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Abstract

Sludge washing and parametric caustic leaching tests were performed on sludge samples from five Hanford tanks: B-101, BX-110, BX-112, C-102, and S-101. These studies examined the effects of both dilute hydroxide washing and caustic leaching on the composition of the residual sludge solids.

Dilute hydroxide washing removed from <1 to 25% of the Al, ~20 to ~45% of the Cr, ~25 to 97% of the P, and 63 to 99% of the Na from the Hanford tank sludge samples examined. The partial removal of these elements was likely due to the presence of water-soluble sodium salts of aluminate, chromate, hydroxide, nitrate, nitrite, and phosphate, either in the interstitial liquid or as dried salts.

The response of Al to caustic leaching was variable. When leached with 3 M NaOH for one week at 95 to 100°C, the cumulative Al removals were 62, 99, 61, 95, and 89% for the B-101, BX-110, BX-112, C-102, and S-101 samples, respectively. For the B-101 and the BX-110 samples, Al dissolution was rapid, with the Al concentrations reaching >80% of their final values within the first 5 h of leaching. Interestingly, for the BX-112 sample, Al removal decreased with increasing leaching time and temperature—a trend contrary to what was expected. We hypothesize that this is due to the formation of aluminosilicate minerals. For the C-102 sludge, there was clearly a benefit in increasing the NaOH concentration from 1 M to 3 M. Leaching with 1 M NaOH removed ~20 to 30% of the Al from the dilute hydroxide-washed solids while 3 M NaOH removed ~95% of the Al. Aluminum dissolved slowly from the S-101 sample, which is consistent with boehmite being the predominant Al-containing phase.

Chromium in the washing and leaching solutions was predominantly present as the chromate ion. For all the sludge samples examined, Cr removal during caustic leaching was highly time-dependent, but the Cr dissolution did not fit simple zero-, first-, or second-order kinetic models. Consistent trends in the effects of temperature and hydroxide concentration on Cr removal were difficult to discern.

A combination of dilute hydroxide washing and caustic leaching was generally effective at removing P from the sludge samples examined. Except for the Tank C-102 sample, cumulative P removals were ≥85%. For C-102, the cumulative P removals were only ~60%. Increasing temperature or hydroxide concentration generally did not result in large improvements in P removal; that is, relatively mild conditions tended to be adequate to remove P.

The projected ^{137}Cs content for the low-level waste (LLW) resulting from immobilizing the sludge washing/leaching solutions would range from ~50 to ~540 Ci/m^3 for the samples examined. Although these concentrations are below the U.S. Nuclear Regulatory Commission Class C LLW limit of 4,600 Ci/m^3, they are well above the proposed guideline of 3 Ci/m^3 for the immobilized LLW product from the proposed private-processing facilities. Thus, it is likely that ^{137}Cs will need to be removed from the washing and leaching solutions. On the other hand, transuranic and Sr removal would likely not be required for the washing and leaching solutions from processing the sludges examined here.

An estimate of high-level waste (HLW) glass produced in immobilizing the washed and leached sludges shows there is a clear benefit in performing caustic leaching. Significant reductions in the HLW glass mass can be achieved by leaching the tank solids with caustic before immobilization.

Finally, the results of the FY 1998 studies reported here indicate the importance of performing parametric washing/leaching studies. The response of the various tank sludges to dilute hydroxide washing and caustic leaching is highly variable. This can be true even for tanks containing similar waste types (e.g., BX-110 and BX-112). Thus, before processing a particular batch of waste, parametric tests should be performed to determine the optimal processing conditions for achieving the process objectives.

Summary

This report describes the sludge washing and caustic leaching tests conducted in FY 1998 at the Pacific Northwest National Laboratory, the Los Alamos National Laboratory, and the Oak Ridge National Laboratory. 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).

Sludge samples from five different Hanford tanks were examined: B-101, BX-110, BX-112, C-102, and S-101. These five tank waste samples showed a wide range of behaviors for Al, Cr, P, and Na under the test conditions examined. The effects of caustic leaching on the quantity of immobilized high-level waste (IHLW) resulting from these wastes were estimated, assuming the following constraints on the IHLW glass: 1) 25 wt% oxide loading (excluding Na_2O and SiO_2), 2) a maximum of 15 wt% Al_2O_3, 3) a maximum of 0.5 wt% Cr_2O_3, and 4) a maximum of 3 wt% P_2O_5. The variable leaching behaviors, along with differences in the sludge compositions, led to estimates of ~20 to ~95% reductions in the quantity of IHLW achieved by caustic leaching for the five wastes examined.

