing or ESW) represents the baseline method for pretreating Hanford tank sludges. 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).

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

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

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.

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

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

Based on its known amphoteric behavior (Rai, Sass, and Moore 1987), Cr(III) is expected to be removed by caustic leaching according to the following equation:

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

However, recent studies conducted at the Pacific Northwest National Laboratory (PNNL) have suggested that the behavior of Cr in the caustic leaching process is more complex. This subject is discussed further in Section 2.0 of this report.

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, Lumetta et al. 1996, Temer and Villarreal 1995 and 1996). 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 tanks AN-104, BY-108, S-101, and S-111. Table 1.1 lists the primary and secondary waste types stored in these tanks. In addition, a repeat ESW test with Tank S-104 sludge was performed using extended leaching times (Section 3.0).

Table 1.1. Primary and Secondary Waste Types

Tank	Primary Waste	Secondary Waste
AN-104	DSSF	N/A
BY-108	TBP-F	EB-ITS
S-101	R	EB
S-111	R	EB

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

Note:

DSSF	Double-shell slurry feed
EB	Evaporator bottoms
F	Ferrocyanide-scavaged waste
ITS	In-tank solidification
R	High-level REDOX process waste
TBP	Waste from tributyl phosphate extraction process

2.0 Behavior of Chromium During Enhanced Sludge Washing

In the last quarter of FY 1996, concern arose over the amount of Cr in the HLW stream resulting from the baseline processing of the Hanford tank wastes. The reason for this concern was 2-fold. First, due to new data considered in the annual ESW evaluation (Colton 1996), the projected Cr removal efficiency for the ESW process was much less than that estimated in the previous year (Colton 1995). Second, ongoing work in revising the tank inventory suggested that the tank wastes contain much more Cr than previously assumed. The combination of these two factors led to a predicted HLW glass volume of 31,260 m^3 compared to 9,100 m^3, which was the prediction made at the end of FY 1995 using the best available information available at that time.[a]

To better understand the behavior of Cr in high-caustic media, we undertook a series of experiments probing the behavior of Cr under conditions analogous to those that would be encountered during enhanced washing of tank sludges. Chromium(VI) is highly soluble under alkaline conditions. However, as a result of these experiments, we have concluded that we should not expect any significant removal of Cr(III) from tank sludges by ESW (as it is currently envisioned). The observations made that led to this conclusion are discussed below.

We have observed during our ESW tests with actual tank waste that the Cr in the caustic leach solutions is in the +6 oxidation state, even when the sludge has been washed to remove Cr(VI) in the interstitial liquid before the caustic leaching step. This would presumably remove all the Cr initially present as Cr(VI) (Lumetta et al. 1996). The exact mechanism by which this occurs was unknown; we thought the most likely mechanism was that the Cr(III) in the sludge dissolved according to Equation 1.4, then was oxidized to Cr(VI) once the Cr was in solution. This led us to perform the first experiment, in which 1 g of $Cr(OH)_3$ was heated overnight at 100°C with 10 mL of 3 M NaOH. After cooling to room temperature, the mixture was filtered yielding a yellow solution. The ultraviolet/visible (UV/vis) spectrum of a 100-fold dilution of this solution revealed the presence of CrO_4^{2-} (2.4×10^{-4} M). Not much could be concluded regarding the presence of Cr(III) because the Cr(III) concentration in the solution that was measured was less than 0.046 M, based on the extinction coefficient for Cr(III) at 595 nm (22 $cm^{-1}M^{-1}$). Although this experiment did not tell us if Equation 1.4 was operating in this system, it did tell us that Cr(VI) can indeed form while Cr(III) is leached with caustic.

The second experiment was designed to demonstrate that $[Cr(OH)_4]^-$ is converted to CrO_4^{2-} in hot aqueous caustic media. A solution of $[Cr(OH)_4]^-$ was prepared by adding aqueous $Cr(NO_3)_3$ (0.4 mL of a 0.1 M solution) to 3 M NaOH (20 mL). This yielded a pale green solution that displayed two bands in the UV/vis spectrum (λ_{max} = 430 nm and 595 nm). This solution was stable at room temperature; no change was observed in the UV/vis spectrum after stirring overnight at room temperature. However, after heating for 2 h at 100°C, a green precipitate had formed, and the solution was pale yellow. The UV/vis

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(a) JO Honeyman. Letter to W. J. Taylor, U.S. Department of Energy, September 9, 1996, Correspondence Number 9654032, Westinghouse Hanford Company, Richland, Washington.

spectra of the solution before and after heating (total heating time was 3 h) are presented in Figure 2.1. The spectrum reveals that the solution contained both Cr(III) and Cr(VI) after heating. This result was reproducible. In a repeat of this experiment, 0.6 mL of 0.1 M $Cr(NO_3)_3$ was added with stirring to 60 mL of 3 M NaOH to give a 0.001 M Cr solution (inductively coupled plasma/atomic emission spectroscopy [ICP/AES] analysis indicated the concentration to be 0.0012 M). Heating this solution for 3 h again resulted in the precipitation of a green solid. The UV/vis spectrum of the resulting solution indicated the Cr(III) concentration to be 2.0×10^{-4} M and the Cr(VI) concentration to be 1.3×10^{-4} M, or a total Cr concentration of 4.3×10^{-4} M. The ICP/AES analysis indicated the total Cr concentration to be $< 2.9 \times 10^{-4}$ M. Thus, the Cr concentration decreased ~75% during heating.

Although we saw Cr(VI) in solution, as expected, the green precipitate was puzzling, and furthermore suggested that the amount of Cr expected to be removed by caustic leaching might be limited. That is, the Cr(III) might dissolve according to Equation 1.4, but subsequently precipitate. Such behavior might also be responsible for the decreased solubility of Cr(III) hydroxide at higher temperatures previously reported in the literature (Rai, Sass, and Moore 1987).

In the third experiment, 0.47 g of $Cr(OH)_3$ was stirred at room temperature for several days with 10 mL of 3 M NaOH. The mixture was filtered to give a green solution. The UV/vis spectrum of this solution indicated the presence of both Cr(III) (7.7×10^{-3} M) and Cr(VI) (1.0×10^{-4} M) (see Figure 2.2). The green precipitate formed when the solution was heated at 100°C for ~3 h. The UV/vis spectrum (Figure 2.2), obtained after cooling, indicated a decrease in the Cr(III) concentration to 5.7×10^{-5} M. The spectrum indicated a slight increase in the Cr(VI) concentration to 1.3×10^{-4} M. Thus, the UV/vis spectra

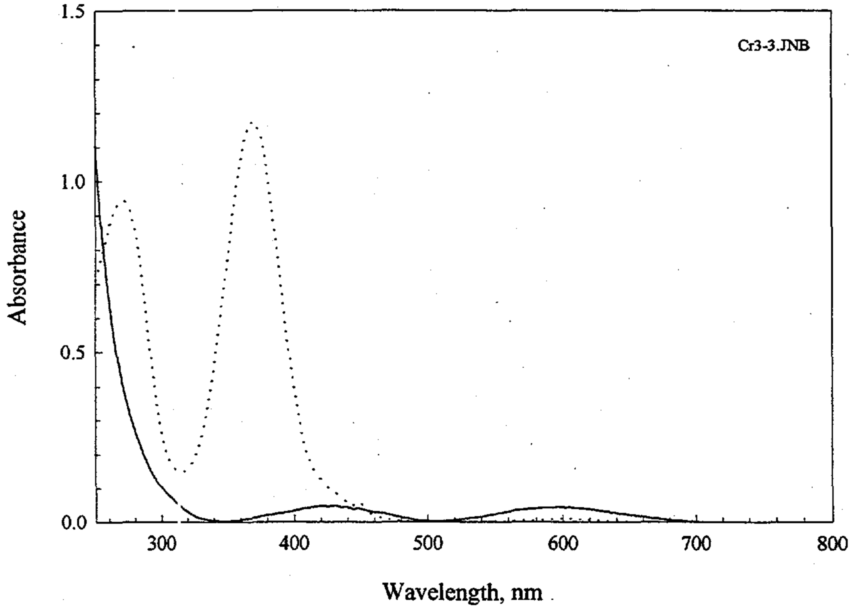


Figure 2.1. Spectra of Cr (III) Solution in 3 M NaOH Before and After Heating at 100°C

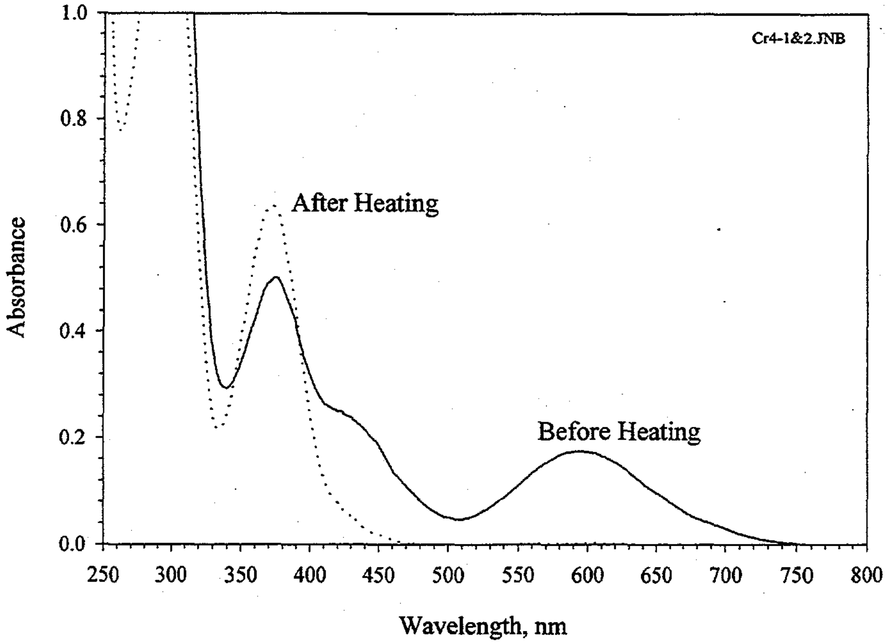


Figure 2.2. Spectra of Solution Formed By Stirring Cr(III) Hydroxide in 3 M NaOH Before and After Heating at 100°C

indicated an overall decrease of 98% in the total Cr concentration in solution. The solution was also analyzed by ICP/AES before and after heating. The Cr concentration dropped from 6.3×10^{-3} M before heating to 4.8×10^{-4} M after heating, which is 92% less Cr. The latter result agrees reasonably well with that obtained by UV/vis spectrophotometry. The green solid has been analyzed by microscopic methods. Although a definitive identification has not been made, it appears to have been an amorphous Cr oxide/ hydroxide species with an O/Cr ratio of 2; the most likely assignment of this species is to guyanaite, syn (CrOOH).

Finally, a test was performed to determine if nitrite ion was involved in the oxidation of Cr(III) to Cr(VI) in high caustic media. A 0.0013 M solution of Cr(III) was prepared by adding 0.2 mL of 0.1 M $Cr(NO_3)_3$ to 15 mL of 3 M NaOH. To this solution was added 0.1 mL of 1.0 M $NaNO_2$ to give 0.0065 M nitrite. No change in the UV/vis spectrum of this solution occurred after stirring overnight at room temperature. However, a green precipitate (like the earlier experiments) had formed after heating the solution at 100°C for about 5 h. The UV/vis spectrum of the solution after heating indicated Cr(VI) at 1.2×10^{-4} M and Cr(III) at $< 6.4 \times 10^{-4}$ M; this was consistent with what was seen in the previous experiments. The green solid was isolated and confirmed to contain Cr(III) by treatment with permanganate. The material rapidly oxidized to Cr(VI) when treated with aqueous permanganate solution. Thus, under the very limited conditions of this experiment, nitrite does not appear to significantly oxidize Cr(III) to Cr(VI). Perhaps higher nitrite concentrations would result in more conversion to Cr(VI), or perhaps other waste components (or even oxygen) are responsible for the observed oxidation of some of the Cr to Cr(VI) during ESW.

In conclusion, it appears that elevated temperatures produce a significant driving force to precipitate Cr(III) from high (3 M) caustic solutions. The precipitation of Cr(O)OH might explain the low removal efficiencies observed for Cr during ESW tests with actual tank waste and the failure to observe any Cr(III) in the leachates (Lumetta et al. 1996; Colton 1996). This observation is consistent with previous reports of low solubility of $Cr(OH)_3$ in acidic and near-neutral solutions at elevated temperature (Rai, Sass, and Moore 1987). It might be possible to remove Cr(III) from the sludges by caustic leaching at ~25°C, but this might not practical because some mechanical heating will likely occur during sludge retrieval (which could lead to the more refractory Cr(O)OH phase). Oxidation to Cr(VI) is likely the best option for ensuring adequate Cr removal. Further work in this area is needed to determine if oxidation is best carried out before, after, or concurrently with caustic leaching.

3.0 Modified Tank S-104 Enhanced Sludge Washing Test

3.1 Background

In FY 1995, two ESW tests were performed on sludge from Hanford Tank S-104. One of these tests was performed at PNNL, while a duplicate test was conducted at Los Alamos National Laboratory (LANL). A significant finding of these tests was that ESW removed relatively little Al. The test conducted at PNNL in FY 1995 indicated that only 38% of the Al was removed (Rapko, Lumetta, and Wagner 1995); this result was substantiated by the duplicate test run at LANL, which revealed 33% Al removal (Temer and Villarreal 1995). Based on thermodynamic models, it was suggested that the low Al removal was due to solubility constraints (Rapko et al. 1996), but microscopic analysis of the leached S-104 residue and a study of the stability of aluminate solutions suggested this was not the case (Lumetta et al. 1996). To determine if additional Al could be removed from S-104 sludge, another test was performed at PNNL in which the S-104 sludge was treated with greater relative volumes of caustic and for longer periods of time. The results of this study are summarized here.

3.2 Experimental

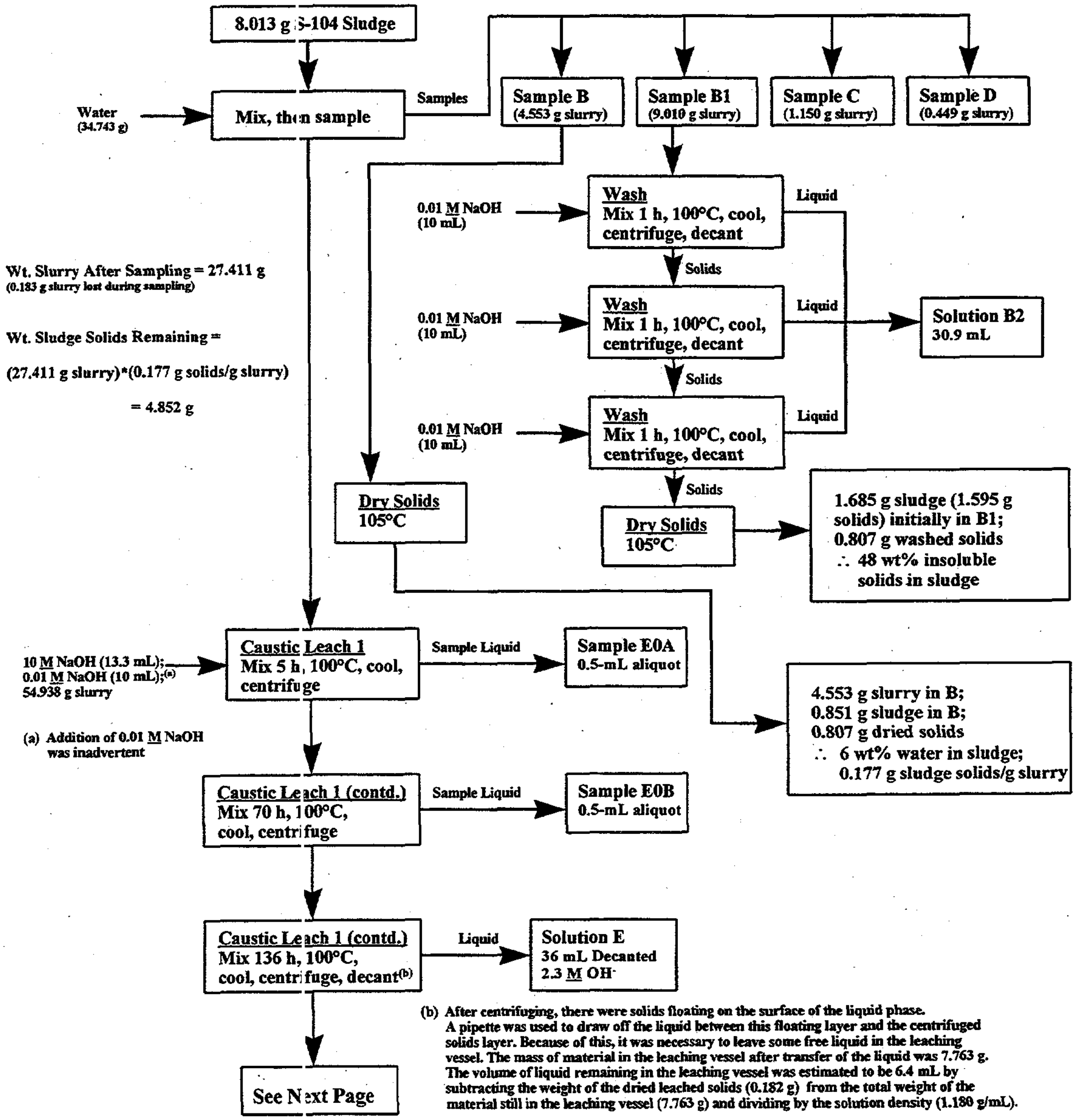
Figure 3.1 summarizes the experimental procedure used in this test. The procedure was essentially the same as the baseline enhanced sludge washing test procedure described previously (Lumetta et al. 1996), except that the first caustic leaching step was performed over a period of ~8 days rather than the usual 5 h. The leachate was sampled at the following intervals: 5 h, 75 h, and 211 h. Also, during the second caustic leaching step, the mixture was heated for 3 days rather than the usual 5 h.

3.3 Results and Discussion

3.3.1 Washing With Dilute NaOH

Table 3.1 summarizes the behavior of important sludge components during washing of the S-104 sludge with 0.01 M NaOH. Only Cr, Na, and P were significantly removed by dilute hydroxide washing. A small fraction of Al (2%), Ni (5%), and Si (8%) were also removed. Iron, Mn, and Sr were largely unaffected by dilute hydroxide washing. Mass recoveries were within 30% for all the components listed, except for P, Ni, and Si.[a] The low mass recoveries for the latter two elements are unexplained at this time. The high mass recovery for P is likely due to experimental uncertainties in determining this component at the low concentrations in the S-104 sludge.

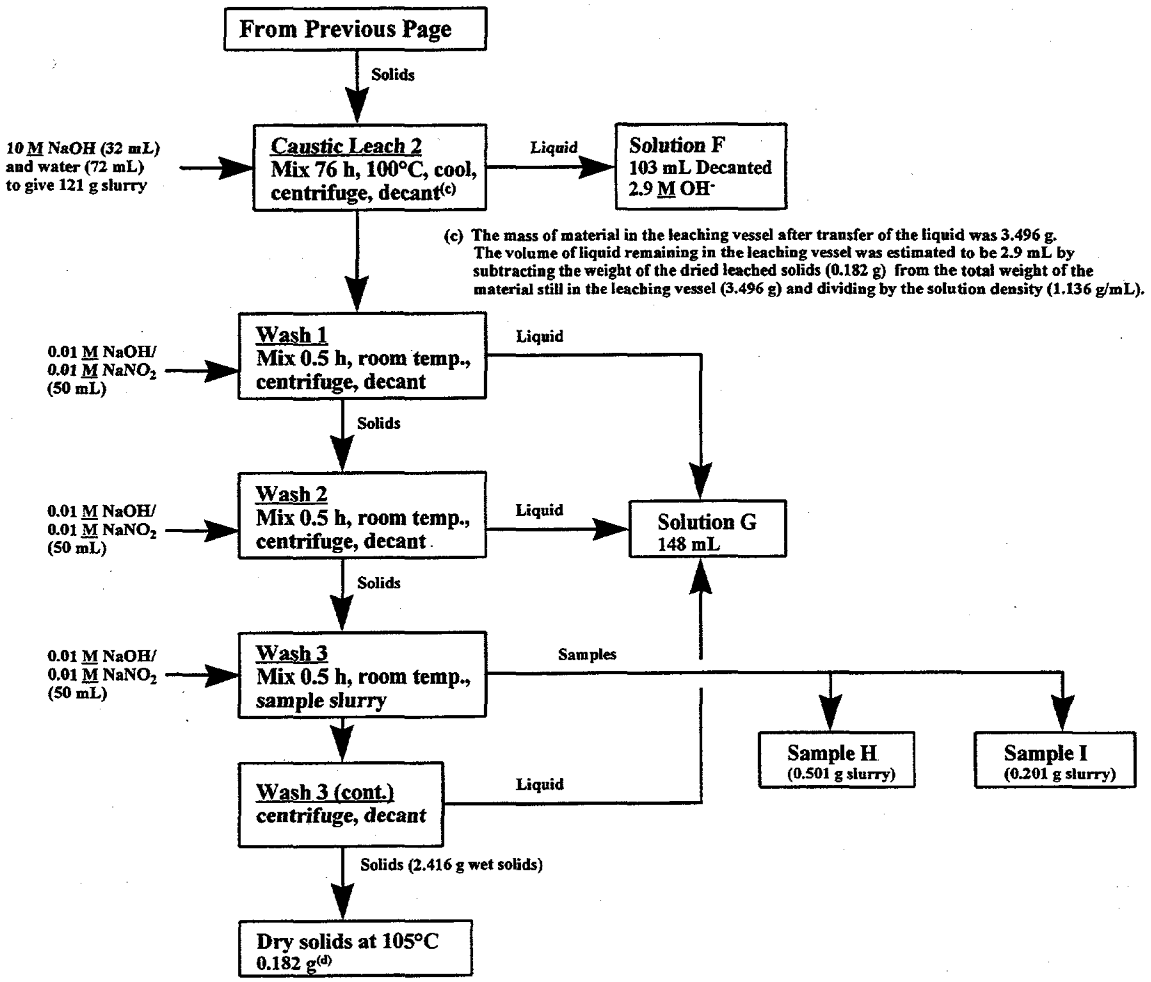
(a) In this report, we define the mass recovery to be the ratio of the concentration determined by the summation method to that determined by direct analysis of the untreated sludge solids multiplied by 100. To determine the concentrations by the summation method, the amount of material found in each process solution and in the residual solids was summed, and the resulting quantity was divided by the mass of solids used in the test.



(a) Addition of 0.01 M NaOH was inadvertent

(b) After centrifuging, there were solids floating on the surface of the liquid phase. A pipette was used to draw off the liquid between this floating layer and the centrifuged solids layer. Because of this, it was necessary to leave some free liquid in the leaching vessel. The mass of material in the leaching vessel after transfer of the liquid was 7.763 g. The volume of liquid remaining in the leaching vessel was estimated to be 6.4 mL by subtracting the weight of the dried leached solids (0.182 g) from the total weight of the material still in the leaching vessel (7.763 g) and dividing by the solution density (1.180 g/mL).

Figure 3.1. Schematic Representation of S-104 Leaching Test



(c) The mass of material in the leaching vessel after transfer of the liquid was 3.496 g. The volume of liquid remaining in the leaching vessel was estimated to be 2.9 mL by subtracting the weight of the dried leached solids (0.182 g) from the total weight of the material still in the leaching vessel (3.496 g) and dividing by the solution density (1.136 g/mL).

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

S104-6.PPT

Figure 3.1. (contd)

Table 3.1. Results of Tank S-104 Sludge Washing: Nonradioactive Components

	Wash Solution		Washed Solids			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[(a)]	Recovery, %
Al	190	5873	380500	0 307064	312936	2	98	1.96E+05	1.53E+05	128
Cr	187	5775	444	0 358	6133	94	6	3.85E+03	4.47E+03	86
Fe	< 0.13	< 4	7675	0 6194	< 6198	0	100	< 3.89E+03	3.02E+03	129
Mn	< 0.26	< 8	5018	0 4049	< 4057	0	100	< 2.54E+03	2.09E+03	122
Na	8117	243900 [(b)]	13550	0 10935	254835	96	4	1.60E+05	1.84E+05	87
Ni	0.44	14	355	0 286	300	5	95	1.88E+02	3.06E+02	61
P	2.73	84	< 133	< 107	191	> 44	< 56	< 1.20E+02	1.70E+01	< 706
Si	9.77	302	4300	0 3470	3772	8	92	2.36E+03	3.95E+03	60
Sr	< 0.08	< 2	1553	0 1253	< 1255	0	100	< 7.87E+02	6.51E+02	121
U[(c)]	0.35	11	21900	0 17673	17684	0	100	1.11E+04	9.36E+03	118

(a) Solids were prepared for analysis by both KOH and Na_2O_2 fusion methods; mean values are given for analytes that can be determined by both these methods.

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

(c) Uranium was determined by laser fluorimetry; all other elements were determined by ICP/AES.

3.3.2 Caustic Leaching

Figure 3.2 depicts the Al and Na concentrations as a function of time in the first caustic leaching step. These results clearly indicate that additional Al dissolved between 5 and 75 hours of leaching. Thus, kinetic factors are important in the removal of Al from the S-104 sludge. The previous studies with the S-104 sludge used two successive leaching steps of 5 h each. The results of the current study suggest that slow Al dissolution kinetics were, at least in part, responsible for the low Al removal efficiencies observed in the earlier studies. The Na concentration remained essentially constant (3.6 M) during the 211 h of leaching.

The Cr concentration also remained essentially constant (~420 µg/mL) throughout the first leaching step. Spectrophotometry indicated that the only Cr species was CrO_4^{2-} ($\lambda_{max} = 372$ nm); no evidence existed for bands at 430 and 595 nm, which would be characteristic of Cr(III) (Figure 3.3). To obtain the spectrum depicted in Figure 3.3, the first leaching solution was diluted by some unknown amount. Based on calibration with standard Cr(VI) solutions, the Cr(VI) concentration in the solution measured for Figure 3.3 was ~10 µg/mL. Nitrite ion displays an absorbance at 354 nm, so it might also be contributing to the absorbance at 371 nm. The detection limit for Cr(III) in the diluted solution is used to measure the spectrum of 10 µg/mL; that is, the Cr(III) concentration would have had to be about the same as that for Cr(VI) for it to have been detected.

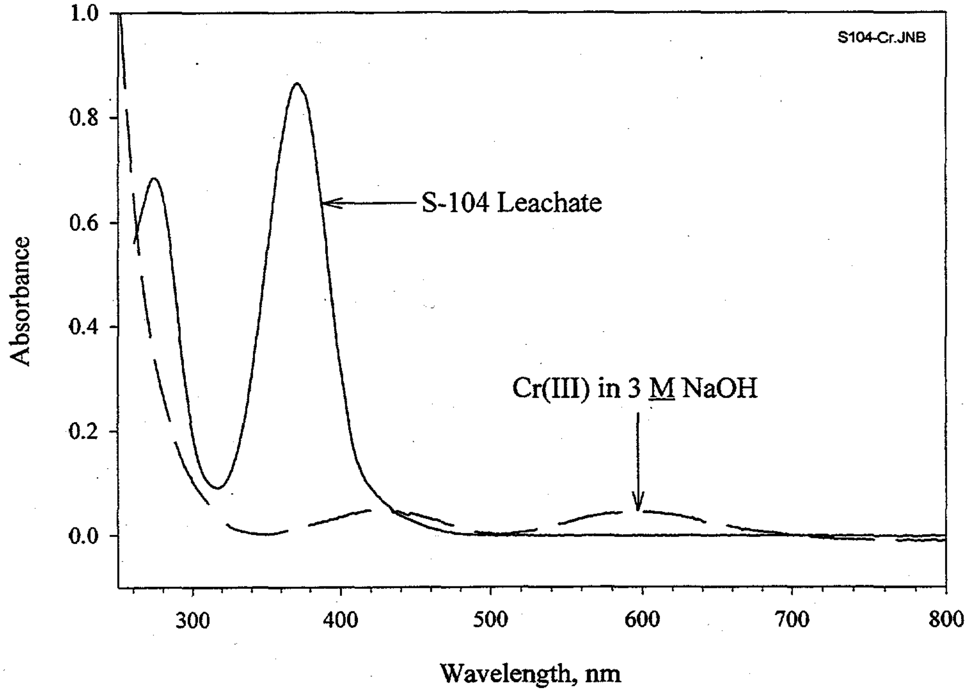


Figure 3.2. Aluminum and Na Concentrations as a Function of Time in the First Caustic Leaching Step

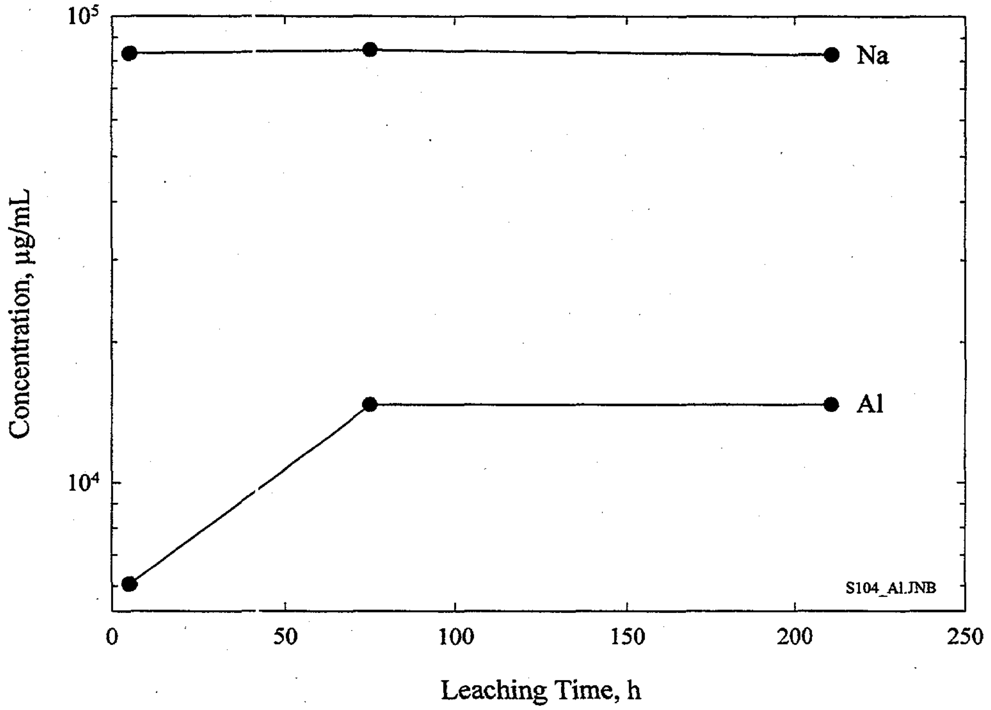


Figure 3.3. UV/Vis Spectra of the First S-104 Caustic Leaching Solution and a Solution Derived From Dissolving $Cr(OH)_3$ in 3 M NaOH

Table 3.2 presents the concentrations of various sludge components in each process stream, and Table 3.3 presents the distribution of the sludge components between the various process streams; the results are not adjusted for the amount of each component carried over from one step to the next in the interstitial liquid. Leaching with caustic under the conditions described here led to much greater Al removal than previously observed. The results indicated 99% of the Al was removed from the S-104 sludge. Virtually all of the Al dissolution occurred in the first leaching step; the amount of Al present in the second leaching step could be accounted for by diluting the interstitial liquid carried over from the first leaching step. In previous studies, the Al removal was indicated to be between 30 and 40%. Thus, longer leaching times, combined with a greater solution-to-solids ratio, led to a dramatic increase in Al removal for the S-104 sludge.

Nearly all of the Cr was removed in the caustic leaching procedure, although the wash with dilute NaOH indicated that caustic leaching is not necessary to remove most of the Cr in the S-104 sludge (see above). Interestingly, a significant fraction of the Ni appeared to be removed by caustic leaching; but because the Ni concentrations were often near the analytical detection limit, this result should be viewed with caution. Likewise, very little P was present in this waste, so definitive conclusions regarding its behavior could not be deduced from this work. Approximately half of the Si was removed by caustic leaching. However, Fe, Mn, and U showed little tendency towards dissolution under these alkaline conditions.

Table 3.2. Concentrations of the Nonradioactive S-104 Sludge Components in the Various Process Streams

	First Leach Solution		Second Leach Solution		Final Wash Solution		Leached Solids		
Component	Conc., µg/mL	Mass, µg[a]	Conc., µg/mL	Mass, µg[b]	Conc., µg/mL	Mass, µg[b]	Conc., µg/g	Mass, µg	Total Mass, µg
Al	14700	539570	150	15429	65.2	9654	30384	5530	570183
Cr	419	15488	22.8	2350	0.48	72	908	165	18075
Fe	2.0	76	2.1	216	< 0.07	< 10	73466	13371	13673
Mn	< 1.8	< 63	< 1.8	< 180	< 0.06	< 8	56203	10229	~ 10480
Na	82600	3057455	62020	6388060	2222	328856	55250	10056	~ 0(c)
Ni	2.1	76	2.1	216	0.70	104	4213	767	1163
P	15.4	566	< 3.5	< 361	< 0.11	< 16	195	35	978
Si	23.8	910	23.8	2451	1.32	195	24100	4386	7942
Sr	0.53	19	0.66	68	< 0.02	< 2	16113	2932	3022
U[d]	0.308	11	0.489	50	0.072	11	254000	46228	46300

(a) Mass of material present in the solution decanted during the first leaching step; the mass value is corrected for the mass of material present in the samples taken at 5 and 75 hrs.

(b) Mass of material present in the solution decanted during the indicated step.

(c) Adjusted for the amount of Na added as NaOH gives a negative mass for Na in the sludge, indicating < 100% mass recovery for Na.

(d) Uranium was determined by laser fluorimetry; all other elements were determined by ICP/AES.

Table 3.3. Distribution of Nonradiactive S-104 Sludge Components Between the Various Process Streams

Component	Component Distribution, % First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids
Al	95	3	2	1
Cr	86	13	0	1
Fe	0.6	1.6	0.1	97.8
Mn	1	2	0	97
Na	--	--	--	1.1[(a)]
Ni	7	19	9	66
P	> 58	< 37	< 2	> 4
Si	11	31	2	55
Sr	1	2	0	97
U	0	0	0	100

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

The test data indicated that 3% of the Sr was in the leach solutions, which might have implications regarding the LLW stream (i.e., by leaching of ^{90}Sr). Radiochemical analysis indicated that the first leach, second leach, and final wash solutions contained 0.326, 0.570, and 0.058 µCi ^{90}Sr/mL, respectively. Assuming the LLW glass form will contain 20 wt% Na_2O (Orme et al. 1996), with a density of 2.7 metric tons/m^3, the LLW form resulting from immobilization of only these solutions would be projected to contain 3 Ci ^{90}Sr/m^3. This would be two orders-of-magnitude above the 0.04 Ci/m^3 U.S. Nuclear Regulatory Commission (NRC) Class A LLW limit for this isotope, but well within the Class C LLW limit of 7000 Ci/m^3. As current plans only require Class C LLW, no ^{90}Sr removal from the S-104 leaching and washing solutions would be required.

Table 3.4 presents the concentrations in the untreated S-104 sludge solids as determined by direct analysis and by summing the components found in each process stream; the table also presents the mass recovery for each component. With the exceptions of P and Si, mass recoveries were all within 30%. The data for P and Si should be viewed with caution based upon the poor mass balance for these components. The concentrations determined by direct analysis agreed well with those obtained in the FY 1995 study (Rapko, Lumetta, and Wagner 1995), except for Si.

Microscopic analysis of untreated S-104 solids indicated boehmite (AlOOH) to be the predominant phase present (Figure 3.4). Some clay, some iron-containing particles, and other minor phases were also observed. Microscopic analysis of treated S-104 solids indicated that boehmite almost completely dissolved. This contrasts with the earlier studies of the S-104 sludge in which boehmite remained after caustic leaching. Again, these observations support the hypothesis that the previously observed low Al

Table 3.4. Concentrations of the Nonradioactive S-104 Sludge Components in the Initial Sludge Solids

	Concentration in Initial Solids, µg/g			
		Direct Analysis		
Component	Summation Method[a]	This Work	Previous Work[b]	Mass Recovery, %
Al	117515	152735	150000	77
Cr	3725	4470	4700	83
Fe	2818	3017	3400	93
Mn	< 2160	2088	2200	--
Na	--	184450	200000	--
Ni	240	306	Not Determined	78
P	202	17	< 200	1186
Si	1637	3950	6800	41
Sr	623	651	610	96
U	9542	9360	10100	102

(a) The value was determined by summing the amount of a given component in the caustic leaching solutions, the subsequent washing solutions, and the leached solids; the total concentration was then determined by dividing the sum by the amount of solids used.

(b) Rapko, Lumetta, and Wagner 1995.

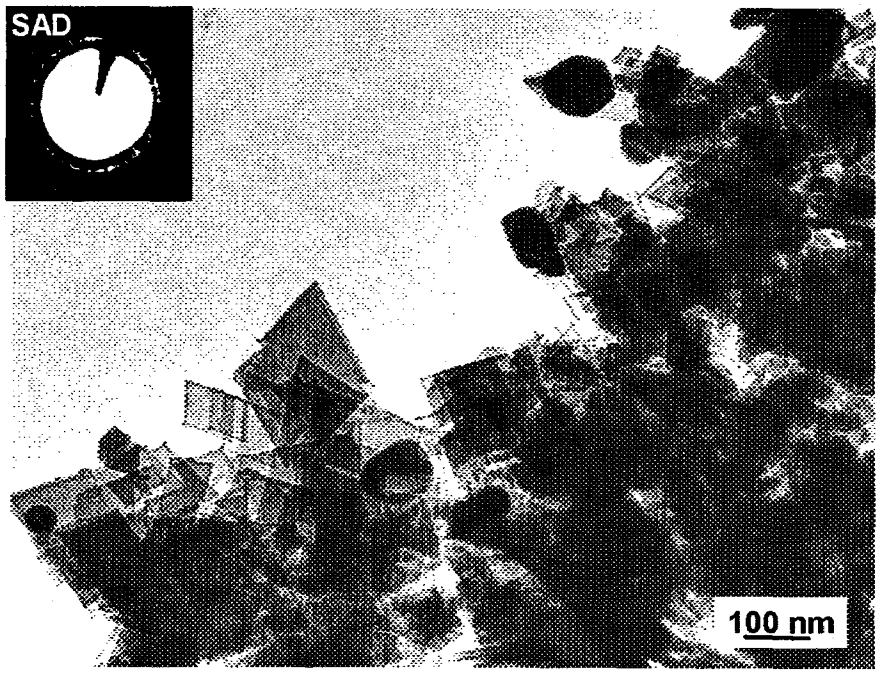


Figure 3.4. Boehmite Particles in the Untreated S-104 Sludge

removal was due to slow boehmite dissolution. Microscopic analysis indicated that Fe, U, Mn, and Si were the major elements in the caustic-leached S-104 solids. Mixed Fe/Mn oxide phases were observed along with aluminosilicates (Figure 3.5). The morphology and structure of the U-containing particles appeared to change during the treatment (Figure 3.6).

