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Caustic Leaching of Composite AZ-101/AZ-102 Hanford Tank Sludge

B. M. Rapko
M. J. Wagner

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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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B. M. Rapko

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

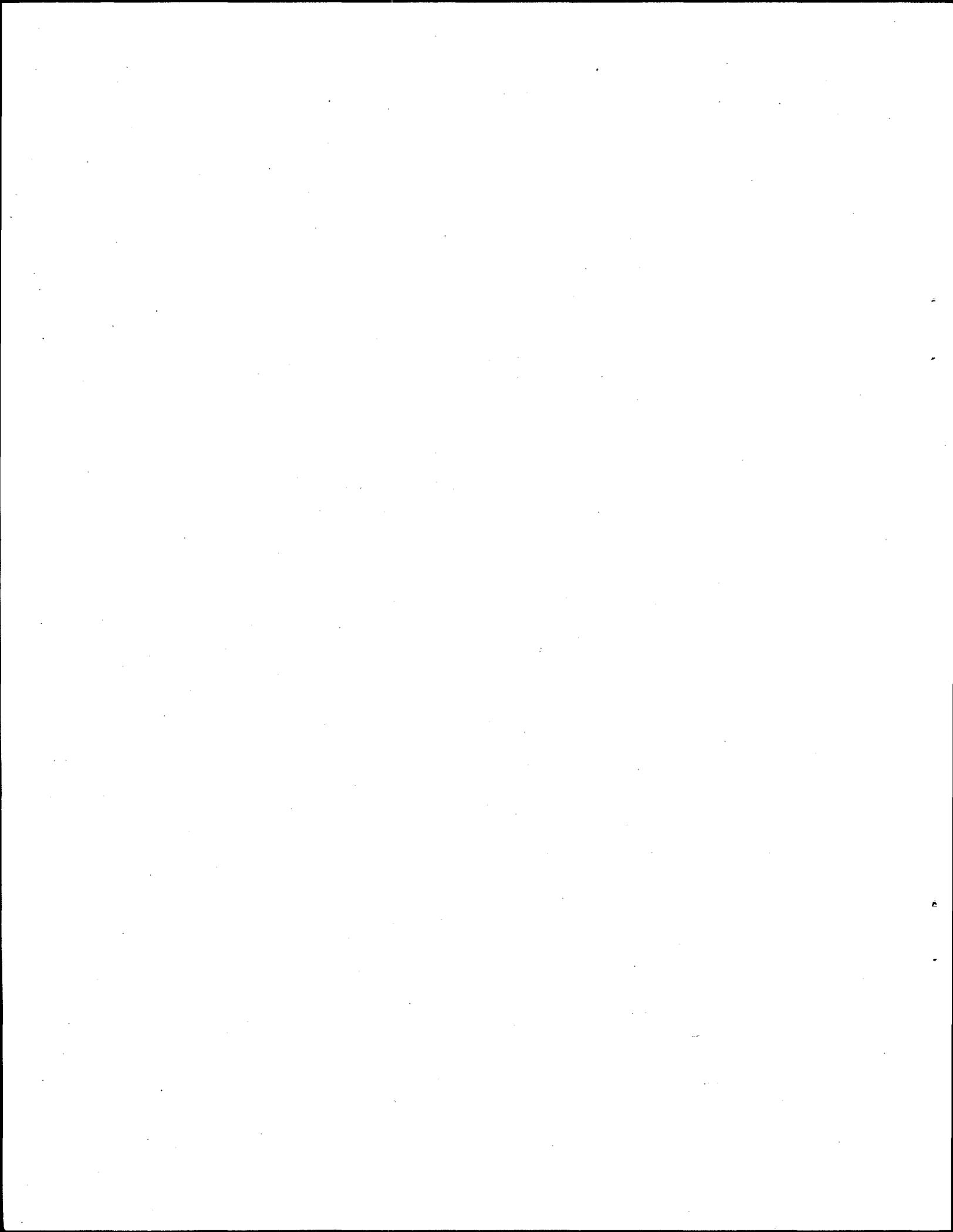
To reduce the quantity (and hence the cost) of glass canisters needed for disposing of high-level radioactive wastes from the Hanford tank farms, pretreatment processes are needed to remove as much nonradioactive material as possible. This report describes the results of a laboratory-scale caustic leaching test performed on a composite derived from a combination of 241-AZ-101 and 241-AZ-102 Hanford Tank sludges. The goals of this FY 1996 test were to evaluate the effectiveness of caustic leaching on removing key components from the sludge and to evaluate the effectiveness of varying the free-hydroxide ($[\text{OH}]^-$) concentrations by incrementally increasing the free- $[\text{OH}]^-$ concentration of the leach steps up to 3 M free $[\text{OH}]^-$. The results of this work can be summarized as follows.

- The major components of the AZ-101/AZ-102 composite sludge were (on a dry weight basis) Fe (14 wt%), Na (12 wt%), Al (6 wt%), Zr (1.8 wt%), Cd (1.3 wt%), and U (1 wt%). For these elements, the cumulative impact of six caustic leaches from 0.23 M NaOH up to 3 M NaOH leaches and three 0.01 M NaOH final washes varied: Fe (0% removed), Al (79% removed), Zr (0% removed), Cd (2% removed), and U (19% removed). Other significant nonradionuclides removed by caustic leaching include Cr (58%), K (69%), P (63%) and Zn (34%). Because of experimental complications, the removal of Na could not be evaluated, but the final Na concentration in the dried, treated solids was 1.6 wt%.
- The transuranic elements and ^{90}Sr showed no tendency to dissolve, either in the 0.23 to 3 M NaOH leach solutions or in the 0.01 M NaOH final washes. Caustic leaching effectively removed the following radioisotopes: ^{137}Cs (97% removed) and ^{99}Tc (93% removed).
- Almost all of the radioactive and nonradioactive materials removed by caustic leaching were removed by completion of the first 3 M NaOH leach; only small additional quantities of Al (5%) and Si (14%) were removed by an additional 3 M NaOH leach.
- Careful comparison of component concentrations for leaching at 0.1, 1, 2, and 3 M free $[\text{OH}]^-$ indicates that substantial changes in the concentrations of dissolved components occurred between 0.1 and 1 M free $[\text{OH}]^-$, but that subsequent increases in the free- $[\text{OH}]^-$ concentration up to 3 M had little additional effect.
- The settling behavior of the AZ-101/AZ-102 sludge solids was favorable. The rate of settling generally decreased as the free- $[\text{OH}]^-$ concentration increased; however, normalized settling behavior was very similar at all $[\text{OH}]^-$ concentrations.

Particle-size analysis of the treated and untreated sludge indicated that the size and range of the sludge particles remained essentially unchanged by the caustic leaching treatment. Both before and after caustic leaching, a particle range of 0.2 μm to 50 μm was observed, with mean particle diameters of 8.5 to 9 μm based on the volume distribution and mean particle diameters of 0.3 to 0.4 μm based on the number distribution.

Acronyms

AAS	alternative acquisition strategy
ACL	Analytical Chemistry Laboratory
EDS	electron dispersion spectroscopy
HDPE	high-density polyethylene
HLW	high-level waste
IC	ion chromatography
ICP/AES	inductively coupled plasma/atomic emission spectroscopy
LLW	low-level waste
PNNL	Pacific Northwest National Laboratory
TEM	transmission electron microscopy
TRU	transuranic
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

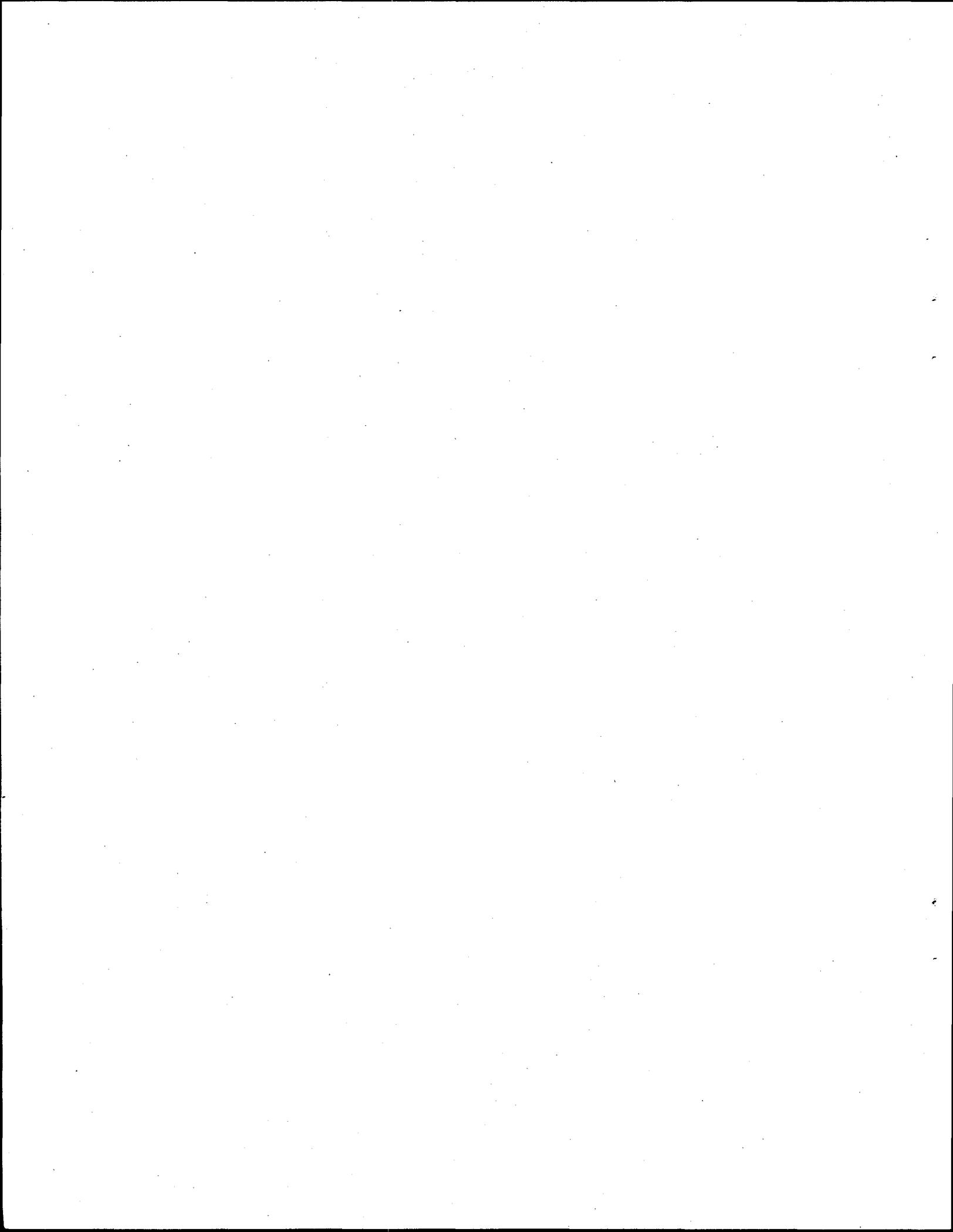


Acknowledgments

The authors gratefully acknowledge the technical assistance of the Analytical Chemistry Laboratory personnel. We also thank the following staff at Pacific Northwest National Laboratory: D. E. Rinehart for technical assistance and G. J. Lumetta and W. C. Cosby for reviewing this document.

This work was supported by the U.S. Department of Energy, through the Tank Waste Remediation System (TWRS; EM-30). The authors would like to thank G. T. MacLean (SGN Eurisys Services Corporation) for his assistance in describing how to present normalized settling behavior and J. L. Swanson for his valuable review of this document.

Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.