The projected ^{137}Cs content for the low-level waste (LLW)[a] resulting from immobilizing the sludge washing/leaching solutions would range from ~50 to ~540 Ci/m^3 for the samples examined. Although these concentrations are below the U.S. Nuclear Regulatory Commission (NRC) Class C LLW limit of 4,600 Ci/m^3, they are well above the proposed guideline of 3 Ci/m^3 for the immobilized LLW product from the proposed private-processing facilities. Thus, it is likely that ^{137}Cs will need to be removed from the washing and leaching solutions. On the other hand, transuranic (TRU) and Sr removal from the washing and leaching solutions generated in processing the sludges examined here would likely not be required.

Another important observation is that the compositions measured for these five sludge samples were often markedly different from the compositions estimated from historical data. Also, different leaching behaviors (as well as compositions) were observed for samples taken from tanks believed to contain similar wastes. These observations emphasize the need of basing processing projections on experimental data rather than estimates.

The sludge samples were first subjected to washing with dilute sodium hydroxide solution at ambient temperature. The removals of the various waste components were measured. Table S.1 summarizes the behaviors of Al, Cr, P, and Na during the dilute hydroxide-washing tests. Highlights of these results include:

- Dilute hydroxide washing removed from <1 to 25% of the Al from the sludge samples examined. The Al removed by such washing was likely present in the samples as soluble aluminate, either in the interstitial liquid or as dried salts.

- Dilute hydroxide washing removed from ~20 to ~45% of the Cr from the sludge samples examined. The Cr removed by such washing was likely present in the samples as soluble chromate ion, either in the interstitial liquid or as dried salts.

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[a] The LLW form is assumed to contain 20 wt% Na_2O and have a density of 2.7 MT/m^3.

Table S.1. Summary of Dilute Hydroxide-Washing Results

	Aluminum		Chromium	
	Conc. In Sample, wt%	Removed, %	Conc. In Sample, wt%	Removed, %
B-101[(a)]	3.04	25	0.23	21
BX-110	3.39	4	0.13	23
BX-112	3.80	5	0.40	19
C-102	10.95	0.4	<0.05	--
S-101	9.41	11	0.47	46

	Phosphorus		Sodium	
	Conc. In Sample, wt%	Removed, %	Conc. In Sample, wt%	Removed, %
B-101	0.65	67	13.7	88
BX-110[(a)]	1.97	97	(b)	99
BX-112	5.55	24	19.8	63
C-102	0.42	25	8.0	74
S-101	0.30	55	12.6	98

(a) For the B-101 and BX-110 samples, the concentrations given are on a wet-weight basis; all others are on a dry-weight basis.

(b) Not determined.

- Chromium in the washing solutions was predominantly present as the chromate ion.

- Dilute hydroxide washing removed from ~25 to 97% of the P from the sludge samples examined. The P removed by such washing was likely present in the samples as soluble phosphate salts, either in the interstitial liquid or dried salts.

- Dilute hydroxide washing removed 88%, 99%, 63%, 74%, and 98% of the Na from B-101, BX-110, BX-112, C-102, and S-101 sludge samples, respectively.

Following the dilute hydroxide washing, the remaining solids were subjected to leaching with 1 or 3 M NaOH at 60 to 100°C for up to 168 h. Again, the removals of the various waste components were measured. Table S.2 summarizes the behaviors of Al, Cr, and P during the caustic leaching tests. Highlights of these results include:

- Caustic leaching removed ~45% of the Al from the dilute hydroxide-washed B-101 solids. Aluminum dissolution was rapid for this waste with the Al concentration reaching >80% of its final value within the first 5 h of leaching. Aluminum removal at 3 M NaOH was slightly better than at 1 M NaOH, but increasing the temperature from 60°C to 100°C did not result in significant improvement. Leaching the B-101 sludge with 1 M NaOH at 60°C is nearly as effective at removing Al as leaching with 3 M NaOH at 100°C.