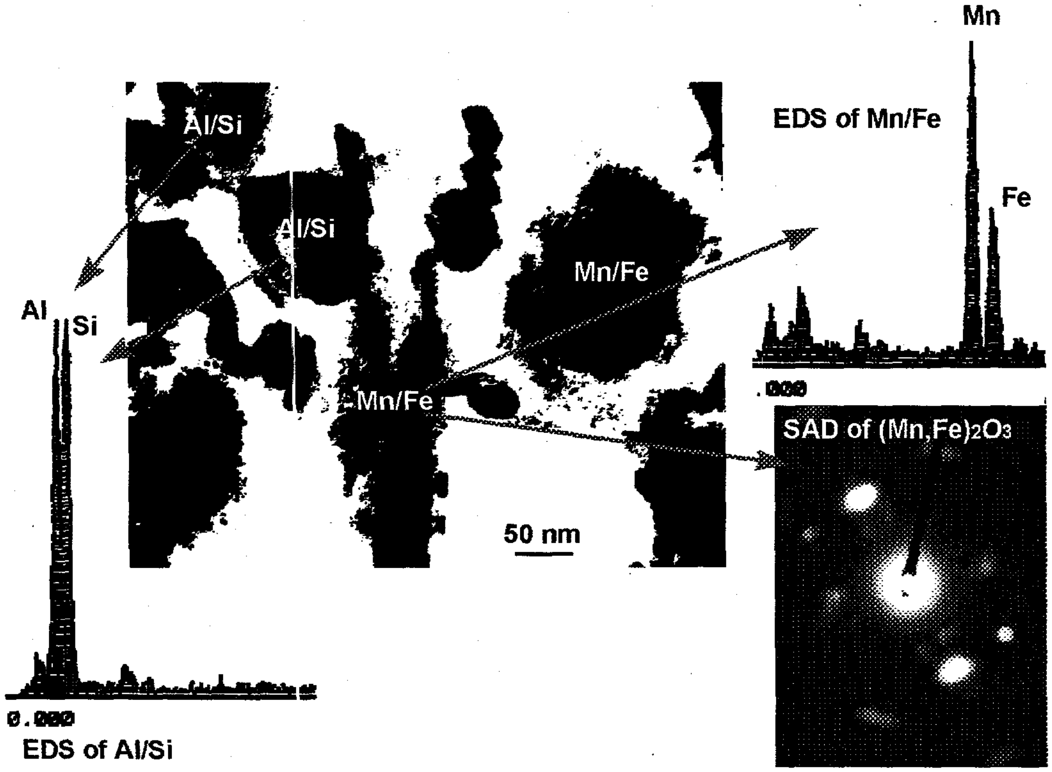
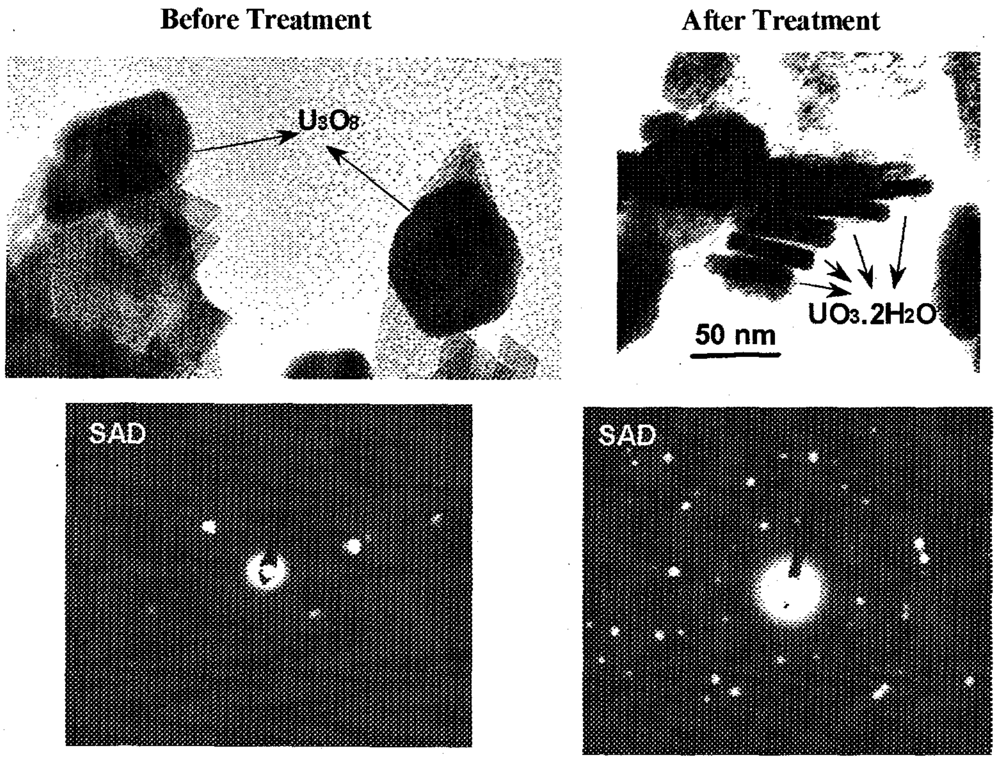


Figure 3.5. Mixed Iron/Manganese Oxide and Amorphous Aluminosilicate Particles in the Caustic-Leached S-104 Sludge. EDS = electron dispersion spectroscopy; SAD = selected area diffraction.



Before Treatment

After Treatment

Figure 3.6. Uranium Oxide Species Before and After Leaching S-104 Sludge

4.0 Tank BY-108 Enhanced Sludge Washing Test

This section presents the results of the ESW test performed on Hanford Tank BY-108 sludge. The sludge sample used in this test was received at PNNL on August 2, 1996; the 222-S laboratory ID for this sample was S96T002035, and the jar number was 10527. This material was a composite of segment 4 from Core 99.

4.1 Experimental

Figure 4.1 summarizes the experimental procedure used in the BY-108 ESW test. The procedure was the same as the baseline ESW test procedure described previously (Lumen et al. 1996), except gravity settling was used rather than centrifugation for solids/liquid separations in the leaching steps. Centrifugation was not used because a suitable centrifuge was not available in the hot cell where the test was performed.(a)

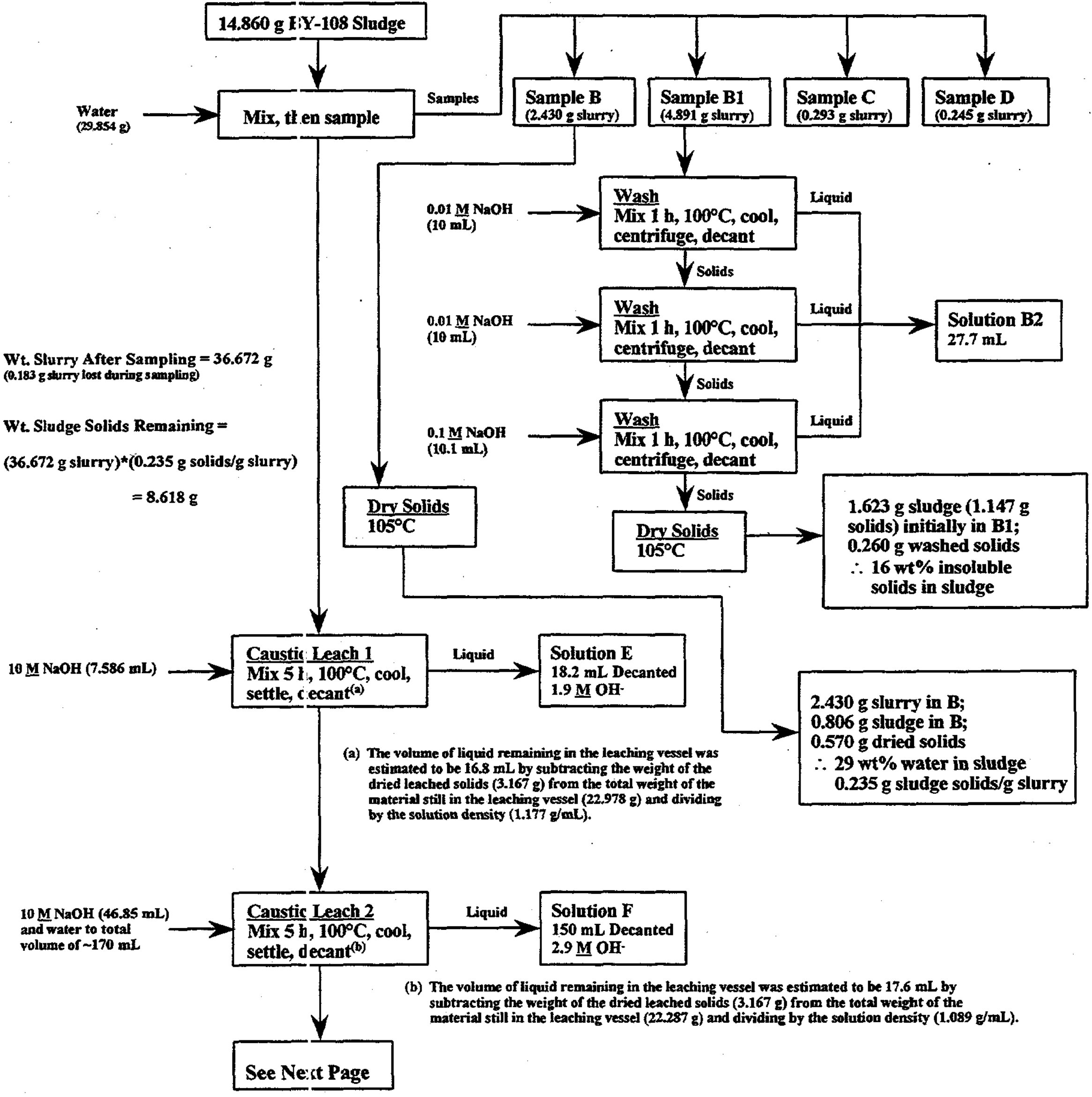
For the dilute hydroxide washing steps (sample B1), the undissolved solids concentrations ranged from 1.7 to 2.9 wt%. The target undissolved solids concentration in the first and second caustic leaching steps were 5 wt% and 1 wt% respectively. Based upon the leached-solids' mass of 3.167 g, the actual concentrations were 7.1 and 1.7 wt%, respectively.

4.2 Results and Discussion

4.2.1 Washing With Dilute NaOH

Table 4.1 summarizes the behavior of most of the nonradioactive sludge components during washing of the BY-108 sludge with 0.01 M NaOH. Sodium was the most soluble element present with 96% being removed by washing with 0.01 M NaOH. A relatively large fraction (63%) of the Al was removed by dilute hydroxide washing. Although most other tanks investigated indicated a smaller percentage of Al removed (see Section 8.0), the value of 63% determined for BY-108 is similar to the value of 65% determined for BY-104, and it is even less than observed for BY-110 (Lumetta et al. 1996). Both BY-104 and BY-110 are reported to contain similar wastes to that stored in BY-108 (Hill, Anderson, and Simpson 1995). Significant fractions of P (73%) and Cr (49%) were also removed from BY-108 sludge by dilute hydroxide washing.

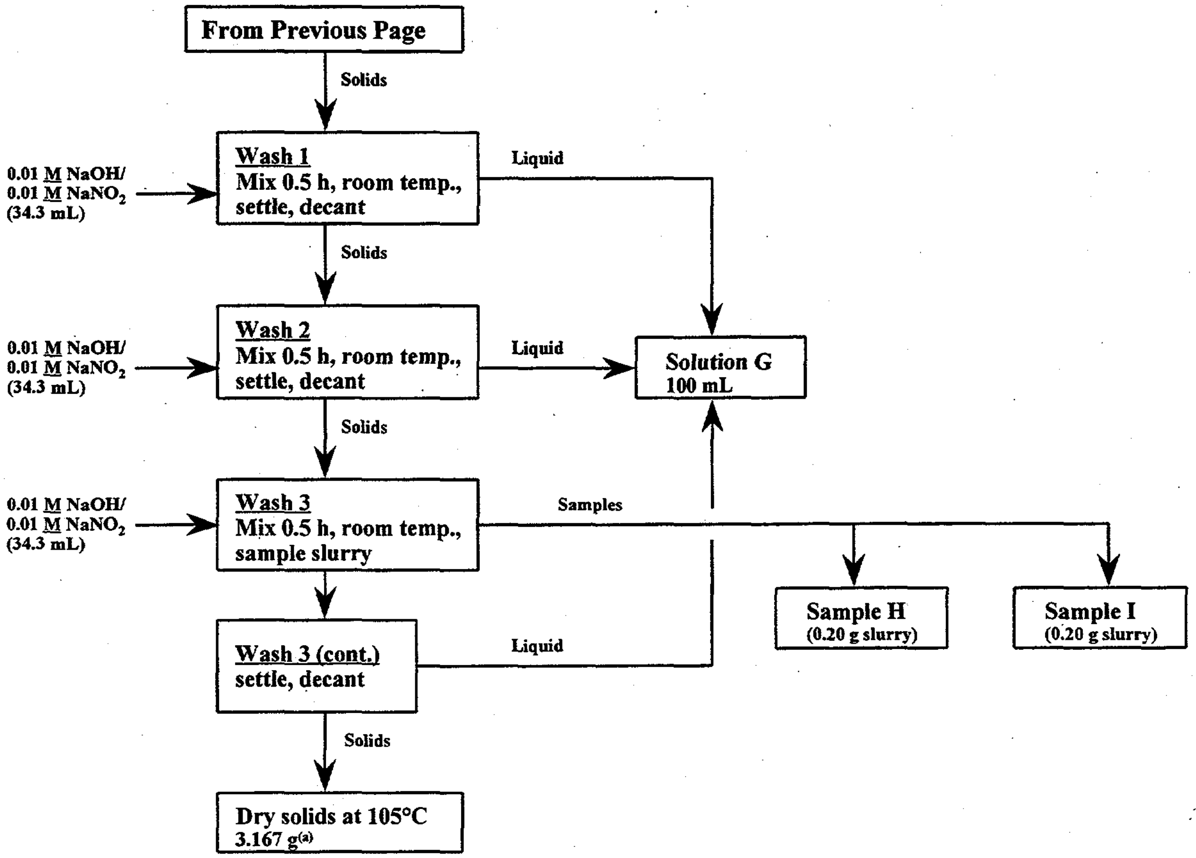
(a) Typically, the ESW tests are performed in fume hoods, but because of the radiological characteristics of the BY-108 sludge, it was necessary to perform this test in the hot cell.



(a) The volume of liquid remaining in the leaching vessel was estimated to be 16.8 mL by subtracting the weight of the dried leached solids (3.167 g) from the total weight of the material still in the leaching vessel (22.978 g) and dividing by the solution density (1.177 g/mL).

(b) The volume of liquid remaining in the leaching vessel was estimated to be 17.6 mL by subtracting the weight of the dried leached solids (3.167 g) from the total weight of the material still in the leaching vessel (22.287 g) and dividing by the solution density (1.089 g/mL).

Figure 4.1. Schematic Representation of the BY-108 ESW Test



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

BY108-1.PPT

Figure 4.1. (contd)

Table 4.1. Results of Dilute Hydroxide Washing of Tank BY-108 Sludge: Nonradioactive Components

	Wash Solution		Washed Solids			Component Distribution, %	
Component	Conc., µg/mL	Mass, µg	Conc., µg/g	Mass, µg	Total Mass, µg	Wash Solution	Washed Solids
Ag	< 0.0825	< 2	< 23	< 6	8	--	--
Al	363	10055	23050	5993	16048	63	37
As	< 0.825	< 23	< 656	< 171	193	--	--
B	0.792	22	< 76	< 20	42	> 53	< 47
Ba	< 0.055	< 2	1018	265	266	< 1	> 99
Be	< 0.0275	< 1	< 8	< 2	3	--	--
Bi	< 0.55	< 15	6215	1616	1631	< 1	> 99
Ca	1.375	38	52710	13705	13743	0	100
Cd	< 0.0825	< 2	28	7	10	< 24	> 76
Ce	< 1.1	< 30	< 444	< 115	146	--	--
Co	0.275	8	< 76	< 20	27	> 28	< 72
Cr	6.259	173	692	180	353	49	51
Cu	< 0.1375	< 4	229	59	63	< 6	> 94
Dy	< 0.275	< 8	< 76	< 20	27	--	--
Eu	< 0.55	< 15	< 152	< 40	55	--	--
Fe	0.1375	4	134500	34970	34974	0	100
K	69.3	1920	< 3046	< 792	2712	> 71	< 29
La	< 0.275	< 8	218	57	64	< 12	> 88
Li	< 0.165	< 5	< 46	< 12	16	--	--
Mg	< 0.55	< 15	3405	885	901	< 2	> 98
Mn	< 0.275	< 8	1556	404	412	< 2	> 98
Mo	< 0.275	< 8	< 76	< 20	27	--	--
Na	9427	(a) 254228	42300	10998	265226	96	4
Nd	< 0.55	< 15	656	171	186	< 8	> 92
Ni	80.74	2235	38600	10036	12272	18	82
P	915.2	25351	35900	9334	34685	73	27
Pb	< 0.55	< 15	3975	1034	1049	< 1	> 99
Pd	< 4.125	< 114	< 1142	< 297	411	--	--
Rh	< 1.65	< 46	< 457	< 119	164	--	--
Ru	< 5.5	< 152	< 1523	< 396	548	--	--
Sb	< 2.75	< 76	< 762	< 198	274	--	--
Se	< 1.375	< 38	< 615	< 160	198	--	--
Si	7.15	198	9245	2404	2602	8	92
Sn	< 8.25	< 229	< 2880	< 749	977	--	--
Sr	< 0.0825	< 2	37450	9737	9739	0	100
Te	< 8.25	< 229	< 2285	< 594	822	--	--
Th	< 5.5	< 152	< 1523	< 396	548	--	--
Ti	< 0.1375	< 4	169	44	48	< 8	> 92
Tl	< 2.75	< 76	< 762	< 198	274	--	--
U(b)	0.0812	2	202000	52520	52522	0	100
V	< 0.275	< 8	< 76	< 20	27	--	--
W	< 11	< 305	< 3046	< 792	1097	--	--
Y	< 0.275	< 8	< 76	< 20	27	--	--
Zn	0.66	18	973	253	271	7	93
Zr	< 0.275	< 8	142	37	45	<17	>83

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

(b) Uranium was determined by laser fluorimetry; all other elements were determined by ICP/AES.

Table 4.2 presents the concentrations determined in the untreated BY-108 sludge solids for most of the nonradioactive sludge components; also given is the mass recovery achieved for each of these components. The ten most abundant elements in the BY-108 sludge, as determined by direct analysis of the sludge, were Na (21.3 wt%), U (8.07 wt%), Fe (5.17 wt%), P (2.35 wt%), Ca (2.08 wt%), Ni (1.77 wt%), Sr (1.36 wt%), Al (1.26 wt%), Si (0.74 wt%), and K (0.26 wt%). Mass recoveries were good for Al and Na, less so for Cr, and poor for all the other components. Mass recoveries obtained in the caustic leaching portion of the test were much better (see below) suggesting the analytical error was not the major cause for this discrepancy. There was a discrepancy between the weight of the dilute hydroxide-washed solids and the weight of the caustic-leached solids. Washing of sample B1 indicated that the sludge contained 16 wt% insoluble solids. Using that value, the weight of the residue from the caustic leaching portion of the test would be expected to be 1.95 g or less; but, the actual weight of the caustic-leached solids was 3.167 g. Furthermore, during the third wash of B1, there was a mass loss of 4.213 g. During the previous two washing steps, the mass lost upon heating was only ~0.1 g. This suggests that vial B1 might have leaked during the third washing step, which would account for the low mass balance.

Table 4.3 summarizes the behavior of the radioactive sludge components during washing of the BY-108 sludge with 0.01 M NaOH. As has been seen with most other Hanford tank sludges, the TRU elements are very insoluble in 0.01 M NaOH. All Np, Pu, Am, and Cm isotopes were below the detection limit in the wash solution. Likewise, ^{60}Co, ^{90}Sr, and ^{154,155}Eu showed little propensity for dissolving in 0.01 M NaOH. Interestingly, ^{137}Cs did not dissolve effectively in 0.01 M NaOH. Tank BY-108 is believed to contain wastes that were treated with ferrocyanide to scavenge ^{137}Cs, which might explain this result. As would be consistent with the behavior of pertechnetate ion, ^{99}Tc was effectively (>95%) dissolved in the dilute NaOH wash.

Table 4.4 presents the concentrations of the various radionuclides in the untreated BY-108 sludge solids along with the mass recovery for each. As was the case with most of the nonradioactive components, the mass recoveries were low for most of the radionuclides.

Table 4.2. Concentrations of Nonradioactive Components in the Untreated BY-108 Solids: Results from the Dilute Hydroxide Wash

	Concentration in Initial Solids µg/g		
Component	Summation Method(a)	Direct Analysis(b)	Recovery, %
Ag	< 7.17E+00	< 2.03E+01	--
Al	1.40E+04	1.26E+04	111
As	< 1.69E+02	< 2.03E+02	--
B	19.1 < x < 36.4	1.60E+03	1 < x < 2
Ba	2.31E+02	3.89E+02	59
Be	< 2.39E+00	< 6.78E+00	--
Bi	1.41E+03	2.35E+03	60
Ca	1.20E+04	2.08E+04	58
Cd	6.36 < x < 8.35	2.60E+01	24 < x < 32
Ce	< 1.27E+02	< 2.71E+02	--
Co	< 2.39E+01	< 6.78E+01	--
Cr	3.08E+02	3.98E+02	77
Cu	51.8 < x < 55.1	1.22E+02	42 < x < 45
Dy	< 2.39E+01	< 6.78E+01	--
Eu	< 4.78E+01	< 1.36E+02	--
Fe	3.05E+04	5.17E+04	59
K	1670 < x < 2360	2.58E+03	65 < x < 92
La	49.3 < x < 55.9	1.03E+02	48 < x < 54
Li	< 1.43E+01	< 4.07E+01	--
Mg	7.72E+02	1.33E+03	58
Mn	3.53E+02	5.34E+02	66
Mo	< 2.39E+01	< 6.78E+01	0 < x < 35
Na	2.31E+05	2.13E+05	108
Nd	149 < x < 162	3.10E+02	48 < x < 52
Ni	1.07E+04	1.77E+04	60
P	3.02E+04	2.35E+04	129
Pb	9.01E+02	1.55E+03	58
Pd	< 3.59E+02	< 1.02E+03	--
Rh	< 1.43E+02	< 4.07E+02	--
Ru	< 4.78E+02	< 1.36E+03	--
Sb	< 2.39E+02	< 6.78E+02	--
Se	< 1.73E+02	< 3.39E+02	--
Si	2.27E+03	7.36E+03	31
Sn	< 8.52E+02	< 2.03E+03	--
Sr	8.49E+03	1.36E+04	63
Te	< 7.17E+02	< 2.03E+03	--
Th	< 4.78E+02	< 1.36E+03	--
Ti	38.3 < x < 41.6	7.05E+01	54 < x < 59
Tl	< 2.39E+02	< 6.78E+02	--
U	4.58E+04	8.07E+04	57
V	< 2.39E+01	< 6.78E+01	--
W	< 9.56E+02	< 2.71E+03	--
Y	< 2.39E+01	< 6.78E+01	--
Zn	2.36E+02	4.03E+02	59
Zr	32.2 < x < 38.8	1.08E+02	30 < x < 36

(a) Values determined by summing the mass of the component found in each process stream and dividing by the amount of sludge solids treated.

(b) Solids were prepared for analysis by both KOH and Na_2O_2 fusion methods; mean values are given for analytes that can be determined by both these methods.

Table 4.3. Results of Dilute Hydroxide Washing of Tank BY-108 Sludge: Radioactive Components

	Wash Solution		Washed Solids			Component Distribution, %	
Component	Conc., µCi/mL	Activity, µCi	Conc., µCi/g	Activity, µCi	Total Activity, µCi	Wash	Washed Solids
Total Alpha	< 3.30E-04	< 9.14E-03	1.26E+00	3.28E-01	< 3.37E-01	< 3	> 97
^{239,240}Pu	< 3.30E-04	< 9.14E-03	7.54E-01	1.96E-01	< 2.05E-01	< 4	> 96
^{241}Am+^{238}Pu	< 3.30E-04	< 9.14E-03	3.73E-01	9.70E-02	< 1.06E-01	< 9	> 91
^{241}Am(g)	< 1.43E-02	< 3.96E-01	< 1.30E-02	< 3.38E-03	< 3.99E-01	--	--
^{137}Cs	1.24E+00	3.44E+01	3.95E+03	1.03E+03	1.06E+03	3	97
^{60}Co	< 4.40E-03	< 1.22E-01	< 4.00E-03	< 1.04E-03	< 1.23E-01	--	--
^{154}Eu	< 1.32E-02	< 3.66E-01	< 4.00E-01	< 1.04E-01	< 4.70E-01	--	--
^{155}Eu	< 1.43E-02	< 3.96E-01	< 1.30E-02	< 3.38E-03	< 3.99E-01	--	--
^{90}Sr	< 2.20E-02	< 6.09E-01	2.54E+03	6.60E+02	< 6.61E+02	0	100
^{99}Tc	8.31E-04	2.30E-02	< 5.00E-03	< 1.30E-03	< 2.43E-02	> 95	< 5
^{243,244}Cm	< 3.30E-04	< 9.14E-03	5.73E-02	1.49E-02	< 2.40E-02	< 38	> 62
^{237}Np	< 3.30E-04	< 9.14E-03	9.50E-03	2.47E-03	< 1.16E-02	< 79	> 21
^{238}U	< 3.30E-04	< 9.14E-03	7.52E-02	1.96E-02	< 2.87E-02	< 32	> 68

Table 4.4. Concentrations of Radioactive Components in the Untreated BY-108 Solids as Determined in the Dilute Hydroxide Washing Test

	Concentration in Initial Solids, µCi/g		
Component	Summation Method	Direct Analysis	Recovery, %
Total Alpha	< 2.94E-01	4.04E-01	71 < x <73
^{239,240}Pu	< 1.79E-01	2.28E-01	75 < x <78
^{241}Am+^{238}Pu	< 9.25E-02	1.36E-01	62 < x <68
^{241}Am(g)	< 3.48E-01	< 1.30E-02	--
^{137}Cs	9.25E+02	1.59E+03	58
^{60}Co	< 1.07E-01	< 4.00E-03	--
^{154}Eu	< 4.09E-01	< 3.00E-01	--
^{155}Eu	< 3.48E-01	< 1.30E-02	--
^{90}Sr	< 5.76E+02	1.04E+03	55
^{99}Tc	< 2.12E-02	1.81E-02	111 < x < 117
^{243,244}Cm	< 2.10E-02	< 3.00E-04	--
^{237}Np	< 1.01E-02	2.59E-02	8 < x < 36
^{238}U	< 2.50E-02	1.47E-02	116 < x < 165

4.2.2 Caustic Leaching

Table 4.5 presents the concentrations of most of the nonradioactive sludge components in each process stream, and Table 4.6 presents the distribution of those sludge components between the various process streams. The values presented in Table 4.6 are not adjusted for material contained in the interstitial liquid, but rather represent the amount of each component contained in the liquid that was decanted in a given step (or in the residual solid).

The cumulative removal of Al was 71%, which was only slightly higher than the 63% removed by washing with 0.01 M NaOH. Hence, caustic leaching did not have a large effect on the removal of Al from BY-108 sludge. Accounting for the 16.8 mL of leachate solution that remained after decanting the first leach solution, 57% of the Al dissolved in the first leaching step; another 14 % dissolved in the second leaching step. Only 43% of the Cr was removed during the caustic leaching test, which was actually somewhat lower than the amount removed by dilute NaOH washing. Thus, caustic leaching did nothing to improve Cr removal. Again, taking into account the interstitial liquid volumes, 37% of the Cr was dissolved during the first leaching step and 6% more during the second leaching step. Caustic leaching did not significantly improve the P removal either as the cumulative P removal (70%) was similar to the amount removed by dilute NaOH washing (73%). Accounting for interstitial liquid, the P removals were 52%, 16%, and 2% in the first leach, second leach, and final wash, respectively. On the other hand, Si removal was improved from 8% for dilute NaOH washing to 42% for caustic leaching. Virtually all of the U, which is the second-most abundant metallic element in the BY-108 sludge, remained in the sludge solids during caustic leaching.

Table 4.7 summarizes the mass recoveries for the various elements analyzed by ICP/AES and for U, which was determined by laser fluorimetry. For the most part, the mass recoveries for the caustic leaching portion of the test were much better than was seen for the dilute hydroxide washing (compare the values in Table 4.7 to those in Table 4.2).

Table 4.8 presents the concentrations of the various anions in each process solution. Also listed are the amount of each anion in solution per gram of sludge solids treated. For the anions determined, in no case did the amount dissolved during caustic leaching exceed that which was removed simply by washing with 0.01 M NaOH. Thus, for Tank BY-108 sludge, ESW would not provide much benefit in terms of removing these anions from the HLW stream.

Table 4.5. Concentrations of the Nonradioactive BY-108 Sludge Components in the Various Process Streams During the Caustic Leaching Portion of the Test

	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/g	Mass, μg	Total Mass, μg
Ag	< 0.098	< 2	< 0.098	< 15	< 0.083	< 8	< 22	< 71	< 95
Al	2210	40222	335	50276	62.6	6290	12421	39336	136124
As	< 0.98	< 18	< 0.98	< 146	< 0.83	< 83	< 671	< 2125	< 2372
B	3.89	71	0.60	90	< 0.28	< 28	< 74	< 235	< 423
Ba	< 0.065	< 1	< 0.065	< 10	< 0.055	< 6	989	3131	< 3147
Be	< 0.033	< 1	< 0.033	< 5	< 0.028	< 3	< 7	< 24	< 32
Bi	< 0.65	< 12	< 0.65	< 97	< 0.55	< 55	5970	18907	< 19072
Ca	< 1.63	< 30	5.59	838	< 1.38	< 138	51087	161793	< 162798
Cd	< 0.098	< 2	< 0.098	< 15	< 0.083	< 8	46	146	< 170
Ce	< 1.3	< 24	< 1.3	< 195	< 1.1	< 111	< 442	< 1400	< 1729
Co	2.08	38	0.36	55	< 0.28	< 28	< 74	< 235	< 356
Cr	34.6	629	4.6	688	0.87	87	598	1894	3298
Cu	1.20	22	0.21	31	< 0.14	< 14	212	670	< 737
Dy	< 0.33	< 6	< 0.33	< 49	< 0.28	< 28	< 74	< 235	< 318
Eu	< 0.65	< 12	< 0.65	< 97	< 0.55	< 55	< 149	< 471	< 635
Fe	85.9	1564	19.8	2962	4.11	413	130000	411710	416649
K	387	7051	49.4	7405	11.0	1106	< 2974	< 9419	< 24980
La	< 0.33	< 6	< 0.33	< 49	< 0.28	< 28	209	662	< 744
Li	< 0.20	< 4	< 0.20	< 29	< 0.17	< 17	< 45	< 141	< 191
Mg	< 0.65	< 12	< 0.65	< 97	< 0.55	< 55	3230	10229	< 10394
Mn	< 0.33	< 6	< 0.33	< 49	< 0.28	< 28	1716	5433	< 5515
Mo	< 0.33	< 6	< 0.33	< 49	< 0.28	< 28	< 74	< 235	< 318
Na	91130	1658566	66430	9957857	12100	1216050	68600	217256	(b) 487579
Nd	< 0.65	< 12	< 0.65	< 97	< 0.55	< 55	628	1987	< 2152
Ni	325	5915	45.1	6762	8.3	835	38800	122880	136391
P	4082	74292	672	100748	178	17909	26300	83292	276241
Pb	< 0.65	< 12	< 0.65	< 97	< 0.55	< 55	3740	11845	< 12009
Pd	< 4.88	< 89	< 4.88	< 731	< 4.13	< 415	< 1115	< 3532	< 4766
Rh	< 1.95	< 35	< 1.95	< 292	< 1.65	< 166	< 446	< 1413	< 1906
Ru	< 6.5	< 118	< 6.5	< 974	< 5.5	< 553	< 1487	< 4709	< 6355
Sb	< 3.25	< 59	< 3.25	< 487	< 2.75	< 276	< 744	< 2355	< 3177
Se	< 1.63	< 30	< 1.63	< 244	< 1.38	< 138	< 629	< 1992	< 2403
Si	26	473	75.8	11361	19.8	1990	5915	18733	32557
Sn	< 9.75	< 177	< 9.75	< 1462	< 8.25	< 829	< 2830	< 8963	< 11431
Sr	< 0.098	< 2	< 0.098	< 15	< 0.083	< 8	36350	115120	< 115145
Te	< 9.75	< 177	< 9.75	< 1462	< 8.25	< 829	< 2231	< 7064	< 9532
Th	< 6.5	< 118	< 6.5	< 974	< 5.5	< 553	< 1487	< 4709	< 6355
Ti	< 0.16	< 3	< 0.16	< 24	< 0.14	< 14	159	504	< 545
Tl	< 3.25	< 59	< 3.25	< 487	< 2.75	< 276	< 744	< 2355	< 3177
U[c]	0.092	2	0.092	14	0.046	5	196000	620732	620752
V	< 0.33	< 6	< 0.33	< 49	< 0.28	< 28	< 74	< 235	< 318
W	< 13	< 237	< 13	< 1949	< 11	< 1106	< 2974	< 9419	< 12709
Y	< 0.33	< 6	< 0.33	< 49	< 0.28	< 28	< 74	< 235	< 318
Zn	2.34	43	1.3	195	< 0.275	< 28	856	2711	< 2976
Zr	< 0.33	< 6	< 0.33	< 49	< 0.28	< 28	258	817	< 899

(a) Mass of material present in the solution decanted during the indicated step.

(b) Adjusted for the amount (12,562,150 μg) of Na added as NaOH.

(c) Uranium was determined by laser fluorimetry; all other elements were determined by ICP/AES.

Table 4.6. Distribution of Nonradioactive BY-108 Sludge Componenets Between the Various Process Streams During Caustic Leaching

Component	Component Distribution, % First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids
Ag	< (a)	< (a)	(a)	(a)
Al	30	37	5	29
As	< (a)	< (a)	(a)	(a)
B	> 17	> 21	< 7	< 55
Ba	< 0	< 0	0	100
Be	< (a)	< (a)	(a)	(a)
Bi	< 0	< 0	0	100
Ca	< 0	0	0	100
Cd	< < 1	< < 9	< 5	> 86
Ce	< (a)	< (a)	(a)	(a)
Co	> 11	> 15	< 8	< 66
Cr	19	21	3	57
Cu	3	4	2	91
Dy	< (a)	< (a)	(a)	(a)
Eu	< (a)	< (a)	(a)	(a)
Fe	0	1	0	99
K	28 < x < 45	30 < x < 48	4 < x < 7	< 38
La	< < 1	< < 7	< 4	> 88
Li	< (a)	< (a)	(a)	(a)
Mg	< < 1	< < 1	< 1	> 97
Mn	< < 1	< < 1	< 1	> 97
Mo	< (a)	< (a)	(a)	(a)
Na	--	--	--	32[(b)]
Nd	< < 1	< < 4	< 3	> 92
Ni	4	5	1	90
P	27	36	6	30
Pb	< < 1	< < 1	< 1	> 97
Pd	< (a)	< (a)	(a)	(a)
Rh	< (a)	< (a)	(a)	(a)
Ru	< (a)	< (a)	(a)	(a)
Sb	< (a)	< (a)	(a)	(a)
Se	< (a)	< (a)	(a)	(a)
Si	1	35	6	58
Sn	< (a)	< (a)	(a)	(a)
Sr	< 0	< 0	0	100
Te	< (a)	< (a)	(a)	(a)
Th	< (a)	< (a)	(a)	(a)
Ti	< < 1	< < 4	< 3	> 92
Tl	< (a)	< (a)	(a)	(a)
U	0	0	0	100
V	< (a)	< (a)	(a)	(a)
W	< (a)	< (a)	(a)	(a)
Y	< (a)	< (a)	(a)	(a)
Zn	1	7	< 1	> 91
Zr	< < 1	< < 5	< 3	> 91

(a) Analyte was below detection limit for all process streams.

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

Table 4.7. Concentrations of the Nonradioactive BY-108 Sludge Components in the Initial Sludge Solids: Results of the Caustic Leaching Portion of the Test

	Concentration in Initial Solids, µg/g		
Component	Summation Method(a)	Direct Analysis	Mass Recovery, %
Ag	< 11	< 20	--
Al	15823	12600	126
As	< 276	< 203	--
B	$19 < x < 49$	1603	$1 < x < 3$
Ba	364	389	94
Be	< 4	< 7	--
Bi	2197	2345	94
Ca	18904	20810	91
Cd	$17 < x < 20$	26	$65 < x < 76$
Ce	< 201	< 271	--
Co	< 41	< 68	--
Cr	383	398	96
Cu	84	122	69
Dy	< 37	< 68	--
Eu	< 74	< 136	--
Fe	48431	51650	94
K	$1809 < x < 2904$	2580	$70 < x < 113$
La	$77 < x < 87$	103	$75 < x < 84$
Li	< 22	< 41	--
Mg	1189	1325	90
Mn	632	534	118
Mo	< 37	< 68	--
Na	56675	213400	27(b)
Nd	$231 < x < 250$	310	$75 < x < 81$
Ni	15854	17700	90
P	32110	23500	137
Pb	1377	1550	89
Pd	< 554	< 1017	--
Rh	< 222	< 407	--
Ru	< 739	< 1356	--
Sb	< 369	< 678	--
Se	< 279	< 339	--
Si	3784	7360	51
Sn	< 1329	< 2034	--
Sr	13381	13550	99
Te	< 1108	< 2034	--
Th	< 739	< 1356	--
Ti	$59 < x < 63$	71	$83 < x < 90$
Tl	< 369	< 678	--
U	72155	80700	89
V	< 37	< 68	--
W	< 1477	< 2712	--
Y	< 37	< 68	--
Zn	343	403	85
Zr	$95 < x < 105$	108	$88 < x < 97$

(a) The value was determined by summing the amount of a given component in the caustic leaching solutions, the subsequent washing solutions, and the leached solids; the total concentration was then determined by dividing the sum by the amount of solids processed.

(b) Adjusted for Na added during testing.