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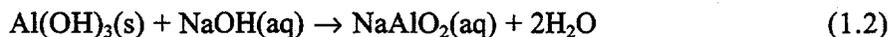
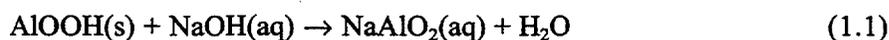
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1.0 Introduction

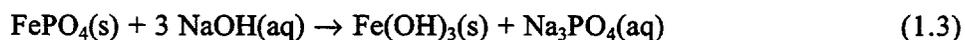
During the past few years, the primary mission at the U.S. Department of Energy's Hanford Site has changed from producing Pu to restoring the environment. Large volumes of high-level radioactive wastes (HLW), generated during past Pu production and other operations, are stored in underground tanks on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

The baseline sludge pretreatment flowsheet involves retrieval of the sludge by sluicing and pumping with inhibited water (0.01 M sodium hydroxide [NaOH]/0.01 M sodium nitrite [NaNO₂]), leaching the sludge with caustic (3 M NaOH), then washing the sludge with inhibited water to remove the added NaOH and the components dissolved during the caustic-leaching step. The retrieval, leach, and wash solutions will be combined and processed to remove ¹³⁷Cs (and possibly other radionuclides). The decontaminated solution will then be routed to the low-level waste (LLW) stream, where it will be immobilized in a glass matrix. The leached solids, which will contain the transuranic (TRU) elements and ⁹⁰Sr, will be handled as HLW (Orme et al. 1996). Several studies of the baseline Hanford sludge washing and caustic-leaching process have been reported to date (Lumetta and Rapko 1994; Rapko et al. 1995; Temer and Villareal 1995a; Temer and Villareal 1995b; Lumetta et al. 1996a; Lumetta et al. 1996b; Temer and Villareal 1996).

A key step in the baseline sludge pretreatment flowsheet is leaching the sludge with caustic. Caustic leaching is expected to remove a large fraction of the Al, which is present in large quantities in Hanford tank sludges. Aluminum is removed when Al oxides/hydroxides convert to sodium aluminate (NaAlO₂). For example, boehmite (AlOOH) and gibbsite (Al(OH)₃) are dissolved according to the following equations (Weber 1982).

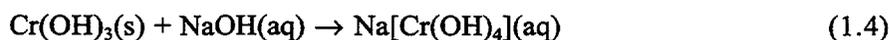


A significant portion of the P is also expected to be removed from the sludge when water-insoluble metal phosphate (PO₄) salts metathesize to insoluble [OH]⁻ salts and soluble Na₃PO₄. An example of this is shown for Fe(III) PO₄ in the following equation.



Sulfate can be removed from the HLW stream as a result of similar metathesis reactions for the insoluble sulfate salts.

Based on the known amphoteric behavior of Cr(III), (Rai et al. 1987) Cr is expected to dissolve because of the formation of the tetrahydroxochromium(III) anion.



However, recent work in our laboratory (Lumetta et. al. 1996a; Rapko et al. 1996; Rapko et al. 1997) has indicated a more complex chemistry for Cr dissolution during the caustic-leaching process. Specifically, ultraviolet visible (UV-vis) spectroscopic measurements of the caustic-leach solutions reveal that the dissolved Cr is present as Cr(VI), not Cr(III), indicating further Cr oxidation during the caustic leach. Furthermore, soluble Cr(III) has been shown to precipitate from caustic solutions at elevated temperatures.¹

Alternative approaches to sludge washing and caustic leaching might be developed and applied as a consequence of the Phase I Alternative Acquisition Strategy (AAS). The sludges proposed for processing during Phase I are a composite of the solids from Tanks AZ-101 and AZ-102, solids from Tank C-106, or a composite of solids from all three of these tanks. Sludge washing and caustic-leaching tests have been performed on Tank C-106 sludge (Lumetta et. al. 1996b).

This report describes the results of a small-scale screening test performed with an actual Hanford tank sludge composite comprised of sludge from tanks AZ-101 and AZ-102. The work was performed under the Sludge Washing of Phase I Feeds Project at the Pacific Northwest National Laboratory (PNNL). The work has two objectives: first, to collect data regarding the efficacy of water washing and caustic leaching in removing certain sludge components from the HLW sludges expected to be processed during the Phase I AAS and second, to collect information on the effects of varying NaOH concentration on the caustic leaching of this sludge composite to evaluate the efficacy of the leaching process under potential alternative caustic-leaching conditions.

¹ G. J. Lumetta, Pacific Northwest National Laboratory, personal communication.

2.0 Experimental Section

The materials and methods used in the leach test are discussed in this section.

2.1 Materials

Composites of sludge from tanks 241-AZ-101 and 241-AZ-102 were used from materials stored in the hot cells of the 325 building. The source of these materials has been previously described (Gray et al. 1993; Peterson et al. 1993). Previous characterization reports (Hodgson 1995; Ryan 1995; Schreiber 1995) indicate that both sludge composites contained a substantial portion of water (40 to 45% for AZ-101 and ca. 50% for AZ-102). Although the AZ-101 sludge was a paste, indicating substantial interstitial fluid, the water appeared to have evaporated from the AZ-102 sludge, leaving a hard, dry, solid residue. Therefore, to "reconstitute" this dry AZ-102 residue to the original state of the core composite, an equal weight of water was added, and the weight of this material then was used to obtain the desired AZ-101/AZ-102 sludge ratio.

Leach and wash solutions were prepared using reagent grade NaOH and NaNO₂. The concentrations of the NaOH solutions were confirmed by titration with standard HCl.

2.2 Analytical Methods

Portions of the sludges were analyzed before and after the sludge washing/caustic-leaching treatment. The solid samples were solubilized for analysis by a well established KOH fusion method.¹ In addition, a sodium peroxide (Na₂O₂) fusion was also conducted; this allowed for the determination of K and Ni and also gave a duplicate analytical result for other sludge components. The mean values are reported for those components determined through both fusion methods. Solution samples were analyzed after acidification with HNO₃. Typically, the samples were acidified 2 or 3 days after being washed or leached. The major metallic elements (Al, Bi, Cr, Fe, Na, etc.) as well as P and Si were determined by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). Anions were determined by ion chromatography. Alpha spectroscopy was used to measure the concentrations of the TRU elements, and gamma spectroscopy was used to measure the gamma-emitting radionuclides, such as ¹³⁷Cs. Uranium concentrations were determined by laser fluorimetry. A proportional beta counter was used to determine ⁹⁰Sr and ⁹⁹Tc after chemical separation of these isotopes from the other radionuclides. Established procedures were used for all these analyses.¹ It has recently been reported that the procedure for ⁹⁹Tc does not always give satisfactory results for Hanford tank wastes containing complexing agents,² but because neither AZ-101 nor AZ-102 tank sludges contain significant quantities of complexing agents, the method should be reliable for these wastes.

¹ Method used was from the Analytical Chemistry Laboratory (ACL) Procedure Compendium, PNL-MA-599, ACL Department. Pacific Northwest National Laboratory, Richland, Washington.

² *Technetium Removal and Speciation: A Progress Report*. Written by D. L. Blanchard and others (1996). Pacific Northwest National Laboratory, Richland, Washington.

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

Free-[OH]⁻ concentrations in the caustic-leach solutions were determined by titration with standard HCl, as described previously (Rapko et al. 1995).

Sludge heights were measured in the hot cells from the bottom of the container by determining visually where the supernatant was clear of suspended particles and comparing the interface level with a standard ruler placed next to the sludge container. Heights were recorded to the near half-millimeter.

2.3 Experimental Procedure

The experimental test procedure used in this study differs in several respects from the test procedures used in other recent caustic-leaching studies (Lumetta et. al. 1996a; Temer and Villareal 1996). Figure 2.1 summarizes the experimental test procedure used in this study. This test procedure consisted of the following steps:

1. Portions of AZ-101 and the reconstituted AZ-102 sludge were placed in a high-density polyethylene (HDPE) bottle in the equivalent ratio of 95 volumes AZ-102 to 35 volumes AZ-101.
2. The sludge was slurried in water (2 g water/g sludge); then three aliquots of the slurry were removed (samples B, C, and D).
3. One of the aliquots (B) was dried at 105°C and submitted for elemental and radiochemical analysis.
4. Two of the slurry aliquots were saved. One was used for particle-size measurements (C); the second was saved for microscopy studies (D).
5. A quantity of 12 M NaOH was added to the remaining sludge slurry with a targeted final free-[OH]⁻ concentration of 0.1 M NaOH. The resulting mixture was stirred and heated at 80°C for 5 hours.
6. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity. The height of the sludge solids was monitored as a function of time.
7. After settling, a small portion of the supernatant was transferred to a second container. This second container was centrifuged, and an aliquot of the centrifuged supernatant was removed, passed through a 0.2 micron filter, and submitted for analysis. This solution will be referred to hereafter as the "first leach" solution (E).
8. A quantity of 12 M NaOH was added to the sludge slurry with a targeted final free-[OH]⁻ concentration of 1 M NaOH. The resulting mixture was stirred and heated at 80°C for 5 hours.
9. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity. The height of the sludge solids was monitored as a function of time.