Table S.2. Summary of Caustic-Leaching Results

Tank	T, °C	[NaOH], M	Removed, %[a] Al	Cr	P
B-101	60	1.1	42	37	60
		3.2	51	38	77
	100	1.0	46	39	56
		3.1	50	48	84
BX-110	60	1.2	95	49	95
		3.2	99	77	97
	80	1.2	98	74	97
		3.1	98	88	97
	95	1.2	99	87	97
		3.2	99	93	98
BX-112	60	1.1	62	52	99
		2.9	68	70	99
	80	1.3	54	85	99
		3.4	63	86	99
	100	1.1	51	83	98
		3.4	59	82	99
C-102	60	1.1	27	(b)	47
		2.9	95	(b)	55
	100	1	20	(b)	41
		2.9	95	(b)	48
S-101	70	1	66	52	(c)
		3	59	75	(c)
	95	1	87	71	(c)
		3	89	76	(c)

(a) Amount removed from the dilute hydroxide-washed solids after leaching for 168 h (72 h for C-102).

(b) Chromium was below the analytical detection limit in this sludge.

(c) No value reported because of low mass recovery for P.

- Caustic leaching removed ≥ 95% of the Al from the dilute hydroxide-washed BX-110 solids. When leached with 3 M NaOH, Al dissolution was rapid with the Al concentration reaching >90% of its final value within the first 5 h of leaching. The results also indicate that, provided sufficient time is allowed, leaching the BX-110 sludge with 1 M NaOH at 60°C is as effective at removing Al as leaching with 3 M NaOH at 95°C.

- Caustic leaching removed 50 to 75% of the Al from the dilute hydroxide-washed BX-112 solids. For the most part, the hydroxide concentration dependence was as expected. That is, Al removal improved with increasing hydroxide concentration, although the increases were small. Interestingly, Al removal decreased with increasing leaching time and temperature—a trend contrary to what was expected. We hypothesize that this is due to the formation of aluminosilicate minerals. This hypothesis is supported by solution analytical data that indicate parallel decreases in Al and Si concentrations. It is also supported by microscopy analyses of the solids before and after leaching. No aluminosilicate phases were seen in the solids before caustic leaching, but such phases were clearly present afterwards.

- For the C-102 sludge, there was clearly a benefit in increasing the NaOH concentration from 1 M to 3 M. Leaching with 1 M NaOH removed ~20 to 30% of the Al from the dilute hydroxide-washed solids while 3 M NaOH removed ~95% of the Al. As expected, the Al concentration generally increased with time. Increasing the temperature from 60°C to 100°C did not result in significant improvement in Al removal from the C-102 sludge. Indeed, leaching the C-102 sludge with 1 M NaOH at 100°C was not as effective at removing Al as leaching with 3 M NaOH at 60°C.

- Caustic leaching removed about 60% to 90% of the Al from the dilute hydroxide-washed S-101 solids. Aluminum dissolved slowly from this sludge, which is consistent with boehmite being the predominant Al-containing phase. The trends were as expected for this sludge; that is, increasing hydroxide concentration, temperature, and time improved Al removal.

- For all the sludge samples examined, Cr removal during caustic leaching was highly time-dependent, but the Cr dissolution did not fit simple zero-, first-, or second-order kinetic models.

- Chromium in the caustic leaching solutions was predominantly present as the chromate ion.

- For the B-101 sludge, only a modest improvement in Cr removal was achieved in going from 1 M NaOH at 60°C to 3 M NaOH at 100°C.

- For the BX-110 sludge, Cr removal increased with increasing NaOH concentration, although such increases were less pronounced at the higher temperatures. Likewise, increasing temperature increased Cr removal from the BX-110 sludge. For this waste, leaching with 3 M NaOH at 60°C was nearly as effective at removing Cr as leaching with 1 M NaOH at 80°C. Likewise, the Cr removal was similar for 3 M NaOH at 80°C and 1 M NaOH at 95°C.

- For the BX-112 sludge, there was marked improvement in Cr removal in going from 60°C to 80°C, but no significant improvement in going from 80°C to 100°C. Furthermore, at a given temperature, there was little difference in Cr removal when leaching with 1 M NaOH or 3 M NaOH.

- After 168 h of leaching, the total Cr removed from the washed S-101 solids was similar when leached with 3 M NaOH at 70°C or 95°C or with 1 M NaOH at 95°C. Chromium removal was markedly less efficient at 1 M NaOH/70°C.