Table 4.8. Anion Concentrations in the Various BY-108 Process Solutions

	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		31,450	N/A[b]	49,980	N/A[b]	Not Determined	
NO_3^-	4,500	108,675	25,700	54,369	1,800	31363	400	4673
NO_2^-	2,200	53,130	12,600	26,656	900	15682	350	N/A[c]
PO_4^{3-}	2500	60,375	4,700	9,943	1400	24394	500	5841
SO_4^{2-}	900	21,735	5000	10,578	400	6970	100	1168
F^-	70	1,690	110	233	90	1568	< 50	<550
Cl^-	80	1,932	370	783	< 50	<610	< 50	<570
Br^-	< 50	<1200	< 250	<530	< 50	<700	< 50	<570

(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 4.9 presents the concentrations of various radioactive sludge components in each process stream, and Table 4.10 presents the distribution of those sludge components between the various process streams. As was the case with the dilute NaOH wash, only ^{137}Cs and ^{99}Tc were detected in the leach and wash solutions. Comparable to what was observed for the dilute NaOH wash, >91% of the ^{99}Tc was removed. Significantly more ^{137}Cs was dissolved by caustic leaching than by dilute NaOH washing; nearly all of the ^{137}Cs was solubilized by caustic leaching compared to only 3% by dilute hydroxide washing. The increased ^{137}Cs dissolution is probably the most important distinction between the dilute hydroxide washing and caustic leaching of the BY-108 sludge. As it would be preferable to have the ^{137}Cs remain with the HLW solids, simply washing with dilute hydroxide would seem the best option for this sludge.

Table 4.11 summarizes the mass recoveries achieved for the various radionuclides during the caustic leaching portion of the test. Except for ^{90}Sr, the mass recoveries were all somewhat greater than 100%.

Table 4.9. Concentrations of the Radioactive BY-108 Sludge Components in the Various Process Streams During Caustic Leaching

	First Leach Solution		Second Leach Solution	
Component	Conc., µCi/mL	Activity, µCi	Conc., µCi/mL	Activity, µCi
Total Alpha	< 2.60E-04	< 4.73E-03	< 2.60E-04	< 3.90E-02
^{239,240}Pu	< 2.60E-04	< 4.73E-03	< 2.60E-04	< 3.90E-02
^{241}Am^{+238}Pu	< 2.60E-04	< 4.73E-03	< 2.60E-04	< 3.90E-02
^{241}Am(g)	< 1.69E-02	< 3.08E-01	< 1.69E-02	< 2.53E+00
^{137}Cs	4.30E+02	7.83E+03	4.15E+01	6.22E+03
^{60}Co	< 5.20E-03	< 9.46E-02	< 5.20E-03	< 7.79E-01
^{154}Eu	< 1.56E-02	< 2.84E-01	< 1.56E-02	< 2.34E+00
^{155}Eu	< 1.69E-02	< 3.08E-01	< 1.69E-02	< 2.53E+00
^{90}Sr	1.52E+00	2.77E+01	4.63E-03	6.94E-01
^{99}Tc	4.78E-03	8.71E-02	4.68E-04	7.02E-02
^{243,244}Cm	< 2.60E-04	< 4.73E-03	< 2.60E-04	< 3.90E-02
^{237}Np	< 2.60E-04	< 4.73E-03	< 2.60E-04	< 3.90E-02
^{238}U	< 2.60E-04	< 4.73E-03	< 2.60E-04	< 3.90E-02

	Final Wash Solution		Leached Solids		
Component	Conc., µCi/mL	Activity, µCi	Conc., µCi/g	Activity, µCi	Total Activity, µCi
Total Alpha	< 2.20E-04	< 2.21E-02	1.38E+00	4.37E+00	< 4.44E+00
^{239,240}Pu	< 2.20E-04	< 2.21E-02	7.95E-01	2.52E+00	< 2.58E+00
^{241}Am^{+238}Pu	< 2.20E-04	< 2.21E-02	4.32E-01	1.37E+00	< 1.43E+00
^{241}Am(g)	< 1.43E-02	< 1.44E+00	< 1.30E-02	< 4.12E-02	< 4.32E+00
^{137}Cs	7.17E+00	7.21E+02	5.67E+01	1.80E+02	1.49E+04
^{60}Co	< 4.40E-03	< 4.42E-01	< 4.00E-03	< 1.27E-02	< 1.33E+00
^{154}Eu	< 1.32E-02	< 1.33E+00	5.71E-01	1.81E+00	< 5.76E+00
^{155}Eu	< 1.43E-02	< 1.44E+00	< 1.30E-02	< 4.12E-02	< 4.32E+00
^{90}Sr	< 6.60E-03	< 6.63E-01	2.35E+03	7.44E+03	< 7.47E+03
^{99}Tc	7.55E-05	7.58E-03	< 5.00E-03	< 1.58E-02	< 1.81E-01
^{243,244}Cm	< 2.20E-04	< 2.21E-02	< 2.00E-04	< 6.33E-04	< 6.64E-02
^{237}Np	< 2.20E-04	< 2.21E-02	7.41E-02	2.35E-01	< 3.00E-01
^{238}U	< 2.20E-04	< 2.21E-02	7.82E-02	2.48E-01	< 3.13E-01

Table 4.10. Distribution of Radioactive BY-108 Sludge Components Between the Various Process Streams During Caustic Leaching

	Component Distribution, %			
Component	First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids
Total Alpha	0	< 1	0	> 99
^{239,240}Pu	0	< 2	< 1	> 97
^{241}Am+^{238}Pu	0	< 3	< 2	> 95
^{241}Am(g)	(a)	(a)	(a)	(a)
^{137}Cs	52	42	5	1
^{60}Co	(a)	(a)	(a)	(a)
^{154}Eu	< 5	< 41	< 23	> 31
^{155}Eu	(a)	(a)	(a)	(a)
^{90}Sr	0	0	0	100
^{99}Tc	> 48	> 39	> 4	< 9
^{243,244}Cm	(a)	(a)	(a)	(a)
^{237}Np	< 2	< 13	< 7	> 78
^{238}U	< 2	< 13	< 7	> 78

(a) Analyte was below detection limit for all solutions.

Table 4.11. Concentrations of the Radioactive Components in the Initial BY-108 Solids: Results of the Caustic Leaching Portion of the Test

	Concentration in Initial Solids, µCi/g		
Component	Summation Method[(a)]	Direct Analysis	Recovery, %
Total Alpha	5.08E-01	4.04E-01	126
^{239,240}Pu	2.93E-01	2.28E-01	129
^{241}Am+^{238}Pu	1.59E-01	1.36E-01	117
^{241}Am(g)	< 5.02E-01	1.30E-02	--
^{137}Cs	1.74E+03	1.59E+03	109
^{60}Co	< 1.54E-01	4.00E-03	--
^{154}Eu	0.21 < x < 0.67	3.00E-01	70 < x < 233
^{155}Eu	< 5.02E-01	1.30E-02	--
^{90}Sr	8.68E+02	1.04E+03	83
^{99}Tc	0.019 < x < 0.021	1.81E-02	106 < x < 116
^{243,244}Cm	< 7.72E-03	3.00E-04	--
^{237}Np	0.027 < 0.035	2.59E-02	105 < x < 135
^{238}U	0.029 < x < 0.036	1.47E-02	196 < x < 248

(a) The value was determined by summing the amount of a given component in the caustic leaching solutions, the subsequent washing solutions, and the leached solids; the total concentration was then determined by dividing the sum by the amount of sludge solids processed.

4.2.3 Particle-Size Analysis

Figure 4.2 presents the particle-size data for the untreated and treated BY-108 sludge solids in terms of the number distributions, and Figure 4.3 presents the data in terms of the volume distributions. Leaching the sludge with caustic slightly reduced the mean particle size. The volume distribution for the untreated BY-108 sludge indicated a mean particle size of 6.5 µm, while that for the treated material was 3.8 µm. Based on the number distribution, the mean particle size was virtually unchanged after leaching (~0.31 µm). The particle-size measurements were repeated after an ultrasonic field was applied. This had very little effect, except to break up some of the largest particles (>20 µm).

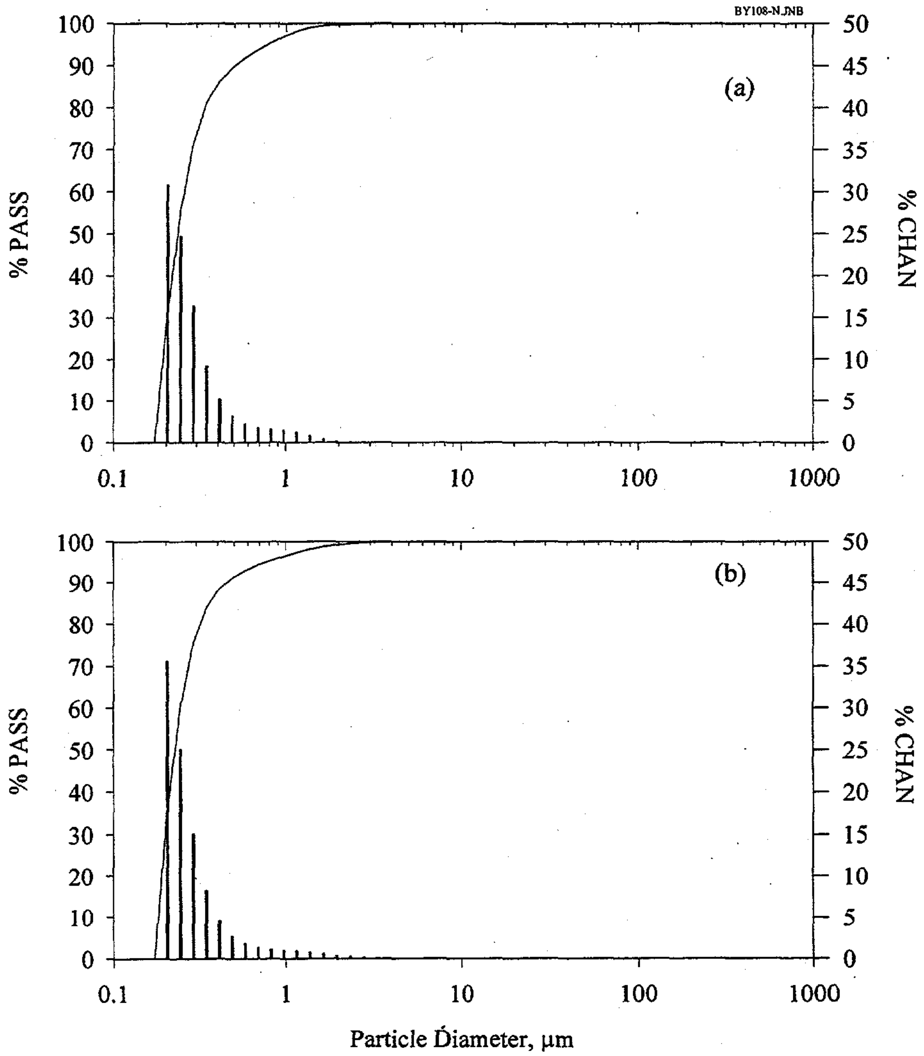


Figure 4.2. Particle-Size Number Distributions for Untreated (a) and Treated (b) BY-108 Sludge

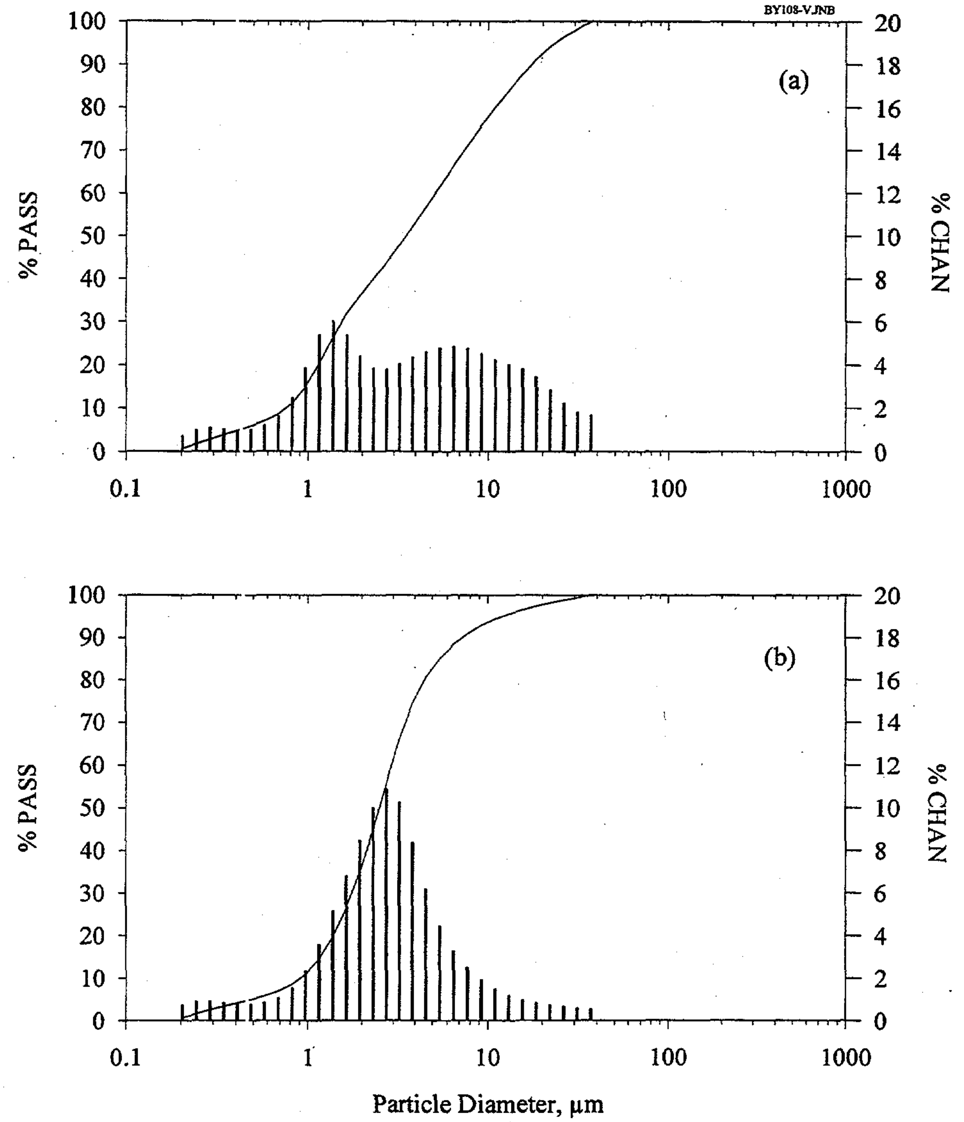


Figure 4.3. Particle-Size Number Distributions for Untreated (a) and Treated (b) BY-108 Sludge

4.2.4 Microscopic Analysis

As expected from the ICP/AES analysis, transmission electron microscopy (TEM) examination of the untreated BY-108 sludge revealed the presence of significant amounts of sodium salts, which existed as irregularly shaped agglomerates. Other phases identified were as follows.

- A single-crystalline phase of FeOOH (orthorhombic, a = 1.07 nm, b = 0.98 nm, and c = 0.296 nm), which has a different size of unit cell than goethite; these particles were approximately 1 µm in diameter

- Multicrystalline phases of maghemite (γ-Fe_2O_3)

- Hexagonal $Ca_xSr_{10-x}(PO_4)_6(OH)_2$ (where $x = 8$ or 9)

- β-U_3O_8, in nanometer-sized single crystalline particles

Except for the sodium salts, these phases remained after caustic leaching.

4.2.5 Settling Data

Table 4.12 and Figures 4.4 and 4.5 present the BY-108 settling data from the caustic leaching steps and the final wash step.[a] The data are presented in terms of the actual sludge height versus time (Figure 4.4) and in terms of normalized sludge height versus a dimensionless time value (Figure 4.5).[b] Wide variability in the settling behavior was observed. Settling was slowest during the first caustic leaching step and fastest during the second caustic leaching step. The settling behavior during the third washing step was in between. The settling behavior qualitatively correlates to the solids concentration in the slurries being settled—7.1 wt% for the first caustic leach, 1.7 wt% for the second caustic leach, and 6.0 wt% for the third wash.

(a) Settling data are not presented for the first and second washing steps because an error was made in reading the scale on the ruler. This error could not be reconciled after-the-fact, so the data are omitted from this report.

(b) Data were normalized according to a formula suggested by G.T. MacLean, SGN Eurisys Services Corp., personal communication, 1996. The formula is given in Table 4.12.

Table 4.12. Settling Data From the BY-108 Caustic Leaching Test[a]

First Caustic Leach				Second Caustic Leach				Third Wash			
t, min	h, mm	T	H	t, min	h, mm	T	H	t, min	h, mm	T	H
0	41	0.00	1.00	0	65	0.00	1.00	0	54	0.00	1.00
1	40	0.02	0.98	1	64	0.01	0.98	1	53	0.02	0.98
2	39	0.05	0.95	2	63	0.03	0.97	2	52	0.04	0.96
5	39	0.12	0.95	3	61	0.04	0.94	5	51	0.09	0.94
10	38	0.24	0.93	4	60	0.06	0.92	10	50	0.19	0.93
20	38	0.49	0.93	5	59	0.07	0.91	15	48	0.28	0.89
30	37	0.73	0.90	6	58	0.08	0.89	20	46	0.37	0.85
40	36	0.98	0.88	8	57	0.11	0.88	25	44	0.46	0.81
50	34	1.22	0.88	10	55	0.14	0.85	30	42	0.56	0.78
60	32	1.46	0.83	15	50	0.21	0.77	35	40	0.65	0.74
70	31	1.71	0.78	20	45	0.28	0.69	40	38	0.74	0.70
80	30	1.95	0.76	30	40	0.34	0.62	45	35	0.83	0.65
110	29	2.68	0.73	35	36	0.41	0.55	60	33	1.11	0.61
140	28	3.41	0.71	45	32	0.48	0.49	75	30	1.39	0.56
170	27	4.15	0.68	55	26	0.62	0.40	90	29	1.67	0.54
200	26	4.88	0.66	65	23	0.76	0.35	120	27	2.22	0.50
260	25	6.34	0.63	95	20	0.90	0.31	180	25	3.33	0.46
1250	19.5	30.49	0.61	125	14	1.31	0.22	240	24	4.44	0.44
				155	13	1.72	0.20	360	22	6.67	0.41
				215	13	2.14	0.20				
				335	13	2.97	0.20				
				395	12	4.62	0.18				
				1400	12	5.45	0.18				

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

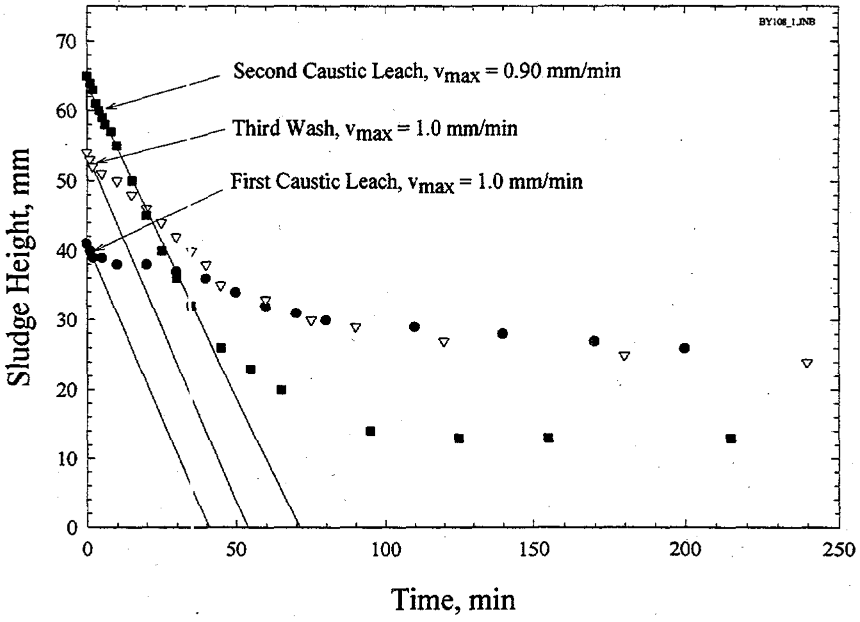


Figure 4.4. Settling Data From the BY-108 Caustic Leaching Test

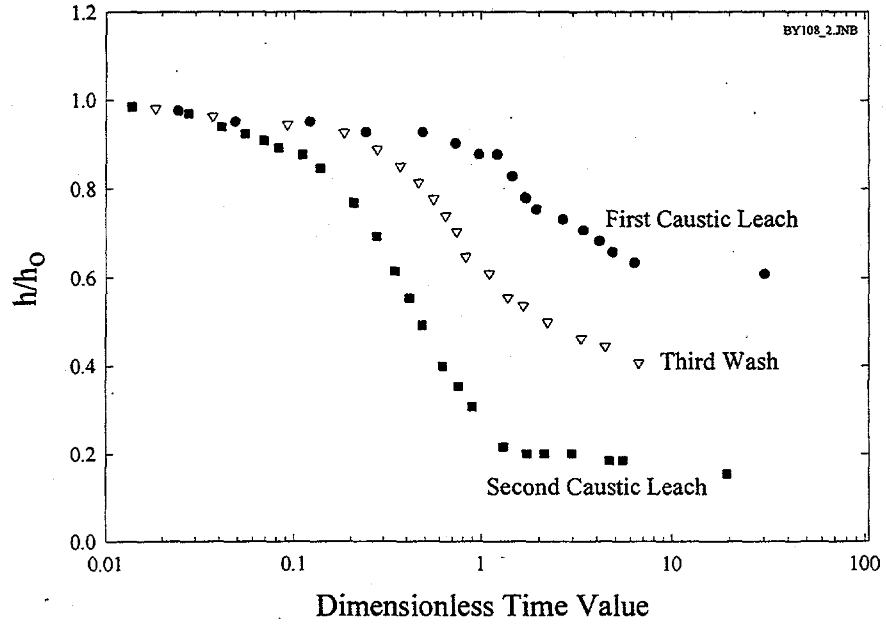


Figure 4.5. Normalized Settling Data From the BY-108 Caustic Leaching Test

5.0 Tank S-101 Enhanced Sludge Washing Test

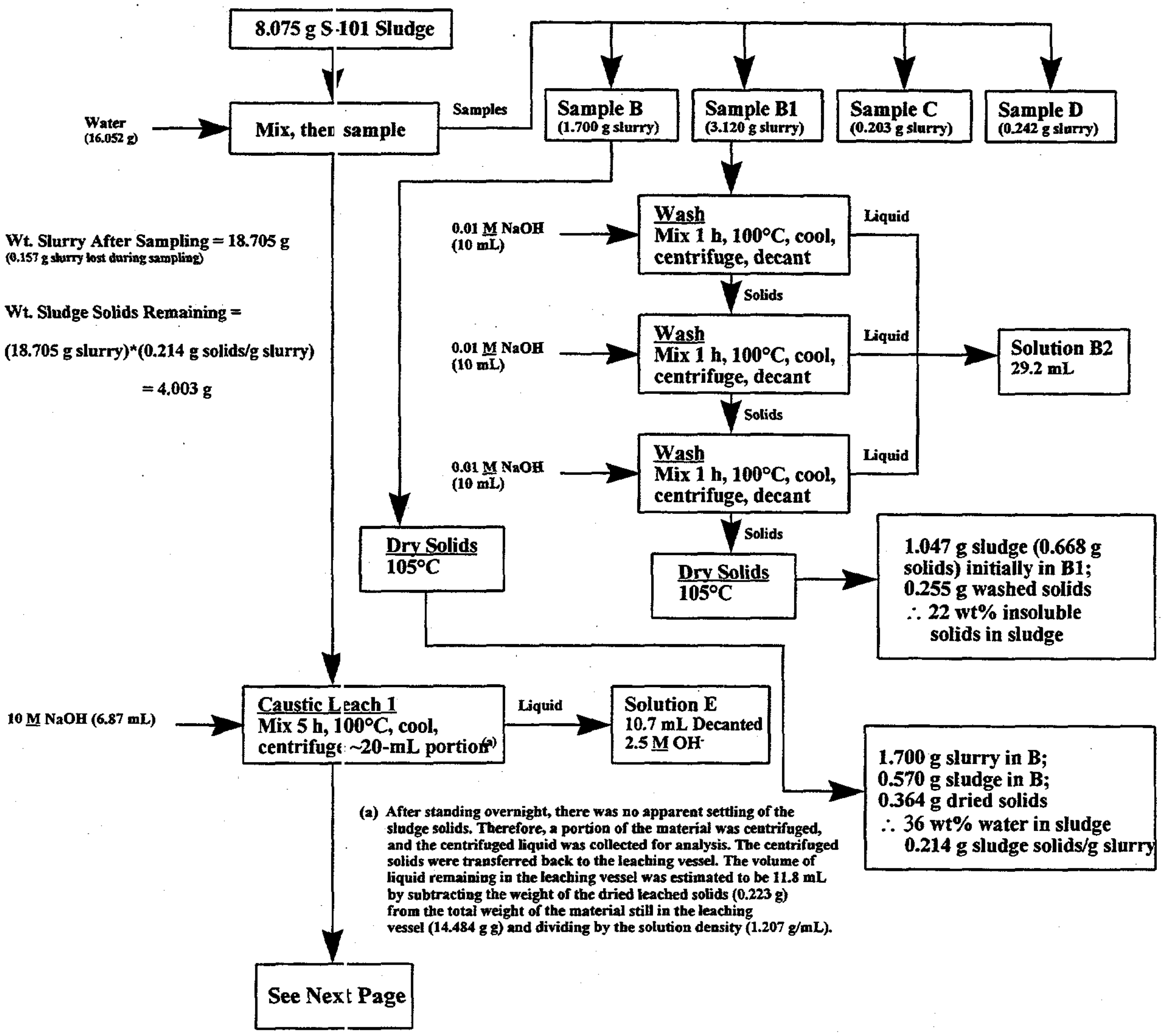
This section presents the results of the ESW test performed on Hanford Tank S-101 sludge. The sludge sample used in this test was received at PNNL on August 2, 1996; the 222-S laboratory ID for this sample was S96T003486, and the jar number was 10519.

5.1 Experimental

Figure 5.1 summarizes the experimental procedure used in the S-101 ESW test. The procedure was the same as the baseline ESW test procedure described previously (Lumetta et al. 1996), except 1) gravity settling was used rather than centrifugation for solids/liquid separations in the leaching steps, and 2) the second caustic leach step was performed for 100 h rather than 5 h. Centrifugation was not used because a suitable centrifuge was not available in the hot cell where the test was performed.[a] An exception to this was the first leaching step. In that case, there was no apparent settling after standing overnight. In order to sample the solution, an approximately 20-mL portion of the slurry was transferred to a vial suitable for centrifugation. This portion was centrifuged, and 10.7 mL of liquid was decanted; the remaining solids were transferred back to the original vial for the second leaching step. The extended leaching time was used because of the previous observation that kinetics plays an important role in the removal of Al from REDOX sludges (see Section 3.0). During the second leaching step, samples were taken after 5 and 100 h of heating.

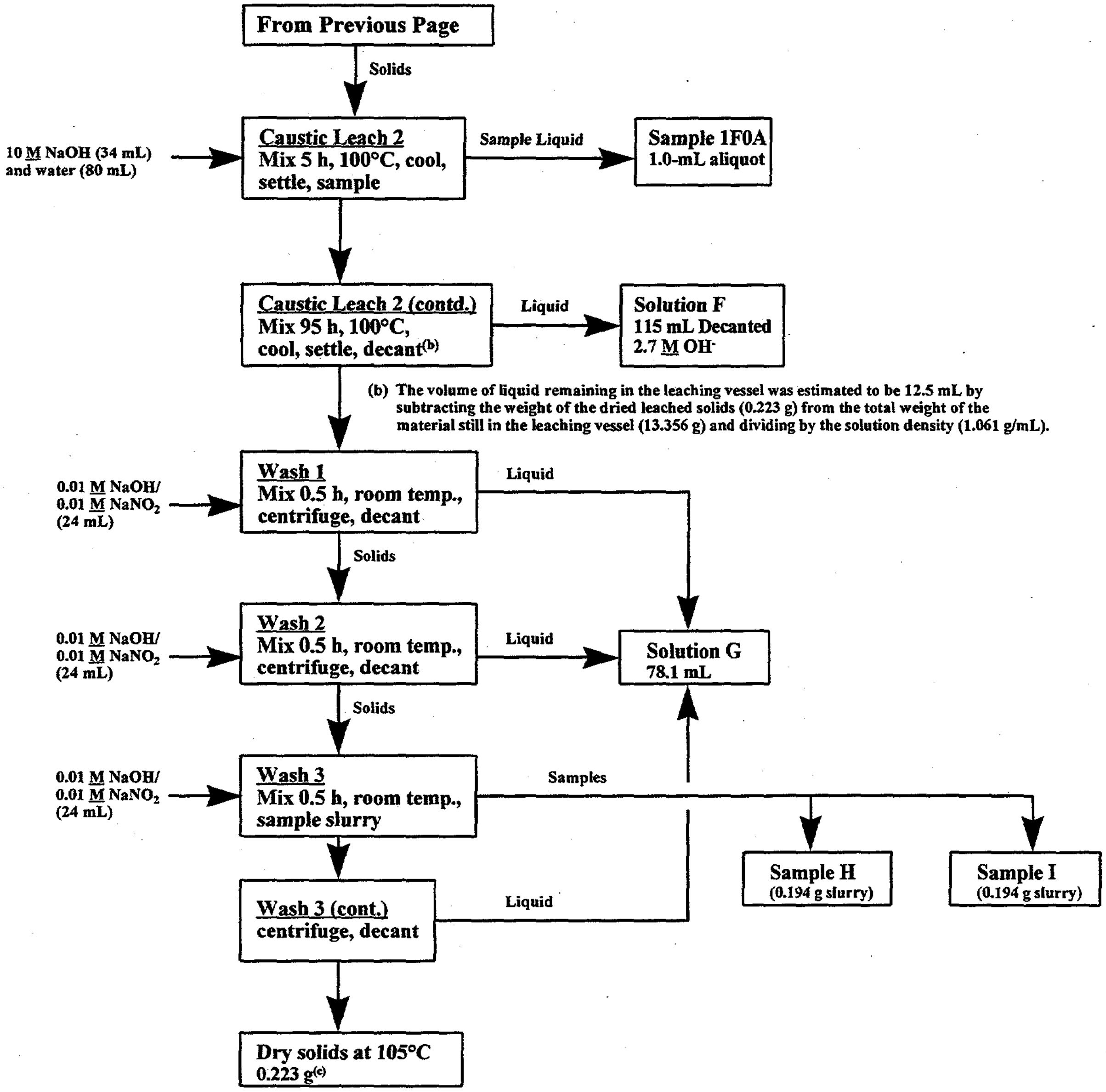
For the dilute hydroxide washing steps (sample B1), the insoluble solids concentrations were ~1.8 wt%. The target undissolved solids concentration in the first and second caustic leaching steps were 5 wt% and 1 wt% respectively. Usually, we estimate the undissolved solids concentration in the first caustic leaching slurry from the weight of the residual caustic-leached solids. But because significant Al dissolution occurred in the second leaching step, using the residual solids weight would give an erroneously low value for the undissolved solids in the first leaching step. However, we can give a range of 0.8 to 5.0 wt% undissolved solids in the first caustic leaching slurry. The former number was determined using the weight of the residual solids, while the latter value was obtained from the expected amount of water-insoluble solids in the S-101 sludge (as determined from washing sample B1). Based upon the leached-solids mass of 0.223 g, the undissolved solids concentrations were 0.2 and 0.9 wt% in the second caustic leaching slurry and the final wash slurries, respectively.

(a) Typically, the ESW tests are performed in fume hoods, but because of the radiological characteristics of the S-101 sludge, it was necessary to perform this test in the hot cell.



(a) After standing overnight, there was no apparent settling of the sludge solids. Therefore, a portion of the material was centrifuged, and the centrifuged liquid was collected for analysis. The centrifuged solids were transferred back to the leaching vessel. The volume of liquid remaining in the leaching vessel was estimated to be 11.8 mL by subtracting the weight of the dried leached solids (0.223 g) from the total weight of the material still in the leaching vessel (14.484 g g) and dividing by the solution density (1.207 g/mL).

Figure 5.1 Schematic Representation of the S-101 ESW Test



(b) The volume of liquid remaining in the leaching vessel was estimated to be 12.5 mL by subtracting the weight of the dried leached solids (0.223 g) from the total weight of the material still in the leaching vessel (13.356 g) and dividing by the solution density (1.061 g/mL).

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

S101_ESW.PPT

Figure 5.1. (contd)

5.2 Results and Discussion

5.2.1 Washing With Dilute NaOH

Table 5.1 summarizes the behavior of most of the nonradioactive sludge components during washing of the S-101 sludge with 0.01 M NaOH. Sodium was the most soluble element present with 97% being removed by washing with 0.01 M NaOH. A small fraction (12%) of the Al was removed by dilute hydroxide washing, which is consistent with the behavior of other REDOX sludges (e.g., see Section 3.0 and Lumetta et al. 1996). Significant fractions of P (87%) and Cr (44%) were also removed from S-101 sludge by dilute hydroxide washing. The value of 44% removal for Cr highlights the variability in Cr removal for REDOX sludges. REDOX sludge is the primary waste type in tanks S-101, S-104, S-107, SX-108, and SX-113; the Cr removals by simple washing of these sludges were 44%, 94%, 24%, 71%, and 2%, respectively. Thus, Cr removal for REDOX sludges varies from practically no removal (SX-113) to nearly complete removal (S-104). SX-108 sludge contained only 0.01 wt% Cr, while the others listed here contained between 0.41 and 0.79 wt%. It would interesting to examine other factors (secondary and tertiary waste types, tank processing history, etc.) in trying to correlate the behavior of Cr in these wastes.

Table 5.2 presents the concentrations determined in the untreated S-101 sludge solids for most of the nonradioactive sludge components; also given is the mass recovery achieved for each of these components. The ten most abundant elements in the S-101 sludge, as determined by direct analysis of the sludge, were Na (18.0 wt%), Al (14.7 wt%), U (9.56 wt%), Cr (7.11 wt%), Mn (2.84 wt%), Si (2.67 wt%), P (2.30 wt%), Fe (2.15 wt%), Ca (1.29 wt%), and Ce (0.80 wt%). Mass recoveries were within 10% for Al, Cr, Mn, P, and Fe, and within 20% for Sr, U, and Si. The mass recovery for Na was slightly high (123%), but reasonable. Mass recoveries were poor for most of the other components.

Table 5.3 summarizes the behavior of the radioactive sludge components during washing of the S-101 sludge with 0.01 M NaOH. As has been seen with most other Hanford tank sludges, the TRU elements are very insoluble in 0.01 M NaOH. All Pu and Am isotopes were below the detection limit in the wash solution. Likewise, ^{60}Co, ^{90}Sr, and ^{154,155}Eu showed little propensity for dissolving in 0.01 M NaOH. Cesium-137 dissolved effectively (97%) in 0.01 M NaOH. Likewise, as would be consistent with the behavior of pertechnetate ion, ^{99}Tc was effectively (97%) dissolved in the dilute NaOH wash.

Table 5.4 presents the concentrations of the various radionuclides in the untreated S-101 sludge solids along with the mass recovery for each. Mass recoveries for ^{137}Cs, ^{90}Sr, and ^{99}Tc were within 30%, but recoveries for the TRUs ^{154,155}Eu and ^{60}Co were much worse. We cannot explain the poor mass recoveries.

Table 5.1. Results of Tank S-101 Sludge Washing Nonradioactive Components

	Wash Solution		Washed Solids			Component Distribution, %	
Component	Conc., µg/mL	Mass, µg	Conc., µg/g	Mass, µg	Total Mass, µg	Wash Solution	Washed Solids
Ag	< 0.033	< 1	< 61	< 16	< 16	--	--
Al	397	11578	342500	87338	98915	12	88
As	< 0.33	< 9	< 609	< 155	< 165	--	--
B	0.85	25	203	52	76	32	68
Ba	< 0.013	< 0	144	37	< 37	< 1	> 99
Be	< 0.013	< 0	< 24	< 6	< 7	--	--
Bi	< 0.13	< 4	250	64	< 68	< 6	> 94
Ca	1.43	42	2169	553	595	7	93
Cd	< 0.020	< 1	38	10	< 10	< 6	> 94
Ce	< 0.26	< 8	642	164	< 171	< 4	> 96
Co	< 0.065	< 2	< 122	< 31	< 33	--	--
Cr	72	2114	10500	2678	4792	44	56
Cu	< 0.033	< 1	180	46	< 47	< 2	> 98
Dy	< 0.065	< 2	< 122	< 31	< 33	--	--
Eu	< 0.13	< 4	< 244	< 62	< 66	--	--
Fe	0.078	2	5509	1405	1407	0	100
K	20	569	< 4872	< 1242	< 1812	> 31	< 69
La	< 0.065	< 2	< 122	< 31	< 33	--	--
Li	< 0.039	< 1	< 73	< 19	< 20	--	--
Mg	< 0.13	< 4	< 244	< 62	< 66	--	--
Mn	< 0.065	< 2	6902	1760	< 1762	0	100
Mo	0.74	22	< 122	< 31	< 53	> 41	< 59
Na	5187	(a) 144560	15240	3886	148447	97	3
Nd	< 0.13	< 4	287	73	< 77	< 5	> 95
Ni	0.10	3	721	184	187	2	98
P	46	1348	763	195	1542	87	13
Pb	< 0.13	< 4	344	88	< 91	< 4	> 96
Pd	< 0.98	< 28	< 1827	< 466	< 494	--	--
Rh	< 0.39	< 11	< 731	< 186	< 198	--	--
Ru	< 1.43	< 42	< 2680	< 683	< 725	--	--
Sb	< 0.65	< 19	< 1218	< 311	< 330	--	--
Se	< 0.325	< 9	< 609	< 155	< 165	--	--
Si	20	585	3500	893	1477	40	60
Sn	< 1.95	< 57	< 3654	< 932	< 989	--	--
Sr	< 0.020	< 1	1098	280	< 280	0	100
Te	< 1.95	< 57	< 3654	< 932	< 989	--	--
Th	< 1.3	< 38	< 2436	< 621	< 659	--	--
Ti	< 0.033	< 1	99	25	< 26	< 4	> 96
Tl	< 0.65	< 19	< 1218	< 311	< 330	--	--
U(b)	0.484	14	21600	5508	5522	0	100
V	0.12	3	< 122	< 31	< 34	10	90
W	< 2.6	< 76	< 4872	< 1242	< 1318	--	--
Y	< 0.065	< 2	< 122	< 31	< 33	--	--
Zn	0.14	4	268	68	73	6	94
Zr	< 0.065	< 2	< 126	< 32	< 34	--	--

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

(b) Uranium was determined by laser fluorimetry; all other elements were determined by ICP/AES.