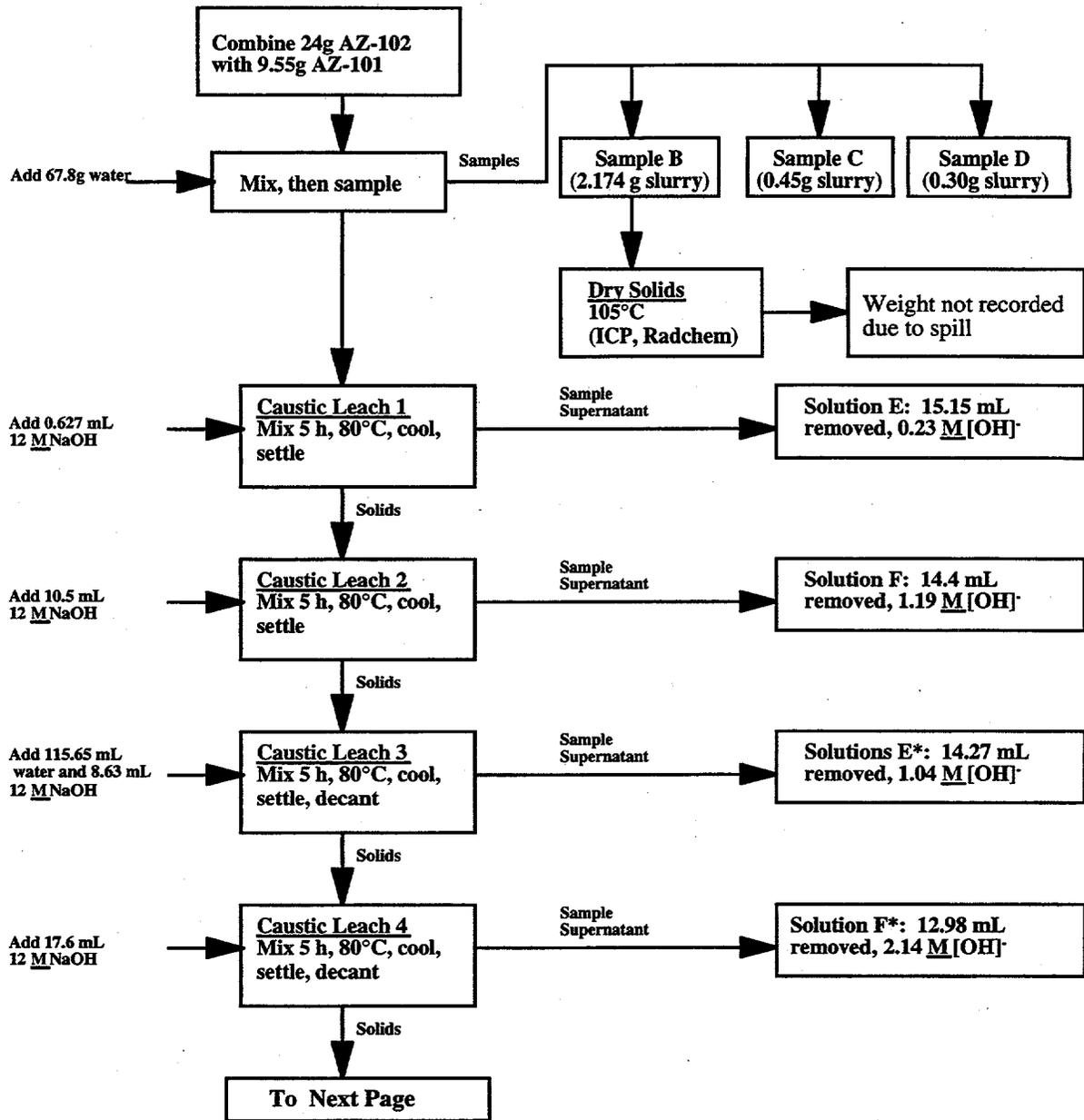


Figure 2.1. Schematic Outline of the AZ-101/AZ-102 Caustic-Leach Test

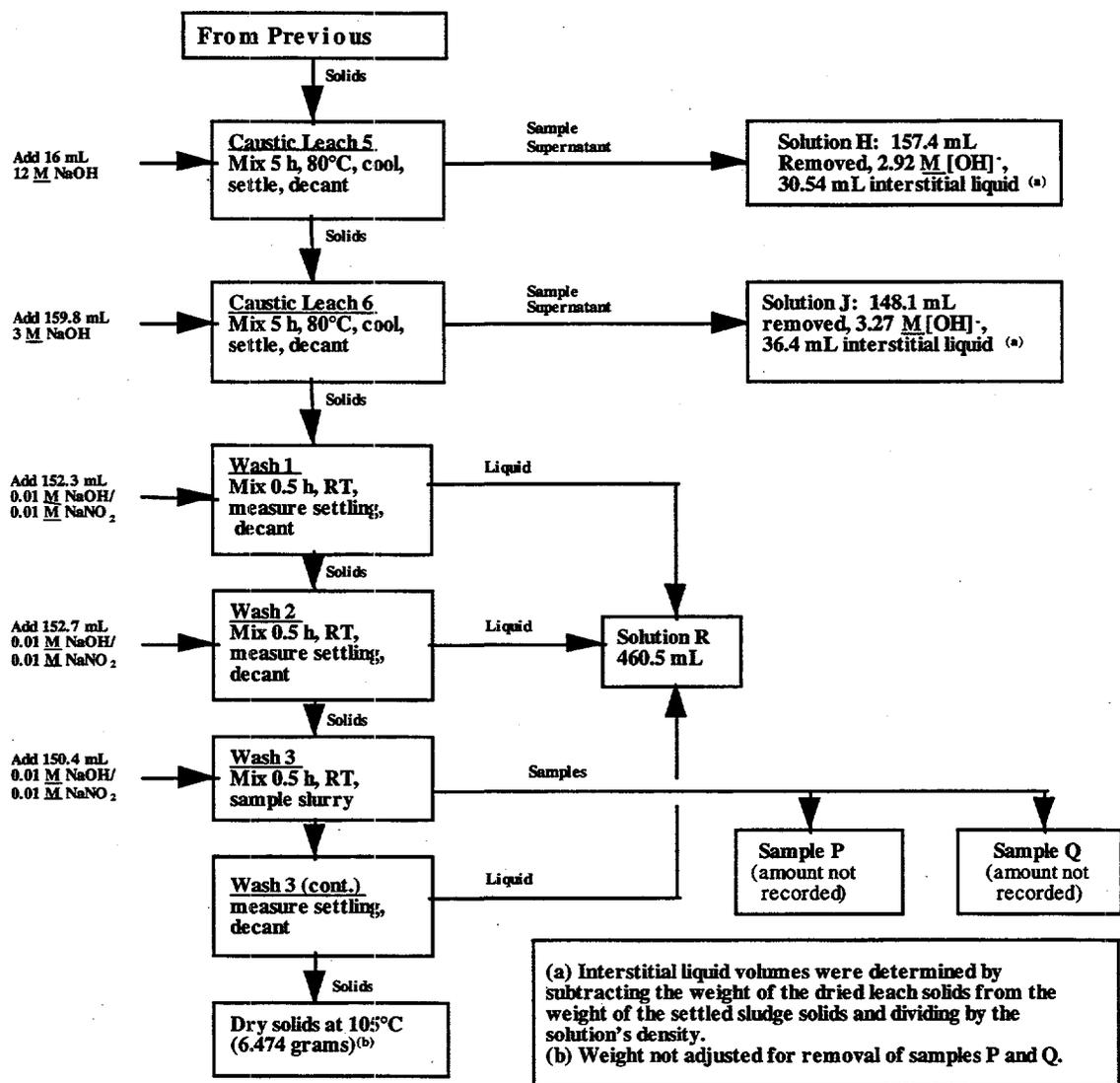


Figure 2.1. (contd)

10. After settling, a small portion of the supernatant was transferred to a second container. This second container was centrifuged, and an aliquot of the centrifuged supernatant was removed, passed through a 0.2 micron filter, and submitted for analysis. This solution will be referred to hereafter as the "second leach" solution (F).
11. Water and 12 M NaOH were added to the sludge slurry with a targeted final free-[OH]⁻ concentration of ca. 1 M NaOH. The resulting mixture was stirred and heated at 80°C for 5 hours.
12. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity. The height of the sludge solids was monitored as a function of time.

13. After settling, a small portion of the supernatant was transferred to a second container. This second container was centrifuged, and an aliquot of the centrifuged supernatant was removed for analysis. This solution will be referred to hereafter as the "third leach" solution (E*).
14. Water and 12 M NaOH were added to the sludge slurry with a targeted final free-[OH]⁻ concentration of 2 M NaOH. The resulting mixture was stirred and heated at 80°C for 5 hours.
15. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity. The height of the sludge solids was monitored as a function of time.
16. After settling, a small portion of the supernatant was transferred to a second container. This second container was centrifuged, and an aliquot of the centrifuged supernatant was removed, passed through a 0.2-micron filter, and submitted for analysis. This solution will be referred to hereafter as the "fourth leach" solution (F*).
17. Water and 12 M NaOH were added to the sludge slurry with a targeted final free-[OH]⁻ concentration of 3 M NaOH. The resulting mixture was stirred and heated at 80°C for 5 hours.
18. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity. The height of the sludge solids was monitored as a function of time.
19. After settling, the entire supernatant was decanted off, and an aliquot of the supernatant was transferred to a separate container. This separate container was centrifuged, and an aliquot of the centrifuged supernatant was removed, passed through a 0.2-micron filter, and submitted for analysis. This solution will be referred to hereafter as the "fifth leach" solution (H).
20. The settled solids were then contacted with a volume of 3 M NaOH comparable to the amount of removed supernatant. The resulting mixture was stirred and heated at 80°C for 5 hours.
21. After cooling to room temperature, mixing was stopped, and the solids were allowed to settle under the force of gravity. The height of the sludge solids was monitored as a function of time.
22. After settling, the entire supernatant was decanted off, and an aliquot of the supernatant was transferred to a separate container. This separate container was centrifuged, and an aliquot of the centrifuged supernatant was removed, passed through a 0.2-micron filter, and submitted for analysis. This solution will be referred to as the "sixth leach" solution (J).
23. The leached sludge was then successively washed with three portions of 0.01 M NaOH/ 0.01 M NaNO₂; the volume of each portion of the wash solution was equal to the volume of previously removed supernatant. For the first two portions, mixing was stopped after stirring for at least 0.5 hours at room temperature, and the solids were allowed to settle under the force of gravity. Again, the height of the sludge solids was monitored as a function of time. In the case of the third wash, two aliquots of the suspension were removed before the solids were allowed to settle. One aliquot (P) was saved for a particle-size measurement; the second (Q) was used for microscopy studies. In each case, after gravity settling, the supernatant was decanted.

24. The wash solutions were combined, and an aliquot of the composite wash solution (R) was removed, passed through a 0.2-micron filter, and submitted for analysis.
25. Finally, the remaining residue was dried to a constant weight at 105°C.

Several mishaps during the testing impacted the interpretation of the test results. One mishap occurred when, because of a sample spill during the transfer of the dried solids in sample B, an accurate dry weight could not be obtained. An unknown initial dry weight for the sludge impacts the mass balance checks usually performed in the data workup and required an alternative approach to presenting this comparison. Details about the alternative workup are given in the appropriate section below. A second mishap occurred when, as the supernatant of the second caustic leach was being prepared for analysis by being acidified, extensive foaming occurred, and most of the analytical sample was lost. The shape of the titration curve is consistent with the presence of considerable amounts (ca. 0.2 M) of bicarbonate in the leach solution. Carbon dioxide is generated when bicarbonate is acidified, and a release of this gas explains the observed foaming. The impact of this on interpreting the results is discussed further below. A final mishap resulted when the amounts of suspended solids in samples P and Q were not recorded. Usually the final dry weight of leached sludge is corrected for the amount removed for the particle size and TEM analyses. In this instance, because of the relatively large amount of residual solids and the small (typically on the order to 10 to 20 mg) amounts of solids removed, the lack of such a correction has a minimal impact on the results.

The quantities of sludge expressed in Figure 2.1 are given in term of weights. However, the relative quantities of AZ-101 to AZ-102 sludge and of the composite AZ-101/AZ-102 sludge to leachate used are given in terms of volumes. Since the specific gravity for these sludges has previously been determined to be 1.62 g/mL for AZ-101 sludge (Hodgson 1995) and 1.49 g/mL for AZ-102 (Schreiber 1995) the relative volumes of sludge used in preparing the AZ-101/AZ-102 sludge composite can be calculated. The calculated volumes of sludge are 16.1 mL for AZ-102 and 5.9 mL for AZ-101, which gives an AZ-102/AZ-101 volume ratio of 2.73 in this test as compared to the target ratio (Hanlon 1996) of 2.71 (95 volumes of AZ-102/35 volumes of AZ-101).

The targeted volumes of leachate to sludge were 850 volumes of leachate to 130 volumes of sludge, or a leachate/sludge volume ratio of 6.54. This ratio is derived from the assumption that the washing/leaching tank can hold 980,000 gallons and that the combined sludges have a volume of 130,000 gallons (Hanlon 1996). The actual ratio of leachate to sludge varied significantly. If the initial sludge volume is assumed to remain constant, then the leachate-to-sludge volumes can be estimated and are summarized below in Table 2.1. As noted in Table 2.1, the first two leaches had significantly lower leachate-to-solids ratios, and the latter leaches and washes were somewhat higher than targeted.

Table 2.1. Estimates of Leachate to Initial Sludge Volume

Test step (from Fig. 2.1)	Targeted Leachate/Sludge Volume Ratio	Found Leachate/Sludge Volume Ratio
Caustic Leach 1	6.54	3.11
Caustic Leach 2	6.54	2.89
Caustic Leach 3	6.54	8.03
Caustic Leach 4	6.54	8.26
Caustic Leach 5	6.54	8.40
Caustic Leach 6	6.54	8.51
Wash 1	6.54	8.71
Wash 2	6.54	8.54
Wash 3	6.54	8.63

3.0 Results

The experimental data are presented in this section.