- For the B-101 sludge, P removal on leaching at 3 M NaOH was better than at 1 M NaOH, but increasing the temperature from 60°C to 100°C did not result in significant improvements.

- Caustic leaching removed ≥95% of the P from the dilute hydroxide-washed BX-110 solids, even under the mildest caustic leaching conditions examined (1 M NaOH, 60°C).

- Phosphorus was essentially completely removed from the washed BX-112 solids by caustic leaching. One molar NaOH at 60°C is an adequately vigorous leaching condition to achieve this level of P removal.

- Caustic leaching removed ~50% of the P from the dilute hydroxide-washed C-102 solids using any of the caustic leaching conditions examined. Slightly more P was removed with 3 M NaOH than with 1 M NaOH at the same temperature.

Table S.3 presents the cumulative removals of Al, Cr, and P achieved by the combined washing and leaching operations. Highlights of these results include the following:

- Because Al was generally not efficiently removed by dilute hydroxide washing, the cumulative removals for this component are dominated by that removed during caustic leaching. Cumulative Al removals covered a broad ranged—from 20 to 99%.

- Cumulative Cr removals ranged from 50 to 95%. Similar to the results for Al, caustic leaching was responsible for most of the Cr removal achieved.

- Except for C-102, cumulative P removal was generally good with removals being > 85%. The contribution of dilute hydroxide washing versus caustic leaching in determining these removals varied. Dilute hydroxide washing was the primary factor for the B-101 and BX-110 samples, but caustic leaching was the main driver for P removal for the other samples.

The results of the FY 1998 studies reported here indicate the importance of performing parametric washing/leaching studies. As can be deduced from the above summary, the response of the various tank sludges to dilute hydroxide washing and caustic leaching is highly variable. This can be true even for tanks containing similar waste types (e.g., BX-110 and BX-112). Thus, before processing a particular batch of waste, parametric tests should be performed to determine the optimal processing conditions for achieving the process objectives.

Table S.3. Summary of Cumulative Removals

Tank	T, °C	[NaOH], M	Removed, %[a] Al	Cr	P
B-101	60	1.1	56	50	87
		3.2	63	51	92
	100	1.0	59	52	85
		3.1	62	59	95
BX-110	60	1.2	95	61	100
		3.2	99	82	100
	80	1.2	98	80	100
		3.1	97	91	100
	95	1.2	99	90	100
		3.2	99	95	100
BX-112	60	1.1	64	62	99
		2.9	69	76	99
	80	1.3	56	88	99
		3.4	65	89	99
	100	1.1	53	86	99
		3.4	61	86	100
C-102	60	1.1	27	(b)	60
		2.9	95	(b)	66
	100	1	20	(b)	56
		2.9	95	(b)	61
S-101	70	1	70	74	(c)
		3	63	86	(c)
	95	1	88	84	(c)
		3	90	87	(c)

(a) Amount removed from the dilute hydroxide-washed solids after leaching for 168 h (72 h for C-102).

(b) Chromium was below the analytical detection limit in this sludge.

(c) No value reported because of low mass recovery for P.

Glossary

CW	cladding waste
EB	evaporator bottoms
ESW	enhanced sludge washing
HDPE	high density polyethylene
HLW	high-level waste
IC	ion chromatography
ICP/AES	inductively coupled plasma/atomic emission spectroscopy
ICP/MS	inductively coupled plasma/mass spectrometry
IHLW	immobilized high level waste
ITS	in-tank solidification
LANL	Los Alamos National Laboratory
LLW	low-level waste
NRC	U.S. Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
PUREX	plutonium uranium extraction process
R	high-level REDOX process waste
REDOX	REDOX process for Pu recovery
SORWT	sort on radioactive waste type
SRS	strontium leached sludge
TBP	tributyl phosphate
TEM	transmission electron microscopy
TRU	transuranic elements
UV/vis	ultraviolet/visible
WHC	Westinghouse Hanford Company
WOL	Waste Oxide Loading

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1.0 Introduction

Over the last decade, 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 onsite. 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 onsite. 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 also 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) was expected to be removed by caustic leaching according to the following equation:

$$\mathrm{Cr(OH)_3(s) + NaOH(aq) \rightarrow Na[Cr(OH)_4](aq)} \tag{1.4}$$

However, studies conducted at the Pacific Northwest National Laboratory (PNNL) have suggested that the behavior of Cr in the caustic leaching process is more complex (Lumetta et al. 1997).