Table 5.2. Concentrations of Nonradioactive Components in the Untreated S-101

Component	Concentration in Initial Solids µg/g Summation Method(a)	Direct Analysis(b)	Recovery, %
Ag	< 2.47E+01	< 6.07E+01	–
Al	1.48E+05	1.47E+05	101
As	< 2.47E+02	< 6.07E+02	–
B	1.14E+02	3.70E+02	31
Ba	55 < x < 231	6.85E+01	80 < x < 337
Be	< 9.87E+00	< 2.43E+01	–
Bi	1.41E+03	< 2.43E+02	–
Ca	8.90E+02	1.29E+03	69
Cd	~13	< 3.64E+01	–
Ce	~220	8.04E+02	~27
Co	< 4.93E+01	< 1.21E+02	–
Cr	7.17E+03	7.11E+03	101
Cu	6.20E+01	9.90E+01	63
Dy	< 4.93E+01	< 1.21E+02	–
Eu	< 9.87E+01	< 2.43E+02	–
Fe	2.11E+03	2.15E+03	98
K	852 < x < 2710	7.20E+02	118 < x < 277
La	< 4.93E+01	< 1.21E+02	–
Li	< 2.96E+01	< 7.28E+01	–
Mg	7.72E+02	< 2.43E+02	–
Mn	2.64E+03	2.84E+03	93
Mo	32 < x < 79	< 1.21E+02	–
Na	2.22E+05	1.80E+05	123
Nd	97 < x < 102	1.61E+02	68 < x < 74
Ni	2.80E+02	< 7.28E+01	–
P	2.31E+03	2.30E+03	101
Pb	131 < x < 901	4.82E+02	27 < x < 187
Pd	< 7.40E+02	< 1.82E+03	–
Rh	< 2.96E+02	< 7.28E+02	–
Ru	< 1.09E+03	< 2.67E+03	–
Sb	< 4.93E+02	< 1.21E+03	–
Se	< 2.47E+02	< 6.07E+02	–
Si	2.21E+03	2.67E+03	83
Sn	< 1.48E+03	< 3.64E+03	–
Sr	4.20E+02	4.93E+02	85
Te	< 1.48E+03	< 3.64E+03	–
Th	< 9.87E+02	< 2.43E+03	–
Ti	3.40E+01	2.13E+02	16
Tl	< 4.93E+02	< 1.21E+03	–
U	8.27E+03	9.56E+03	86
V	< 5.16E+01	< 1.21E+02	–
W	< 1.97E+03	< 4.85E+03	–
Y	< 4.93E+01	< 1.21E+02	–
Zn	1.09E+02	1.51E+02	72
Zr	< 5.10E+01	< 1.21E+02	–

(a) The values were determined by summing the mass of the component found in each process stream and dividing by the amount of sludge solids treated.

(b) Solids were prepared for analysis by both KOH and Na_2O_2 fusion methods; mean values are given for analytes that can be determined by both these methods.

Table 5.3. Results of Tank S-101 Sludge Washing Radioactive Components

	Wash Solution		Washed Solids			Component Distribution, %	
Component	Conc., µCi/mL	Activity, µCi	Conc., µCi/g	Activity, µCi	Total Activity, µCi	Wash	Washed Solids
Total Alpha	< 2.60E-04	< 7.59E-03	1.10E+00	2.81E-01	< 2.88E-01	< 3	> 97
^{239,240}Pu	< 2.60E-04	< 7.59E-03	7.81E-01	1.99E-01	< 2.07E-01	< 4	> 96
^{241}Am+^{238}Pu	< 2.60E-04	< 7.59E-03	3.19E-01	8.13E-02	< 8.89E-02	< 9	> 91
^{241}Am(g)	< 3.90E-03	< 1.14E-01	3.56E-01	9.08E-02	< 2.05E-01	< 56	> 44
^{137}Cs	3.85E+00	1.12E+02	1.27E+01	3.24E+00	1.16E+02	97	3
^{60}Co	< 5.20E-05	< 1.52E-03	3.29E-02	8.39E-03	< 9.91E-03	< 15	> 85
^{154}Eu	< 2.60E-04	< 7.59E-03	2.08E-01	5.30E-02	< 6.06E-02	< 13	> 87
^{155}Eu	< 3.90E-03	< 1.14E-01	< 2.00E-01	< 5.10E-02	< 1.65E-01	--	--
^{90}Sr	< 2.60E-02	< 7.59E-01	9.10E+02	2.32E+02	< 2.33E+02	0	100
^{99}Tc	2.70E-03	7.90E-02	1.06E-02	2.70E-03	8.17E-02	97	3

Table 5.4. Concentrations of Radioactive Components in the Untreated S-101 Solids as Determined in the Simple Washing Test

	Concentration in Initial Solids, µCi/g		
Component	Summation Method	Direct Analysis	Recovery, %
Total Alpha	0.374 < x < 0.384	1.36E+00	~31
^{239,240}Pu	0.265 < x < 0.275	4.80E-01	~63
^{241}Am+^{238}Pu	0.108 < x < 0.118	6.28E-01	~20
^{241}Am(g)	0.121 < x < 0.273	< 7.00E-01	--
^{137}Cs	1.73E+02	1.38E+02	125
^{60}Co	0.011 < x < 0.013	< 5.00E-02	--
^{154}Eu	0.071 < x < 0.081	< 2.00E-01	--
^{155}Eu	< 2.47E-01	< 5.00E-01	--
^{90}Sr	3.49E+02	4.41E+02	79
^{99}Tc	1.22E-01	1.40E-01	87

5.2.2 Caustic Leaching

Table 5.5 presents the concentrations of most of the nonradioactive sludge components in each process stream, and Table 5.6 presents the distribution of those sludge components between the various process streams. The values presented in Table 5.6 are not adjusted for material contained in the interstitial liquid, but rather represent the amount of each component contained in the liquid that was decanted in a given step (or in the residual solid).

The cumulative removal of Al was 96%, most of which occurred in the second leaching step. The decanted liquid from the first caustic leaching step contained only 11% of the Al; the interstitial liquid contained another ~13% of the Al. Thus, approximately 24% of the Al was dissolved in the first leaching step. During the second caustic leaching step, the Al concentration increased from 1115 µg/mL at 5 h to 4240 µg/mL after 100 h at 100°C. Thus, the Al concentration increased nearly 4-fold between 5 and 100 h of leaching; this translated to an additional dissolution of 72% of the Al. This result is similar to what was seen with S-104 sludge (see Section 3.0), again indicating the importance of kinetics in removing Al from REDOX sludges. The second caustic leaching solution was stable toward precipitation for at least 210 days.

The cumulative removal of Cr was 89%, which indicated a significant increase over that removed by simple washing. During the second caustic leaching step, the Cr concentration increased from 105 µg/mL at 5 h to 155 µg/mL after 100 h at 100°C, indicating a 1.5-fold increase in the dissolved Cr in that leaching step. Taking into the interstitial liquid volumes, 48% of the Cr was removed in the first leaching step and 41% in the second leaching step.

No spectrophotometry was performed on the second leaching solution immediately after the test was completed, but it was examined by UV/vis spectrophotometry ~210 days afterwards. The spectrum was obtained for the undiluted solution. No evidence existed for Cr(III) in the aged solution; the Cr(III) concentration was less than 25 µg/mL. The spectrum was also obtained for a diluted solution so that the Cr(VI) concentration could be determined. This measurement indicated that the second leaching solution contained 210 µg Cr(VI)/mL. As indicated above, the ICP/AES measurement indicated that the total Cr concentration was 155 µg/mL. It appears likely that all the Cr in the aged leaching solution was in the Cr(VI) form. Although the vial was tightly sealed, evaporation could not be ruled out as a possible reason for the increase in the Cr concentration.

The cumulative P removal (97%) was somewhat better than achieved by dilute NaOH washing (87%). The amount of P removed in the first leaching step was 88% (when adjusted for that in the interstitial liquid), which was very similar to that achieved in the dilute NaOH wash. An additional 9% of the P dissolved in the second leaching step, suggesting that kinetics were important for removing that fraction of the P. Silicon removal was improved from 40% by dilute NaOH washing to 71% for caustic leaching. Virtually all of the U, which is the third-most abundant metallic element in the S-101 sludge, remained in the sludge solids during caustic leaching.

Table 5.5. Concentrations of the Nonradioactive S-101 Sludge Components in the Various Process Streams During Caustic Leaching

	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/g	Mass, μg	Total Mass, μg
Ag	< 0.16	< 2	< 0.16	< 19	< 0.14	< 11	68	15	< 46
Al	6798	72742	4238	488485	699	54553	115000	25645	641425
As	< 1.61	< 17	< 1.63	< 187	< 1.38	< 107	< 529	< 118	< 429
B	6.81	73	0.70	82	< 0.28	< 21	147	33	< 209
Ba	< 0.065	< 1	< 0.065	< 7	< 0.055	< 4	927	207	< 219
Be	< 0.065	< 1	< 0.065	< 7	< 0.055	< 4	< 21	< 5	< 17
Bi	0.86	9	< 0.65	< 75	< 0.55	< 43	829	185	< 312
Ca	1.94	21	9.10	1059	< 1.38	< 107	9669	2156	< 3343
Cd	0.15	2	0.10	12	< 0.083	< 6	121	27	< 47
Ce	< 1.29	< 14	< 1.30	< 150	< 1.1	< 86	1005	224	< 473
Co	0.39	4	< 0.33	< 37	< 0.28	< 21	< 106	< 24	< 87
Cr	640	6846	153	17748	26.1	2036	14650	3267	29898
Cu	9.06	97	1.90	220	< 0.14	< 11	487	109	< 437
Dy	< 0.32	< 3	< 0.33	< 37	< 0.28	< 21	< 106	< 24	< 86
Eu	< 0.65	< 7	< 0.65	< 75	< 0.55	< 43	< 211	< 47	< 172
Fe	4.5	48	5.9	685	0.31	24	36269	8088	8845
K	217	2319	24.7	2877	< 11.0	< 859	< 4228	< 943	< 6998
La	< 0.32	< 3	< 0.33	< 37	< 0.28	< 21	416	93	< 155
Li	0.22	2	< 0.20	< 22	< 0.17	< 13	< 63	< 14	< 52
Mg	< 0.65	< 7	< 0.65	< 78	< 0.55	< 43	471	105	< 233
Mn	0.54	6	< 0.33	< 37	< 0.28	< 21	46137	10289	< 10353
Mo	5.56	59	0.38	43	< 0.28	< 21	< 106	< 24	< 148
Na	109779	1174635	74750	8668410	12430	970783	61240	13657	(b) 1394485
Nd	0.70	7	< 0.65	< 75	< 0.55	< 43	1142	255	< 380
Ni	< 0.19	< 2	< 0.2	< 22	< 0.2	< 13	2091	466	< 504
P	375	4017	41	4766	7	552	1268	283	9617
Pb	5.03	54	1.56	179	< 0.55	< 43	517	115	< 391
Pd	< 4.84	< 52	< 4.88	< 561	< 4.13	< 322	< 1586	< 354	< 1288
Rh	< 1.94	< 21	< 1.95	< 224	< 1.65	< 129	< 634	< 141	< 515
Ru	< 7.10	< 76	< 7.15	< 822	< 6.05	< 473	< 2325	< 519	< 1889
Sb	< 3.23	< 35	< 3.25	< 374	< 2.75	< 215	< 1057	< 236	< 859
Se	< 1.61	< 17	< 1.63	< 187	< 1.38	< 107	< 529	< 118	< 429
Si	55	594	29.9	3488	5.3	412	8420	1878	6372
Sn	< 9.68	< 104	< 9.75	< 1121	< 8.25	< 644	< 3171	< 707	< 2576
Sr	0.12	1	0.10	12	< 0.08	< 6	7780	1735	< 1755
Te	< 9.68	< 104	< 9.75	< 1121	< 8.25	< 644	< 3171	< 707	< 2576
Th	< 6.45	< 69	< 6.5	< 748	< 5.5	< 430	< 2114	< 471	< 1717
Ti	< 0.16	< 2	< 0.16	< 19	< 0.14	< 11	313	70	< 101
Tl	< 3.23	< 35	< 3.25	< 374	< 2.75	< 215	< 1057	< 236	< 859
U(c)	0.325	3	3.86	444	1.05	82	168000	37464	37994
V	0.72	8	< 0.33	< 37	< 0.28	< 21	< 106	< 24	< 90
W	< 12.9	< 138	< 13	< 1495	< 11	< 859	< 4228	< 943	< 3435
Y	< 0.32	< 3	< 0.33	< 37	< 0.28	< 21	152	34	< 96
Zn	1.81	19	0.74	87	0.36	28	1003	224	358
Zr	< 0.32	< 3	< 0.33	< 37	< 0.28	< 21	752	168	< 230

(a) Mass of material present in the solution decanted during the indicated step.

(b) Adjusted for the amount (9,433,000 μg) of Na added as NaOH.

(c) Uranium was determined by laser fluorimetry; all other elements were determined by ICP/AES.

Table 5.6. Distribution of Nonradioactive S-101 Sludge Components Between the Various Process Streams During Caustic Leaching

	Component Distribution, %			
Component	First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids
Ag	< 4	< 40	< 23	> 33
Al	11	76	9	4
As	(a)	(a)	(a)	(a)
B	$35 < x < 39$	$39 < x < 43$	< 10	$16 < x < 18$
Ba	< 1	< 3	< 2	> 94
Be	(a)	(a)	(a)	(a)
Bi	$3 < x < 5$	< 24	< 14	$59 < x < 95$
Ca	1	32	0	67
Cd	4	$25 < x < 30$	< 14	$57 < x < 66$
Ce	< 3	< 32	< 18	> 47
Co	> 5	< 43	< 25	< 27
Cr	23	59	7	11
Cu	23	52	0	26
Dy	(a)	(a)	(a)	(a)
Eu	(a)	(a)	(a)	(a)
Fe	1	8	0	91
K	$33 < x < 45$	$41 < x < 55$	< 12	< 14
La	< 2	< 24	< 14	> 60
Li	> 5	< 43	< 25	< 27
Mg	< 3	< 33	< 19	> 46
Mn	0	0	0	100
Mo	$40 < x < 58$	$29 < x < 42$	< 15	< 16
Na	–	–	–	34(b)
Nd	$2 < x < 3$	< 20	< 11	$67 < x < 97$
Ni	0	< 4	< 3	> 93
P	42	50	6	3
Pb	$14 < x < 15$	$46 < x < 51$	< 11	$29 < x < 33$
Pd	(a)	(a)	(a)	(a)
Rh	(a)	(a)	(a)	(a)
Ru	(a)	(a)	(a)	(a)
Sb	(a)	(a)	(a)	(a)
Se	(a)	(a)	(a)	(a)
Si	9	55	6	29
Sn	(a)	(a)	(a)	(a)
Sr	0	1	0	> 69
Te	(a)	(a)	(a)	(a)
Th	(a)	(a)	(a)	(a)
Ti	< 2	< 19	< 11	> 92
Tl	(a)	(a)	(a)	(a)
U	0	1	0	99
V	(a)	(a)	(a)	(a)
W	(a)	(a)	(a)	(a)
Y	< 4	< 39	< 22	> 35
Zn	5	24	< 1	> 91
Zr	< 2	< 16	< 9	> 73

(a) Analyte was below detection limit for all process streams.

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

Table 5.7 summarizes the mass recoveries achieved for the various elements analyzed by ICP/AES and for U, which was determined by laser fluorimetry. For the most part, the mass recoveries for the caustic leaching portion of the test were better than was seen for the dilute hydroxide washing (compare the values in Table 5.7 to those in Table 5.2). Good mass recoveries were obtained for Al, Cr, Fe, Mn, P, and U. Recoveries for Ca, Ce, and Si were low.

Table 5.8 presents the concentrations of the various anions in each process solution. Also listed is the amount of each anion in solution as a function of the amount of sludge solids treated. Although the amounts of NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-} in solution during the caustic leaching portion of the test were greater (on a per gram of sludge processed basis) than in the dilute hydroxide wash, in no case did this difference exceed 20%. These results indicate that ESW would not provide much benefit in terms of removing these anions from the HLW stream.

Table 5.9 presents the concentrations of various radioactive sludge components in each process stream, and Table 5.10 presents the distribution of those sludge components between the various process streams. As was the case with the dilute NaOH wash, only ^{137}Cs and ^{99}Tc were detected in the leach and wash solutions; these radioisotopes were virtually quantitatively dissolved during caustic leaching. Table 5.11 summarizes the mass recoveries achieved for the various radionuclides during the caustic leaching portion of the test. Mass recoveries were good for ^{239,240}Pu, ^{137}Cs, and ^{90}Sr, but the mass recovery for ^{99}Tc was low.

Table 5.7. Concentrations of the Nonradioactive S-101 Sludge Components in the Initial Sludge Solids: Results From the Caustic Leaching Portion of the Text

	Concentration in Initial Solids, µg/g		
Component	Summation Method(a)	Direct Analysis	Mass Recovery, %
Ag	4 < x < 12	< 61	--
Al	160236	147000	109
As	< 107	< 607	--
B	47 < x < 52	370	13
Ba	52 < x < 55	69	75 < x < 80
Be	< 4	< 24	--
Bi	2197	< 243	905
Ca	806 < x < 833	1294	62 < x < 64
Cd	10 < x < 12	< 36	--
Ce	56 < x < 118	804	7 < x < 15
Co	< 22	< 121	--
Cr	7469	7110	105
Cu	109	99	110
Dy	< 21	< 121	--
Eu	< 43	< 243	--
Fe	2209	2149	103
K	1290 < x < 1740	720	179 < x < 242
La	23 < x < 39	< 121	--
Li	< 13	< 73	--
Mg	26 < x < 57	< 243	--
Mn	2574	2842	91
Mo	26 < x < 37	< 121	--
Na	348360	180140	193
Nd	66 < x < 95	161	41 < x < 59
Ni	117 < x < 126	< 73	17
P	2402	2295	105
Pb	87 < x < 98	482	18 < x < 20
Pd	< 322	< 1820	--
Rh	< 129	< 728	--
Ru	< 472	< 2670	--
Sb	< 215	< 1214	--
Se	< 107	< 607	--
Si	1592	2670	60
Sn	< 644	< 3641	--
Sr	438	493	89
Te	< 644	< 3641	--
Th	< 429	< 2427	--
Ti	17 < x < 25	213	8 < x < 12
Tl	< 215	< 1214	--
U	9491	9560	99
V	< 23	< 121	--
W	< 858	< 4854	--
Y	8 < x < 24	< 121	--
Zn	89	151	59
Zr	42 < x < 57	< 121	--

(a) The value was determined by summing the amount of a given component in the caustic leaching solutions, the subsequent washing solutions, and the leached solids; the total concentration was then determined by dividing the sum by the amount of solids processed.

Table 5.8. Anion Concentrations in the Various S-101 Process Solutions

	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		43,010	N/A(b)	46,240	N/A(b)	Not Determined	
NO_3^-	4,800	186,631	40,000	107,000	3,500	101500	560	10920
NO_2^-	1,620	62,988	12,600	33,705	1210	35090	280	N/A(c)
PO_4^{3-}	180	6,999	1,400	3,745	140	4060	25	488
SO_4^{2-}	270	10,498	2150	5,751	190	5510	29	566
F^-	30	1,166	300	803	< 250	< 7250	< 13	< 255
Cl^-	110	4,277	900	2,408	< 250	< 7250	20	390
Br^-	< 25	< 970	< 250	< 670	< 25	< 725	< 13	< 255

(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 5.9. Concentrations of the Radioactive S-101 Sludge Components in the Various Process Streams During Caustic Leaching

	First Leach Solution		Second Leach Solution	
Component	Conc., µCi/mL	Activity, µCi	Conc., µCi/mL	Activity, µCi
Total Alpha	< 2.58E-04	< 2.76E-03	< 2.60E-04	< 2.99E-02
$^{239,240}Pu$	< 2.58E-04	< 2.76E-03	< 2.60E-04	< 2.99E-02
$^{241}Am+^{238}Pu$	< 2.58E-04	< 2.76E-03	< 2.60E-04	< 2.99E-02
$^{241}Am(g)$	< 3.87E-02	< 4.14E-01	< 3.90E-03	< 4.49E-01
^{137}Cs	2.88E+01	3.08E+02	2.77E+00	3.18E+02
^{60}Co	< 3.87E-04	< 4.14E-03	< 3.90E-05	< 4.49E-03
^{154}Eu	< 2.58E-03	< 2.76E-02	< 2.60E-04	< 2.99E-02
^{155}Eu	< 3.87E-02	< 4.14E-01	< 2.60E-03	< 2.99E-01
^{90}Sr	< 9.03E-02	< 9.66E-01	6.81E-02	7.83E+00
^{99}Tc	1.14E-02	1.22E-01	2.11E-03	2.42E-01

	Final Wash Solution		Leached Solids		
Component	Conc., µCi/mL	Activity, µCi	Conc., µCi/g	Activity, µCi	Total Activity, µCi
Total Alpha	< 3.30E-04	< 2.57E-02	1.06E+01	2.36E+00	< 2.42E+00
$^{239,240}Pu$	< 3.30E-04	< 2.57E-02	7.20E+00	1.61E+00	< 1.66E+00
$^{241}Am+^{238}Pu$	< 3.30E-04	< 2.57E-02	3.23E+00	7.20E-01	< 7.79E-01
$^{241}Am(g)$	< 2.20E-03	< 1.72E-01	3.43E+00	7.65E-01	< 1.80E+00
^{137}Cs	4.31E-01	3.36E+01	1.23E+01	2.74E+00	6.63E+02
^{60}Co	< 3.30E-05	< 2.57E-03	3.01E-01	6.71E-02	< 7.83E-02
^{154}Eu	< 2.20E-04	< 1.72E-02	3.39E+00	7.56E-01	< 8.31E-01
^{155}Eu	< 8.80E-04	< 6.86E-02	2.19E+00	4.88E-01	< 1.27E+00
^{90}Sr	2.94E-02	2.29E+00	7.94E+03	1.77E+03	< 1.78E+03
^{99}Tc	2.82E-04	2.20E-02	< 6.00E-02	< 1.34E-02	< 4.00E-01

Table 5.10. Distribution of Radioactive S-101 Sludge Components Between the Various Process Streams During Caustic Leaching

	Component Distribution, %			
Component	First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids
Total Alpha	0	< 1	< 1	> 98
^{239,240}Pu	0	< 2	< 2	> 96
^{241}Am+^{238}Pu	0	< 4	< 3	> 93
^{241}Am(g)	< 23	< 25	< 10	> 43
^{137}Cs	46	48	5	0
^{60}Co	< 5	< 6	< 3	> 86
^{154}Eu	< 3	< 4	< 2	> 91
^{155}Eu	(a)	(a)	(a)	(a)
^{90}Sr	0	0	0	100
^{99}Tc	> 32	> 63	> 6	0

(a) Analyte was below detection limit for all solutions.

Table 5.11. Concentrations of the Radioactive Components in the Initial S-101 Sludge Solids: Results of the Caustic Leaching Portion of the Test

	Concentration in Initial Solids, µCi/g		
Component	Summation Method(a)	Direct Analysis	Recovery, %
Total Alpha	$0.59 < x < 0.61$	1.36E+00	$43 < x < 45$
^{239,240}Pu	$0.40 < x < 0.42$	4.80E-01	$84 < x < 87$
^{241}Am+^{238}Pu	$0.18 < x < 0.20$	6.28E-01	~30
^{241}Am(g)	$0.19 < x < 0.45$	< 7.00E-01	--
^{137}Cs	1.66E+02	1.38E+02	120
^{60}Co	$0.017 < x < 0.020$	< 5.00E-02	--
^{154}Eu	$0.19 < x < 0.21$	< 2.00E-01	--
^{155}Eu	< 3.17E-01	< 5.00E-01	--
^{90}Sr	4.45E+02	4.41E+02	101
^{99}Tc	$0.097 < x < 0.10$	1.40E-01	$69 < x < 71$

(a) The value was determined by summing the amount of a given component in the caustic leaching solutions, the subsequent washing solutions, and the leached solids; the total concentration was then determined by dividing the sum by the amount of sludge solids processed.

5.2.3 Particle-Size Analysis

Figure 5.2 presents the particle-size data for the untreated and treated S-101 sludge solids in terms of the number distributions, and Figure 5.3 presents the data in terms of the volume distributions. Leaching the sludge with caustic slightly reduced the mean particle size. The volume distribution for the untreated S-101 sludge indicated a mean particle size of 6.8 µm, while that for the treated material was 4.8 µm. Based on the number distribution, the mean particle decreased from 0.51 µm to 0.32 µm upon caustic leaching.

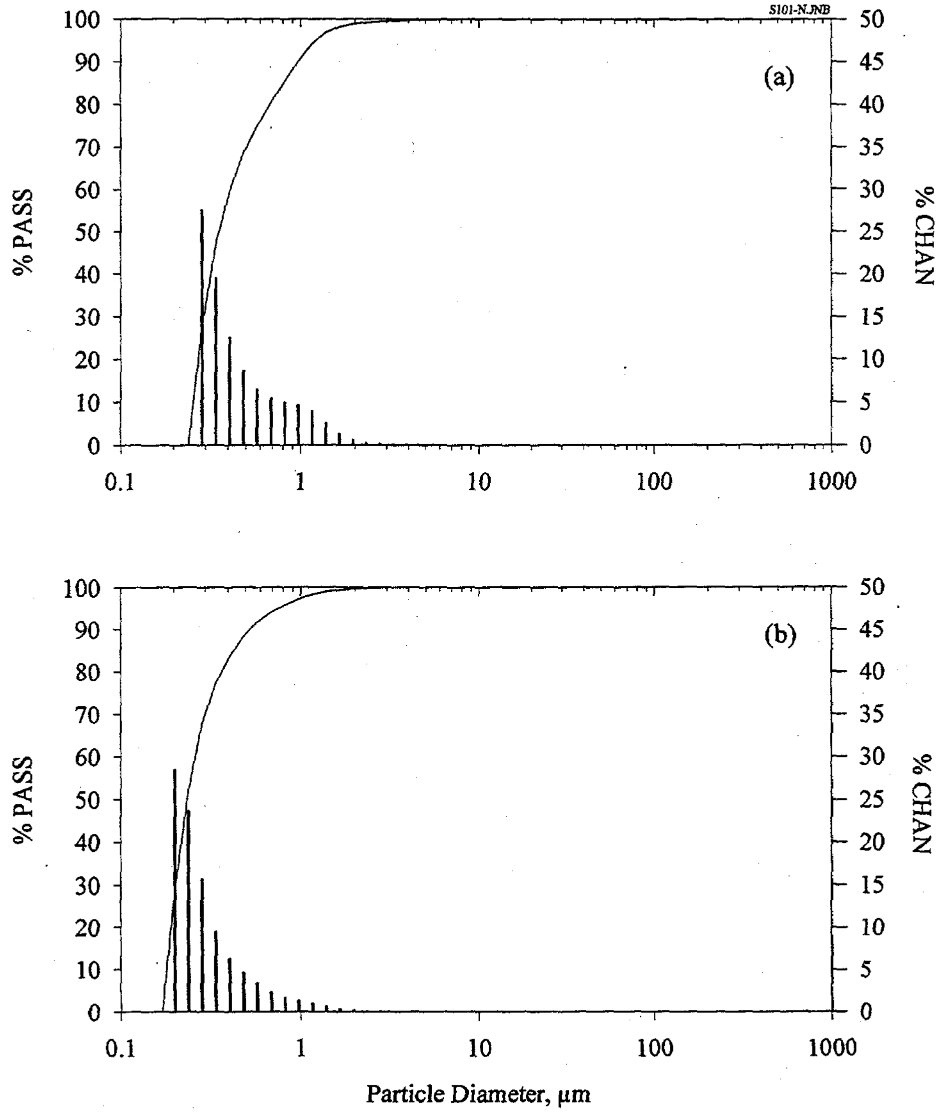


Figure 5.2. Particle-Size Number Distribution for Untreated (a) and Treated (b) S-101 Sludge

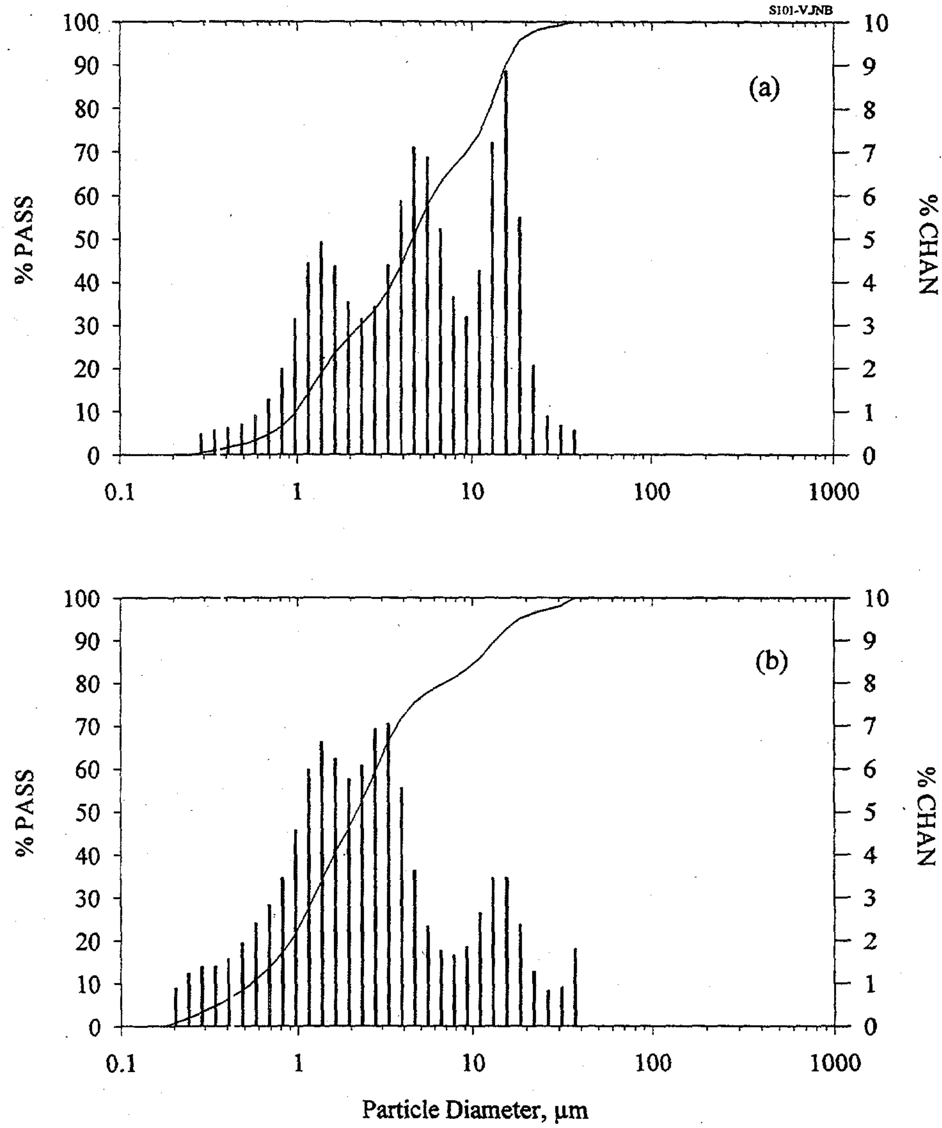


Figure 5.3. Particle-Size Volume Distribution for Untreated (a) and Treated (b) S-101 Sludge

5.2.4 Microscopic Analysis

Similar to S-107 (Lumetta et al. 1996) and S-104 (Section 3.0), boehmite was the predominant solid phase in the S-101 sludge. During leaching, the size of the boehmite particles decreased dramatically, and the edges of the particles became more rounded (Figure 5.4). Examination of the leached solids revealed the presence of amorphous aluminosilicates and rod-like aluminum oxyhydroxide (diaspore) (Figure 5.5). A mixed Mn(Fe)OOH phase was observed in the leached solids as were spherical particles of uranium oxides (Figure 5.4).

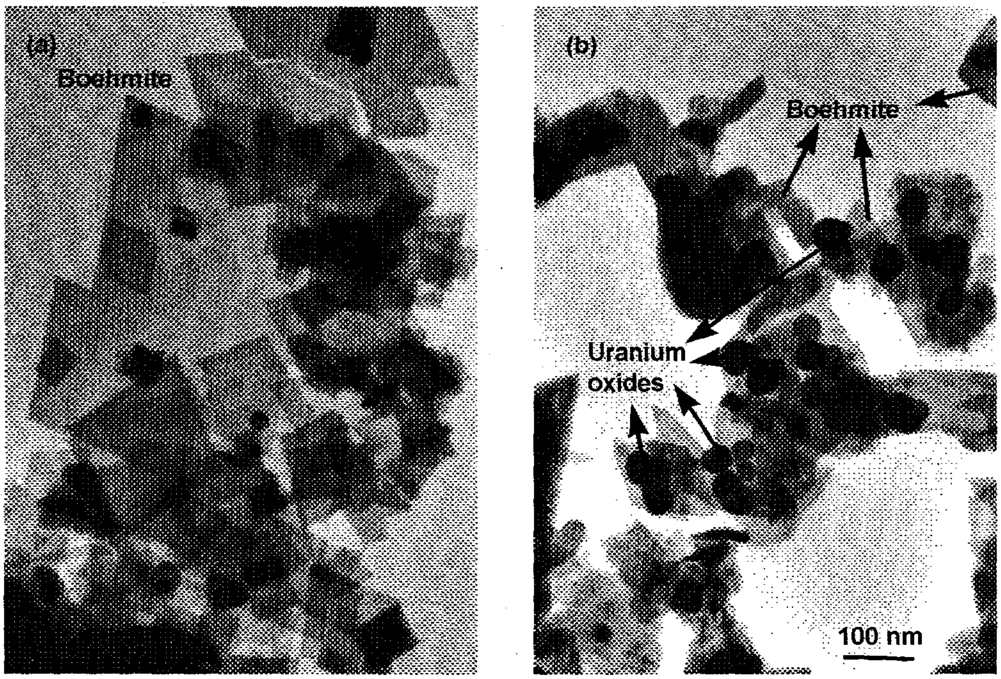


Figure 5.4. Micrograph of S-101 Sludge Boehmite Particles Before (a) and After (b) Leaching

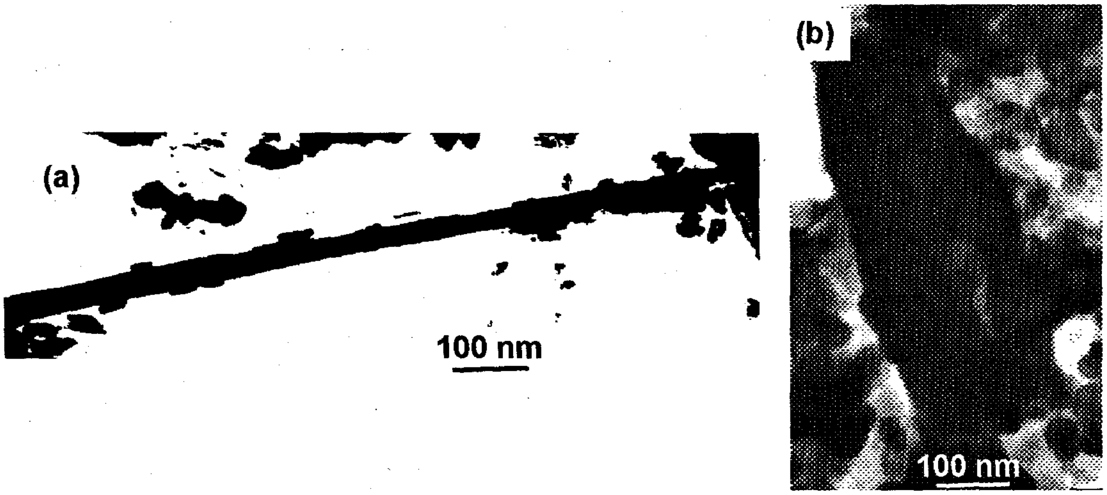


Figure 5.5. Rod-like Diaspore (a) and Amorphous Aluminosilicate (b) in the Leached S-101 Sludge

5.2.5 Settling Data

For the first leaching step, no settling occurred after the mixture had stood overnight. For the second leaching step, initial indications were that the settling was slow for this slurry as well, but the solids did settle after standing overnight. Because the second caustic leaching slurry had a very low undissolved solids concentration (0.2 wt%), it is likely that this slurry was in a regime where the particles fall freely through the solution. That is, the heavier particles settle to the bottom of the vessel first, and finer particles remain suspended, giving the solution a very cloudy appearance (this behavior would be difficult to observe through the hot cell window and the high-density polyethylene bottle used). Such behavior has been documented for other Hanford sludges; e.g., for S-107 sludge where the undissolved solids concentration in the second leaching slurry was 0.35 wt% (Lumetta et al. 1996). Table 5.12 and Figures 5.6 and 5.7 present the S-101 settling data from the final three washing steps. For the final washing steps, the undissolved solids concentration was 0.9 wt%. The data are presented in terms of the actual sludge height versus time (Figure 5.6) and in terms of normalized sludge height versus a dimensionless time value (Figure 5.7).[a] The settling behavior was similar for all three washes.

Table 5.12. Settling Data From the S-101 Caustic Leaching Test[a]

First Wash				Second Wash				Third Wash			
t, min	h, mm	T	H	t, min	h, mm	T	H	t, min	h, mm	T	H
0	35	0.0	1.0	0	35	0.00	1.00	0	38	0.00	1.00
1	33	0.14	0.94	1	30	0.14	0.86	1	35	0.13	0.92
2	31	0.29	0.89	2	25	0.29	0.71	2	30	0.26	0.79
3	25	0.43	0.71	3	20	0.43	0.57	3	25	0.39	0.66
4	20	0.57	0.57	4	17	0.57	0.49	4	19	0.53	0.50
5	15	0.71	0.43	5	15	0.71	0.43	5	16	0.66	0.42
6	14	0.86	0.40	6	14	0.86	0.40	6	14	0.79	0.37
8	13	1.14	0.37	7	13	1.00	0.37	7	13	0.92	0.34
10	12	1.43	0.34	10	12	1.43	0.34	10	12	1.32	0.32
13	11	1.86	0.31	15	11	2.14	0.31	15	11	1.97	0.29
30	9	4.29	0.26	35	10	5.00	0.29	25	10	3.29	0.26
45	9	6.43	0.26	95	9	13.6	0.26	55	10	7.24	0.26
75	9	10.7	0.26	1130	8	161	0.23	115	9	15.1	0.24
135	8	19.3	0.23								
1320	8	189	0.23								

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

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[a] Data were normalized according to a formula suggested by G.T. MacLean, SGN Eurisys Services Corp., personal communication, 1996. The formula is given in Table 5.12.