3.1 AZ-101/AZ-102 Sludge Settling Behavior

Tables 3.1 through 3.7 and Figures 3.1 and 3.2 present the settling data for the various caustic-leaching steps and the final three washing steps. Settling data were not obtained for the first two leach steps shown in Figure 2.1: at these relatively low solution-to-solids ratios, little (< 10%), if any, settling was observed. Lacking a good estimate for the mass of leached insoluble solids for these steps prevents estimating the wt% solids value for these tests. For the other steps, the solids generally settled at reasonable rates. The maximum rate was roughly inversely proportional to the $[\text{OH}^-]$ concentration, with the maximum velocity decreasing as the $[\text{OH}^-]$ concentration was increased and then increasing as the lower $[\text{OH}^-]$ washes were performed. The settling data for all of these tests were normalized according to a formula recommended by personnel at Westinghouse Hanford Company (WHC).¹ These normalized settling data (Figure 3.2) give a different picture of sludge settling behavior compared to the raw settling data (Figure 3.1). Figure 3.2 suggests that the raw settling data can be correlated with dimensionless time provided that the free settling rate of the sludge is known.

Since the bulk of the supernatant was not separated from the settled solids until the 3 M leach steps, no direct measurement of the wt% settled solids is possible. However, if the assumption is made that the mass of leached solids at the end of the test corresponds to the weight of insoluble solids at each leach step, then knowing the weight of the total leach suspension and the change in sludge height during settling allows for a rough estimate of the wt% settled solids to be made. These values are remarkably constant for each step, ranging only from 12 to 15 wt% solids for these settled suspensions.

3.2 Particle Size Data for the AZ-101/AZ-102 Leach Test

Figures 3.3 and 3.4 present the number and volume distributions of the particle-size data for the untreated and treated AZ-101/AZ-102 sludge composite. Leaching the sludge had little effect on the particle-size distribution; in both cases, a broad range of particles spanning from 0.2 to 50 microns was observed. The volume distribution indicated the mean particle diameter to be 8.57 microns for the untreated sludge and 8.85 microns for the treated sludge. The number distribution indicated the mean particle diameter to be 0.3 microns for the untreated and 0.4 microns for the treated solids. Particle sizes were also measured after applying an ultrasonic field for 5 minutes. No significant changes in the particle-size distribution were observed following sonication.

¹ G. T. MacLean, Westinghouse Hanford Company, personal communication, 1996.

Table 3.1. Settling Data from the 1 M Caustic Leach of the AZ-101/AZ-102 Test

t (min)	h (mm)	T	H
0	73	0.00	1.00
1.22	70	0.02	0.96
2.55	68	0.05	0.93
4.35	66	0.08	0.90
5.58	64	0.10	0.88
8.01	62	0.15	0.85
9.2	60	0.17	0.82
11.05	58	0.21	0.79
14.15	54	0.26	0.74
15.41	52	0.29	0.71
17.41	50	0.32	0.68
19.28	48	0.36	0.66
21.12	46	0.39	0.63
24.45	42	0.45	0.58
31.38	36	0.58	0.49
41.3	32	0.77	0.44
47.29	30	0.88	0.41
54.45	28	1.01	0.38
65	26	1.21	0.36
80	24	1.49	0.33
110	21.5	2.05	0.29
170	19	3.16	0.26
230	17.5	4.28	0.24
320	17	5.95	0.23
375	16.5	6.97	0.23
1380	16	25.66	0.22

(a) t = time, h = sludge height, T= normalized time value = $t \cdot v_{\max} / h_0$, H = normalized height = h/h_0 . $V_{\max} = 1.36$ mm/min

3.3 Nonradionuclide Distribution During the AZ-101/AZ-102 Leach Test

Tables 3.8 through 3.11 summarize the results for the distribution of nonradionuclides during the AZ-101/AZ-102 leaching test. Table 3.8 reports the actual component concentrations in each of the test solutions as determined by ICP-AES (elements) or ion chromatography (anions). Tables 3.9 and 3.10 reveal the amount of each element remaining in the residue and the amount that dissolved in leach solutions as determined by ICP-AES. The inability to obtain good quality ion chromatography (IC) data for the dissolved sludge solids prevents calculating both anion mass balance and component distributions. Table 3.9 describes the relative amounts of each component in each of the

Table 3.2. Settling Data from the 2 M Caustic Leach of the AZ-101/AZ-102 Test

t (min)	h (mm)	T	H
0	78	0.00	1.00
2	75	0.03	0.96
3.36	73	0.05	0.94
6.17	70	0.09	0.90
9.45	68	0.14	0.87
11.3	65	0.17	0.83
14.35	63	0.21	0.81
17.15	60	0.25	0.77
20	58	0.29	0.74
24.3	55	0.36	0.71
26.3	53	0.39	0.68
30.01	50	0.44	0.64
35.15	45	0.52	0.58
43.3	40	0.64	0.51
53.1	35	0.78	0.45
62.55	30	0.92	0.38
90	25	1.33	0.32
165	20	2.43	0.26
255	19	3.76	0.24
355	19	5.24	0.24

(a) t = time, h = sludge height, T = normalized time value = $t \cdot v_{\max} / h_0$, H = normalized height = h/h_0 . $V_{\max} = 1.15$ mm/min.

decanted solutions and in the residual solids; Table 3.10 corrects these amounts for contributions due to carryover of interstitial liquids from the previous step. The tables describe the amounts of component removed by decanting the liquid from four sources: the first 3 M NaOH leach, the second 3 M NaOH leach, the combined 0.01 M NaOH washes, and the amount remaining in the residual leached solids. The amount removed during the first 3 M NaOH leach includes the contributions due to removal of analysis aliquots from the previous leach steps.

The final table in this series, Table 3.11, compares component concentrations as determined by summation of all the contributions from the residual solids and the individual leach and wash steps and compares them with the concentrations determined by direct analysis of the initial solids. However, to determine a concentration based on knowledge of the total sum of a component, the amount of initial solids also must be known. As previously mentioned, a sample spill prevented accurately knowing the initial amount of dried solids. The total component amounts were converted to concentrations by assuming that the value for a single, chosen component obtained by direct analysis was correct. Then the other elemental concentrations were "normalized" to this "correct" value by

Table 3.3. Settling Data from the 1st 3 M Caustic Leach of the AZ-101/AZ-102 Test

t (min)	h (mm)	T	H
0	77	0.00	1.00
1.3	75	0.01	0.97
3.49	73	0.04	0.95
7.22	70	0.07	0.91
10.45	68	0.11	0.88
13	66	0.13	0.86
16	64	0.16	0.83
19	62	0.19	0.81
22	60	0.22	0.78
24	58	0.24	0.75
27	56	0.27	0.73
31	54	0.31	0.70
35.15	50	0.36	0.65
38	48	0.38	0.62
42.15	45	0.43	0.58
46	43	0.46	0.56
50.15	40	0.51	0.52
54.19	38	0.55	0.49
60	35.5	0.61	0.46
65	33.5	0.66	0.44
70	31.5	0.71	0.41
80	28.5	0.81	0.37
90	26	0.91	0.34
105	24	1.06	0.31
120	24	1.21	0.31
180	20	1.82	0.26
240	18.5	2.42	0.24
1320	16	13.33	0.21

(a) t = time, h = sludge height, T = normalized time value = $t \cdot v_{\max} / h_0$, H = normalized height = h/h_0 . $v_{\max} = 0.78$ mm/min.

Table 3.4. Settling Data from the 2nd 3 M Caustic Leach of the AZ-101/AZ-102 Test

t (min)	h (mm)	T	H
0	76	0.00	1.00
3.27	72	0.04	0.95
6.05	70	0.07	0.92
8.25	68	0.09	0.89
11	66	0.12	0.87
13.3	64	0.15	0.84
16	62	0.18	0.82
18.17	60	0.20	0.79
20.19	58	0.23	0.76
23.1	56	0.26	0.74
25.07	54	0.28	0.71
27.57	52	0.31	0.68
29.45	50	0.33	0.66
32.25	48	0.36	0.63
34.39	46	0.39	0.61
36.59	44	0.41	0.58
39.5	42	0.44	0.55
42.29	40	0.47	0.53
45.35	38	0.51	0.50
49	36	0.55	0.47
52.5	34	0.59	0.45
56.54	32	0.63	0.42
61.4	30	0.69	0.39
67.26	28	0.75	0.37
75.5	26	0.85	0.34
83.15	24	0.93	0.32
120	22	1.34	0.29
180	20	2.02	0.26
240	18	2.69	0.24

(a) t = time, h = sludge height, T = normalized time value = $t \cdot v_{\max} / h_0$, H = normalized height = h/h_0 . $v_{\max} = 0.85$ mm/min.

Table 3.5. Settling Data from the 1st Wash of the AZ-101/AZ-102 Test

t (min)	h (mm)	T	H
0	76	0.00	1.00
1.1	72	0.03	0.95
2.08	70	0.06	0.92
3.1	68	0.09	0.89
3.58	66	0.10	0.87
4.52	64	0.13	0.84
5.51	62	0.15	0.82
6.45	60	0.18	0.79
7.46	58	0.21	0.76
8.41	56	0.23	0.74
10.14	53	0.28	0.70
10.52	52	0.29	0.68
11.39	50	0.32	0.66
12.44	48	0.34	0.63
13.42	46	0.37	0.61
14.5	44	0.40	0.58
16	42	0.44	0.55
17.12	40	0.47	0.53
18.43	38	0.51	0.50
20.29	36	0.56	0.47
21.59	34	0.60	0.45
24.1	32	0.67	0.42
25.48	30	0.70	0.39
28.46	28	0.79	0.37
34.15	26	0.94	0.34
46.15	24	1.28	0.32
60	22	1.66	0.29
91	20	2.52	0.26
150	19	4.15	0.25

(a) t = time, h = sludge height, T = normalized time value = $t \cdot v_{\max} / h_0$, H = normalized height = h / h_0 . $v_{\max} = 2.10$ mm/min.

Table 3.6. Settling Data from the 2nd Wash of the AZ-101/AZ-102 Test

t (min)	h (mm)	T	H
0	75	0.00	1.00
0.44	71	0.01	0.95
2.12	68	0.07	0.91
2.53	66	0.08	0.88
3.46	64	0.11	0.85
5.06	62	0.17	0.83
6.16	58	0.20	0.77
7.1	56	0.23	0.75
7.53	54	0.25	0.72
8.59	52	0.28	0.69
9.31	50	0.31	0.67
10.36	48	0.34	0.64
11.22	46	0.37	0.61
12.2	44	0.40	0.59
13.24	42	0.44	0.56
14.17	40	0.47	0.53
15.36	38	0.51	0.51
16.34	36	0.54	0.48
17.55	34	0.58	0.45
19.14	32	0.63	0.43
20.31	30	0.67	0.40
23.2	28	0.76	0.37
28.37	26	0.93	0.35
37.37	24	1.23	0.32
51.16	22	1.68	0.29
111.16	19	3.66	0.25
171.16	18.5	5.64	0.25
1311.56	17	43.19	0.23

(a) t = time, h = sludge height, T= normalized time value = $t \cdot v_{\max} / h_0$, H = normalized height = h/h_0 . $v_{\max} = 2.47$ mm/min.

applying the measured ratio of the other component masses to the chosen component with the direct analysis value of the chosen component. This correction is illustrated below in equation form:

$$\{[\text{Component}]_{\text{sum}}/[\text{chosen component}]_{\text{sum}}\} \cdot [\text{chosen component}]_{\text{direct analysis}} = [\text{component}]_{\text{corrected}} \quad (3.1)$$

The component chosen as correct was Fe. Iron was selected because of its large abundance in this sample and the historically good agreement between direct analysis and summation values for this element in previous caustic-leaching studies. It should be emphasized that such a data analysis results in the recovery for Fe being 100%, by definition.