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 and 1997, Temer and Villarreal 1995, 1996, and 1997). In the previous work, a standard set of test conditions was examined for each sludge. In FY 1998, the focus of the testing effort shifted to performing parametric tests on selected sludge samples. The purpose of the parametric tests is to provide data that process engineers can use to optimize process flowsheets for specific waste types. The parameters being considered are time, temperature, and caustic (NaOH) concentration. This report describes the results of the sludge washing and parametric caustic-leaching tests performed in FY 1998 at the Pacific Northwest National Laboratory, the Los Alamos National Laboratory, and the Oak Ridge National Laboratory. The sludges used in this study were taken from Hanford tanks B-101, BX-110, BX-112, C-102, and S-101. Table 1.1 lists the reported primary and secondary waste types stored in these tanks along with the percentage of the total sludge inventory contained in each tank.

Table 1.1. Primary and Secondary Waste Types[(a)]

Tank	Primary Waste	Secondary Waste	Percentage of Total Sludge Inventory
B-101	EB	CW	0.9
BX-110	1C	EB-ITS	1.5
BX-112	1C	EB	1.3
C-102	CW	TBP	3.4
S-101	R	EB	2.0

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

EB	Evaporator bottoms
CW	cladding waste
1C	First decontamination cycle Bi phosphate
ITS	In-tank solidification
R	High-level REDOX process waste
TBP	Waste from tributyl phosphate extraction process
SRS	Strontium-leached sludge
SR-WASH	Particulates from Sr wash of PUREX waste in the AR vault.

2.0 Tank B-101 Test

2.1 B-101 Experimental

The B-101 sludge sample used was a composite mixture of two segments from Core #90 and two segments from Core #91. The composite sample was prepared at the Hanford 222-S laboratory and shipped to Los Alamos National Laboratory (LANL) in January 1998. The as-received sludge sample contained 19-wt% water as determined by drying a pre-weighed aliquot to a constant weight at 105°C.

Initial Wash: A 50.15-g portion of the B-101 composite sample was placed in a 225-mL plastic centrifuge bottle labeled as "B101." One hundred milliliters of 0.1 M NaOH was added to the bottle. The mixture was stirred 30 min at ambient temperature and centrifuged for 15 minutes at 1,200 G; then the centrifuged liquid was decanted. Another 100-mL of fresh 0.1 M NaOH was added to B101. The mixture was stirred for 30 minutes, then centrifuged for 15 minutes at 1,200 G. Again, the centrifuged liquid was decanted. This washing procedure was repeated for a total of seven wash cycles. The wash solutions were yellow, but became progressively less so, and the final wash solution was colorless. During the course of the washing procedure, it became necessary to change the bottle in which the washing solutions were being collected. An additional amount of 0.1 M NaOH was used to quantitatively transfer the liquids from the original collection bottle to the new bottle. The final volume of the combined wash solution was 793 mL (815 g of solution at a density of 1.028 g/mL).

Division of the Washed Solids: The washed B-101 solids were diluted with 50 mL of deionized water and stirred for 30 min to homogenize. The total weight of the slurry was 78.3591 g, corresponding to 0.640 g of as-received B-101 sample/g of slurry. Aliquots (~15 g) were distributed between five 125-mL polymethylpentene (PMP) bottles (labeled as B101-A0, A1, A2, A3, and A4, respectively). The method for dividing the slurry was to use a 10-mL auto pipette with a tip that had been trimmed so that the bore was large enough to accommodate the thick and granular nature of the slurry. While the slurry in B101 stirred, 5 mL was removed successively into the five tared containers. This process was continued until all the slurry had been dispensed. The amount of B-101 sludge solids calculated to be in each vial is given in Table 2.1. Sample B101-A0 contained 15.5041 g of slurry, corresponding to 9.923 g of as-received B-101 sludge. When dried at 105°C, B101-A0 yielded 2.7525 g of dried solids, corresponding to 27.7-wt% (13.89 g) dry washed solids in the as-received sludge. Based on this value, the amount of washed solids in each of the bottles was determined. Sample B101-A0 was analyzed by inductively coupled plasma/atomic emission spectroscopy (ICP/AES) and radiochemical methods.