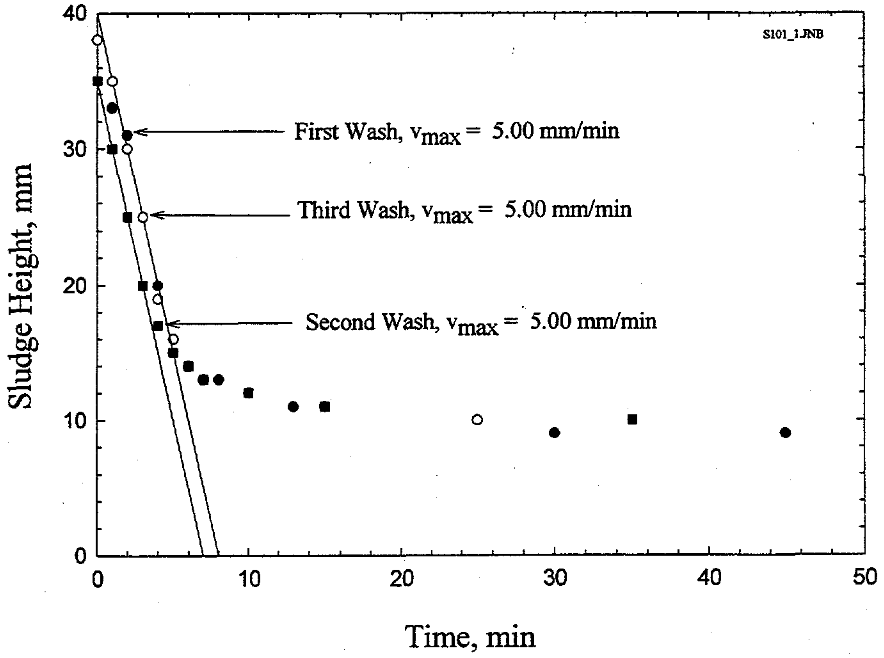


Figure 5.6. Settling Data From the S-101 Caustic Leaching Test

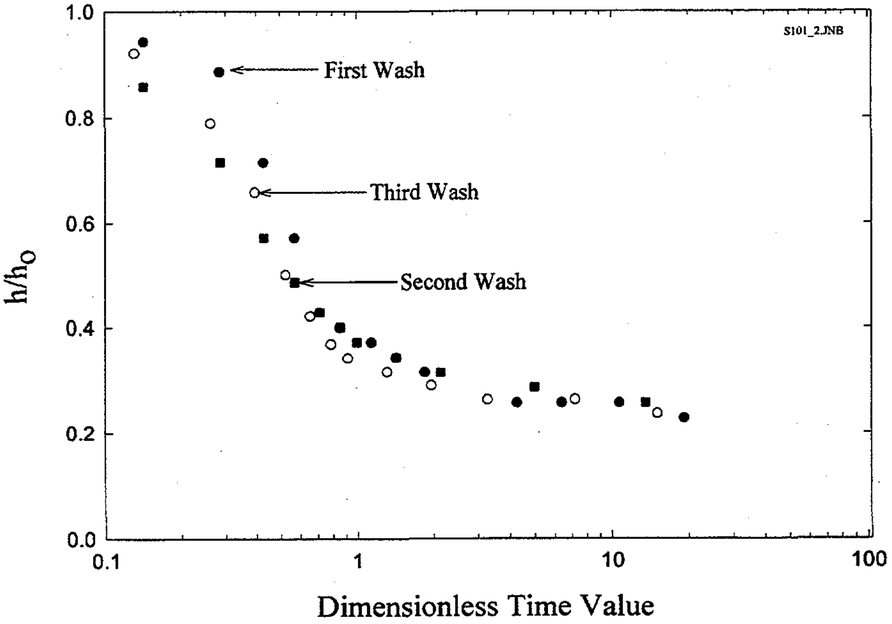


Figure 5.7. Normalized Settling Data From the S-101 Caustic Leaching Test

6.0 Tank S-111 Enhanced Sludge Washing Test

This section presents the results of the ESW test performed on Hanford Tank S-111 sludge. The sludge sample used in this test was received at PNNL on December 5, 1996; the 222-S laboratory ID for this sample was S96T005106, and the jar number was 11150.

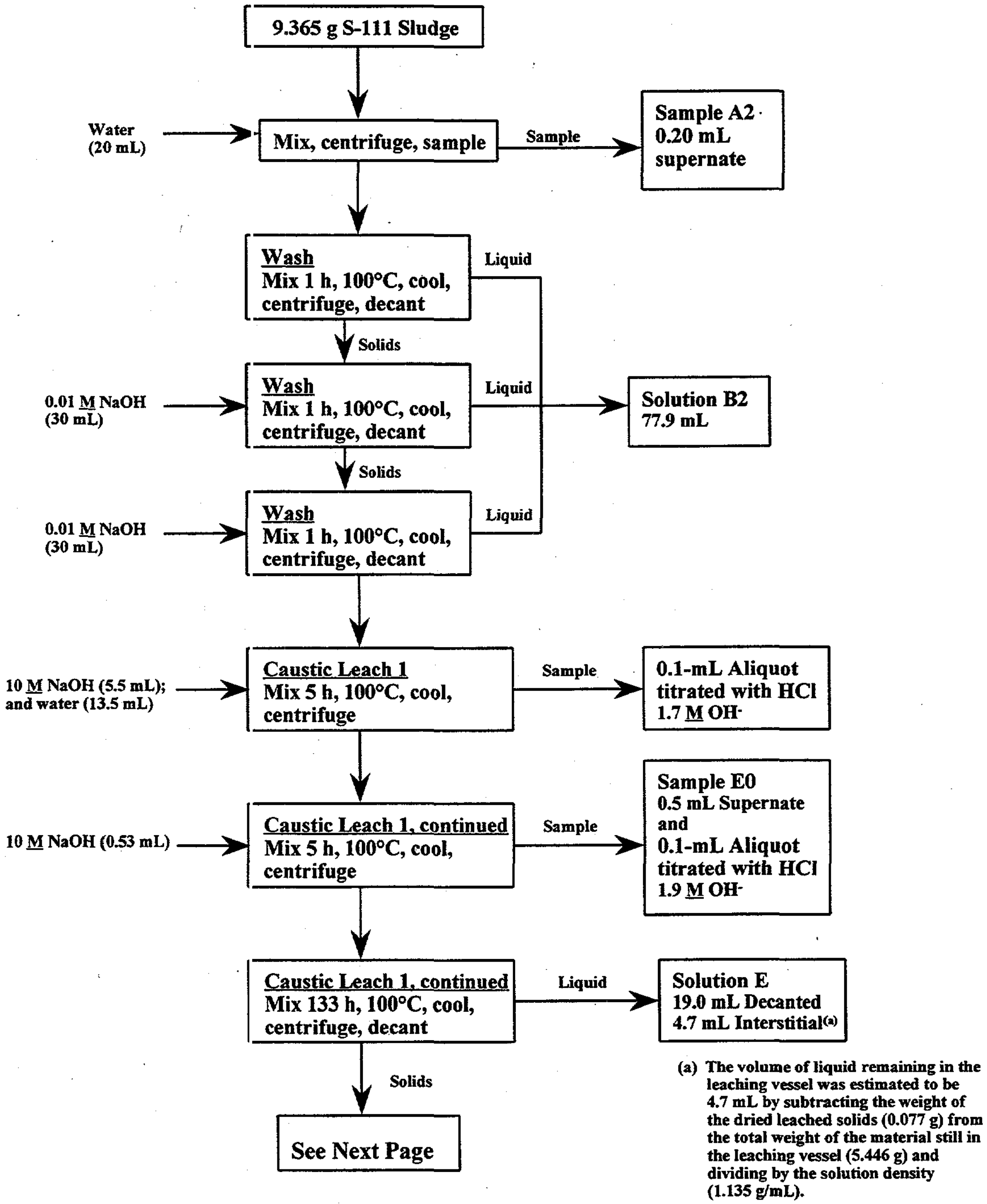
6.1 Experimental

Figure 6.1 summarizes the experimental procedure used in the S-111 ESW test. When the sludge was mixed in water for the initial sampling, the sludge particles partitioned between those that were readily mixed and heavier particles that stayed near the bottom of the vial. Hence, it was impossible to withdraw aliquots that would be representative of the entire sludge sample. Because of this, no samples were taken for the untreated sludge. Due to this complication, the procedure used deviated somewhat from the standard baseline ESW test procedure. In this test, the sludge was first washed with dilute sodium hydroxide solution. Two successive caustic leaching steps were then performed; as the S-111 is a REDOX sludge, extended leaching times were used to assess the kinetics of Al dissolution. To determine the leaching volumes, it was assumed that 35 wt% of the material left after the initial washing steps would remain undissolved after caustic leaching. The weight of the wet-washed sludge was 3.074 g; thus it was estimated that a leaching slurry of ~19 mL would yield 5 wt% solids in the first leaching step and a leaching slurry of ~95 mL would give 1 wt% solids in the second leaching step. Following the second caustic leaching step, the leached sludge was washed with 0.01 M NaOH/0.01 M $NaNO_2$. Settling rates for the solids could not be determined because the heavier solids settled very rapidly, and the liquid phase generally could not be clearly distinguished from the solid phase as the smaller solids settled.

6.2 Results and Discussion

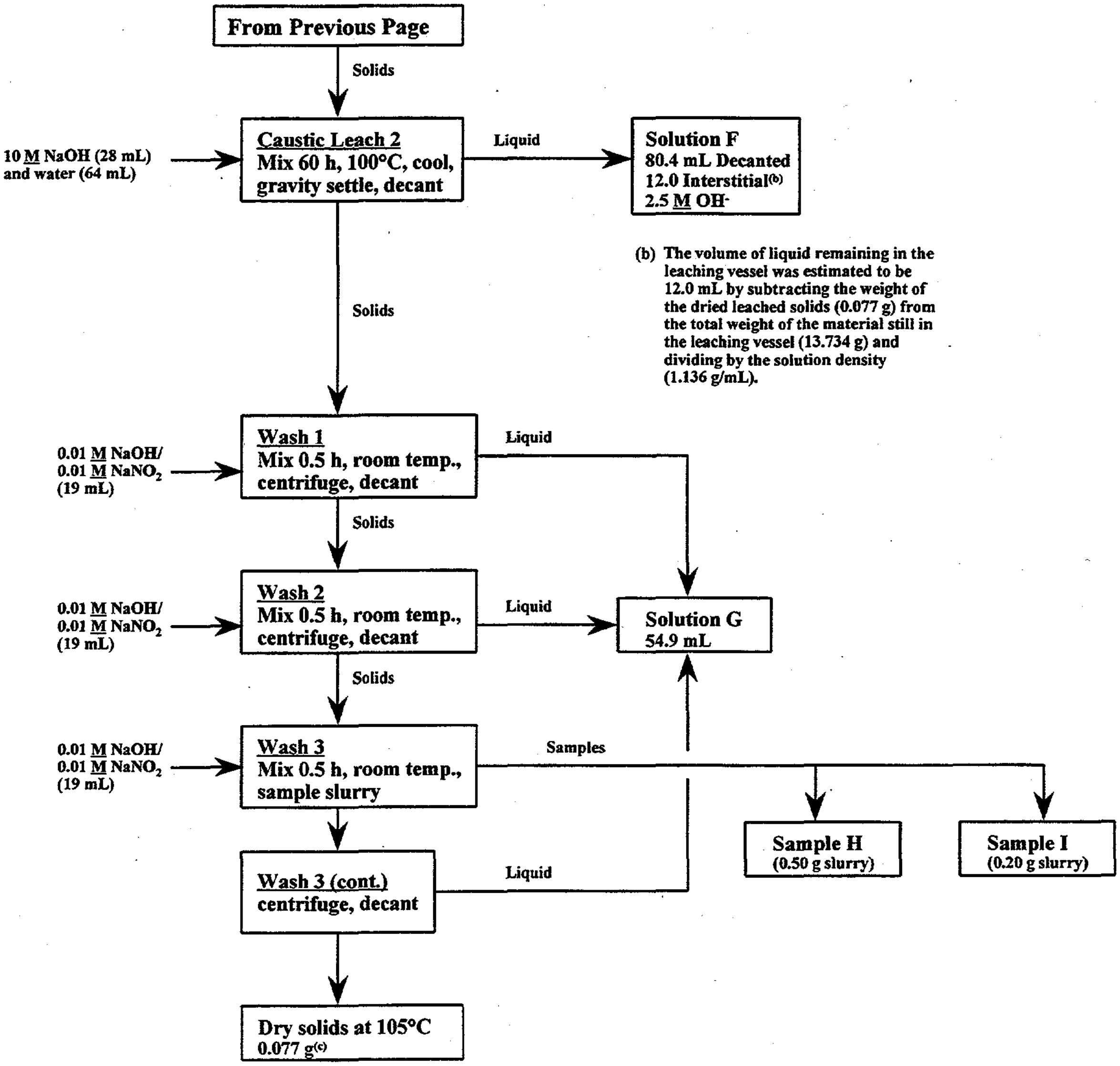
Table 6.1 presents the concentrations of most of the nonradioactive sludge components in each process stream, Table 6.2 presents the concentrations of those components in the untreated S-111 sludge, and Table 6.3 presents the distribution of those sludge components between the various process streams. The values presented in Table 6.3 are not adjusted for material contained in the interstitial liquid, but rather represent the amount of each component contained in the liquid that was decanted in a given step (or in the residual solid).

Excluding Na, the most abundant metallic element in the S-111 sludge was Al; the as-received (wet) sludge sample contained 16.0 wt% Al. The Al was largely water-insoluble, with only 10% being removed by dilute hydroxide washing. However, caustic leaching was very effective at dissolving the Al. As was the case with S-104 (Section 3.0) and S-101 (Section 5.0) sludges, kinetics played an important role in determining the amount of Al removed from the S-111 sludge by caustic leaching. After a total of 10 h of leaching at 100°C, the Al concentration in the first leaching step was 20,500 µg/mL. The Al concentration had increased to 37,200 µg/mL after a total of 143 h of leaching at 100°C, representing



(a) The volume of liquid remaining in the leaching vessel was estimated to be 4.7 mL by subtracting the weight of the dried leached solids (0.077 g) from the total weight of the material still in the leaching vessel (5.446 g) and dividing by the solution density (1.135 g/mL).

Figure 6.1. Schematic Representation of the S-111 ESW Test



(b) The volume of liquid remaining in the leaching vessel was estimated to be 12.0 mL by subtracting the weight of the dried leached solids (0.077 g) from the total weight of the material still in the leaching vessel (13.734 g) and dividing by the solution density (1.136 g/mL).

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

S111_IB.PPT

Figure 6.1. (contd)

Table 6.1. Concentrations of the Nonradioactive S-111 Sludge Components in the Various Process Streams

	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	Conc., μg/mL	Mass, μg	Conc., μg/g	Mass, μg	Total Mass, μg
Ag	< 0.13125	< 11	0.279	6	< 0.125	< 10	< 0.125	< 7	< 85	< 7	< 40
Al	1806	141897	37200	717046	6740	541896	1760	96448	40500	3131	1500417
As	< 1.3125	< 106	< 1.9375	< 41	< 1.25	< 101	< 1.25	< 69	< 853	< 66	< 382
B	3.759	295	0.7285	15	0.41	33	0.25	14	< 171	< 13	< 370
Ba	< 0.0525	< 4	< 0.0775	< 2	< 0.05	< 4	< 0.05	< 3	189	15	< 27
Be	< 0.0525	< 4	< 0.0775	< 2	< 0.05	< 4	< 0.05	< 3	< 34	< 3	< 15
Bi	< 0.525	< 42	4.495	87	1.2	96	< 0.5	< 27	< 341	< 26	< 280
Ca	2.52	200	4.96	98	< 1.25	< 101	1.3	71	8810	681	< 1151
Cd	< 0.07875	< 6	4.6655	89	0.24	19	< 0.075	< 4	105	8	< 127
Ce	< 1.05	< 85	< 1.55	< 33	< 1	< 80	< 1	< 55	< 682	< 53	< 305
Co	< 0.2625	< 21	0.6975	14	< 0.25	< 20	< 0.25	< 14	< 171	< 13	< 82
Cr	81.585	6407	1215.2	23181	52.1	4189	13.7	751	7090	548	35076
Cu	< 0.13125	< 11	< 0.19375	< 4	0.27	22	< 0.125	< 7	< 85	< 7	< 50
Dy	< 0.2625	< 21	< 0.3875	< 8	< 0.25	< 20	< 0.25	< 14	< 171	< 13	< 76
Eu	< 0.525	< 42	< 0.775	< 16	< 0.5	< 40	< 0.5	< 27	< 341	< 26	< 153
Fe	0.357	28	1.054	20	2.03	163	0.36	20	2500	193	425
K	72.45	5680	17.05	355	< 10	< 804	< 10	< 548	(b)	(b)	< 7387
La	< 0.2625	< 21	< 0.3875	< 8	< 0.25	< 20	< 0.25	< 14	< 171	< 13	< 76
Li	< 0.1575	< 13	0.248	5	< 0.15	< 12	< 0.15	< 8	< 102	< 8	< 46
Mg	< 0.525	< 42	3.41	66	< 0.5	< 40	< 0.5	< 27	936	72	< 249
Mn	< 0.2625	< 21	0.806	16	< 0.25	< 20	< 0.25	< 14	5450	421	< 492
Mo	2.415	190	< 0.3875	< 8	< 0.25	< 20	< 0.25	< 14	< 171	< 13	< 245
Na	15750	1236623	73625	1430185	49500	3979800	12400	679520	220200	17021	(c) -615851
Nd	< 0.525	< 42	0.9145	19	< 0.5	< 40	< 0.5	< 27	416	32	< 161
Ni	< 0.1575	< 13	< 0.2325	< 9	< 0.15	< 12	< 0.15	< 8	(b)	(b)	< 42
P	237.3	18642	< 0.775	< 16	< 0.5	< 40	< 0.5	< 27	< 341	< 26	< 18752
Pb	< 0.525	< 42	< 0.775	< 16	< 0.5	< 40	< 0.5	< 27	412	32	< 158
Pd	< 3.9375	< 318	< 5.8125	< 122	< 3.75	< 302	< 3.75	< 206	< 2560	< 198	< 1145
Rh	< 1.575	< 127	< 2.325	< 49	< 1.5	< 121	< 1.5	< 82	< 1024	< 79	< 458
Ru	< 5.775	< 467	< 8.525	< 179	< 5.5	< 442	< 5.5	< 301	< 3754	< 290	< 1679
Sb	< 2.625	< 212	< 3.875	< 81	< 2.5	< 201	< 2.5	< 137	< 1707	< 132	< 763
Se	< 1.3125	< 106	< 1.9375	< 41	< 1.25	< 101	< 1.25	< 69	< 853	< 66	< 382
Si	37.905	2982	82.15	1574	12	965	< 2.5	< 137	9650	746	< 6404
Sn	< 7.875	< 636	< 11.625	< 244	< 7.5	< 603	< 7.5	< 411	< 5120	< 396	< 2290
Sr	< 0.07875	< 6	< 0.11625	< 2	0.12	10	< 0.075	< 4	179	14	< 36
Te	< 7.875	< 636	< 11.625	< 244	< 7.5	< 603	< 7.5	< 411	< 5120	< 396	< 2290
Th	< 5.25	< 424	38.75	752	< 5	< 402	< 5	< 274	< 3413	< 264	< 2116
Ti	< 0.13125	< 11	0.3565	7	< 0.125	< 10	< 0.125	< 7	106	8	< 43
Tl	< 2.625	< 212	< 3.875	< 81	< 2.5	< 201	< 2.5	< 137	< 1707	< 132	< 763
U	4.5885	388	10.0905	223	1.88	151	7.25	397	3790	293	< 1452
V	< 0.2625	< 21	< 0.3875	< 8	< 0.25	< 20	< 0.25	< 14	< 171	< 13	< 76
W	< 10.5	< 848	< 15.5	< 326	< 10	< 804	< 10	< 548	< 6826	< 528	< 3053
Y	< 0.2625	< 21	< 0.3875	< 8	< 0.25	< 20	< 0.25	< 14	< 171	< 13	< 76
Zn	1.89	148	2.79	54	0.79	64	0.28	15	416	32	314
Zr	< 0.2625	< 21	< 0.3875	< 8	< 0.25	< 20	< 0.25	< 14	< 171	< 13	< 76

(a) Includes mass in analytical sample

(b) The Na_2O fusion could not be done due to lack of sample. Therefore K and Ni data on the solids are not available.

(c) Mass of Na added in leaching and washing is subtracted.

Table 6.2. Concentrations of the Nonradioactive S-111 Sludge Components in the Untreated Sludge (a)

Component	Concentration in Sludge, μg/g wet sludge
Ag	$1 < x < 4$
Al	160215
As	< 41
B	$38 < x < 39$
Ba	$2 < x < 3$
Be	< 2
Bi	$20 < x < 30$
Ca	$112 < x < 123$
Cd	$12 < x < 14$
Ce	< 33
Co	$1 < x < 9$
Cr	3745
Cu	$2 < x < 5$
Dy	< 8
Eu	< 16
Fe	45
K	> 644
La	< 8
Li	$1 < x < 5$
Mg	$15 < x < 27$
Mn	$47 < x < 53$
Mo	$20 < x < 26$
Na	(b)
Nd	$5 < x < 17$
Ni	< 5
P	$1991 < x < 2002$
Pb	$3 < x < 17$
Pd	< 122
Rh	< 49
Ru	< 179
Sb	< 82
Se	< 41
Si	$669 < x < 684$
Sn	< 245
Sr	$3 < x < 4$
Te	< 245
Th	$80 < x < 226$
Ti	$2 < x < 5$
Tl	< 82
U	< 155
V	< 8
W	< 326
Y	< 8
Zn	34
Zr	< 8

(a) Concentrations detemined by summing the amount of component found in each process step and dividing by the amount of sludge used in the test component.

(b) Due to the amount of Na added in leaching and washing steps, the Na concentration in the untreated sludge could not be determined.

Table 6.3. Distribution of Nonradioactive S-111 Sludge Components Between the Various Process Streams

	Component Distribution, %				
Component	Initial Wash	First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids
Ag	<27	>14	<26	<17	<17
Al	9	48	36	6	0
As	(a)	(a)	(a)	(a)	(a)
B	$80<x<83$	4	9	4	<4
Ba	<16	<6	<15	<10	>53
Be	(a)	(a)	(a)	(a)	(a)
Bi	<15	$31<x<47$	$35<x<53$	<10	<9
Ca	$17<x<19$	9	<9	$6<x<7$	$59<x<65$
Cd	<5	$70<x<76$	$15<x<17$	<3	$6<x<7$
Ce	(a)	(a)	(a)	(a)	(a)
Co	<26	>17	<24	<17	<16
Cr	18	66	12	2	2
Cu	<21	<8	>44	<14	<13
Dy	(a)	(a)	(a)	(a)	(a)
Eu	(a)	(a)	(a)	(a)	(a)
Fe	7	5	38	5	45
K	(b)	(b)	(b)	(b)	(b)
La	(a)	(a)	(a)	(a)	(a)
Li	<28	>11	<26	<18	<17
Mg	<17	$27<x<48$	<16	<11	$29<x<52$
Mn	<4	$3<x<4$	<4	<3	$86<x<96$
Mo	>77	<3	<8	<6	<5
Na	(c)	(c)	(c)	(c)	(c)
Nd	<26	$12<x<37$	<25	<17	$20<x<63$
Ni	(b)	(b)	(b)	(b)	(b)
P	100	0	0	0	0
Pb	<27	<10	<25	<17	>20
Pd	(a)	(a)	(a)	(a)	(a)
Rh	(a)	(a)	(a)	(a)	(a)
Ru	(a)	(a)	(a)	(a)	(a)
Sb	(a)	(a)	(a)	(a)	(a)
Se	(a)	(a)	(a)	(a)	(a)
Si	$47<x<48$	25	15	<2	12
Sn	(a)	(a)	(a)	(a)	(a)
Sr	<17	<7	$27<x<41$	<11	$38<x<59$
Te	(a)	(a)	(a)	(a)	(a)
Th	<20	>36	<19	<13	<12
Ti	<25	$17<x<47$	<23	<16	$19<x<53$
Tl	(a)	(a)	(a)	(a)	(a)
U	27	15	10	27	20
V	(a)	(a)	(a)	(a)	(a)
W	(a)	(a)	(a)	(a)	(a)
Y	(a)	(a)	(a)	(a)	(a)
Zn	47	17	21	5	10
Zr	(a)	(a)	(a)	(a)	(a)

(a) Analyte was below detection limit for all process streams.

(b) The Na_2O fusion could not be done due to lack of sample. Therefore K and Ni data on the solids are not available.

(c) Percentage of Na in each solution could not be tracked because of Na added during testing.

nearly a 2-fold increase in the amount of Al dissolved. The solution decanted from the first leaching step contained 47% of the Al, but if the amount of dissolved Al in the interstitial liquid is included, a total of 59% of the Al was dissolved in the first leaching step.

The first caustic leaching solution was stable for up to 12 days, but a white precipitate had formed after 100 days. Based on published data for gibbsite solubility in aqueous NaOH (LaFemina 1995), the first caustic leaching solution was indeed supersaturated with respect to Al. At 25°C, the solubility for gibbsite is 0.25 m at 2.8 m Na (which was the Na concentration in the leaching solution). The Al concentration of 37,200 μg/mL reported in Table 6.1 corresponds to 1.21 m Al, which is nearly 5 times the thermodynamic solubility at 25°C. Interestingly, the gibbsite solubility is 1.4 m at 2.8 m Na and 100°C. Thus, it appears likely that Al removal in the first caustic leaching step was solubility limited.

Again, because the previous studies with S-104 and S-101 sludges indicated slow Al dissolution for REDOX sludges, the second leaching step for S-111 sludge was conducted for 60 h at 100°C, rather than the usual 5 h. The solution decanted after the second leaching step contained 36% of the Al. Accounting for carry-over of interstitial liquid from the first leaching step and that left in the interstitial liquid after decanting, 30% more Al dissolved in the second leaching step. The data indicate than another 1% of the Al dissolved in the final washing step, so the cumulative Al removal was virtually 100%.

Regarding the behavior of Cr, the initial dilute hydroxide washing removed only 18% of the Cr from the sludge. Spectrophotometry (UV/vis) indicated the presence of Cr(VI) in the dilute hydroxide wash solution, but the presence of Cr(III) could not be ruled out. Caustic leaching significantly increased the amount of Cr removed. The solution decanted in the first leaching step contained 66% of the Cr, but accounting for that contained in the interstitial liquid after decanting, 80% of the Cr was actually dissolved in the first leaching step. Little or no additional Cr dissolution occurred in the subsequent leaching and washing steps. The cumulative Cr removal was 98%. As with Al, kinetics played a significant role in the removal of Cr from the S-111 sludge. During the first leaching step, the Cr concentration increased from 185 μg/mL at 10 h of leaching to 1215 μg/mL at 143 h of leaching, representing nearly a 6.6-fold increase in the amount of Cr dissolved.

The UV/vis spectrum was recorded on a 100-fold dilution of the first caustic leaching solution. Again, UV/vis spectrophotometry indicated that the dissolved Cr was mostly Cr(VI), so the mechanism of Cr removal appeared to involve oxidation from Cr(III) to Cr(VI). The concentration of Cr determined spectrophotometrically as CrO_4^{2-} was 1080 μg/mL, which is slightly less than the value of 1215 μg/mL determined by ICP/AES, but within the 15% experimental uncertainty in the ICP/AES measurement. It could not be determined if the 135 μg/mL difference was due to Cr(III) in solution or simply to analytical uncertainty. Based on the UV/vis spectrum, the Cr(III) concentration in the first leaching solution was less than 490 μg/mL. The spectrophotometric measurements were repeated 166 days after the first leaching solution had first been sampled.(a) In this case, the solution was not diluted before measuring the spectrum. Again, no Cr(III) was detected in the undiluted solution. For the undiluted solution, the

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(a) As noted previously, a white precipitate (presumably aluminum hydroxide) had precipitated from the solution during this interval. The solution was filtered through a 0.2-μm membrane before measuring the spectrum.

detection limit for Cr(III) was 25 µg/mL. A 128-fold dilution was made so that the Cr(VI) concentration could be determined again; a value of 1200 µg Cr(VI)/mL was obtained. This value was even closer to the total Cr concentration determined by ICP/AES. But due to the uncertainties in the measurements, it was impossible to determine if this reflected a more accurate measurement, or if some Cr(III) was indeed originally in the leach solution that oxidized over the 166-day period. Also, evaporation could not be ruled out as a reason for the slight increase in the measured Cr(VI) concentration.

The P concentration in the S-111 sludge was quite low (< 0.2 wt % in the wet sludge). Virtually all of the P was removed by dilute hydroxide washing.

Table 6.4 presents the anion concentrations in the various process solutions. The data suggest that no further nitrate, nitrite, sulfate, phosphate, or chloride were removed after the initial dilute hydroxide washing step.

Table 6.5 presents the concentrations of various radioactive sludge components in each process stream, and Table 6.6 presents the distribution of those sludge components between the various process streams. Strontium-90 and ^{137}Cs accounted for most of the activity in the sludge; the TRU content in the sludge was quite low—less than 0.016 µCi/g of wet sludge. About half of the ^{137}Cs was removed by dilute hydroxide washing, and most of the rest was removed by caustic leaching. The ^{90}Sr in the S-111 sludge displayed unusual behavior. The ^{90}Sr concentration in the initial washing step was below the detection limit, which is usually the case for the alkaline Hanford sludges. However, appreciable ^{90}Sr dissolved in the first, and especially, the second caustic leaching steps. The reason for this is not clear. Assuming the LLW glass form will contain 20 wt% Na_2O (Orme et al. 1996) with a density of 2.7 metric tons/m^3, the LLW form resulting from immobilization of only these solutions would be projected to contain 5 Ci ^{90}Sr/m^3. As current plans target a LLW form with less than 20 Ci ^{90}Sr/m^3, no ^{90}Sr removal from the S-111 leaching and washing solutions would be required.

Table 6.4. Anion Concentrations in the Various S-111 Process Solutions

	Concentration, µg/mL			
Component	Wash Solution	First Leach Solution	Second Leach Solution	Final Wash Solution
OH^-	Not Determined	32,640	42,500	Not Determined
NO_3^-	8,100	80	< 20	< 20
NO_2^-	2,890	40	< 20	80$^{(a)}$
PO_4^{3-}	670	30	< 20	< 20
SO_4^{2-}	1970	< 20	< 20	< 20
F^-	< 50	< 50	< 50	< 50
Cl^-	270	< 50	< 50	< 50
Br^-	< 50	< 5	< 5	< 5

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

Table 6.5. Concentrations of the Radioactive S-111 Sludge Components in the Various Process Streams

Component	Initial Wash Solution		First Leach Solution		Second Leach Solution	
	Conc., µCi/mL	Activity, µCi	Conc., µCi/mL	Activity, µCi	Conc., µCi/mL	Activity, µCi
Total Alpha	< 2.00E-04	< 2.60E-04	< 4.00E-05	< 7.60E-04	< 2.00E-04	< 1.61E-02
^{239,240}Pu	< 2.00E-04	< 2.60E-04	< 4.00E-05	< 7.60E-04	< 2.00E-04	< 1.61E-02
^{241}Am+^{238}Pu	< 2.00E-04	< 2.60E-04	< 4.00E-05	< 7.60E-04	< 2.00E-04	< 1.61E-02
^{241}Am(g)	< 3.00E-03	< 3.90E-03	< 6.00E-04	< 1.14E-02	< 5.00E-04	< 4.02E-02
^{137}Cs	2.96E+00	3.85E+00	1.29E-01	2.45E+00	1.44E-02	1.16E+00
^{60}Co	< 4.00E-05	< 5.20E-05	< 2.00E-05	< 3.80E-04	< 3.00E-05	< 2.41E-03
^{154}Eu	< 2.00E-04	< 2.60E-04	< 1.00E-04	< 1.90E-03	< 9.00E-05	< 7.24E-03
^{155}Eu	< 3.00E-03	< 3.90E-03	< 4.00E-04	< 7.60E-03	< 3.00E-04	< 2.41E-02
^{90}Sr	< 2.00E-02	< 2.60E-02	1.73E-02	3.29E-01	7.71E-01	6.20E+01
^{99}Tc	2.08E-03	2.70E-03	9.35E-04	1.78E-02	8.44E-05	6.79E-03

Component	Final Wash Solution		Leached Solids		Total Activity, µCi	Concentration, µCi/g wet sludge
	Conc., µCi/mL	Activity, µCi	Conc., µCi/g	Activity, µCi		
Total Alpha	< 3.00E-04	< 1.64E-02	1.46E+00	1.13E-01	< 1.46E-01	$0.012 < x < 0.016$
^{239,240}Pu	< 3.00E-04	< 1.64E-02	4.11E-01	3.18E-02	< 6.53E-02	$0.0034 < x < 0.0070$
^{241}Am+^{238}Pu	< 3.00E-04	< 1.64E-02	< 8.00E-03	< 6.18E-04	< 3.42E-02	< 3.65E-03
^{241}Am(g)	< 3.00E-04	< 1.64E-02	1.06E+00	8.19E-02	< 1.54E-01	$0.0087 < x < 0.0164$
^{137}Cs	2.97E-03	1.63E-01	4.11E+00	3.18E-01	7.94E+00	8.48E-01
^{60}Co	< 3.00E-05	< 1.64E-03	1.35E-01	1.04E-02	< 1.49E-02	$0.0011 < x < 0.0016$
^{154}Eu	< 7.00E-05	< 3.84E-03	1.01E+00	7.81E-02	< 9.13E-02	$0.008 < x < 0.010$
^{155}Eu	< 2.00E-04	< 1.10E-02	7.08E-01	5.47E-02	< 1.01E-01	$0.006 < x < 0.011$
^{90}Sr	3.88E-01	2.13E+01	1.01E+03	7.81E+01	< 1.62E+02	1.73E+01
^{99}Tc	1.78E-05	9.75E-04	6.04E-03	4.67E-04	2.87E-02	3.06E-03

Table 6.6. Distribution of Radioactive S-111 Sludge Components Between the Various Process Steams

Component	Component Distribution, %(a)				
	Initial Wash Solution	First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids
Total Alpha	< 1	< 1	< 11	< 11	> 76
^{239,240}Pu	< 1	< 1	< 25	< 25	> 48
^{241}Am+^{238}Pu	(a)	(a)	(a)	(a)	(a)
^{241}Am(g)	< 3	< 7	< 26	< 11	> 53
^{137}Cs	48	31	15	2	4
^{60}Co	< 1	< 3	< 16	< 11	> 69
^{154}Eu	< 1	< 2	< 8	< 4	> 85
^{155}Eu	< 4	< 8	< 24	< 11	> 53
^{90}Sr	0	0	38	13	48
^{99}Tc	9	62	24	3	2

(a) Analyte was below detection limit for all solutions.

The ^{99}Tc behavior was also interesting. Only 9% of the ^{99}Tc was removed in the initial dilute hydroxide washing step, but caustic leaching resulted in nearly complete ^{99}Tc dissolution. This suggests that most of the ^{99}Tc was either tied up with Al (as pertechnetate) and was released as the Al dissolved, or was present in a lower oxidation state and was oxidized to pertechnetate during the caustic leaching steps (much in the same way Cr was oxidized to Cr(VI) during the leaching steps).

6.2.1 Particle-Size Analysis

As explained in Section 6.1, we were not able to obtain a representative sample of the untreated sludge solids; thus particle-size measurements were only made on the leached solids. Figures 6.2 and 6.3 present the particle-size data for the leached S-111 sludge solids in terms of the number and volume distributions, respectively, both before and after sonicating for 5 min. Previous measurements with

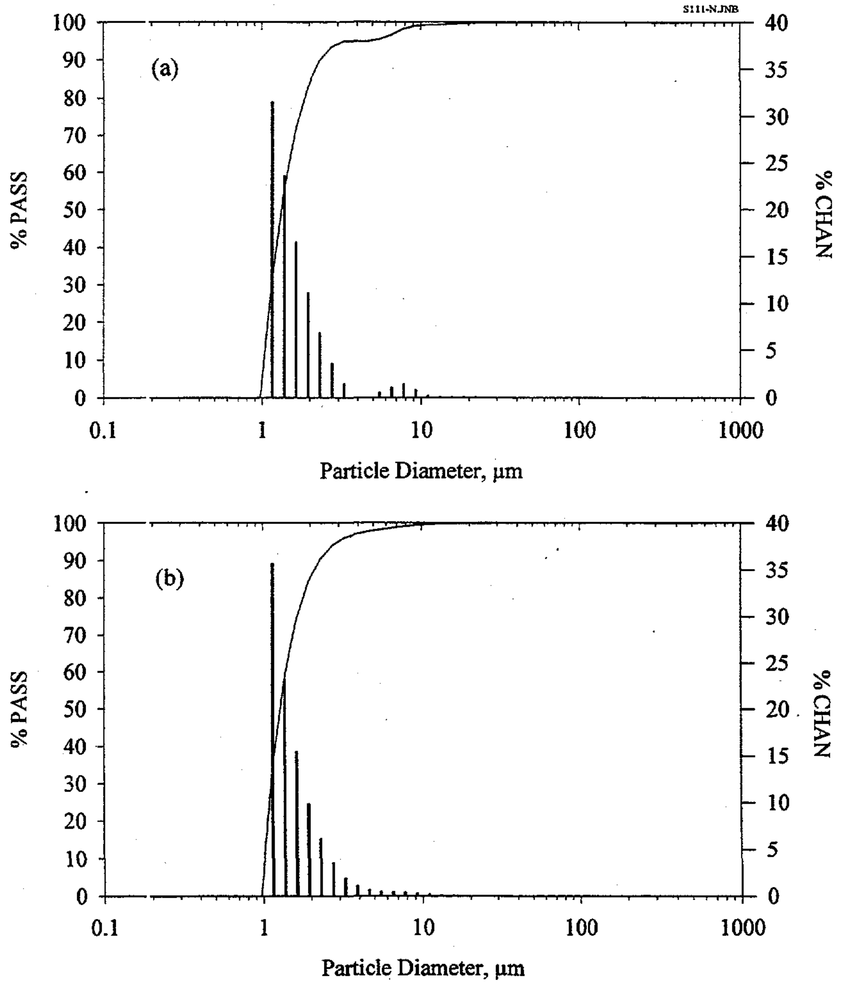


Figure 6.2. Particle-Size Number Distribution for Treated S-111 Sludge Before (a) and After (b) Sonication

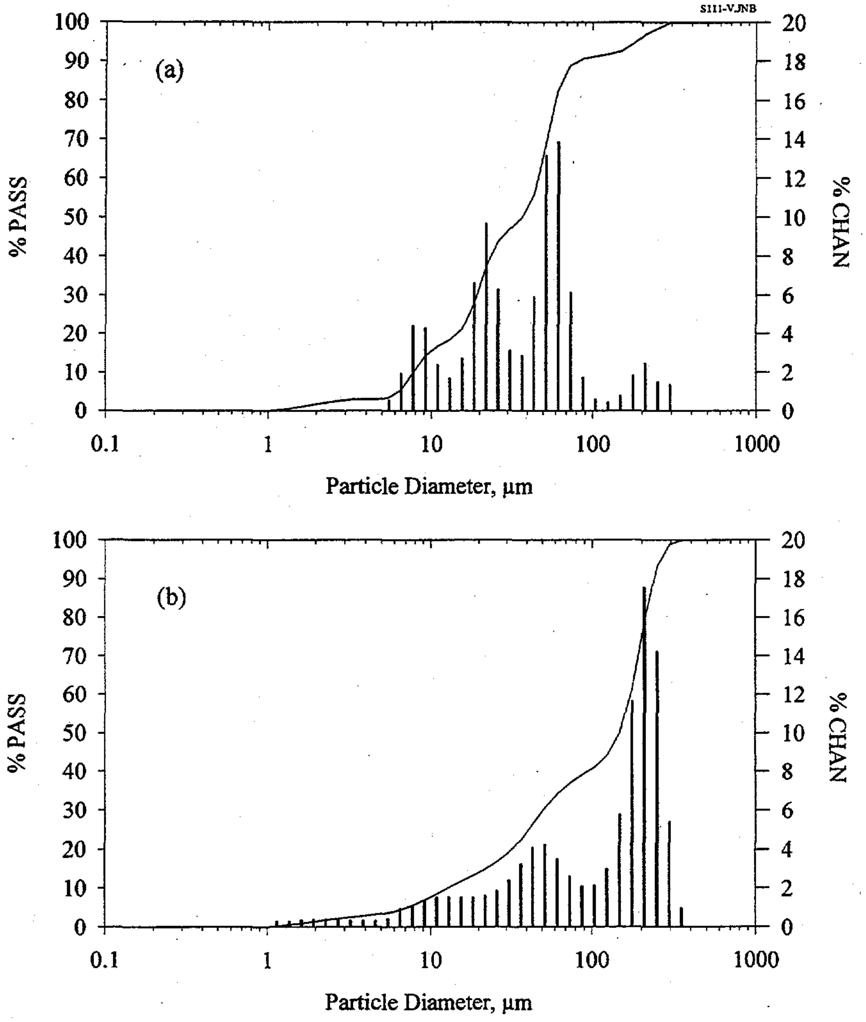


Figure 6.3. Particle-Size Volume Distribution for Treated S-111 Sludge Before (a) and After b) Sonication

Hanford sludges usually indicated that sonicating breaks up some of the larger sludge particles (e.g., see the BY-108 results in Section 4.2). However, in the case of S-111, the volume distribution suggests that sonicating increased the mean particle size from 47.7 µm to 129 µm. Based on the number distribution, sonicating had little effect with the mean particle size being 1.8 µm before sonication and 1.6 µm after. The reason for this unusual behavior is unknown.