Table 3.7. Settling Data from the 3rd Wash of the AZ-101/AZ-102 Test

t (min)	h (mm)	T	H
0	74	0.00	1.00
0.41	72	0.01	0.97
1.01	70	0.03	0.95
2.13	68	0.06	0.92
3.06	66	0.08	0.89
3.55	64	0.09	0.86
4.56	62	0.12	0.84
5.57	60	0.15	0.81
6.59	58	0.17	0.78
8.08	56	0.21	0.76
9.01	54	0.24	0.73
10.57	50	0.28	0.68
13.06	46	0.35	0.62
14.09	44	0.37	0.59
15.06	42	0.40	0.57
22.44	30	0.59	0.41
26.27	28	0.70	0.38
34.21	26	0.91	0.35
57	22	1.51	0.30
72	20.5	1.91	0.28
112	19.5	2.97	0.26
192	18.5	5.09	0.25

(a) t = time, h = sludge height, T = normalized time value = $t \cdot v_{\max} / h_0$, H = normalized height = h/h_0 . $v_{\max} = 1.96$ mm/min.

Sodium was not included in Tables 3.9 through 3.11 because of the large amount of Na added in the form of NaOH during the leaching test. Theoretically, this amount could be subtracted out, as had been performed in previous reports (Lumetta et al. 1996a), but because of the unusually large numbers of steps where Na was added in this test and because of the additional assumptions required to perform the usual mass balance check, the uncertainty associated with such a calculation seemed excessively large and so was not performed.

The component concentrations described in Table 3.8 cover solutions with free $[\text{OH}^-]$ of ca. 0.2, 1, 2, and 3 M. In two cases, two sets of measurements were made at similar free- $[\text{OH}^-]$ concentrations. The first two sets of measurements, caustic leaches 2 and 3 in Figure 2.1, respectively, were performed at free $[\text{OH}^-]$ equals ca. 1 M, but at differing solution-to-sludge ratios and with relatively little supernatant removed between contacts. The second two sets of measurements, caustic leaches 5 and 6 in Figure 2.1, respectively, were both performed at ca. 3 M free $[\text{OH}^-]$ and at the same solution-to-sludge ratios, but with most of the supernatant removed between contacts.

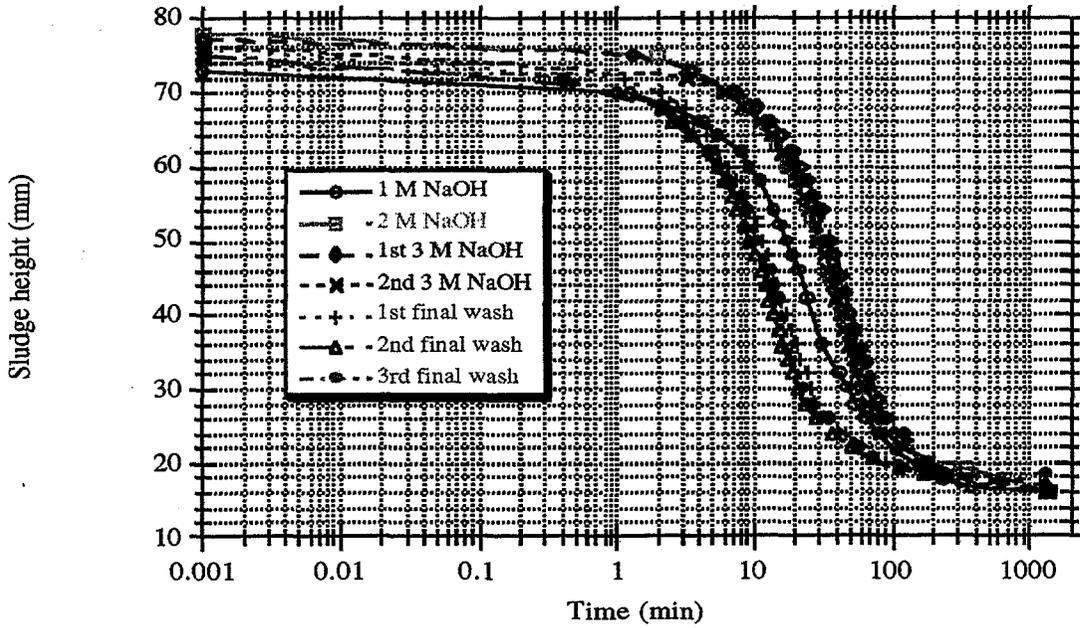


Figure 3.1. Settling for AZ-101/AZ-102 Sludge

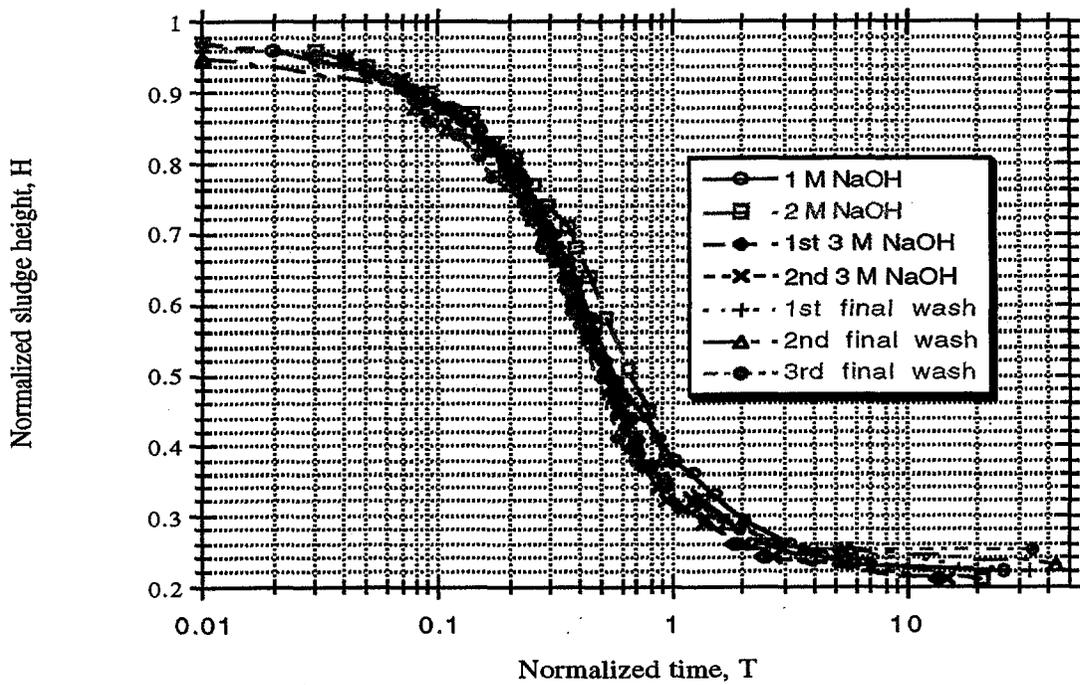


Figure 3.2. Normalized Settling for AZ-101/AZ-102 Sludge. Normalized height of sludge, $H = \text{normalized height} = h/h_0$. Normalized time, $T = t \cdot v_{\text{max}}/h_0$

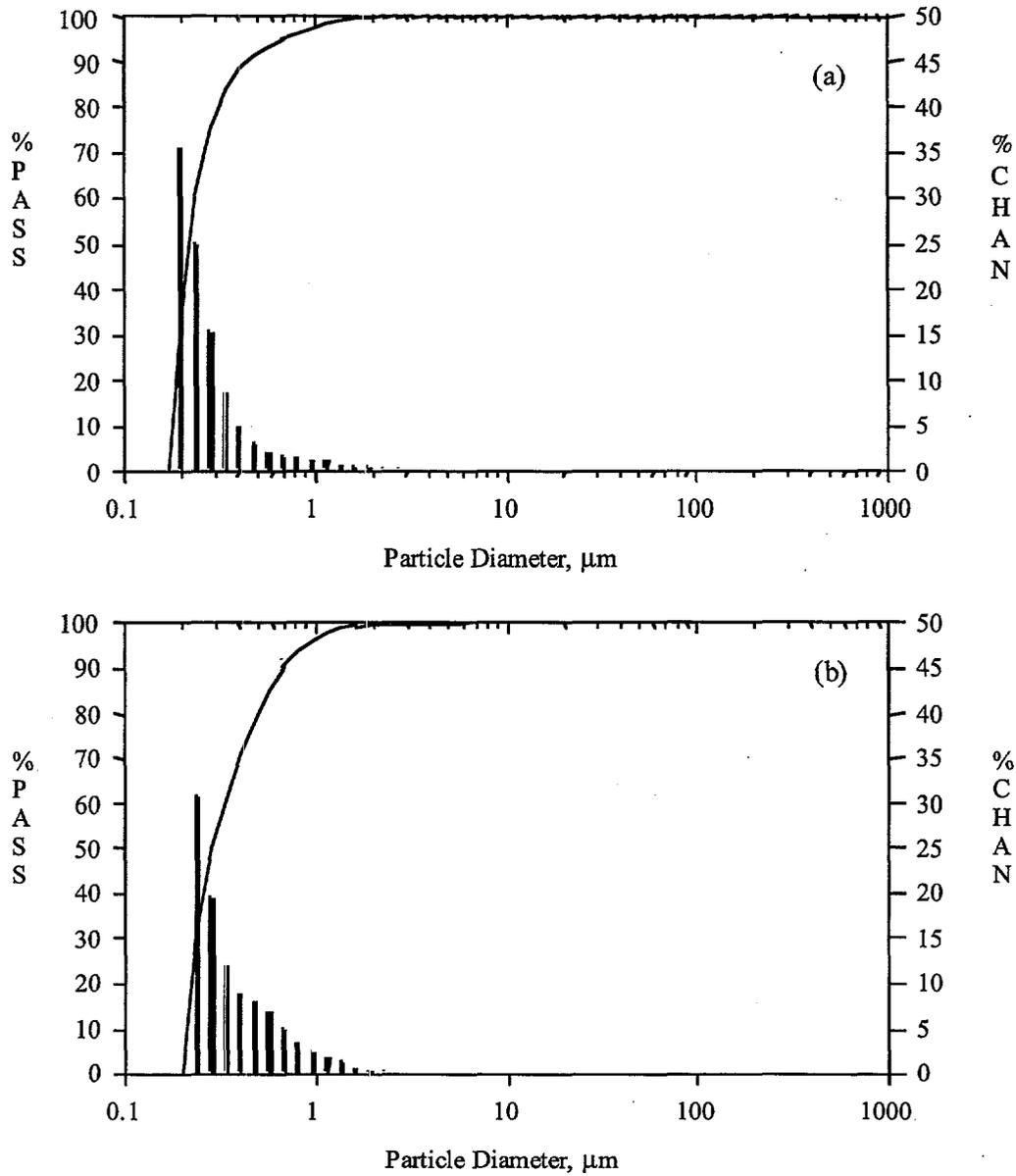


Figure 3.3. Particle Size Number Distribution for the (a) Untreated and (b) Treated AZ-101/AZ-102 Sludge Composite

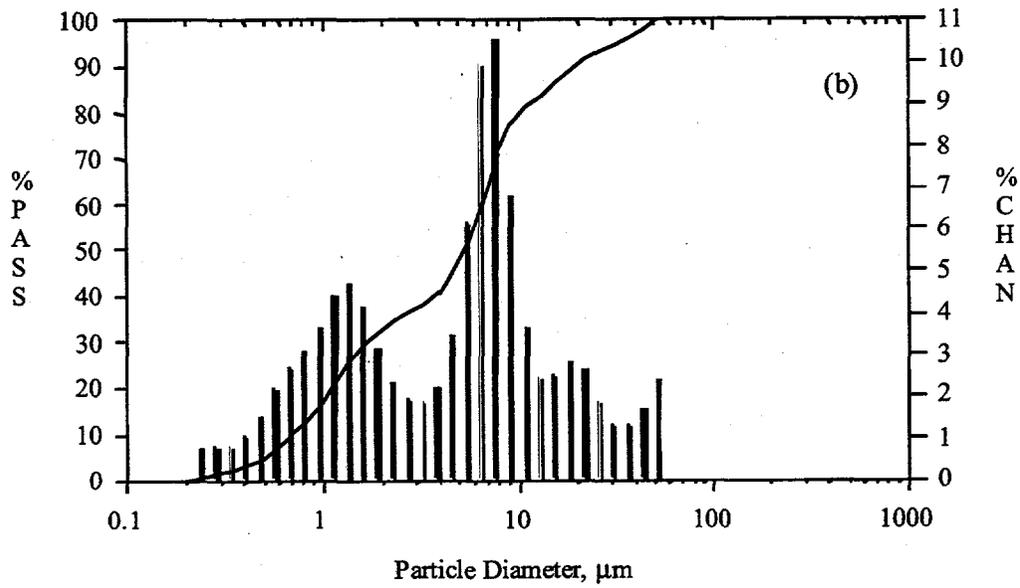
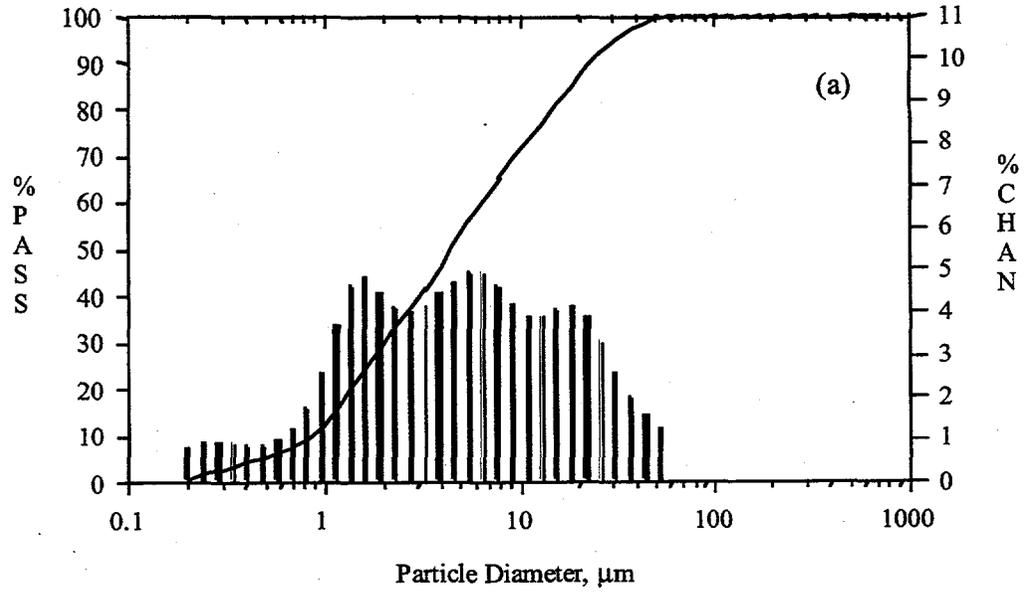


Figure 3.4. Particle Size Volume Distribution for the (a) Untreated and (b) Treated AZ-101/AZ-102 Sludge Composite

Table 3.8. Concentrations of Non-radioactive Components During the AZ-101/AZ-102 Test

Component	1st Caustic Leach Solution (µg/mL)	2nd Caustic Leach Solution (µg/mL)	3rd Caustic Leach Solution (µg/mL)	4th Caustic Leach Solution (µg/mL)	5th Caustic Leach Solution (µg/mL)	6th Caustic Leach Solution (µg/mL)	Final Wash Solution (µg/mL)	Dried Residue (µg/g)
Solution Vol (mL)	86.8	80.6	189.2	189	187.9	184.5	460.5	NA
[OH], M	0.23	1.19	1.04	2.14	2.92	3.27	NA	NA
Ag	1.562	18.91	7.722	2.16	1.118	2.6	0.231	859
Al	222.2	5797	2343	2580	2769	864.5	76.89	30325
As	2.2	11.16	3.85	5.4	5.2	< 2.6	0.132	429
B	2.09	4.34	1.65	1.56	< 1.625	< 1.625	0.066	172
Ba	0.055	< 7.75	< 0.055	< 0.012	< 0.325	< 0.325	0.011	1205
Be	< 0.0275	< 3.875	0.066	0.18	0.286	< 1.625	< 0.0055	< 25.2
Bi	2.86	< 77.5	< 0.55	< 0.12	< 3.25	< 3.25	< 0.11	< 1680
Ca	4.84	11.16	5.61	14.4	40.3	< 8.125	2.882	9645
Cd	0.231	1.55	0.539	3.36	9.958	8.996	< 0.0165	27875
Ce	0.682	< 77.5	< 0.55	< 0.12	< 3.25	< 3.25	< 0.11	2700
Co	< 0.275	< 38.75	< 0.275	< 0.06	< 1.625	< 1.625	< 0.055	187
Cr	168.3	230.64	83.71	84	83.85	16.12	1.375	2653
Cu	0.319	< 38.75	0.319	< 0.06	< 1.625	< 1.625	< 0.055	519
Dy	< 0.275	< 38.75	< 0.275	< 0.06	< 1.625	< 1.625	< 0.055	< 126
Eu	< 0.55	< 77.5	< 0.55	< 0.12	< 3.25	< 3.25	< 0.11	< 336
Fe	< 0.275	< 38.75	< 0.275	< 0.06	1.69	1.69	0.143	291250
K	599.5	638.6	218.9	216	195	< 65	< 2.2	3730
La	< 0.275	< 38.75	< 0.275	< 0.06	< 1.625	< 1.625	< 0.055	7618
Li	< 0.165	< 23.25	< 0.165	< 0.036	< 0.975	< 0.975	< 0.033	< 84
Mg	< 0.55	< 77.5	< 0.55	< 0.12	< 3.25	< 3.25	0.198	< 4200
Mn	< 0.275	< 38.75	< 0.275	< 0.06	< 1.625	< 1.625	< 0.055	7145
Mo	13.64	13.02	4.279	4.2	4.03	< 0.975	0.055	< 210
Na	19360	63240	33110	53640	77090	67080	5698	16300
Ni	0.605	< 77.5	< 0.55	< 0.12	< 3.25	< 3.25	< 0.11	5770
Ni	0.814	< 23.25	0.396	< 0.036	2.08	2.21	0.682	18400
P	25.96	356.5	134.2	145.2	153.4	45.5	2.53	3775
Pb	< 0.55	15.19	6.336	8.16	9.88	5.33	0.209	3230
Pd	8.03	< 232.5	1.87	< 0.36	< 9.75	< 9.75	< 0.33	< 3360
Rh	3.52	< 232.5	< 1.65	< 0.36	< 9.75	< 9.75	< 0.33	< 1260

Table 3.8. (contd)

Ru	1.32	< 77.5	0.814	< 1.2	< 3.25	< 3.25	< 0.11	1155
Sb	3.08	4.34	1.32	< 1.2	< 3.25	< 3.25	< 0.11	< 1260
Se	3.41	20.15	7.689	9.96	11.18	4.55	0.286	< 840
Si	8.58	40.3	24.2	36	48.1	91	9.185	9475
Sn	13.2	< 77.5	6.93	< 12	< 32.5	< 32.5	< 1.1	< 8400
Sr	0.11	< 11.625	< 0.0825	< 0.018	< 0.4875	< 0.4875	< 0.0165	714
Te	< 2.75	< 387.5	3.96	< 0.6	< 16.25	< 16.25	< 0.55	< 1260
Th	< 4.4	< 620	< 4.4	< 0.96	< 26	< 26	< 0.88	< 2100
Ti	< 0.1375	< 19.375	< 0.1375	< 0.03	< 0.8125	< 0.8125	< 0.0275	297
Tl	< 2.75	< 387.5	< 2.75	< 0.6	< 16.25	< 16.25	< 0.55	< 840
U	1232	511.5	16.72	1.0884	17.03	23.92	1.683	21110
V	0.374	1.86	0.759	1.128	1.222	0	0.022	< 126
W	129.8	139.5	52.47	48	46.8	< 16.25	0.66	< 1680
Y	< 0.055	< 7.75	< 0.055	< 0.012	< 0.325	< 0.325	< 0.011	384
Zn	0.594	3.72	1.276	3.12	5.59	3.25	0.748	559
Zr	0.165	< 19.375	< 0.1375	< 0.03	0.832	< 0.8125	< 0.0275	18000
NO ₃ ⁻	1254	NA	396	420	390	689	286	NA
NO ₂ ⁻	13860	NA	4180	4440	4290	117	33	NA
PO ₄ ³⁻	64.9	NA	363	492	513.5	143	6.6	NA
SO ₄ ²⁻	3080	NA	1012	1032	981.5	156	14.3	NA
F ⁻	627	NA	176	216	214.5	52	< 13.75	NA
Cl ⁻	88	NA	22	< 15	< 12.5	< 16.25	< 13.75	NA
Br ⁻	< 13.75	NA	< 1.375	< 1.5	< 1.25	< 1.625	< 1.375	NA

NA= Not Available or Applicable

Table 3.9. Distribution of Nonradioactive Components in the AZ-101/AZ-102 Test: Uncorrected for Carryover of Interstitial Liquids^(a)

% Component Found

Component	To 1st 3 M Caustic Leach		2nd 3 M Caustic Leach		Final Washes		Dried Residue	
Ag	9		6		2		84	
Al	62		14		4		21	
As	28	(26)	0	(9)	2	(1)	70	(64)
B	10	(22)	0	(14)	2	(2)	87	(62)
Ba	0	(2)	0	(1)	0	(0)	100	(97)
Be	100	(34)	0	(8)	0	(1)	0	(57)
Bi	100	(12)	0	(4)	0	(0)	0	(84)
Ca	10	(10)	0	(2)	2	(2)	88	(86)
Cd	1	(1)	1	(1)	0	(0)	98	(98)
Ce	0	(8)	0	(2)	0	(0)	100	(90)
Co	0	(34)	0	(11)	0	(1)	100	(54)
Cr	51		6		2		42	
Cu	0	(17)	0	(5)	0	(1)	100	(77)
Dy	^(b)	(41)	^(b)	(13)	^(b)	(1)	^(b)	(45)
Eu	^(b)	(36)	^(b)	(11)	^(b)	(1)	^(b)	(52)
Fe	0	(0)	0	(0)	0	(0)	100	(100)
K	69	(61)	0	(11)	0	(1)	31	(27)
La	0	(2)	0	(0)	0	(0)	100	(98)
Li	^(b)	(39)	^(b)	(12)	^(b)	(1)	^(b)	(48)
Mg	0	(5)	0	(2)	100	(0)	0	(93)
Mn	0	(2)	0	(1)	0	(0)	100	(97)
Mo	98	(42)	0	(5)	2	(1)	0	(52)
Nd	0	(4)	0	(1)	0	(0)	100	(95)
Ni	0	(1)	0	(0)	0	(0)	99	(99)
P	50		10		2		37	(38)
Pb	8	(8)	3	(3)	0	(0)	88	(89)
Pd	100	(17)	0	(5)	0	(1)	0	(77)
Rh	100	(32)	0	(10)	0	(1)	0	(57)
Ru	0	(16)	0	(5)	0	(1)	100	(78)
Sb	100	(7)	0	(5)	0	(1)	0	(87)
Se	74	(27)	22	(8)	4	(2)	0	(63)
Si	10		15		5		70	
Sn	100	(20)	0	(6)	0	(1)	0	(73)
Sr	0	(5)	0	(1)	0	(0)	100	(94)
Te	100	(41)	0	(13)	0	(1)	0	(45)

Table 3.9. (contd)

Component	To 1st 3 M Caustic Leach	2nd 3 M Caustic Leach	Final Washes	Dried Residue
Th	(b) (41)	(b) (13)	(b) (1)	(b) (45)
Ti	0 (16)	0 (5)	0 (1)	100 (78)
Tl	(b) (48)	(b) (15)	(b) (2)	(b) (35)
U	17 (17)	2 (2)	0 (0)	81 (81)
V	96 (22)	0 (6)	4 (1)	0 (71)
W	98 (48)	0 (9)	2 (1)	0 (42)
Y	0 (6)	0 (2)	0 (0)	100 (92)
Zn	18	9	6	67
Zr	0 (0)	0 (0)	0 (0)	100 (100)

(a) Values in parenthesis represent the distribution if component concentrations in the process streams that were below detection limits are recalculated with the component concentrations at their detection limits.