6.2.2 Microscopic Analysis

As with the particle-size measurement, only the leached S-111 solids were examined by TEM. Bayerite [$Al(OH)_3$] and boehmite (AlOOH) were major phases identified in the leached sludge (Figure 6.4). This observation is consistent with the ICP analysis of the residual sludge solids, which revealed Al to be the

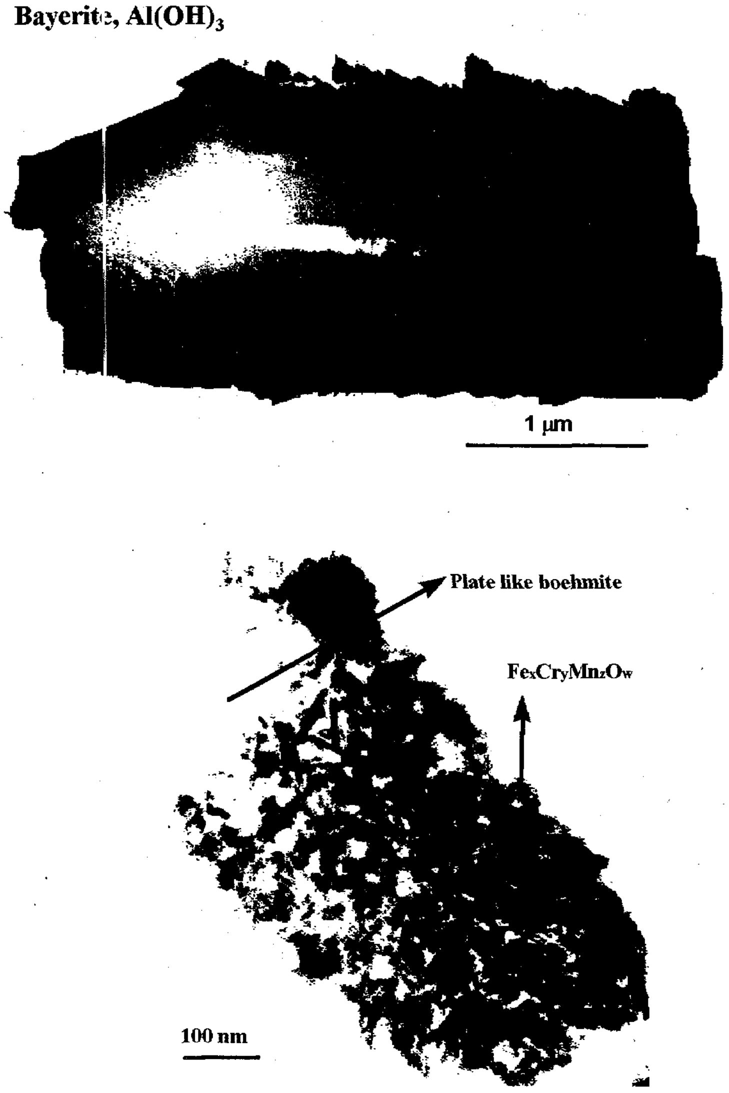


Figure 6.4. Aluminum-Containing Phases in Leached S-111 Sludge

most abundant metallic element besides Na (see Table 6.1). Although these were major phases in the leached solids, they represent a very small percentage of the mass of the untreated solids. A mixture of Fe, Cr, and Mn oxides were present in the leached S-111 solids (Figure 6.5). These elements can form a range of compounds with similar crystalline structure, such as $MnFe_2O_4$, $FeCr_2O_4$, Mn_2CrO_4, and $Mn_{1.5}Cr_{1.5}O_4$. The diffraction patterns obtained from the samples are consistent with these phases. Single-crystal UO_3 was also in the leached S-111 sludge solids.

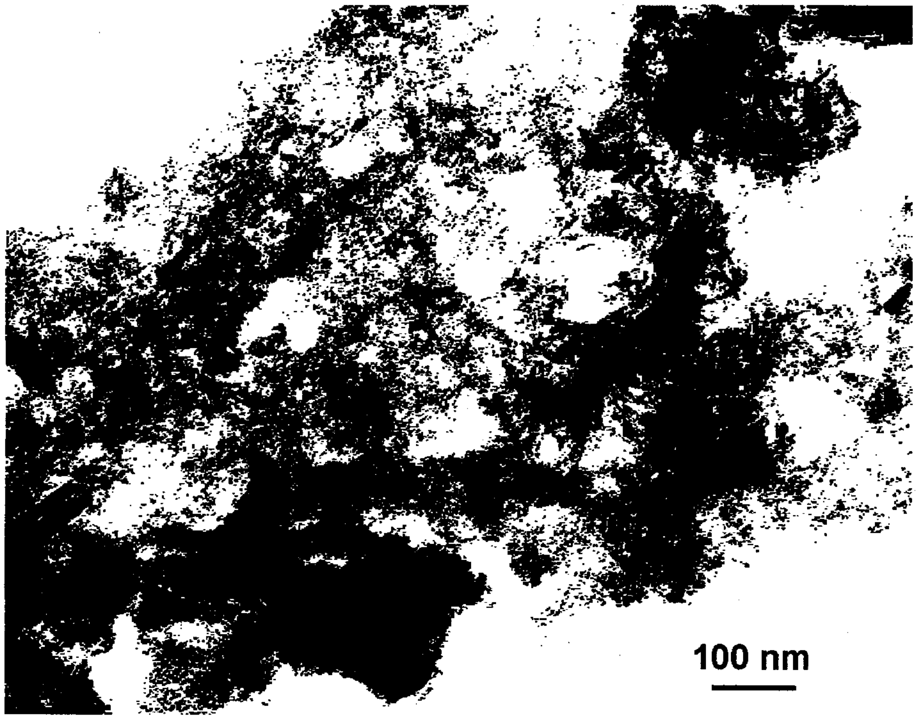


Figure 6.5. Mixed Fe, Cr, and Mn Phases in Leached S-111 Sludge

7.0 Tank AN-104 Enhanced Sludge Washing Test

This section presents the results of the ESW test performed on Hanford Tank AN-104 sludge. The sludge sample used in this test was received at PNNL on February 6, 1997; the 222-S laboratory ID for this sample was S96T005974, and the jar number was 12039. This material was a composite from Core 164.

7.1 Experimental

Figure 7.1 summarizes the experimental procedure used in the AN-104 ESW test. The procedure was the same as the baseline ESW test procedure described previously (Lumetta et al. 1996). The mass of solid material remaining after washing portion B1 was very small and could not be measured with certainty. Hence, the weight percent of water-insoluble solids could not be determined, but clearly a large

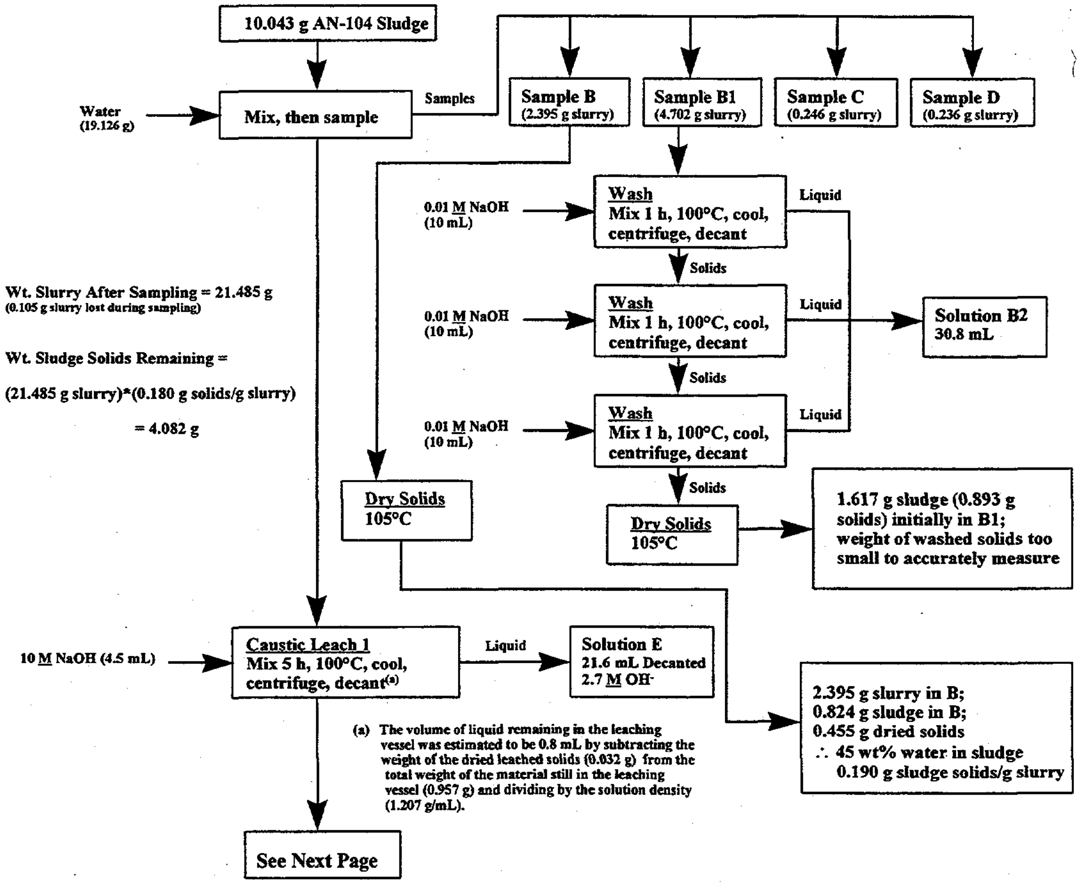
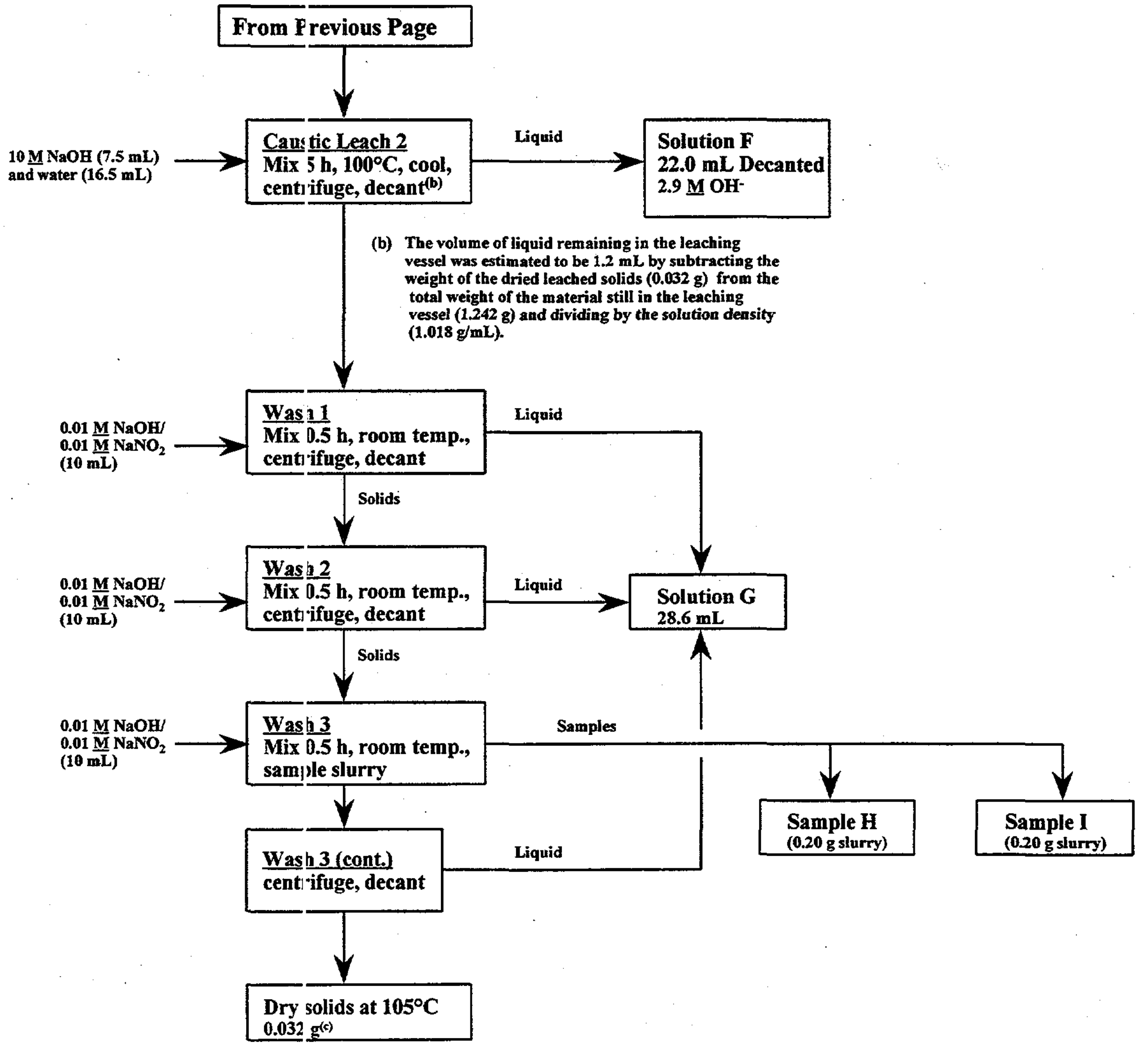


Figure 7.1. Schematic Representation of the AN-104 ESW Test



(b) The volume of liquid remaining in the leaching vessel was estimated to be 1.2 mL by subtracting the weight of the dried leached solids (0.032 g) from the total weight of the material still in the leaching vessel (1.242 g) and dividing by the solution density (1.018 g/mL).

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

AN104_ESW.PPT

Figure 7.1. (contd)

percentage of the sludge solids was water soluble. Consequently, the volume of leaching solution required to yield a slurry with 5 wt% undissolved solids in the first leaching step (as called for by the baseline test procedure) was likely less than 1 mL. This volume was too small to work with. Because the volume of slurry available after the initial sampling was ~20 mL, 4.5 mL of 10 M NaOH were added, which should have given an initial hydroxide concentration of ~1.8 M. However, the measured free-hydroxide concentration after the first leaching step was 2.7 M; presumably the additional hydroxide was in the sludge to begin with. The volume for the second leaching step was kept the same as the first leaching step (~25 mL). The undissolved solids concentration in the both the first and second leaching slurries was 0.12 wt%.

Also as a consequence of the small amount of material left after washing and caustic leaching, the residues, as well as the untreated solids sample, were dissolved in their entirety for chemical and radiochemical analysis. An acid-dissolution procedure was used rather than the KOH and Na_2O_2 fusion procedures normally used for dissolving the sludge solids. In each case, the solid sample (the untreated material, the washed solids, or the leached solids) was treated with ~7 mL of aqua regia and evaporated to dryness at 100°C. The treatment with aqua regia was repeated, then the residues were dissolved and diluted to 15 mL with 0.1 M HCl.

7.2 Results and Discussion

7.2.1 Washing With Dilute NaOH

Interpreting the data from the dilute hydroxide washing of AN-104 sludge was complicated by the fact that very little residual solids remained after washing. To determine the amount of each component removed, the amount of each component in the washed and untreated solids was normalized to the amount of Fe present. The concentrations (gram of component/g of Fe) in the washed and untreated solids were then compared to determine how much of the component was removed by washing. This treatment of the data assumes that no appreciable amount of Fe is removed by dilute hydroxide washing. This assumption is supported by the fact that the Fe concentration in the wash solution was only 0.1 µg/mL. Table 7.1 summarizes the behavior of most of the nonradioactive sludge components during washing of the AN-104 sludge with 0.01 M NaOH. Sodium was essentially completely removed by washing with 0.01 M NaOH. Similarly, 99% of the Al and 98% of the P were removed by dilute hydroxide washing. These observations suggest that the AN-104 solids consist primarily of "salt cake," which has been predicted from tank historical records (Agnew 1997). On the other hand, dilute hydroxide washing removed only 34% of the Cr.

Table 7.2 summarizes the behavior of the radioactive sludge components during washing of the AN-104 sludge with 0.01 M NaOH. Studies with most other Hanford tank sludges have consistently indicated that the TRU elements are very insoluble in 0.01 M NaOH. However, when analyzed as above in terms of radioactivity per gram of Fe in the washed versus the untreated solids, the AN-104 washing data suggested that a significant fraction (38 to 58%) of the TRU radioisotopes were removed from the sludge solids. But all Pu, Am, and Cm isotopes were below the detection limit in the wash solution. Assuming the LLW glass form will contain 20 wt% Na_2O (Orme et al. 1996), with a density of 2.7 metric tons/m^3, the LLW form resulting from immobilizing only the wash solution would be projected to contain <3.1 nCi TRU/g. This would be within the 10 nCi/g NRC Class A LLW limit for TRU. Analyzing the data in terms of the maximum amount of a given isotope in the wash solution, versus the total amount present in the solids that were washed, indicated that < 18% of the TRU elements (based on the total alpha activity) were removed. Similar observations were made for ^{60}Co, ^{90}Sr, and ^{154,155}Eu. Both methods of analyzing the data indicated essentially complete removal of ^{137}Cs and ^{99}Tc by dilute hydroxide washing.

Table 7.1. Results of Tank AN-104 Sludge Washing: Nonradioactive Components

	Wash Solution	Washed Solids		Untreated Solids		
Component	Conc., μg/mL	Conc., μg/mL[(a)]	g/g Fe	Conc., μg/mL[(b)]	g/g Fe	Removed, %
Ag	< 0.0	0.04	0	0.06	0	(c)
Al	951	30.4	3	791	288	99
As	< 0.3	< 0.25	< 0	< 0.50	< 0	(c)
B	1.3	0.11	0	23.7	9	(c)
Ba	< 0.0	0.53	0	0.30	0	46
Be	< 0.0	0.02	0	< 0.02	< 0	(c)
Bi	< 0.1	0.42	0	0.29	0	(c)
Ca	1.2	26.8	3	18.2	7	55
Cd	< 0.0	1.35	0	0.66	0	38
Ce	< 0.2	< 0.20	< 0	< 0.40	< 0	(c)
Co	< 0.1	0.18	0	0.12	0	(c)
Cr	10.7	164	18	75.5	27	34
Cu	0.1	0.93	0	0.67	0	58
Dy	< 0.1	< 0.05	< 0	< 0.10	< 0	(c)
Eu	< 0.1	< 0.10	< 0	< 0.20	< 0	(c)
Fe	0.1	9.08	1	2.75	1	--
K	154	< 2	< 0	188	68	(c)
La	< 0.1	0.34	0	0.22	0	(c)
Li	0.6	0.04	0	0.63	0	(c)
Mg	< 0.1	1.46	0	2.00	1	78
Mn	< 0.1	2.34	0	1.13	0	37
Mo	1.9	< 0.05	< 0	1.37	0	(c)
Na	10028	107	12	10400	3782	100
Nd	< 0.1	0.57	0	0.44	0	(c)
Ni	0.2	10.5	1	6.77	2	53
P	56.0	2.09	0	36.80	13	98
Pb	< 0.1	3.58	0	2.00	1	46
Pd	< 0.8	< 0.8	< 0	< 1.5	< 1	(c)
Rh	< 0.3	< 0.30	< 0	< 0.60	< 0	(c)
Ru	< 1.2	< 1.1	< 0	< 2.2	< 1	(c)
Sb	< 0.5	< 0.50	< 0	< 1.00	< 0	(c)
Se	< 0.3	< 0.25	< 0	< 0.50	< 0	(c)
Si	18.2	< 0.50	< 0	7.90	3	(c)
Sn	< 1.6	< 1.5	< 0	< 3.0	< 1	(c)
Sr	< 0.0	0.14	0	0.09	0	(c)
Te	< 1.6	< 1.5	< 0	< 3.0	< 1	(c)
Th	< 1.1	< 1.0	< 0	< 2.0	< 1	(c)
Ti	< 0.0	0.03	0	0.06	0	(c)
Tl	< 0.5	< 0.50	< 0	< 1.00	< 0	(c)
U[(d)]	1.4	12.1	1	7.96	3	54
V	< 0.1	< 0.05	< 0	< 0.10	< 0	(c)
W	< 2.1	< 2	< 0	< 4.0	< 1	(c)
Y	< 0.1	0.07	0	< 0.10	< 0	(c)
Zn	0.1	6.60	1	4.44	2	55
Zr	< 0.1	1.15	0	0.23	0	(c)

(a) Concentration in 15 mL of solution obtained by dissolving the entire washed solids residue in acid.

(b) Concentration in 15 mL of solution obtained by dissolving a 0.455-g portion of untreated solids in acid.

(c) Value not reliable because the concentration in either the washed or untreated solids was near the detection limit.

(d) Uranium was determined by laser fluorimetry; all other elements were determined by ICP/AES.

Table 7.2. Results of Tank AN-104 Sludge Washing: Radioactive Components

	Wash Solution		Washed Solids	
Component	Conc., μCi/mL	Dissolved, μCi/g Solids	Conc., μCi/mL(a)	μCi/g Fe
Total Alpha	< 2.10E-04	< 7.24E-03	2.53E-03	2.79E-04
^{239,240}Pu	< 2.10E-04	< 7.24E-03	2.99E-04	3.29E-05
^{241}Am+^{238}Pu	< 2.10E-04	< 7.24E-03	1.62E-03	1.78E-04
^{241}Am(g)	< 2.10E-02	< 7.24E-01	1.61E-03	1.77E-04
^{137}Cs	1.75E+01	6.05E+02	1.38E-01	1.52E-02
^{60}Co	< 2.10E-04	< 7.24E-03	1.67E-03	1.84E-04
^{154}Eu	< 9.45E-04	< 3.26E-02	5.19E-03	5.72E-04
^{155}Eu	< 2.10E-02	< 7.24E-01	4.53E-03	4.99E-04
^{90}Sr	< 2.10E-02	< 7.24E-01	2.87E+00	3.16E-01
^{99}Tc	5.23E-03	1.80E-01	2.23E-04	2.46E-05
^{243,244}Cm	< 2.10E-04	< 7.24E-03	6.13E-04	6.75E-05

	Untreated Solids			Removed, %	
Component	Conc., μCi/mL(b)	Conc., μCi/g	μCi/g Fe	Based on μCi/g Fe	Based on Amount in Wash Solution
Total Alpha	1.24E-03	4.09E-02	4.51E-04	38	< 18
^{239,240}Pu	2.15E-04	7.09E-03	7.82E-05	58	< 102
^{241}Am+^{238}Pu	9.46E-04	3.12E-02	3.44E-04	48	< 23
^{241}Am(g)	< 3.00E-02	< 9.89E-01	< 1.09E-02	(c)	< 73
^{137}Cs	1.82E+01	6.00E+02	6.62E+00	100	101
^{60}Co	1.07E-03	3.53E-02	3.89E-04	53	< 21
^{154}Eu	3.71E-03	1.22E-01	1.35E-03	58	< 27
^{155}Eu	< 2.00E-02	< 6.59E-01	< 7.27E-03	(c)	< 110
^{90}Sr	1.48E+00	4.88E+01	5.38E-01	41	< 1
^{99}Tc	4.47E-03	1.47E-01	1.63E-03	98	122
^{243,244}Cm	7.85E-05	2.59E-03	2.85E-05	-137	< 280

(a) Concentration in 15 mL of solution obtained by dissolving the entire washed solids residue in acid.

(b) Concentration in 15 mL of solution obtained by dissolving a 0.455-g portion of untreated solids in acid.

(c) Value not reliable because the concentration in the untreated solids was below the detection limit.

7.2.2 Caustic Leaching

Table 7.3 presents the concentrations of most of the nonradioactive sludge components in each process stream, and Table 7.4 presents the distribution of those sludge components between the various process streams. The values presented in Table 7.4 are not adjusted for material contained in the interstitial liquid, but rather represent the amount of each component contained in the liquid that was decanted in a given step (or in the residual solid). For most of the minor sludge components, the data are not particularly meaningful due to the very small amount of those materials in the residual solids. However, the data are informative for the key components Al, Cr, P, and Na.

Table 7.3. Concentrations of the Nonradioactive AN-104 Sludge Components in the Various Process Streams

	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/g	Mass, µg	Total Mass, µg
Ag	< 3.75	< 81	< 0.16	< 4	< 0.03	< 1	56	2	< 87
Al	7260	156816	255	5606	14	406	15609	500	163327
As	< 37.50	< 810	< 1.63	< 36	< 0.28	< 8	389	12	< 866
B	< 7.50	< 162	< 0.33	< 7	< 0.06	< 2	84	3	< 173
Ba	< 1.500	< 32	< 0.065	< 1	< 0.011	< 0	1083	35	< 69
Be	< 1.500	< 32	< 0.065	< 1	< 0.011	< 0	< 5	< 0	< 34
Bi	< 15.00	< 324	< 0.65	< 14	< 0.11	< 3	670	21	< 363
Ca	< 37.50	< 810	3.38	74	0.75	21	45844	1467	< 2373
Cd	< 2.25	< 49	< 0.10	< 2	< 0.017	< 0	2747	88	< 139
Ce	< 30	< 648	< 1.30	< 29	< 0.22	< 6	< 94	< 3	< 686
Co	< 7.50	< 162	< 0.33	< 7	< 0.06	< 2	352	11	< 182
Cr	162	3499	91	1996	5.2	149	102656	3285	8930
Cu	< 3.75	< 81	0.72	16	0.11	3	745	24	< 124
Dy	< 7.50	< 162	< 0.33	< 7	< 0.06	< 2	28	1	< 172
Eu	< 15.00	< 324	< 0.65	< 14	< 0.11	< 3	52	2	< 343
Fe	< 3.8	< 81	0.6	12	0.06	2	19875	636	< 731
K	1170	25272	33.8	744	< 2.2	< 63	< 938	< 30	< 26109
La	< 7.50	< 162	< 0.33	< 7	< 0.06	< 2	722	23	< 194
Li	6.00	130	0.38	8	< 0.03	< 1	23	1	< 140
Mg	< 15.00	< 324	< 0.65	< 14	< 0.11	< 3	628	20	< 362
Mn	< 7.50	< 162	< 0.33	< 7	< 0.06	< 2	4828	155	< 325
Mo	13.50	292	< 0.33	< 7	< 0.06	< 2	< 23	< 1	< 301
Na	128100	2766960	74620	1641640	3949	112941	24844	795	(b) 1749766
Nd	< 15.00	< 324	< 0.65	< 14	< 0.11	< 3	1181	38	< 379
Ni	< 4.50	< 97	0.6	13	0.2	6	16969	543	< 660
P	406	8770	12	261	1	19	769	25	9074
Pb	< 15.00	< 324	2.34	51	< 0.11	< 3	1214	39	< 417
Pd	< 112.50	< 2430	< 4.88	< 107	< 0.83	< 24	7781	249	< 2810
Rh	< 45.00	< 972	< 1.95	< 43	< 0.33	< 9	469	15	< 1039
Ru	< 165.00	< 3564	< 7.15	< 157	< 1.21	< 35	< 516	< 17	< 3772
Sb	< 75.00	< 1620	< 3.25	< 72	< 0.55	< 16	< 234	< 8	< 1715
Se	< 37.50	< 810	< 1.63	< 36	< 0.28	< 8	< 117	< 4	< 857
Si	< 75	< 1620	57.5	1264	2.8	79	< 234	< 8	< 2970
Sn	< 225.00	< 4860	< 9.75	< 215	< 1.65	< 47	< 703	< 23	< 5144
Sr	< 2.25	< 49	< 0.10	< 2	< 0.02	< 0	483	15	< 67
Te	< 225.00	< 4860	< 9.75	< 215	< 1.65	< 47	< 703	< 23	< 5144
Th	< 150	< 3240	< 6.5	< 143	< 1.1	< 31	< 469	< 15	< 3429
Ti	< 3.75	< 81	< 0.16	< 4	< 0.03	< 1	< 12	< 0	< 86
Tl	< 75.00	< 1620	< 3.25	< 72	< 0.55	< 16	< 234	< 8	< 1715
U[(c)]	14.600	315	7.31	161	0.41	12	19688	630	1118
V	< 7.50	< 162	< 0.33	< 7	< 0.06	< 2	< 23	< 1	< 171
W	< 300	< 6480	< 13	< 286	< 2.2	< 63	< 938	< 30	< 6859
Y	< 7.50	< 162	< 0.33	< 7	< 0.06	< 2	145	5	< 175
Zn	< 7.50	< 162	1.18	26	0.30	8	2761	88	< 285
Zr	< 7.50	< 162	0.51	11	< 0.06	< 2	3038	97	< 272

(a) Mass of material present in the solution decanted during the indicated step.

(b) Adjusted for the amount (2,772,570 µg) of Na added as NaOH.

(c) Uranium was determined by laser fluorimetry; all other elements were determined by ICP/AES.

Table 7.4. Distribution of Nonradioactive AN-104 Sludge Components Between Various Process Streams During Caustic Leaching

	Component Distribution, %			
Component	First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids
Ag	< 93	< 4	< 1	> 2
Al	96	3	0	0
As	< 94	< 4	< 1	> 1
B	< 93	< 4	< 1	> 2
Ba	< 47	< 2	0	> 50
Be	(a)	(a)	(a)	(a)
Bi	< 89	< 4	< 1	> 6
Ca	< 34	3 < x < 5	1	62 < x < 94
Cd	< 35	< 2	0	> 63
Ce	(a)	(a)	(a)	(a)
Co	< 89	< 4	< 1	> 6
Cr	39	22	2	37
Cu	< 65	13 < x < 37	3 < x < 7	19 < x < 56
Dy	< 94	< 4	< 1	> 1
Eu	< 94	< 4	< 1	> 1
Fe	< 11	2	0	87 < x < 98
K	97	3	0	0
La	< 84	< 4	< 1	> 12
Li	93	6	0	1
Mg	< 90	< 4	< 1	> 6
Mn	< 50	< 2	0	> 48
Mo	> 97	< 2	< 1	0
Na	--	--	--	7(b)
Nd	< 85	< 4	< 1	> 10
Ni	< 15	2	1	82 < x < 97
P	97	3	0	0
Pb	< 78	12 < x < 57	< 1	9 < x < 43
Pd	< 86	< 4	< 1	> 9
Rh	< 94	< 4	< 1	> 1
Ru	(a)	(a)	(a)	(a)
Sb	(a)	(a)	(a)	(a)
Se	(a)	(a)	(a)	(a)
Si	< 55	43 < x < 94	3 < x < 6	0
Sn	(a)	(a)	(a)	(a)
Sr	< 73	< 3	< 1	> 23
Te	(a)	(a)	(a)	(a)
Th	(a)	(a)	(a)	(a)
Ti	(a)	(a)	(a)	(a)
Tl	(a)	(a)	(a)	(a)
U	28	14	1	56
V	(a)	(a)	(a)	(a)
W	(a)	(a)	(a)	(a)
Y	< 92	< 4	< 1	> 3
Zn	< 57	9 < x < 21	3 < x < 7	31 < x < 72
Zr	< 60	4 < x < 10	< 1	36 < x < 90

(a) Analyte was below detection limit for all process streams.

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

Since dilute hydroxide washing removed 99% of the Al, it was not surprising that caustic leaching removed Al efficiently. Leaching with caustic appeared to remove most of the small Al fraction not readily removed by dilute hydroxide washing. The Al in the caustic-leached solids represented only 0.3% of the total Al. Accounting for the Al in the interstitial liquid after decanting the first leaching solution, all of the Al dissolution occurred in the first leaching step. Similarly, caustic leaching helped to remove the small amount of water-insoluble P present in the AN-104 sludge, with only 0.3% of the P remaining in the residue. Again, the P that was removed was dissolved in the first leaching step. The 7% residual Na was likely due to incomplete washing of the added sodium from the leached solids.

Caustic leaching significantly improved Cr removal. The cumulative Cr removal was 63% for the caustic leaching and subsequent washing steps. Hence, caustic leaching nearly doubled the amount of Cr removed from the AN-104 sludge (only 34% was removed by dilute hydroxide washing). In this case, significant Cr was dissolved in the second leaching step. Accounting for the interstitial liquid volumes, 41% of the Cr dissolved during the first leaching step, while 22% dissolved in the second leaching step.

The data were also analyzed in terms of grams of component per gram of Fe in the untreated and caustic-leached solids (Table 7.5). The results of this analysis were in general agreement with those in Table 7.4, except that higher Cr and Na removals were indicated.

Table 7.6 summarizes the mass recoveries achieved for the various elements analyzed by ICP/AES and for U, which was determined by laser fluorimetry. For the minor components, the mass recoveries tended to be poor, which was likely because the residual solids contained only a small amount of these elements. Mass recoveries for Cr, Na, and U were all good. But those for Al, Fe, and P were somewhat high.

Table 7.7 presents the concentrations of the various anions in each process solution. Also listed are the amount of each anion in solution as a function of the amount of sludge solids treated. For the most part, the quantity of the anions in solution during the caustic leaching and subsequent washing steps were the same as those in the dilute hydroxide washing step; i.e., caustic leaching did not result in significantly improved removal. However, the amount of sulfate dissolved increased by ~ 25% upon leaching with caustic, suggesting some improved removal for that component.

Table 7.5. Results of AN-104 Caustic Leaching Based on Iron Normalization Procedure

	Leached Solids		Untreated Solids		
Component	Conc., µg/mL[a]	g/g Fe	Conc., µg/mL[b]	g/g Fe	Removed, %
Al	33.3	1	791	288	100
Cr	219	5	75.5	27	81
Fe	42.4	1	2.75	1	--
Na	53.0	1	10400	3782	100
P	1.64	0	36.8	13	100

(a) Concentration in 15 mL of solution obtained by dissolving the entire washed solids residue in acid.

(b) Concentration in 15 mL of solution obtained by dissolving a 0.455-g portion of untreated solids in acid.

Table 7.6. Concentrations of the Nonradioactive AN-104 Sludge Components in the Initial Sludge Solids: Results of the Caustic Leaching Portion of the Test

Component	Concentration in Initial Solids, μg/g		Mass Recovery, %
	Summation Method(a)	Direct Analysis	
Ag	< 21	2	--
Al	40031	26077	154
As	< 212	< 16	--
B	< 43	781	< 5
Ba	8 < x < 17	10	86 < x < 170
Be	< 8	< 1	--
Bi	5 < x < 89	10	55 < x < 930
Ca	383 < x < 582	600	64 < x < 97
Cd	22 < x < 34	22	100 < x < 157
Ce	< 168	< 13	--
Co	3 < x < 45	4	70 < x < 1127
Cr	2189	2489	88
Cu	10 < x < 30	22	47 < x < 137
Dy	< 42	< 3	--
Eu	< 84	< 7	--
Fe	159 < x < 179	91	176 < x < 198
K	6376 < x < 6399	6198	103
La	6 < x < 48	7	78 < x < 655
Li	34	21	165
Mg	5 < x < 89	66	7 < x < 134
Mn	38 < x < 80	37	102 < x < 214
Mo	38 < x < 80	45	158 < x < 163
Na	428864	342857	125
Nd	9 < x < 93	15	64 < x < 641
Ni	138 < x < 162	223	62 < x < 72
P	2224	1213	183
Pb	22 < x < 102	66	34 < x < 155
Pd	< 689	< 49	--
Rh	< 255	< 20	--
Ru	< 925	< 73	--
Sb	< 420	< 33	--
Se	< 210	< 16	--
Si	329 < x < 728	260	126 < x < 280
Sn	< 1261	< 99	--
Sr	4 < x < 16	3	128 < x < 551
Te	< 1261	< 99	--
Th	< 841	< 66	--
Ti	< 21	2	1062
Tl	< 420	< 33	--
U	274	262	104
V	< 42	< 3	--
W	< 1681	< 132	--
Y	< 43	< 3	--
Zn	30 < x < 70	146	21 < x < 48
Zr	27 < x < 67	8	350 < x < 879

(a) The value was determined by summing the amount of a given component in the caustic leaching solutions, the subsequent washing solutions, and the leached solids; the total concentration was then determined by dividing the sum by the amount of solids processed.

Table 7.7. Anion Concentrations in the Various AN-104 Process Solutions

	Wash Solution		First Leach Solution		Second Leach Solution		Final Wash Solution	
Component	Conc., µg/mL	µg/g sludge solids[(a)]	Conc., µg/mL	µg/g sludge solids[(a)]	Conc., µg/mL	µg/g sludge solids[(a)]	Conc., µg/mL	µg/g sludge solids[(a)]
OH^-	Not Determined		46,100	N/A[(b)]	48,600	N/A[(b)]	Not Determined	
NO_3^-	4,950	170,728	30,000	158,824	1,000	5392	50	350
NO_2^-	2,800	95,573	17,000	90,000	500	2696	130	N/A[(c)]
PO_4^{3-}	140	4,829	< 750	< 3980	30	< 162	< 10	< 70
SO_4^{2-}	500	17,245	4000	21,176	90	485	< 10	< 70
F^-	41	1,414	< 375	< 1990	7	38	< 2.5	< 18
Cl^-	195	6,726	1300	6,882	18	97	3	390
Br^-	< 25	< 860	< 375	< 1990	< 5	< 27	< 2.5	< 18

(a) Amount of component in solution per gram of sludge solids processed.