(b) Component was not detected.

The dilution factors resulting from preparing the supernatant for analysis were similar for all of the wash and leach steps, except for caustic leach 2. In this instance, the sample foamed considerably as it was being acidified in preparation for analysis. Consequently, a very dilute sample had to be acidified to avoid sample spillover, so the dilution factor in the analysis of caustic leach 2 is much greater than with the other samples. For this reason, and, unlike with leaches 5 and 6, because no gross separation of the liquid and solid phases occurred during this step, the results from caustic leach 3 only are used when discussing the effect of changing free $[\text{OH}^-]$ on component dissolution.

Another consideration of note when comparing the solution concentrations of each leach step is the volumes of solution added and removed. Between caustic leaches 1 and 2, little additional solution was added. Between caustic leaches 2 and 3, a large quantity of additional liquid was added. Between caustic leaches 3 and 4 and 4 and 5, relatively little additional liquid was added. Between caustic leaches 5 and 6, and 6 and the final washes, large amounts of liquid were added, especially when compared to the relatively small volumes of interstitial liquid remaining from the settle/decant of the previous step.

These differences impact the observed concentrations even in the absence of changes in any actual amount of dissolved component. For example, even with the same amount of dissolved material, a substantial decrease in component concentration is expected between caustic leaches 1 and 3 because a much larger leachate-to-solids ratio was introduced. On the contrary, between leach steps 3 to 5, changes in component concentration should generally reflect the relative amounts of dissolved materials. Finally, from leach steps 5 to 6 and from 6 to the final washes, even with the same amount of dissolved material, a substantial decrease in the observed component concentration would again occur.

With the above in mind, the concentrations of key dissolved components as a function of free- $[\text{OH}^-]$ concentration can be more readily explained and understood. With Al, ca. 80% of the material

Table 3.10. Distribution of Nonradioactive Components in the AZ-101/AZ-102 Test: Corrected for Carryover of Interstitial Liquids^(a)

% Component Found

Component	Up to 1st 3 M Caustic Leach		2nd 3 M Caustic Leach		Final Washes		Dried Residue	
Ag	(9)		(7)		(0)		84	(84)
Al	(71)		(8)		0		21	
As	28	(30)	0	(7)	2	(-1)	70	(64)
B	10	(25)	0	(14)	2	(-2)	87	(63)
Ba	0	(2)	0	(1)	0	(0)	100	(97)
Be	100	(37)	0	(7)	0	(-1)	0	(57)
Bi	100	(13)	0	(4)	0	(-1)	0	(84)
Ca	10	(11)	0	(0)	2	(1)	88	(87)
Cd	1	(1)	1	(1)	0	(0)	98	(98)
Ce	0	(8)	0	(3)	0	(0)	100	(89)
Co	0	(36)	0	(11)	0	(-1)	100	(54)
Cr	59		0		0		42	
Cu	0	(18)	0	(6)	0	(-1)	100	(77)
Dy	^(b)	(44)	^(b)	(14)	^(b)	(-2)	^(b)	(44)
Eu	^(b)	(38)	^(b)	(12)	^(b)	(-2)	^(b)	(51)
Fe	0	(0)	0	(0)	0	(0)	100	(100)
K	69	(67)	0	(7)	0	(-2)	31	(27)
La	0	(2)	0	(0)	0	(0)	100	(98)
Li	^(b)	(42)	^(b)	(13)	^(b)	(-2)	^(b)	(47)
Mg	0	(98)	0	(2)	100	(0)	0	(0)
Mn	0	(2)	0	(1)	0	(0)	100	(97)
Mo	98	(47)	0	(2)	2	(0)	0	(51)
Nd	0	(4)	0	(1)	0	(0)	100	(95)
Ni	0	(1)	0	(0)	0	(0)	99	(99)
P	59		3		0		37	
Pb	10	(9)	2	(3)	0	(0)	88	(89)
Pd	100	(18)	0	(5)	0	(-1)	0	(78)
Rh	100	(34)	0	(10)	0	(-1)	0	(57)
Ru	0	(17)	0	(5)	0	(-1)	100	(78)
Sb	100	(8)	0	(5)	0	(-1)	0	(88)
Se	89	(31)	11	(6)	0	(0)	0	(64)
Si	16		14		1		70	
Sn	100	(22)	0	(7)	0	(-1)	0	(72)
Sr	0	(5)	0	(2)	0	(0)	100	(93)
Te	100	(44)	0	(14)	0	(-2)	0	(44)

Table 3.10. (contd)

Component	Up to 1st 3 M Caustic Leach		2nd 3 M Caustic Leach		Final Washes		Dried Residue	
Th	(b)	(43)	(b)	(13)	(b)	(-2)	(b)	(46)
Ti	0	(17)	0	(5)	0	(-1)	100	(79)
Tl	(b)	(52)	(b)	(16)	(b)	(-2)	(b)	(35)
U	17	(17)	2	(2)	0	(0)	81	(81)
V	96	(25)	0	(5)	4	(-1)	0	(71)
W	98	(53)	0	(6)	2	(-1)	0	(42)
Y	0	(6)	0	(2)	0	(0)	100	(92)
Zn	24		6		4		66	
Zr	0	(0)	0	(0)	0	(0)	100	(100)

- (a) Values in parenthesis represent the distribution if component concentrations in the process streams that were below detection limits are recalculated with the component concentrations at their detection limits.
- (b) Component was not detected in any of the process streams.
- (c) Carryover was estimated by assuming that the amount of insoluble solids left at the end of each step (1st and 2nd 3 M caustic leaches, the final washes and the dried residue) was approximated by the amount of insoluble solids left at the end of the test. The mass of insoluble solids was subtracted from the total mass of the suspension to obtain the mass of the carryover. The density of the supernatant was used to then determine the volume of the carryover solution. The component concentration in the leachate (in $\mu\text{g/mL}$) \cdot (volume leachate) gives the mass of each component carried over to the next leach step. This mass was subtracted from the total amount present in the next leach step's leachate solution (supernatant + interstitial liquid) to determine the amount of the component present in the leachate (or residual solids) in the absence of carryover.

was removed by caustic leaching. Increasing the free-[OH]⁻ concentration from 0.2 to 1 M (1st to 2nd caustic-leach solution in Table 3.8) gave a marked increase in the concentration of dissolved Al. However, neither increasing the solution-to-sludge ratio at 1 M free [OH]⁻ nor increasing the free-[OH]⁻ concentration from 1 to 3 M (3rd through 5th caustic-leach solutions in Table 3.8) has appreciable additional benefit. Adding a second 3 M leach resulted in only a modest increase (5%) in the amount of Al dissolved (Table 3.9). Given the relatively low Al concentrations observed, a likely explanation for this behavior is that 80% of the Al is in a readily dissolvable phase, such as gibbsite, and the other 20% would be in an Al phase that is either slow to dissolve (e.g., boehmite) or is present in an Al phase whose solubility is much lower under these conditions.

Caustic leaching removed ca. 60% of the Cr in the AZ-101/AZ-102 composite sludge. Essentially all of the dissolved Cr in this test was dissolved by the initial 0.2 M free-[OH]⁻ solution, consistent with the hypothesis that only Cr(VI) dissolves to any significant extent during caustic leaching.

Table 3.11. Nonradionuclide Mass Balances and Composition of the AZ-101/AZ-102 Sludge Composite (dry weight basis)

Element Concentration (g element/g dried sludge)

Component	Direct Analysis	Summation ^(a)	Mass Recovery, %
Ag	8.44E-04	4.83E-04	57
Al	6.04E-02	6.85E-02	113
As	(b)	2.89E-04	(b)
B	2.86E-04	9.29E-05	32
Ba	5.58E-04	5.69E-04	102
Be	(b)	3.52E-06	(b)
Bi	(b)	3.16E-06	(b)
Ca	6.29E-03	5.15E-03	82
Cd	1.30E-02	1.34E-02	103
Ce	1.37E-03	1.28E-03	93
Co	1.20E-04	8.81E-05	74
Cr	2.80E-03	3.00E-03	107
Cu	2.77E-04	2.46E-04	89
Dy	(b)	(b)	(b)
Eu	(b)	(b)	(b)
Fe	1.38E-01	1.38E-01	100.0 ^(c)
K	8.14E-03	5.69E-03	70
La	3.57E-03	3.60E-03	101
Li	(b)	(b)	(b)
Mg	(b)	6.65E-06	(b)
Mn	3.66E-03	3.37E-03	92
Mo	(b)	8.37E-05	(b)
Na	1.21E-01	1.97E+00	(d)
Nd	2.76E-03	2.72E-03	99
Ni	8.47E-03	8.76E-03	103
P	(b)	4.76E-03	(b)
Pb	1.62E-03	1.73E-03	107
Pd	(b)	1.08E-05	(b)
Rh	(b)	3.89E-06	(b)
Ru	6.16E-04	5.47E-04	89
Sb	(b)	8.82E-06	(b)
Se	(b)	2.27E-04	(b)
Si	8.49E-03	6.42E-03	76
Sn	(b)	2.18E-05	(a)
Sr	3.52E-04	3.37E-04	96
Te	(b)	4.12E-06	(b)

Table 3.11. (contd)

Component	Direct Analysis	Summation ^(a)	Mass Recovery, %
Th	(b)	(b)	(b)
Ti	1.73E-04	1.40E-04	81
Tl	(b)	(b)	(b)
U	1.01E-02	1.23E-02	122
V	(b)	1.88E-05	(b)
W	(b)	9.32E-04	(b)
Y	(b)	1.81E-04	(b)
Zn	4.08E-04	3.96E-04	97
Zr	1.80E-02	8.50E-03	47

(a) As determined by Equation 3.1.
 (b) Element not detected.
 (c) Mass Recovery for Fe is 100% by definition as all summation data were normalized to the Fe concentration as determined by direct analysis. See text for further explanation.
 (d) Not calculated due to addition of large amount of Na during leaching.

Caustic leaching removed around two-thirds of the P. The amount of P in solution increased significantly upon increasing the free-[OH]⁻ concentration from 0.2 to 1 M, consistent with metathesis of metal PO₄ salts with NaOH taking place. In addition, the changes in PO₄ concentration (as determined by IC analysis) parallel the changes in total P concentration (as determined by ICP-AES analysis), consistent with PO₄ being present as the primary P containing species in solution. Further increases in the free-[OH]⁻ concentration or additional leaching steps seem to have no impact on the amount of P dissolved. In certain previous instances (Rapko et al. 1995), increases in P concentration in the final wash after caustic leaching have been observed. These have been explained by noting the limited dissolution of Na₃PO₄ in solutions with high Na concentration (Rapko et al. 1996). Although evidence exists for metathesis of metal PO₄ salts to Na₃PO₄ by NaOH in the AZ-101/AZ-102 leach test, no exceptional changes in P concentration during the final wash were noted.

Tables 3.9 and 3.10 examine the impact of carryover of interstitial fluid upon the component distribution in each leach step. If carryover is taken into account, then the impact of additional wash and leach steps upon component removal is revealed. Table 3.10 indicates that almost all sludge component dissolution occurs by completion of the first 3 M caustic leach. The second 3 M leach mostly dissolves some additional Si and a small amount of Al. Almost no additional component removal occurs during the final washes. However, the major intended impact of the final washes is simply to remove excess Na and other leached components present in the interstitial liquid. As noted above, the effectiveness of Na removal was not evaluated in this study.

3.4 Radionuclide Distribution During the AZ-101/AZ-102 Leach Test

Tables 3.12 through 3.15 summarize the behavior of the radionuclides during the AZ-101/AZ-102 caustic-leaching test. Table 3.12 reports the actual radionuclide concentrations in each of the test solutions. Tables 3.13 and 3.14 reveal the portion of each radionuclide remaining in the residue and the portion that dissolved in the leach solutions. Table 3.13 describes the relative amounts of the radionuclides in each of the decanted solutions and in the residual solids; Table 3.14 corrects these values for contributions due to carryover of interstitial liquids from the previous step. As noted previously, the analysis reports the amounts of radionuclides removed by decanting the liquid from the first 3 M NaOH leach, from the second 3 M NaOH leach, from the combined 0.01 M NaOH washes, and the amount remaining in the residual leached solids. The amount removed during the first component leach includes contributions due to removal of analysis aliquots from previous leach steps. Finally, Table 3.15 compares radionuclide concentrations as determined by summation of the contributions from the residual solids and the individual leach and wash steps and compares them with the concentrations determined by direct analysis of the initial solids. As with the nonradionuclides, to make this comparison, the summation results have to be normalized to one of the radionuclide concentrations determined by direct analysis. In this table, radionuclide concentrations were normalized to the total alpha concentration. It should be emphasized that such a data analysis results in the recovery for total alpha being 100%, by definition.

The distribution Tables 3.13 and 3.14 show the typical trends observed in previous caustic-leaching tests on Hanford Tank sludges, with little dissolution of TRUs or ⁹⁰Sr and effective dissolution of Tc and Cs. While the uncorrected radionuclide distribution of Table 3.13 would indicate that both the first and second caustic leaches are significant for Cs and Tc removal, the corrections for carryover provided in Table 3.14 reveal that essentially all of the Cs and Tc dissolution occurs by completion of the first 3 M caustic leach, consistent with Cs and Tc being present as simple, aqueous soluble, salts.

Table 3.12. Concentrations of Radioactive Components During the AZ-101/AZ-102 Test

Component	1st Caustic Leach Solution (μCi/mL)	2nd Caustic Leach Solution (μCi/mL)	3rd Caustic Leach Solution (μCi/mL)	4th Caustic Leach Solution (μCi/mL)	5th Caustic Leach Solution (μCi/mL)	6th Caustic Leach Solution (μCi/mL)	Final Wash Solution (μCi/mL)	Dried Residue (μCi/g)
Total Alpha	1.03E-03	3.58E-04	1.32E-04	2.47E-04	2.77E-04	3.77E-04	2.76E-06	2.05E+02
^{239,240} Pu	8.73E-04	3.14E-04	1.17E-04	2.20E-04	2.46E-04	3.35E-04	1.28E-06	1.24E+01
²⁴¹ Am	5.39E-05	3.27E-06	4.27E-07	9.73E-07	7.49E-07	1.18E-06	1.28E-06	1.90E+02
²⁴¹ Am(γ)	< 2.20E-01	< 2.79E-01	< 8.80E-02	< 8.40E-02	< 7.80E-02	< 2.60E-02	< 3.30E-03	2.61E+02
¹³⁷ Cs	2.45E+02	2.74E+02	9.76E+01	9.41E+01	8.93E+01	2.54E+01	2.20E+00	1.36E+02
⁹⁰ Sr	8.25E-01	5.64E-01	4.57E-01	5.98E-01	8.44E-01	1.57E+00	5.96E-02	2.35E+04
⁹⁹ Tc	7.73E-02	6.94E-02	2.17E-02	2.47E-02	2.21E-02	3.22E-03	< 1.43E-04	7.20E-02
^{243,244} Cm	1.98E-07	< 2.00E-08	< 2.00E-08	< 2.00E-08	< 2.00E-08	< 3.00E-08	< 3.00E-08	5.18E-01
¹⁵⁴ Eu	< 8.80E-03	< 1.55E-02	< 3.30E-03	< 6.00E-03	< 5.20E-03	< 1.04E-03	< 8.80E-05	1.33E+02
¹⁵⁵ Eu	< 2.20E-01	< 3.10E-01	< 2.20E-01	< 2.40E-01	< 1.30E-01	< 2.60E-02	< 2.20E-03	3.22E+02
¹²⁵ Sb	< 4.40E-01	< 6.20E-01	< 2.20E-01	< 2.40E-01	< 2.60E-01	< 2.60E-02	1.44E-02	2.00E+02
⁶⁰ Co	1.33E-02	< 1.24E-02	< 3.30E-03	< 3.60E-03	< 3.90E-02	< 2.60E-04	< 2.20E-03	1.83E+01
²⁴² Cm	< 2.00E-07	< 2.00E-08	< 2.00E-08	< 2.00E-08	< 2.00E-08	< 3.00E-08	< 3.00E-08	1.67E-01
²³⁸ Pu	1.03E-04	4.06E-05	1.46E-05	2.69E-05	3.02E-05	4.02E-05	2.08E-07	2.63E+00
¹³⁴ Cs	6.37E-01	7.25E-01	2.57E-01	2.54E-01	2.31E-01	6.10E-02	5.29E-03	0.00E+00
¹⁰⁶ Ru/ ¹⁰⁶ Rh	< 5.50E-01	< 6.20E-01	< 3.30E-01	< 3.60E-01	< 3.90E-01	< 3.90E-01	< 4.40E-03	9.61E+01
¹⁴⁴ Ce	< 4.40E-01	< 6.20E-01	< 3.30E-01	< 3.60E-01	< 2.60E-01	< 3.90E-02	< 3.30E-03	1.27E+02

Table 3.13. Distribution of Radionuclide Components in the AZ-101/AZ-102 Caustic-Leach Test: Uncorrected for Carryover of Interstitial Liquids

% Component Found^(a)

Component	Up to 1st 3 M Caustic Leach	2nd 3 M Caustic Leach	Final Washes	Dried Residue
Total Alpha	0 (0)	0 (0)	0 (0)	100 (100)
^{239,240} Pu	0 (0)	0 (0)	0 (0)	100 (100)
²⁴¹ Am	0 (0)	0 (0)	0 (0)	100 (100)
²⁴¹ Am(γ)	0 (1)	0 (0)	0 (0)	100 (98)
¹³⁷ Cs	81 (81)	13 (13)	3 (3)	3 (3)
⁹⁰ Sr	0 (0)	0 (0)	0 (0)	100 (100)
⁹⁹ Tc	87 (86)	7 (7)	0 (1)	7 (6)
^{243,244} Cm	0 (0)	0 (0)	0 (0)	100 (100)
¹⁵⁴ Eu	0 (0)	0 (0)	0 (0)	100 (100)
¹⁵⁵ Eu	0 (2)	0 (0)	0 (0)	100 (98)
¹²⁵ Sb	0 (5)	0 (0)	1 (0)	99 (95)
⁶⁰ Co	0 (5)	0 (0)	0 (0)	100 (95)
²⁴² Cm	0 (0)	0 (0)	0 (0)	100 (100)
²³⁸ Pu	0 (0)	0 (0)	0 (0)	100 (100)
¹³⁴ Cs	84 (84)	12 (12)	3 (3)	0 (0)
¹⁰⁶ Ru/ ¹⁰⁶ Rh	0 (12)	0 (1)	0 (0)	100 (87)
¹⁴⁴ Ce	0 (7)	0 (1)	0 (0)	100 (92)

(a) Values in parenthesis represent the distribution if component concentrations in the process streams that were below detection limits are recalculated with the component concentrations at their detection limits.

Table 3.14. Distribution of Radionuclide Components in the AZ-101/AZ-102 Caustic-Leach Test: Corrected for Carryover of Interstitial Liquids

% Component Found^(a)

Component	Up to 1st 3 M Caustic Leach	2nd 3 M Caustic Leach	Final Washes	Dried Residue
Total Alpha	0 (0)	0 (0)	0 (0)	100 (100)
^{239,240} Pu	0 (0)	0 (0)	0 (0)	100 (100)
²⁴¹ Am	0 (0)	0 (0)	0 (0)	100 (100)
²⁴¹ Am(γ)	0 (1)	0 (0)	0 (0)	100 (98)
¹³⁷ Cs	93 (90)	3 (7)	0 (0)	3 (3)
⁹⁰ Sr	0 (0)	0 (0)	0 (0)	100 (100)
⁹⁹ Tc	93 (94)	0 (0)	0 (0)	7 (6)
^{243,244} Cm	0 (0)	0 (0)	0 (0)	100 (100)
¹⁵⁴ Eu	0 (0)	0 (0)	0 (0)	100 (100)
¹⁵⁵ Eu	0 (2)	0 (0)	0 (0)	100 (98)
¹²⁵ Sb	0 (5)	0 (0)	1 (0)	99 (95)
⁶⁰ Co	0 (6)	0 (-1)	0 (0)	100 (95)
²⁴² Cm	0 (0)	0 (0)	0 (0)	100 (100)
²³⁸ Pu	0 (0)	0 (0)	0 (0)	100 (100)
¹³⁴ Cs	97 (94)	3 (6)	0 (0)	0 (0)
¹⁰⁶ Ru/ ¹⁰⁶ Rh	0 (14)	0 (-1)	0 (0)	100 (87)
¹⁴⁴ Ce	0 (8)	0 (0)	0 (0)	100 (92)

(a) Values in parenthesis represent the distribution if component concentrations in the process streams that were below detection limits are recalculated with the component concentrations at their detection limits.

Table 3.15. Radionuclide Mass Balances and Composition of the AZ-101/AZ-102 Sludge Composite (dry weight basis)

Radionuclide Concentration, μCi radionuclide/g dried sludge

Component	Direct Analysis	Summation Method	Recovery, %
Total Alpha	9.91E+01	9.91E+01	100.0(a)
^{239,240} Pu	6.11E+00	5.99E+00	98
²⁴¹ Am	9.14E+01	9.15E+01	100
²⁴¹ Am(γ)	1.31E+02	1.26E+02	97
¹³⁷ Cs	1.98E+03	2.20E+03	111
⁹⁰ Sr	2.16E+04	1.14E+04	53
⁹⁹ Tc	5.44E-01	5.30E-01	98
^{243,244} Cm	2.27E-01	2.50E-01	110
¹⁵⁴ Eu	5.98E+01	6.42E+01	107
¹⁵⁵ Eu	1.46E+02	1.55E+02	107
¹²⁵ Sb	1.03E+02	9.70E+01	95
⁶⁰ Co	8.68E+00	8.85E+00	102
²⁴² Cm	6.75E-02	8.06E-02	119
²³⁸ Pu	1.28E+00	1.27E+00	99
¹³⁴ Cs	4.96E+00	5.50E+00	111
¹⁰⁶ Ru/ ¹⁰⁶ Rh	5.14E+01	4.64E+01	90
¹⁴⁴ Ce	5.02E+01	6.13E+01	122

(a) Normalized values: expressed as μCi isotope(s)/ μCi total α . Mass recovery for total α is 100% by definition as all summation data were normalized to the total α concentration as determined by direct analysis. See text for further explanation.

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