(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 7.8 presents the concentrations of various radioactive sludge components in each process stream, and Table 7.9 presents the distribution of those sludge components between the various process streams. As was the case with the dilute NaOH wash, ^{137}Cs and ^{99}Tc were the primary radioisotopes detected in the leach and wash solutions; however, some ^{90}Sr was also detected in the two caustic leaching solutions. Comparable to what was observed for the dilute NaOH wash, caustic leaching removed 99% of the ^{99}Tc and virtually all of the ^{137}Cs. The amount of ^{90}Sr in the caustic leaching solutions is not expected to present a problem. Assuming the LLW glass form will contain 20 wt% Na_2O, with a density of 2.7 metric tons/m^3, the resulting LLW form would be projected to contain 0.35 Ci $^{90}Sr/m^3$, which is well within the NRC Class C LLW limit of 7000 Ci/m^3 and the current planning target of 20 Ci/m^3.

Table 7.10 summarizes the mass recoveries achieved for the various radionuclides during the caustic leaching portion of the test. Excellent mass recoveries were obtained for ^{137}Cs and ^{90}Sr, but that for ^{99}Tc and the total alpha activity were high. The recovery for $^{243,244}Cm$ was very high, but this is a relatively minor component, and the high recovery is likely due to analytical uncertainty.

Table 7.8. Concentrations of the Radioactive AN-104 Sludge Components in the Various Process Streams During Caustic Leaching

	First Leach Solution		Second Leach Solution	
Component	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/mL	Activity, µCi[(a)]
Total Alpha	< 5.00E-04	< 1.08E-02	< 1.17E-04	< 2.57E-03
^{239,240}Pu	< 5.00E-04	< 1.08E-02	< 1.17E-04	< 2.57E-03
^{241}Am+^{238}Pu	< 5.00E-04	< 1.08E-02	< 1.17E-04	< 2.57E-03
^{241}Am(g)	< 1.00E-01	< 2.16E+00	< 1.17E-02	< 2.57E-01
^{137}Cs	1.09E+02	2.35E+03	3.89E+00	8.55E+01
^{60}Co	< 4.00E-03	< 8.64E-02	< 2.60E-04	< 5.72E-03
^{154}Eu	< 8.00E-03	< 1.73E-01	< 5.20E-04	< 1.14E-02
^{155}Eu	< 8.00E-02	< 1.73E+00	< 7.80E-03	< 1.72E-01
^{90}Sr	1.15E-01	2.48E+00	6.63E-02	1.46E+00
^{99}Tc	3.83E-02	8.27E-01	1.11E-03	2.45E-02
^{243,244}Cm	< 5.00E-04	< 1.08E-02	< 1.17E-04	< 2.57E-03

	Final Wash Solution		Leached Solids		
Component	Conc., µCi/mL	Activity, µCi[(a)]	Conc., µCi/g	Activity, µCi	Total Activity, µCi
Total Alpha	< 4.40E-06	< 1.26E-04	8.16E+00	2.61E-01	< 2.74E-01
^{239,240}Pu	< 4.40E-06	< 1.26E-04	6.56E-01	2.10E-02	< 3.45E-02
^{241}Am+^{238}Pu	< 4.40E-06	< 1.26E-04	4.62E+00	1.48E-01	< 1.61E-01
^{241}Am(g)	< 5.50E-04	< 1.57E-02	3.41E+00	1.09E-01	< 2.54E+00
^{137}Cs	1.98E-01	5.66E+00	2.93E+00	9.38E-02	2.45E+03
^{60}Co	< 3.30E-05	< 9.44E-04	3.41E+00	1.09E-01	< 2.02E-01
^{154}Eu	< 5.50E-05	< 1.57E-03	1.11E+01	3.56E-01	< 5.41E-01
^{155}Eu	< 3.30E-04	< 9.44E-03	1.03E+01	3.30E-01	< 2.24E+00
^{90}Sr	< 2.20E-05	< 6.29E-04	5.72E+03	1.83E+02	< 1.87E+02
^{99}Tc	6.63E-05	1.90E-03	1.98E-01	6.35E-03	8.60E-01
^{243,244}Cm	< 4.40E-06	1.26E-04	2.88E+00	9.21E-02	< 1.06E-01

(a) Activity of radioisotope present in the solution decanted during the indicated step.

Table 7.9. Concentrations of the Radioactive Components in the Initial AN-104 Sludge Solids as Determined From the Caustic Leaching Portion of the Test

	Component Distribution, %			
Component	First Leach Solution	Second Leach Solution	Final Wash Solution	Leached Solids
Total Alpha	< 4	< 1	0	> 95
^{239,240}Pu	< 31	< 7	0	> 61
^{241}Am+^{238}Pu	< 7	< 2	0	> 92
^{241}Am(g)	< 85	< 10	< 1	> 4
^{137}Cs	96	3	0	0
^{60}Co	< 43	< 3	0	> 54
^{154}Eu	< 32	< 2	0	> 66
^{155}Eu	< 77	< 8	0	> 15
^{90}Sr	1	1	0	98
^{99}Tc	96	3	0	1
^{243,244}Cm	< 10	< 3	0	> 87

Table 7.10. Anion Concentrations in the Various AN-104 Process Solutions

	Concentration in Initial Solids, µCi/g		
Component	Summation Method[(a)]	Direct Analysis	Recovery, %
Total Alpha	0.064 < x < 0.067	4.09E-02	156 < x < 165
^{239,240}Pu	0.0051 < x < 0.0085	7.09E-03	73 < x < 119
^{241}Am+^{238}Pu	0.036 < x < 0.040	3.12E-02	116 < x < 127
^{241}Am(g)	0.027 < x < 0.623	< 9.89E-01	--
^{137}Cs	5.99E+02	6.00E+02	100
^{60}Co	0.027 < x < 0.049	3.53E-02	76 < x < 140
^{154}Eu	0.087 < x < 0.133	1.22E-01	71 < x < 108
^{155}Eu	5.49E-01	< 6.59E-01	12 < x < 83
^{90}Sr	4.58E+01	4.88E+01	94
^{99}Tc	2.11E-01	1.47E-01	143
^{243,244}Cm	0.023 < x < 0.026	2.59E-03	872 < x < 1000

(a) The value was determined by summing the amount of a given component in the caustic leaching solutions, the subsequent washing solutions, and the leached solids; the total concentrations was then determined by dividing the sum by the amount of sludge solids processed.

7.2.3 Particle-Size Analysis

Figure 7.2 presents the particle-size data for the untreated and treated AN-104 sludge solids in terms of the number distributions, and Figure 7.3 presents the data in terms of the volume distributions. Caustic leaching resulted in rather minor changes in the particle-size distributions. The number distributions indicated the mean particle size decreased from 1.47 μm to 1.01 μm during caustic leaching. On the other hand, the volume distributions indicated an increase in the mean particle size from 4.08 μm to 6.03 μm. The particle-size measurements were repeated after an ultrasonic field was applied. This resulted in only minor changes in the particle-size distributions.

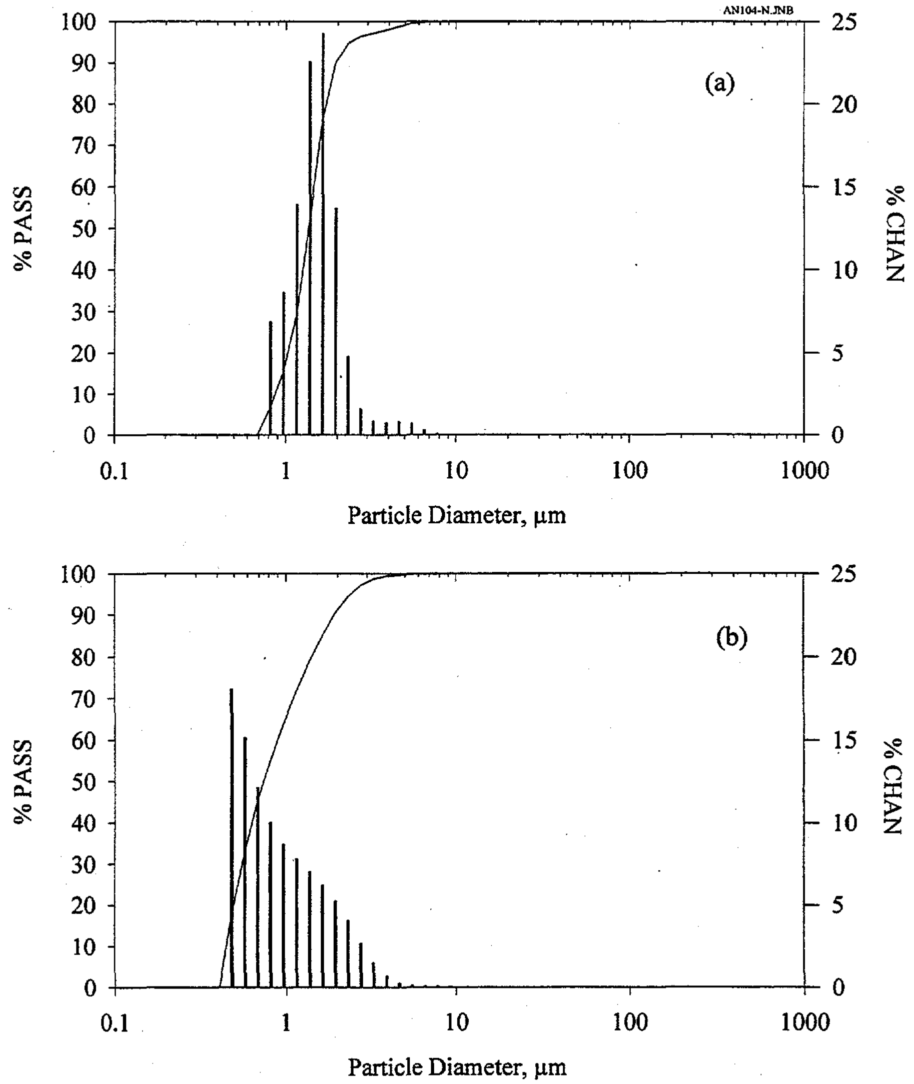


Figure 7.2. Particle-Size Number Distributions for Untreated (a) and Treated (b) AN-104 Sludge

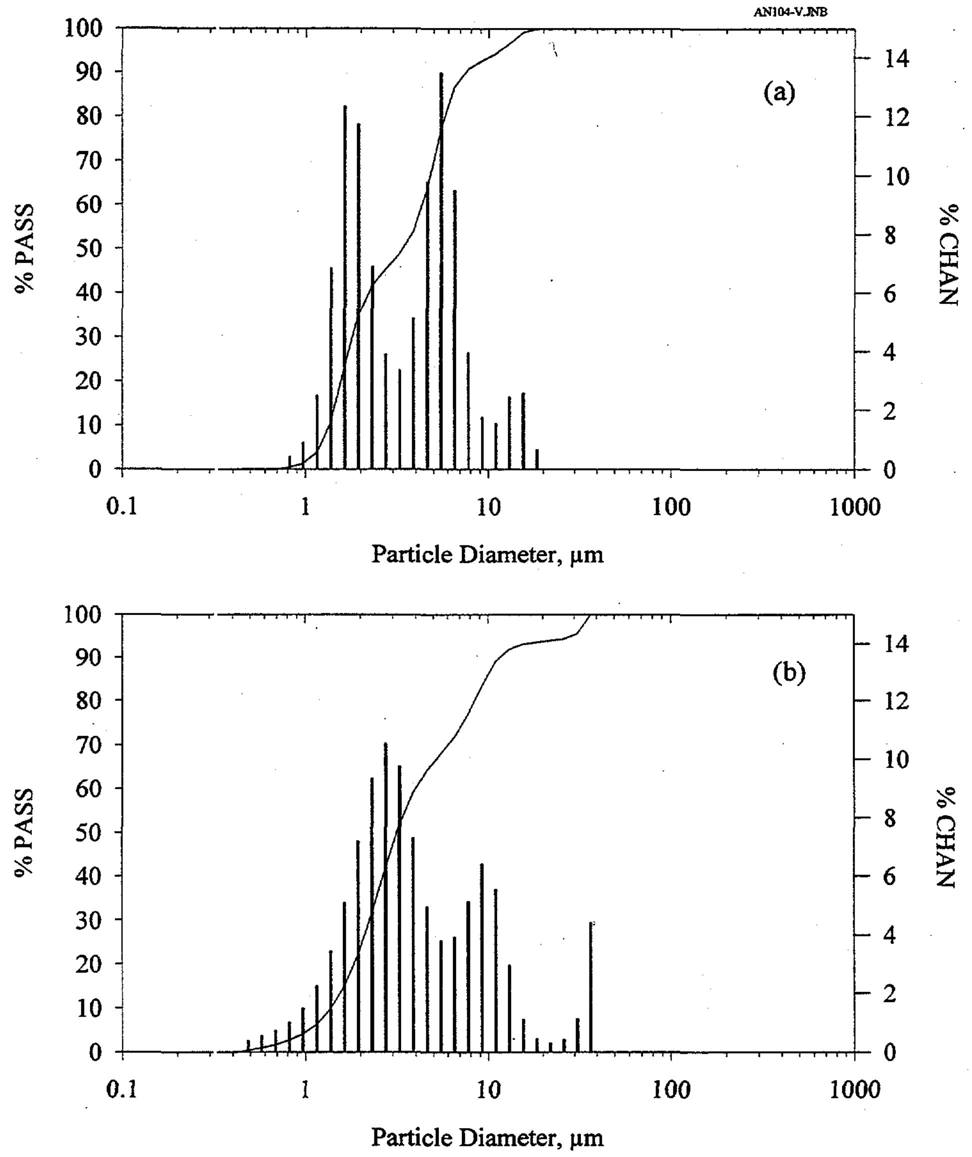


Figure 7.3. Particle-Size Volume Distributions for Untreated (a) and Treated (b) AN-104 Sludge

7.2.4 Microscopic Analysis

The TEM analysis indicated that the untreated AN-104 sludge solids were mainly a mixture of amorphous particles, with Na, Al, Cr, and Si being the dominant elements present (Figure 7.4). Some Fe- and Zr-containing nanoparticles were also present in small quantities. This assessment agrees with the ICP/AES analysis, except that the ICP/AES analysis detected relatively little Si (see Table 7.6). In the untreated solids, Cr-containing particles were fine amorphous particles, mixed with fine particles containing Al and Na (likely sodium aluminate) (Figure 7.5). Al and Si species with clay-like (or film-like) morphologies were also observed in the untreated solids (Figure 7.6).

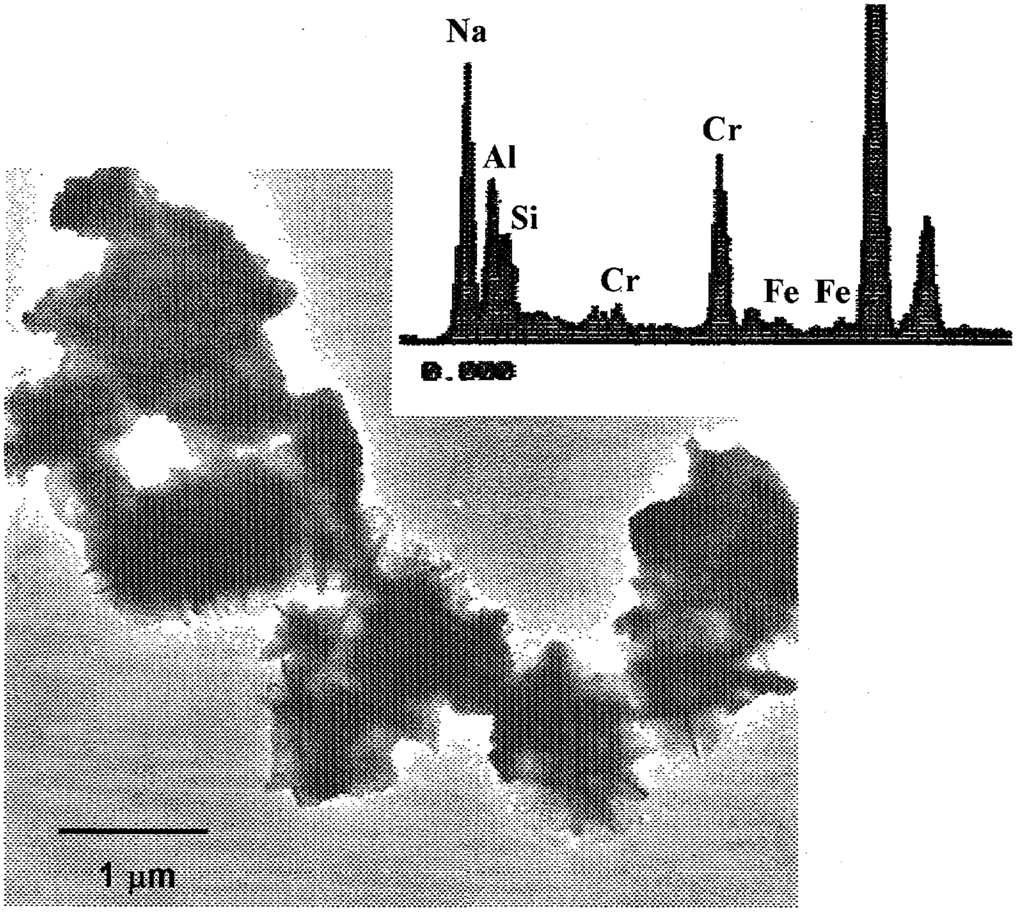


Figure 7.4. Transmission Electron Micrograph and EDS Spectrum of the Mixed Cr and Al Phases in the Untreated AN-104 Solids

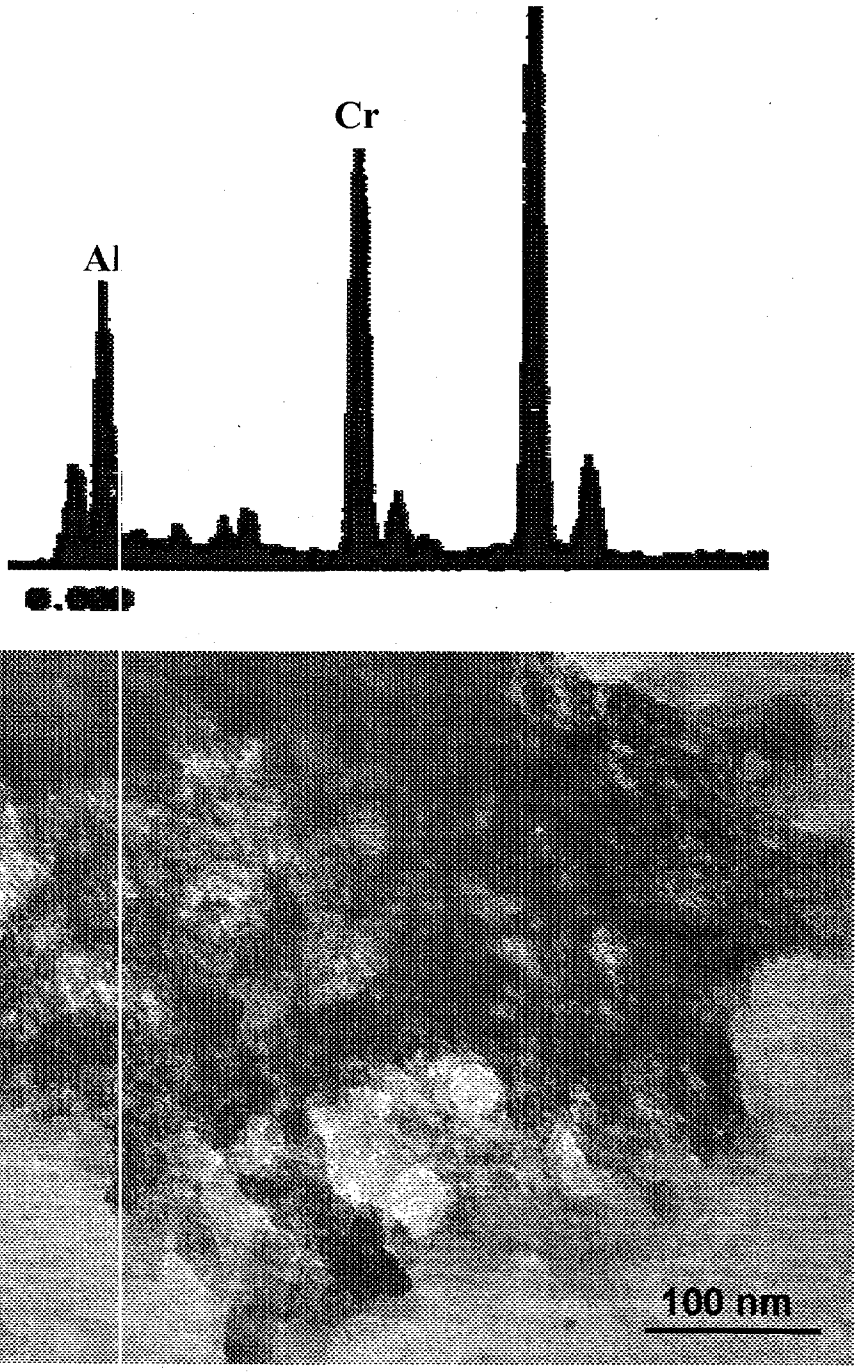


Figure 7.5. Transmission Electron Micrograph and EDS Spectrum of the Untreated AN-104 Solids

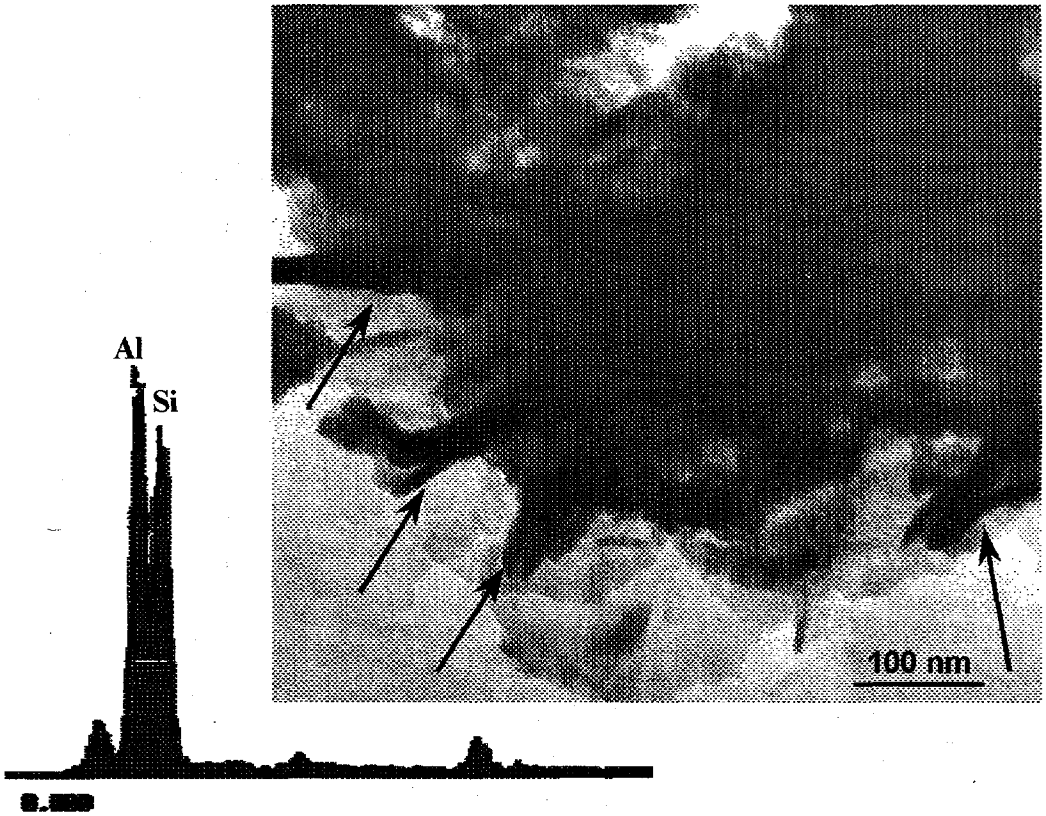


Figure 7.6. Transmission Electron Micrograph and EDS Spectrum of the Clay-Like Al/Si Phase in the Untreated AN-104 Solids

The TEM analysis of the caustic-leached solids indicated that a significant fraction of the Cr remained in the solids. It also suggested that the Si content was reduced and that Al and Na were almost eliminated. Again, these observations are consistent with the ICP/AES analysis (Table 7.3), except for the presence of Si in the leached solids. The ICP/AES analysis indicated little or no Si in the leached solids. The Cr in the leached solids appeared to be mixed with very fine silica particles (Figure 7.7). It is not clear whether these fine silica particles were present before leaching (but undetected in the TEM analysis) or if they formed during the leaching (or subsequent cooling) step.

Some of the Cr in the leached solids was associated with Ca in amorphous particles (Figure 7.8). The only crystalline material identified in either the untreated or caustic-leached solids was a U-containing phase (Figure 7.9). This phase was UO_2 or U_3O_7, or a mixture of both.

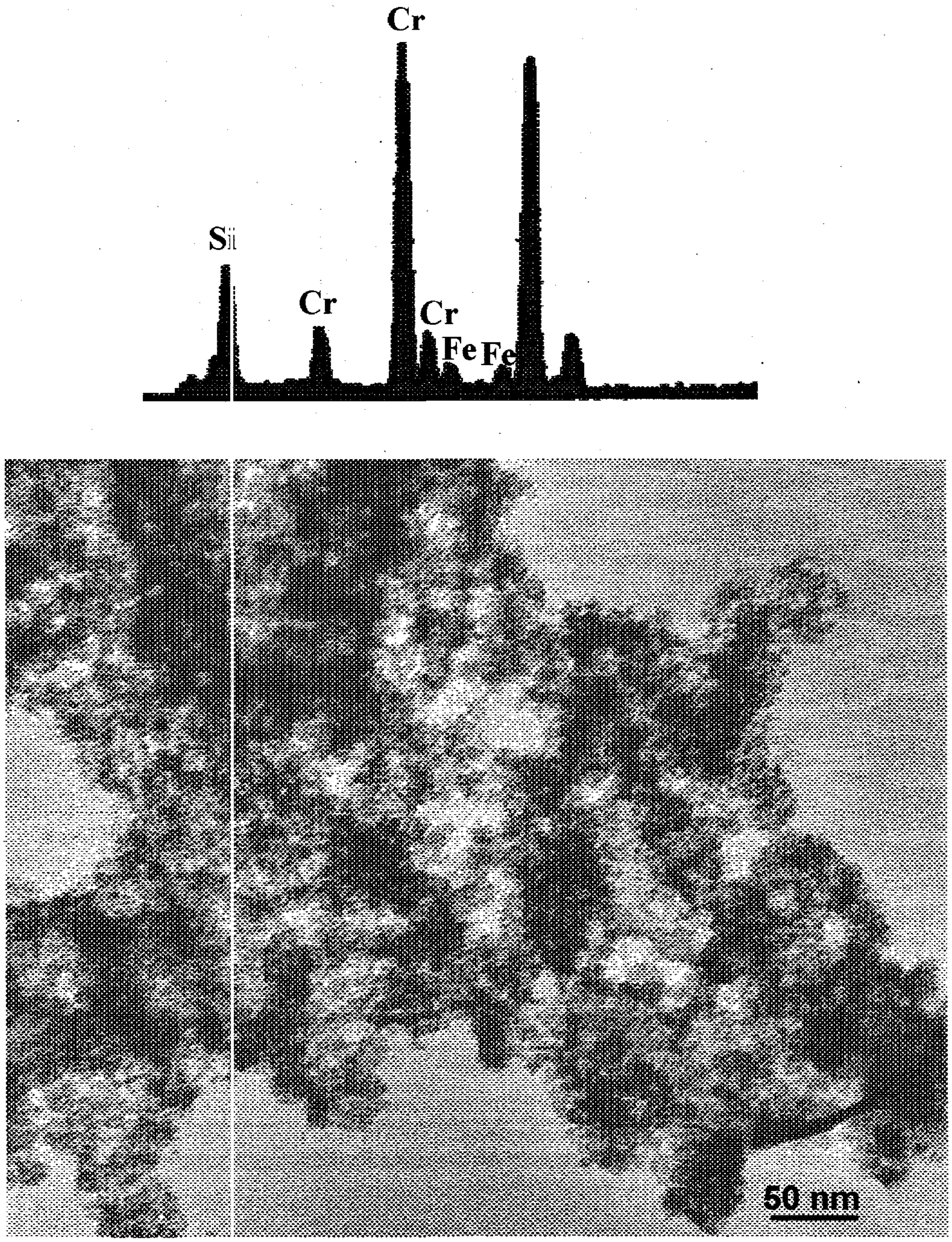


Figure 7.7. Transmission Electron Micrograph and EDS Spectrum of the Mixed Cr and Si Phases in the Caustic-Leach AN-104 Solids

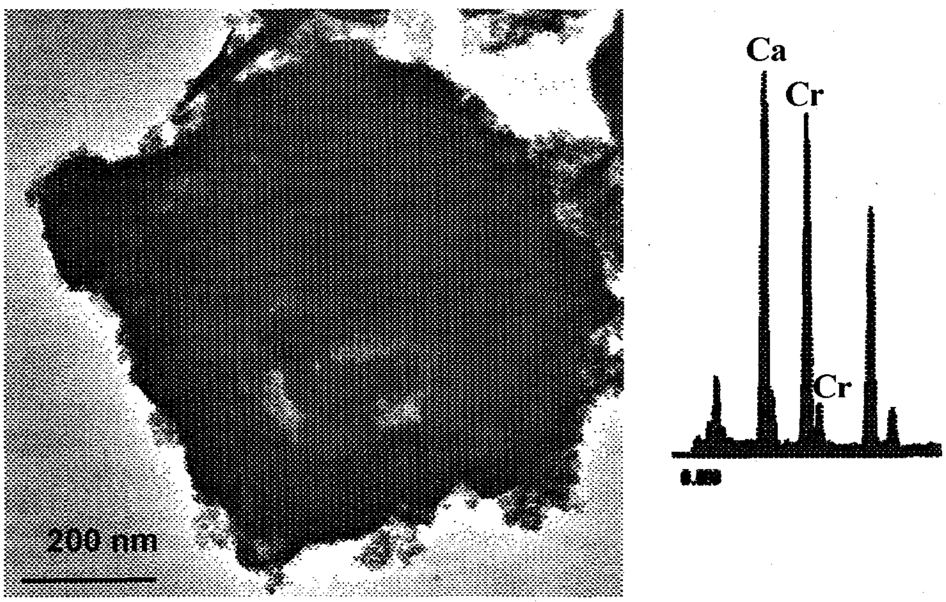


Figure 7.8. Transmission Electron Micrograph and EDS Spectrum of the Mixed Cr and Ca Phase in the Caustic-Leached AN-104 Solids

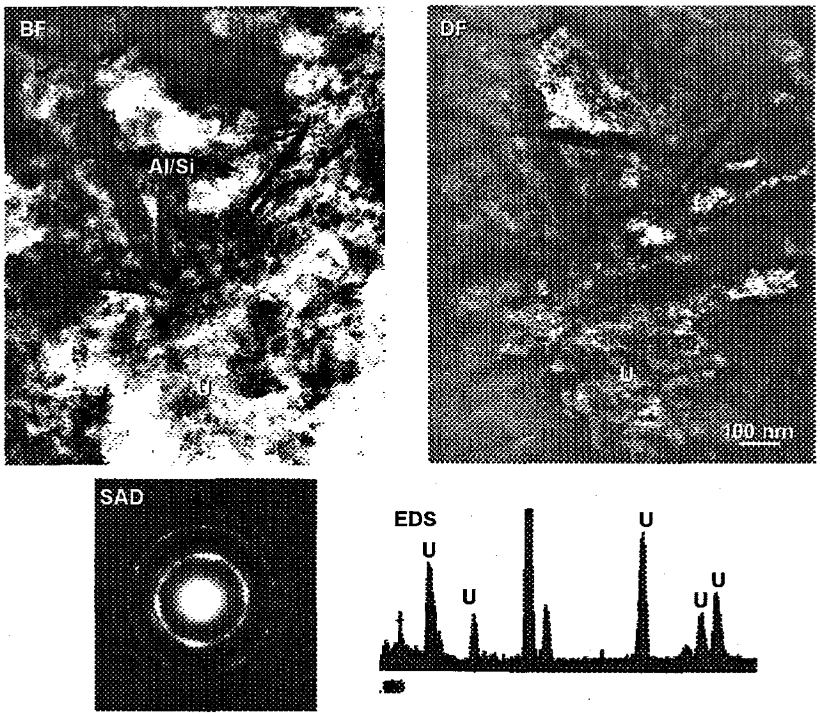


Figure 7.9. Transmission Electron Micrograph and EDS Spectrum of the Crystalline Uranium-Containing Particles in the Caustic-Leached AN-104 Solids

8.0 Discussion

This section presents a review of the key ESW test to date. This discussion is organized in terms of the behavior of the specific sludge components Al, Cr, P, Na, and radionuclides. Observations concerning particle size are also discussed.

8.1 Aluminum

Table 8.1 summarizes the amounts of Al removed by dilute hydroxide washing (simple wash) and by caustic leaching (ESW). The reader should bear in mind that the experimental procedure from one tank sludge to the next was not necessarily the same, as the standard baseline ESW test procedure has evolved over the last few years. In all cases, the caustic leaching steps were performed at 100°C, with cooling to ambient temperature before sampling. The solids-to-liquid ratios and the caustic concentrations may vary from test-to-test. In spite of the differing experimental conditions, some general observations can be made. First, dilute hydroxide washing was generally ineffective at removing Al from the tank sludges. The exceptions to this were the sludges from the SORWT group 3 tanks,[a] and Tank BX-109. Second, caustic leaching was generally effective at removing Al. In the case of REDOX sludges (SORWT groups 1, 4, and 24), extended leaching times significantly improved Al removal. For example, when S-104 was subjected to two successive 5-h caustic leaches, only 38% of the Al was removed. But when leaching was carried out for more than three days, 99% of the Al was removed. Similar improved removals were observed for S-101 and S-111 sludges upon extending leaching (see Sections 5.1 and 6.1). Only three groups of sludges displayed consistently low (< 50%) Al removal: SORWT groups 7, 16, and 20. Finally, the Al removal data generally indicate good agreement for tanks within a given SORWT group.

Table 8.2 summarizes the Al-containing phases that have been identified in the Hanford tank sludges by microscopic examination coupled with X-ray diffraction techniques. Clearly, the sludges contain a variety of chemical species containing Al. Boehmite is the dominant Al-containing species in the REDOX sludges. As mentioned in the previous paragraph, this boehmite can largely be removed by caustic leaching, provided adequate leaching times and temperatures are employed. Microscopic examinations have suggested that species such as $Al(OH)_3$ (amorphous or crystalline), $Al_2O_3 \cdot xH_2O$, and $AlPO_4$ are readily removed by caustic leaching, even at relatively short leaching times. If any of these species do remain after a short leaching time, it is not unreasonable to presume that more would be removed with longer leaching times. As might be expected, the aluminosilicate minerals appear to be the most difficult of the Al-containing species to dissolve by caustic leaching, but it can be inferred from analyses of the leaching solutions that some fraction of the aluminosilicates is also likely dissolved by caustic leaching.

(a) SORWT refers to "sort on radioactive waste type," which is a statistical method for grouping the Hanford single-shell tanks (Hill, Anderson, Simpson 1995).

Table 8.1. Aluminum Removal As a Function of Waste Type

		Waste Types[b]			Removed, %		
Tank	SORWT Group[a]	Primary	Secondary	Initial, wt %[c]	Simple Wash[d]	ESW[e]	References
S-101[f]	1	R	EB	14.7	12	96	(g)
S-107	1	R	EB	20.5	8	73	(h)
S-111[f]	1	R	EB	16	10	100	(g)
BY-104	3	TBP-F	EB-ITS	1.88	65	98	(h)
BY-110	3	TBP-F	EB-ITS	3.37	94	96	(h)
BY-108	3	TBP-F	EB-ITS	1.26	63	71	(g)
S-104	4	R	N/A	15.0	2	38	(i)
S-104[f]	4	R	N/A	15.3	2	99	(g)
SX-108	4	R	N/A	9.02	6	29	(h)
BX-105	5	TBP	CW	30.5	2	100	(j)
BX-109	5	TBP	CW	0.14	61	97	(k)
B-201	7	224	N/A	0.81	0	25	(l)
B-202	7	224	N/A	0.26	< 3	19	(j)
C-107	10	1C	CW	8.70	1	78	(h)
T-107	10	1C	CW	5.67	4	78	(j)
U-110	10	1C	CW	18.0	1	82	(l)
B-106	12	1C	TBP	0.73	28	86	(m)
BX-107	12	1C	TBP	3.50	1	68	(i)
C-108	13	TBP-F	1C	15.1	3	94	(j)
C-109	13	TBP-F	1C	16.1	8	81	(n)
C-112	13	TBP-F	1C	3.09	34	85	(n)
B-110	16	2C	5-6	0.29	0	18	(n)
B-111	16	2C	5-6	0.30	0	2	(i)
C-103	20	SRS	SR-WASH	14.0	0	48	(i)
C-106	20	SRS	SR-WASH	4.85	24	47	(o)
T-104	Ungrouped	1C	N/A	5.35	1	64	(j)
T-111	15	2C	224	0.49	0	13	(i)
B-104	Ungrouped	2C	EB	0.25	6	63	(k)
TY-104	22	TBP	1C-F	4.28	9	63	(k)

Table 8.1. (contd)

Tank	SORWT Group[a]	Waste Types[b]		Initial, wt %[c]	Removed, %		References
		Primary	Secondary		Simple Wash[d]	ESW[e]	
SX-113	24	R	DIA	2.12	0	89	(m)
C-104	Ungrouped	CW	OWW	6.32	9	97	(m)
C-105	Ungrouped	TBP	SR-WASH	27.2	0	99	(m)
AN-104	N/A	DSSF		2.61	99	100	(g)
SY-103	N/A	CC		4.70	9	90	(i)

(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
DIA = Diatomaceous earth
DSSF = Double-shell slurry feed
EB = Evaporator bottoms
ITS = In-tank solidification
F = Ferrocyanide-scavenged waste
OWW = Organic solvent wash from PUREX
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, except for S-111, which is on a wet-sludge basis

(d) Simple washing refers to washing with dilute NaOH (0.01 to 0.1 M)

(e) Enhanced sludge washing (ESW) refers to high caustic (~3 M) leaching followed by washing with dilute NaOH

(f) Extended leaching time used

(g) This work

(h) Lumetta et al. 1996

(i) Rapko, Lumetta, Wagner 1995

(j) Temer and Villarreal 1995

(k) Temer and Villarreal 1996

(l) Lumetta and Rapko 1994

(m) D.J. Temer. 1997. Personal communication. Los Alamos National Laboratory, Los Alamos, New Mexico

(n) Compositional data from Colton 1995, percent removal data from Lumetta and Rapko 1994

(o) Lumetta, Wagner, Hoopes, and Steele 1996

Table 8.2. Aluminum-Containing Phases Identified in Hanford Sludges

Phase	Tank	Reference
Al(O)OH (boehmite)	S-101	This report
	S-104	This report
	S-107	Lumetta et al. 1996
	S-111	This report
	SX-108	Lumetta et al. 1996
Al(O)OH (diaspore)	S-101	This report
$Al(OH)_3$(am)	BX-107	LaFemina 1995
	C-106	Lumetta, Wagner, Hoopes, Steele 1996
	SY-103	LaFemina 1995
	T-104	LaFemina 1995
$Al(OH)_3$(crystalline)	BX-107	LaFemina 1995
	BX-113	(a)
	C-105	(a)
	C-112	LaFemina 1995
	S-101	This report
	S-111	This report
	SY-103	LaFemina 1995
$Al_2O_3 \times xH_2O$(crystalline)	BY-104	Lumetta et al. 1996
	C-107	Lumetta et al. 1996
	SX-108	Lumetta et al. 1996
	SY-103	Rapko et al. 1996
$AlPO_4$	BX-107	LaFemina 1995
	T-104	LaFemina 1995
Aluminosilicate(am)	AN-104	This report
	BX-107	LaFemina 1995
	BY-104	Lumetta et al. 1996
	C-106	Lumetta, Wagner, Hoopes, Steele 1996
	C-107	Lumetta et al. 1996
	S-101	This report
	S-107	Lumetta et al. 1996
	SX-108	Lumetta et al. 1996
	T-104	LaFemina 1995
Aluminosilicate(crystalline)	B-111	Rapko et al. 1996
	BX-107	Rapko et al. 1996
	T-104	Rapko et al. 1996
$Ca_3Al_2O_6$	SX-108	Lumetta et al. 1996

(a) D.J. Temer. 1997. Personal communication. Los Alamos National Laboratory, Los Alamos, New Mexico

8.2 Chromium

Table 8.3 summarizes the amounts of Cr removed by dilute hydroxide washing and by caustic leaching. Here the trends are much less clear than with Al. There is considerable variability in the amount of Cr removed both by simple washing and by caustic leaching, even within the various SORWT groups. As has been indicated throughout this report, the Cr in the wash and leach solutions is invariably present as Cr(VI). Hence, the Cr removal is likely sensitive to the REDOX chemistry (i.e., the presence of oxidants) of the waste itself and of the washing or leaching solutions. The results of the S-101 and S-111 tests suggest that kinetics can also play a role in the efficacy of Cr removal (see Sections 5.1 and 6.1).

Table 8.4 summarizes the Cr-containing phases that have been identified in the Hanford tank sludges by microscopic examination coupled with X-ray diffraction techniques. As with Al, a variety of chemical species containing Cr are present in the sludges. In many cases, the Cr is bound up with other transition metals in spinel-type structures. It might be difficult to dissolve the Cr contained in such species, even under oxidative conditions, because the structure of these mineral phases would physically prevent the oxidant from reaching the Cr. For cases where Cr is bound up in Al hydroxides, such as in SY-103, caustic leaching would dissolve the Al hydroxide matrix and should expose the Cr to any oxidants present. Indeed, although caustic leaching removed only 12% of the Cr from SY-103 sludge (Rapko, Lumetta, and Wagner 1995), treating the caustic-leached SY-103 sludge with permanganate or ozone removed ~90% of the remaining Cr (Rapko, Lumetta, and Wagner 1996).

8.3 Phosphorus

Table 8.5 summarizes the amounts of P removed by dilute hydroxide washing and by caustic leaching. Simple washing removes very different amounts of P, even within the various SORWT groups. But agreement in the P removal for tanks within a given group generally improves after caustic leaching. For many of the tank sludges investigated to date, P removal by caustic leaching exceeds 90%. Only for BY-110, SX-108, B-201, B-202, and C-109 did P removal fall below 50%.

Microscopy studies have revealed several P-containing species in the Hanford sludges (Table 8.6). The microscopy data have indicated that the chemical behavior for these phosphate species appears to be normal. For example, the calcium phosphate phases are typically not affected by caustic leaching. Evidence for the type of metathesis reaction depicted in Equation 1.3 was found for the C-112 sludge. Microscopic examination of the C-112 sludge revealed a uranium-rich phosphate phase with diameters on the order of several µm. Caustic leaching caused these particles to break up into nm-sized particles, and the P was removed (LaFemina 1995). This suggests that the uranium phosphate was converted to uranium hydroxide, and the P was removed as Na_3PO_4. Sodium phosphate is easily removed by dilute hydroxide washing, provided adequate wash solution is used to sufficiently lower the Na activity (Rapko et al. 1996).

Table 8.3. Chromium Removal As a Function of Waste Type

		Waste Types[b]			Removed, %		
Tank	SORWT Group[a]	Primary	Secondary	Initial, wt %[c]	Simple Wash[d]	ESW[e]	References
S-101[f]	1	R	EB	0.71	44	89	(g)
S-107	1	R	EB	0.60	24	53	(h)
S-111[f]	1	R	EB	0.37	18	98	(g)
BY-104	3	TBP-F	EB-ITS	0.51	69	71	(h)
BY-110	3	TBP-F	EB-ITS	0.37	47	48	(h)
BY-108	3	TBP-F	EB-ITS	0.04	49	43	(g)
S-104	4	R	N/A	0.41	90	97	(i)
S-104[f]	4	R	N/A	0.45	94	99	(g)
SX-108	4	R	N/A	0.79	71	78	(h)
BX-105	5	TBP	CW	0.05	52	96	(j)
BX-109	5	TBP	CW	0.03	36	81	(k)
B-201	7	224	N/A	0.73	37	56	(l)
B-202	7	224	N/A	1.12	21	29	(j)
C-107	10	1C	CW	0.12	34	48	(h)
T-107	10	1C	CW	0.07	42	61	(j)
U-110	10	1C	CW	0.1	60	82	(l)
B-106	12	1C	TBP	0.07	12	78	(m)
BX-107	12	1C	TBP	0.23	21	29	(i)
C-108	13	TBP-F	1C	0.06	76	80	(j)
C-109	13	TBP-F	1C	0.03	80	85	(n)
C-112	13	TBP-F	1C	0.04	48	88	(n)
B-110	16	2C	5-6	0.23	10	52	(n)
B-111	16	2C	5-6	0.31	27	40	(i)
C-103	20	SRS	SR-WASH	0.16	2	11	(i)
C-106	20	SRS	SR-WASH	0.06	2	32	(o)
T-104	Ungrouped	1C	N/A	0.21	17	27	(j)
T-111	15	2C	224	0.45	24	63	(i)
B-104	Ungrouped	2C	EB	0.12	3	72	(k)
TY-104	22	TBP	1C-F	0.38	72	86	(k)

Table 8.3. (contd)

Tank	SORWT Group[(a)]	Waste Types[(b)]		Initial, wt %[(c)]	Removed, %		References
		Primary	Secondary		Simple Wash[(d)]	ESW[(e)]	
SX-113	24	R	DIA	0.01	2	40	(m)
C-104	Ungrouped	CW	OWW	0.23	13	52	(m)
C-105	Ungrouped	TBP	SR-WASH	0.07	81	86	(m)
AN-104	N/A	DSSF		0.25	34	63	(g)
SY-103	N/A	CC		1.30	5	12	(i)

(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
DIA = Diatomaceous earth
DSSF = Double-shell slurry feed
EB = Evaporator bottoms
ITS = In-tank solidification
F = Ferrocyanide-scavenged waste
OWW = Organic solvent wash from PUREX
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, except for S-111, which is on a wet-sludge basis

(d) Simple washing refers to washing with dilute NaOH (0.01 to 0.1 M)

(e) Enhanced sludge washing (ESW) refers to high caustic (~3 M) leaching followed by washing with dilute NaOH

(f) Extended leaching time used

(g) This work

(h) Lumetta et al. 1996

(i) Rapko, Lumetta, Wagner 1995

(j) Temer and Villarreal 1995

(k) Temer and Villarreal 1996

(l) Lumetta and Rapko 1994

(m) DJ Temer. 1997. Personal communication. Los Alamos National Laboratory, Los Alamos, New Mexico

(n) Compositional data from Colton 1995, percent removal data from Lumetta and Rapko 1994

(o) Lumetta, Wagner, Hoopes, and Steele 1996

Table 8.4. Chromium-Containing Phases Identified in Hanford Sludges

Phase	Tank	Reference
$Bi_{38}CrO_{60}$	B-111	LaFemina 1995
Cr(O)OH (grimaldite)	BY-110	Lumetta et al. 1996
$Al/Cr(OH)_3(am)$[(a)]	SY-103	LaFemina 1995
$NaAlO_2/Cr(OH)_3(am)$[(b)]	AN-104	This report
Ca/Cr Phase	AN-104	This report
$Fe(Cr,Fe)_2O_4$ (donathite)	BY-104	Lumetta et al. 1996
$FeCr_2O_4$	S-111	This report
Mn_2CrO_4	S-111	This report
$Mn_{1.5}Cr_{1.5}O_4$	S-111	This report

(a) Cr associated with amorphous Al hydroxide.

(b) Cr associated with amorphous Sodium Aluminate

Table 8.5. Phosphorus Removal As a Function of Waste Type

Tank	SORWT Group[a]	Waste Types[b]		Initial, wt %[c]	Removed, %		References
		Primary	Secondary		Simple Wash[d]	ESW[e]	
S-101[f]	1	R	EB	0.23	87	97	(g)
S-107	1	R	EB	0.20	> 91	98	(h)
S-111[f]	1	R	EB	0.2	100	--	(g)
BY-104	3	TBP-F	EB-ITS	0.31	93	95	(h)
BY-110	3	TBP-F	EB-ITS	0.56	19	23	(h)
BY-108	3	TBP-F	EB-ITS	2.35	73	70	(g)
S-104	4	R	N/A	< 0.02	--	--	(i)
S-104[f]	4	R	N/A	0.002	> 44	> 58	(g)
SX-108	4	R	N/A	0.12	9	37	(h)
BX-105	5	TBP	CW	0.09	91	100	(j)
BX-109	5	TBP	CW	4.50	76	96	(k)
B-201	7	224	N/A	1.25	8	26	(l)
B-202	7	224	N/A	1.00	28	44	(j)
C-107	10	1C	CW	0.95	69	94	(h)
T-107	10	1C	CW	5.42	85	99	(j)
U-110	10	1C	CW	1.1	90	> 98	(l)
B-106	12	1C	TBP	5.21	60	94	(m)
BX-107	12	1C	TBP	5.60	20	93	(i)
C-108	13	TBP-F	1C	5.95	75	80	(j)
C-109	13	TBP-F	1C	2.54	30	42	(n)
C-112	13	TBP-F	1C	4.91	44	84	(n)
B-110	16	2C	5-6	3.93	42	98	(n)
B-111	16	2C	5-6	4.10	43	91	(i)
C-103	20	SRS	SR-WASH	0.50	27	66	(i)
C-106	20	SRS	SR-WASH	0.21	66	68	(o)
T-104	Ungrouped	1C	N/A	6.68	26	55	(j)
T-111	15	2C	224	2.60	50	72	(i)
B-104	Ungrouped	2C	EB	3.46	45	99	(k)
TY-104	22	TBP	1C-F	4.04	83	98	(k)

Table 8.5. (contd)

		Waste Types(b)			Removed, %		
Tank	SORWT Group(a)	Primary	Secondary	Initial, wt %(c)	Simple Wash(d)	ESW(e)	References
SX-113	24	R	DIA	< 0.01	--	--	(m)
C-104	Ungrouped	CW	OWW	0.63	27	89	(m)
C-105	Ungrouped	TBP	SR-WASH	0.20	100	100	(m)
AN-104	N/A	DSSF		0.12	98	100	(g)
SY-103	N/A	CC		0.78	74	98	(i)

(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
DIA = Diatomaceous earth
DSSF = Double-shell slurry feed
EB = Evaporator bottoms
ITS = In-tank solidification
F = Ferrocyanide-scavenged waste
OWW = Organic solvent wash from PUREX
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, except for S-111, which is on a wet-sludge basis

(d) Simple washing refers to washing with dilute NaOH (0.01 to 0.1 M)

(e) Enhanced sludge washing (ESW) refers to high caustic (~3 M) leaching followed by washing with dilute NaOH

(f) Extended leaching time used

(g) This work

(h) Lumetta et al. 1996

(i) Rapko, Lumetta, Wagner 1995

(j) Temer and Villarreal 1995

(k) Temer and Villarreal 1996

(l) Lumetta and Rapko 1994

(m) DJ Temer. 1997. Personal communication. Los Alamos National Laboratory, Los Alamos, New Mexico

(n) Compositional data from Colton 1995, percent removal data from Lumetta and Rapko 1994

(o) Lumetta, Wagner, Hoopes, and Steele 1996

Table 8.6. Phosphorus-Containing Phases Identified in Hanford Sludges

Phase	Tank	Reference
$AlPO_4$	B-111	Rapko et al. 1996
	BX-107	LaFemina 1995
	T-104	LaFemina 1995
Bi/Fe Phosphate	T-111	LaFemina 1995
$Ca_5(OH)(PO_4)_3$	BY-104	Lumetta et al. 1996
	BY-110	Lumetta et al. 1996
	T-111	LaFemina 1995
$Ca_xSr_{10-x}(PO_4)_6(OH)_2$(x=8 or 9)	BY-108	This report
$Ca_3(PO_4)_2$	C-112	LaFemina 1995
$La_4(P_2O_7)_3$	T-111	LaFemina 1995
$Pb_5(OH)(PO_4)_3$	C-107	Lumetta et al. 1996
Na_3PO_4	B-111	LaFemina 1995
	BX-107	LaFemina 1995
	T-104	LaFemina 1995
	T-111	LaFemina 1995
U Phosphate	C-112	LaFemina 1995

8.4 Sodium

The minimum sludge pretreatment that would be applied at Hanford is dilute hydroxide washing. The goal of such washing would be to remove most of the Na from the waste. Thus, it is of interest to examine the effectiveness of dilute hydroxide washing at removing Na. Because of the significant additions of Na during caustic leaching tests, it is difficult to quantify how much Na is actually removed from the waste by caustic leaching. Hence, this discussion will focus only on the Na behavior in dilute hydroxide washing.

Table 8.7 summarizes the amount of Na removed by dilute hydroxide washing. In some cases, the percent Na removal could not be determined because of the nature of the experiment. Hence, some of the tanks listed in Tables 8.1, 8.3, and 8.5 are absent from Table 8.7. Except for U-110, Na removal was always greater than 70%; even with U-110, it was close to 70%. Greater than 90% of the Na was removed for over half of the tanks listed.

Table 8.7. Sodium Removal By Dilute Hydroxide Washing As a Function of Waste Type

		Waste Types(b)				
Tank	SORWT Group(a)	Primary	Secondary	Initial, wt %(c)	Removed, %	References
S-101	1	R	EB	18	97	(d)
S-107	1	R	EB	16	93	(e)
BY-110	3	TBP-F	EB-ITS	29	98	(e)
BY-108	3	TBP-F	EB-ITS	21	96	(d)
S-104	4	R	N/A	18	96	(d)
SX-108	4	R	N/A	23	96	(e)
BX-109	5	TBP	CW	20	96	(f)
B-201	7	224	N/A	10	73	(g)
U-110	10	1C	CW	11	69	(g)
B-106	12	1C	TBP	20	95	(h)
C-109	13	TBP-F	1C	11	76	(i)
C-112	13	TBP-F	1C	20	73	(i)
B-110	16	2C	5-6	23	96	(j)
C-106	20	SRS	SR-WASH	23	82	(j)
B-104	Ungrouped	2C	EB	25	93	(f)
SX-113	24	R	DIA	0.2	73	(h)
C-104	Ungrouped	CW	OWW	17	88	(h)
C-105	Ungrouped	TBP	SR-WASH	5.3	78	(h)

(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
DIA = Diatomaceous earth
EB = Evaporator bottoms
ITS = In-tank solidification
F = Ferrocyanide-scavenged waste
OWW = Organic solvent wash from PUREX
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) This work

(e) Lumetta et al. 1996

(f) Temer and Villarreal 1996

(g) Lumetta and Rapko 1994

(h) DJ Temer. 1997. Personal communication. Los Alamos National Laboratory, Los Alamos, New Mexico

(i) Compositional data from Colton 1995, percent removal data from Lumetta and Rapko 1994

(j) Lumetta, Wagner, Hoopes, Steele 1996

8.5 Radionuclides

In general, only ^{137}Cs and ^{99}Tc display appreciable solubility in the alkaline washing and leaching solutions. This is what would be expected based on the solubility of simple Cs and TcO_4^- salts. However, in many cases, only a relatively small fraction of the ^{137}Cs is removed from the sludge solids by dilute-hydroxide washing (Table 8.8). For example, ≤5% of the ^{137}Cs is removed from Tanks BY-108, U-110, C-109, C-112, T-104, and SX-113 by dilute-hydroxide washing. Leaching with caustic generally improves the removal of ^{137}Cs from the sludges; in many cases, the amount of ^{137}Cs removed dramatically increases (e.g., BY-108, C-108, C-109, C-112, and SX-113). One possible explanation for this behavior is that the ^{137}Cs is tied up in one or more mineral forms that act as ion exchangers. Upon raising the Na ion concentration, the Cs is "eluted" from the ion exchanger.

Interestingly, wastes in Tanks BY-108, C-108, C-109, and C-112 were scavenged with ferrocyanide to precipitate the ^{137}Cs as $NaCsNiFe(CN)_6$ or $Cs_2NiFe(CN)_6$. The Cs being present would explain the ^{137}Cs behavior during washing and caustic leaching as the nickel ferrocyanide salts in these wastes. Recent studies have shown that $Na_2NiFe(CN)_6$ decomposes by both radiolytic and hydrolytic mechanisms under conditions that would be expected in the Hanford tanks, and it has been suggested that these pathways would have led to a reduction in the overall ferrocyanide concentrations in the sludges (Lilga et al. 1995). However the cesium nickel ferrocyanide salts are less soluble in aqueous NaOH (Bryan et al. 1993; Lilga et al. 1995), so their decomposition might be slower than the Na analog. Indeed, ferrocyanide has been detected in actual C-109 and C-112 sludges at levels close to 1 wt% (Bryan et al. 1995).

The increased removal of ^{137}Cs upon caustic leaching is actually an undesirable feature of ESW. It would be preferable for the ^{137}Cs to remain in the solids, which would be immobilized as HLW. Because much of the ^{137}Cs partitions to the wash and leach solutions, it will likely need to be removed from these solutions before LLW immobilization (see below).

Table 8.9 presents projected radionuclide concentrations in the LLW that would be produced by immobilizing the combined washing and leaching solutions from the various ESW tests. The projected concentrations are based on a waste form that contains 20 wt% Na_2O and has a density of 2.7 MT/m^3 (Orme et al. 1996). The values listed in Table 8.9 should be used only as indicators rather than definitive values for the radionuclide concentrations in the LLW because the test conditions used (NaOH concentrations, solution-to-solids ratios, etc.) were not necessarily the optimal process conditions.

The projected ^{137}Cs contents are well below the NRC Class C LLW limit of 4,600 Ci/m^3, but in most cases it is well above the proposed guideline of 3 Ci/m^3 for the immobilized LLW product from the proposed private processing facilities. Hence, it appears likely that ^{137}Cs will need to be removed from the combined washing and leaching solutions before LLW immobilization. For the vast majority of the tanks, the projected TRU concentrations in the LLW fall below the 0.1 µCi/g limit for Class C LLW. The tanks with potential of coming close to this limit include C-103 and C-106. Likewise, the projected ^{90}Sr concentrations are below the NRC Class C limit of 7,000 Ci/m^3 and in most cases are well below the proposed guideline of 20 Ci/m^3 for the immobilized LLW product from the proposed private processing facilities. The exception to this is C-103, which is near the 20 Ci/m^3 ^{90}Sr guideline. The proposed

Table 8.3. Cesium-137 Removal As a Function of Waste Type

		Waste Types(b)			Removed, %		
Tank	SORWT Group(a)	Primary	Secondary	Initial, μCi/g(c)	Simple Wash(d)	ESW(e)	References
S-101(f)	1	R	EB	138	97	100	(g)
S-107	1	R	EB	141	77	100	(h)
S-111(f)	1	R	EB	0.85	48	96	(g)
BY-104	3	TBP-F	EB-ITS	84	100	100	(h)
BY-110	3	TBP-F	EB-ITS	181	98	100	(h)
BY-108	3	TBP-F	EB-ITS	1590	3	99	(g)
S-104	4	R	N/A	91.6	90	98	(i)
SX-108	4	R	N/A	45	63	87	(h)
BX-105	5	TBP	CW	58.6	97	100	(j)
BX-109	5	TBP	CW	25.30	54	100	(k)
B-201	7	224	N/A	2.3	17	25	(n)
B-202	7	224	N/A	0.11	52	76	(j)
C-107	10	1C	CW	127	13	70	(h)
T-107	10	1C	CW	15.6	25	91	(j)
U-110	10	1C	CW	22	5	10	(l)
B-106	12	1C	TBP	59.3	51	100	(m)
BX-107	12	1C	TBP	38.1	17	94	(i)
C-108	13	TBP-F	1C	614	4	99	(j)
C-109	13	TBP-F	1C	950	5	98	(n)
C-112	13	TBP-F	1C	1360	5	98	(n)
B-110	16	2C	5-6	35	48	92	(n)
B-111	16	2C	5-6	372	52	95	(i)
C-103	20	SRS	SR-WASH	236	20	44	(i)
C-106	20	SRS	SR-WASH	681	38	60	(o)
T-104	Ungrouped	1C	N/A	2.39	0	69	(j)
T-111	15	2C	224	1.16	25	66	(i)
B-104	Ungrouped	2C	EB	9.44	36	99	(k)
TY-104	22	TBP	1C-F	128	41	54	(k)

Table 8.8. (contd)

Tank	SORWT Group[a]	Waste Types[b]		Initial, µCi/g[c]	Removed, %		References
		Primary	Secondary		Simple Wash[d]	ESW[e]	
SX-113	24	R	DIA	45.5	3	88	(m)
C-104	Ungrouped	CW	OWW	174	56	100	(m)
C-105	Ungrouped	TBP	SR-WASH	293	54	92	(m)
AN-104	N/A	DSSF		600	100	100	(g)
SY-103	N/A	CC		361	97	100	(i)

(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
DIA = Diatomaceous earth
DSSF = Double-shell slurry feed
EB = Evaporator bottoms
ITS = In-tank solidification
F = Ferrocyanide-scavenged waste
OWW = Organic solvent wash from PUREX
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, except for S-111, which is on a wet-sludge basis
(d) Simple washing refers to washing with dilute NaOH (0.01 to 0.1 M)
(e) Enhanced sludge washing (ESW) refers to high caustic (~3 M) leaching followed by washing with dilute NaOH
(f) Extended leaching time used
(g) This work
(h) Lumetta et al. 1996
(i) Rapko, Lumetta, Wagner 1995
(j) Temer and Villarreal 1995
(k) Temer and Villarreal 1996
(l) Lumetta and Rapko 1994
(m) DJ Temer. 1997. Personal communication. Los Alamos National Laboratory, Los Alamos, New Mexico
(n) Compositional data from Colton 1995, percent removal data from Lumetta and Rapko 1994
(o) Lumetta, Wagner, Hoopes, and Steele 1996

Table 8.9. Projected Radionuclide Content for LLW From Immobilization of Combined Wash and Leach Solutions

		TRU		^{137}Cs		^{90}Sr		^{99}Tc	
Tank	Na, g[(a)]	Total, µCi[(a)]	LLW, µCi/g[(b)]	Total, µCi[(a)]	LLW, Ci/m^3 [(b)]	Total, µCi[(a)]	LLW, Ci/m^3 [(b)]	Total, µCi[(a)]	LLW, Ci/m^3 [(b)]
AN-104	4.522	< 1.35E-02	< 4.42E-04	2.44E+03	2.16E+02	3.94E+00	3.48E-01	8.53E-01	7.54E-02
B-104	7.552	< 4.93E-02	< 9.66E-04	5.54E+01	2.93E+00	< 9.13E-02	< 4.83E-03	< 5.48E-02	< 2.90E-03
B-106	7.284	< 1.50E-02	< 3.05E-04	2.15E+02	1.18E+01	< 7.75E-01	< 4.25E-02	< 2.60E-02	< 1.43E-03
B-111	2.197	< 1.73E-03	< 1.17E-04	1.48E+03	2.69E+02	3.30E-01	6.00E-02	1.29E+00	2.35E-01
B-202	0.727	< 2.75E-02	< 5.60E-03	1.95E-01	1.07E-01	< 3.11E-01	< 1.71E-01	< 7.60E-02	< 4.18E-02
BX-105	4.935	< 2.58E-01	< 7.74E-03	5.46E+02	4.42E+01	< 6.92E+00	< 5.60E-01	< 9.36E-01	< 7.58E-02
BX-107	2.666	< 3.46E-03	< 1.92E-04	1.50E+02	2.25E+01	1.61E-01	2.41E-02	3.50E-01	5.25E-02
BX-109	3.416	< 2.20E-02	< 9.53E-04	6.04E+01	7.07E+00	< 4.08E-01	< 4.77E-02	< 2.45E-02	< 2.87E-03
BY-104	17.04	< 3.74E-02	< 3.25E-04	4.82E+04	1.13E+03	< 7.15E+00	< 1.68E-01	1.75E+01	4.10E-01
BY-108	12.83	< 6.60E-02	< 7.61E-04	1.48E+04	4.60E+02	2.90E+01	9.03E-01	1.65E-01	5.14E-03
BY-110	4.785	< 1.63E-02	< 5.04E-04	8.10E+02	6.76E+01	2.09E+01	1.75E+00	6.49E-01	5.42E-02
C-103	1.492	5.22E-01	5.18E-02	8.74E+01	2.34E+01	7.34E+01	1.97E+01	2.38E-01	6.37E-02
C-104	19.22	< 4.52E-02	< 3.48E-04	7.28E+02	1.51E+01	< 2.33E+00	< 4.84E-02	< 1.35E-01	< 2.81E-03
C-105	2.717	< 8.80E-02	< 4.79E-03	6.77E+02	9.96E+01	< 1.63E+00	< 2.40E-01	< 1.96E-01	< 2.88E-02
C-106	2.497	< 1.73E+00	< 1.03E-01	1.97E+03	3.16E+02	< 1.62E+01	< 2.59E+00	3.22E-01	5.15E-02
C-107	7.557	6.46E-01	1.26E-02	3.63E+02	1.92E+01	2.23E+01	1.18E+00	2.61E-01	1.38E-02
C-108	3.12	< 4.76E-01	< 2.26E-02	3.84E+03	4.92E+02	< 8.80E+01	< 1.13E+01	< 4.91E-01	< 6.29E-02
S-101	10.81	< 5.84E-02	< 8.00E-04	6.60E+02	2.44E+01	1.10E+01	4.07E-01	3.86E-01	1.43E-02
S-104	9.774	< 7.18E-02	< 1.09E-03	4.26E+02	1.74E+01	7.93E+01	3.24E+00	1.46E-01	5.97E-03
S-107	14.34	< 1.12E-02	< 1.16E-04	4.63E+02	1.29E+01	2.13E-01	5.93E-03	3.96E-01	1.10E-02
S-111	7.326	< 3.35E-02	< 6.77E-04	7.62E+00	4.16E-01	8.40E+01	4.58E+00	2.83E-02	1.54E-03
SX-108	24.45	< 8.10E-02	< 4.90E-04	2.41E+03	3.93E+01	9.54E+01	1.56E+00	2.65E+00	4.33E-02
SX-113	10.81	< 7.77E-02	< 1.06E-03	6.39E+01	2.36E+00	2.90E+00	1.07E-01	< 8.64E-02	< 3.19E-03
SY-103	2.545	7.42E-02	4.31E-03	2.38E+03	3.74E+02	1.77E+01	2.78E+00	7.40E-01	1.16E-01
T-104	1.691	< 3.10E-03	< 2.71E-04	1.21E+00	2.86E-01	< 1.67E+00	< 3.95E-01	< 9.22E-04	< 2.18E-04
T-107	3.652	< 1.80E-01	< 7.29E-03	7.89E+01	8.63E+00	< 8.21E-01	< 8.98E-02	< 3.34E-01	< 3.65E-02
T-111	2.728	< 4.36E-03	< 2.37E-04	3.21E+00	4.70E-01	< 8.71E-02	< 1.28E-02	< 1.09E-03	< 1.60E-04
TY-104	2.865	< 2.74E-01	< 1.42E-02	3.07E+02	4.28E+01	< 5.05E-01	< 7.04E-02	< 2.02E-01	< 2.82E-02

(a) Total amount of component in combined process streams from ESW test: retrieval wash (where applicable) + first caustic leach + second caustic leach + final wash

(b) Assumes LLW waste form contains 20 wt% Na_2O, and has a density of 2.7 MT/m^3

guideline for ^{99}Tc is 0.3 Ci/m^3 for the immobilized LLW product from the proposed private processing facilities. For the vast majority of the tanks, the projected ^{99}Tc concentrations in the immobilized LLW are within this guideline. The tanks with the potential of coming close to or exceeding this limit include B-111, BY-104, and SY-103.

8.6 Particle Size

Table 8.10 summarizes the particle-size data for selected Hanford tank sludges. This list only includes measurements made at PNNL in FY 1996 and FY 1997. These measurements were all made using a Microtrac 7 X 100 particle-size analyzer (Leeds & Northrup, North Wales, Pennsylvania) with the particles being slurried in water for the measurement. Measurements made at PNNL before FY 1996 were made on slurries prepared using 1:1 glycerin/water, so those measurements are not directly comparable to the more recent measurements. Although water slurries were used for particle-size measurements at LANL, the instrument used there only measured particles up to 10 µm; so the LANL measurements also are not directly comparable to the recent measurements at PNNL.

The particle-size data in Table 8.10 are presented in terms of both the number and volume distributions. Three key pieces of information are presented: 1) the mean particle diameter, 2) the particle diameter for which 95% of the particles are larger (5th percentile), and 3) the particle diameter for which 95% of the particles are smaller (95th percentile). Based on the number distributions, the mean particle sizes were generally less than 1 µm. Exceptions to this were the untreated AN-104 sludge and the leached S-111 sludge. The unusual behavior of the untreated S-111 solids was noted earlier in this report. The untreated S-111 material contained very large particles with the appearance of sand. These particles were so heavy that it was not possible to homogenize the sample to get a representative aliquot for analysis. It is likely that the untreated S-111 sludge had mean particle sizes larger than 1 µm as well. The volume distributions indicated more of a spread in the mean particle diameter, but they were generally less than 10 µm. Again, the leached S-111 sludge was an exception.

In terms of the number distributions, ESW had relatively little impact on the mean particle diameters. The volume distributions generally indicated a decrease in the mean particle diameter, with dramatic decreases being seen for BY-104 and S-107. Interestingly, the mean particle size (based on the volume distribution) increased upon leaching AN-104 sludge.

Sonicating the samples usually resulted in minor decreases in the mean particle diameters. Inspection of the histograms indicated these decreases were generally due to break up of the largest particles in the samples. Once again, the leached S-111 sludge proved an exception to this, highlighting the unusual behavior of the particles in this particular sludge. The mean particle diameter, based on the volume distribution, nearly tripled after the sample had been sonicated. The reason for this behavior is not known.

Table 8.10. Summary of Particle Size Data

	Particle Diameter, µm						
	Number Distribution			Volume Distribution			
Tank	Mean	Percentile(a)	95th Percentile(b)	Mean	5th Percentile(a)	95th Percentile(b)	Reference
AN-104 - Untreated	1.47	0.8	2.34	4.08	1.2	11.7	(e)
AN-104 - Untreated(b)	1.19	0.55	2.19	5.68	1.1	13.6	(e)
AN-104 - Leached	1.01	0.45	2.37	6.03	1.0	29.6	(e)
AN-104 - Leached(b)	0.74	0.35	1.88	6.96	0.7	30.3	(e)
BY-104 - Untreated	0.68	0.35	1.35	10.5	1.0	28.8	(f)
BY-104 - Untreated(b)	0.49	0.25	1.08	6.98	0.6	30.7	(f)
BY-104 - Leached	0.83	0.38	1.6	1.96	0.65	4.51	(f)
BY-104 - Leached(b)	0.70	0.38	1.31	1.54	0.55	3.58	(f)
BY-108 - Untreated	0.31	0.18	0.78	6.53	0.4	23.2	(e)
BY-108 - Untreated(b)	0.31	0.18	0.62	4.23	0.3	15.9	(e)
BY-108 - Leached	0.31	0.18	0.75	3.80	0.5	12.1	(e)
BY-108 - Leached(b)	0.34	0.18	0.75	3.03	0.3	10.4	(e)
BY-110 - Untreated	0.52	(c)	(c)	6.15	0.7	22.4	(f)
BY-110 - Untreated(b)	0.39	(c)	(c)	4.84	0.4	21.2	(f)
BY-110 - Leached	(c)	(c)	(c)	(c)	(c)	(c)	
S-101 - Untreated	0.51	0.25	1.21	6.80	0.7	17.9	(e)
S-101 - Leached	0.32	0.18	0.74	4.75	0.35	18.2	(e)
S-104 - Untreated	0.29	0.18	0.61	6.78	0.3	28.6	(e)
S-104 - Untreated(b)	0.2	0.12	0.36	3.53	0.17	14.3	(e)
S-104 - Leached	0.31	0.18	0.74	5.21	0.3	27.9	(e)
S-107 - Untreated	0.58	(c)	(c)	13.48	0.8	45.7	(f)
S-107 - Untreated(b)	0.48	(c)	(c)	10.69	0.7	44.6	(f)
S-107 - Leached	0.13	(c)	(c)	0.31	0.1	0.83	(f)
S-111 - Leached	1.79	1.0	3.25	47.7	6	181	(e)
S-111 - Leached(b)	1.62	1.0	2.94	129	7	256	(e)
SX-108 - Untreated	0.61	0.31	1.21	12.8	0.65	33.8	(f)
SX-108 - Untreated(b)	0.25	0.15	0.5	9.64	0.28	31.0	(f)
SX-108 - Leached	0.32	0.18	0.68	3.05	0.3	9.87	(f)
SX-108 - Leached(b)	0.28	(c)	(c)	3.07	0.25	15.8	(f)

(a) 95% of the particles have diameters larger than this value

(b) 95% of the particles have diameters smaller than this value

(c) Sample sonicated for 5 minutes

(d) Data not available

(e) This work

(f) Lumetta et al. 1996

8.7 Conclusions

The following are the key conclusions from the work presented in this report.

- Chromium(III) hydroxide can dissolve in high caustic solutions at room temperature, but heating such solutions precipitates guyanaite, syn (CrOOH), which does not readily redissolve in aqueous caustic media. Thus, caustic leaching in and of itself (i.e., in the absence of oxidants) is not likely to remove much Cr from the Hanford tank sludges as Cr(III).

- However, additional Cr is often removed (as chromate) during caustic leaching, apparently because of some oxidative pathway.

- Dilute hydroxide washing was generally ineffective at removing Al from the tank sludges. The exceptions to this were the sludges from the SORWT group 3 tanks and Tank BX-109.

- Caustic leaching was generally effective at removing Al. Only three groups of sludges displayed consistently low (< 50%) Al removal—SORWT groups 7, 16, and 20.

- Extended caustic leaching (several days at 100°C) significantly improves Al removal (and in some cases Cr removal) from REDOX sludge when compared to previous testing methods, which used only 5-h leaching durations. This can be attributed to slow dissolution of boehmite. Nearly all of the Al was removed from the three REDOX sludges examined (S-101, S-104, and S-111) when longer leaching times were used.

- The Al removal data generally indicate good agreement for tanks within a given SORWT group.

- For many of the tank sludges investigated to date, caustic leaching removed more than 90% of the P. Only for BY-110, SX-108, B-201, B-202, and C-109 did P removal fall below 50%.

- Dilute hydroxide washing was generally effective at removing Na from the Hanford tank sludges. More than 90% of the Na was removed for over half of the tanks tested.

- Cesium-137 will likely need to be removed from the sludge washing and leaching solutions before these solutions are immobilized as LLW. The behavior of ^{137}Cs in sludges from ferrocyanide-scavenged tanks suggests that the ^{137}Cs might still be present as the cesium nickel ferrocyanide salt.

- The quantities of TRU, ^{90}Sr, and ^{99}Tc in the washing and leaching solutions are generally low, and removal of these isotopes from the LLW stream probably will not be necessary.

- Particle-volume distributions indicate that the mean particle diameters generally tend to decrease upon leaching with caustic. Sludge from AN-104 is an exception to this rule.

- The behavior of the S-111 particles was unusual in several respects. These particles were much larger than those seen for other sludges, and the mean particle size increased dramatically when the sample was sonicated. For the other sludges measured, sonication tended to break up the larger particles, resulting in a slight decrease in the mean particle diameter.

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Appendix A

Analytical Methods

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Analytical Methods

This appendix describes the analytical methods used in the enhanced sludge washing tests. Portions of the sludge solids were analyzed before and after the dilute hydroxide washing and the caustic leaching treatments. The solid samples were solubilized for analysis by well established KOH and sodium peroxide fusion methods.[1] The sodium peroxide fusion method was used to determine K and Ni and also gave a duplicate analytical result for the other sludge components. Throughout this report, the mean values are reported for those components determined through both fusion methods.

Samples of the dilute hydroxide wash, the first and second leach, and the final wash solutions were analyzed after acidification with HNO_3. Typically, samples were acidified within two or three days after the washing or leaching step was complete. 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). Alpha spectroscopy was used to determine the TRU elements, and gamma spectroscopy was used to measure gamma-emitting radionuclides (e.g., ^{137}Cs, ^{154}Eu, and ^{155}Eu). Uranium concentrations were determined by laser fluroimetry. A proportional beta counter was used to determine ^{90}Sr and ^{99}Tc after chemical separation of these isotopes from the other radionuclides. Treatment with Ce(IV) ensured that all Tc was in the +7 oxidation state before chemical separation because the separation employed relied on the Tc being present as pertechnetate. Anions were determined by ion chromatography on solutions that were not acidified. Established procedures were used for all these analyses.[1]

Particle-size measurements were made using a Microtrac 7 X100 particle-size analyzer (Leeds & Northrup, North Wales, Pennsylvania) with the particles being slurried in water for the measurement. 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 sample slurry on TEM copper grids covered with carbon films. This work was performed using a JEOL 1200 analytical TEM operating at 120 kV. The analyses proceeded as follows: 1) the morphology, distribution, and sizes of the particles were evaluated by electron imaging; 2) the chemical compositions of the particles were identified by electron dispersive spectroscopy (EDS); 3) the crystal structures of the particles were studied by electron diffraction; and 4) the diffraction patterns were compared with the JCPS-EDD Database published by the International Center for Diffraction Data.

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[1] Methods used were from the *Analytical Chemistry Laboratory (ACL) Procedure Compendium.* PNL-MA-599. Analytical Chemistry Laboratory Department, Pacific Northwest National Laboratory, Richland, Washington.

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