Leaching: Table 2.2 summarizes the leaching conditions for each aliquot of B-101 sludge. The amount of NaOH added to each reaction vessel was determined by the desired final NaOH concentration assuming that 1) each mole of Al consumes one mole of hydroxide, 2) each mole of Cr consumes one mole of hydroxide, and 3) each mole of phosphate consumes three moles of hydroxide. A slight excess of NaOH was actually used to allow for uncertainties in the estimated Al, Cr, and P concentrations. The estimated Al, Cr, and P concentrations in the as-received sludge were obtained from Agnew (1997) (Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 4). These estimates were 10,100 μg Al/g, 136 μg Cr/g, and 14,500 μg P/g; these values are based on wet sludge solids. The appropriate amount of 10 M NaOH and water was added to each reaction vessel to give the desired NaOH concentration and 5 mL of leachate per gram of as-received sludge. Based on the solubility of gibbsite at 60°C, it was estimated that this volume of leaching solution was sufficient to avoid Al saturation if all the Al dissolved.

Table 2.1. Weight of B-101 Waste in Each Bottle

Bottle #	Wt. B-101 Sample, g[(a)]	Wt. Washed Solids, g[(b)]
B-101-1	9.96	2.76
B-101-2	10.07	2.79
B-101-3	10.00	2.77
B-101-4	9.39	2.61

(a) Weight of untreated sludge on as-received wet-weight basis.
(b) Weight of washed sludge solids on a dry-weight basis.

Table 2.2. Leaching Conditions for Each Aliquot of Washed B-101

Bottle #	[NaOH], M[(a,b)]	T, °C
B-101-1	1.1	60
B-101-2	1.0	100
B-101-3	3.2	60
B-101-4	3.1	100

(a) Concentrations determined by titration with standard HCl immediately after NaOH additions.
(b) 5 mL per gram of untreated sample.

The slurry was mixed for 5 min, and then allowed to settle for 5 min. A 100-μL portion of supernatant was removed for free-hydroxide determination. If the $[OH^-]$ was not within 0.2 M of the target value, appropriate adjustments were made. The liquid level was marked on each reaction vessel, and each vessel was closed with a cap equipped with a tube-condenser. The vessels were placed in an Al heating block at the appropriate temperature and stirred with a magnetic stirrer. Evaporation was minimal over several hours; occasionally, deionized water was added to bring the liquid level up to its original position. The leachates were sampled at intervals of 5, 24, 72, and 168 h. For each sampling, the stirrer was stopped, and the solids were settled at temperature. The upper portion of the solution was typically clear enough to sample within 30 min. The transfer pipette and the syringe filter assembly (0.2-μm PVDF membrane) were preheated by inserting in a boiling water bath. These were then used to filter ~2.5 mL of the leachate solution. A 2-mL aliquot of the filtered solution was immediately acidified with 1.5 mL of conc. HNO_3 and 16.5 mL deionized water. The remaining filtered solution was added back to the reaction vessel, and the leaching was continued.

At the conclusion of the test, the reaction vessels were removed from the heating block, allowed to cool to ambient temperature, and then centrifuged for 15 min. A pipette was used to draw off the solution above the centrifuged solids. The leached solids were washed thrice with 10-mL portions of 0.01 M NaOH/0.01 M $NaNO_2$, then were dried at 105°C. Table 2.3 gives the weights of the leached solids and the weight reductions achieved after leaching for168 h. The weight reduction with respect to the washed solids treated was generally ~15%.

Table 2.3. Weight of the Leached B-101 Solids

Bottle #	Wt. Leached Solids, g	Wt. Reduction, %[(a)]
B-101-1	2.339	15
B-101-2	2.464	12
B-101-3	2.389	14
B-101-4	2.196	16

(a) Weight reduction with respect to the dry weight of washed solids treated, which was achieved after leaching for 168 h.

2.2 B-101 Results

The following two sections provide results of dilute hydroxide washing and caustic leaching of B-101 sludge.

2.2.1 Dilute Hydroxide Washing of B-101 Sludge

Table 2.4 presents the concentrations of some important nonradioactive B-101 sludge components in the combined dilute hydroxide wash solution and in the washed solids. The table also lists the total mass of each component present in each process stream (wash solution or washed solids) and the amount of each component removed by the dilute hydroxide washing in terms of percent. The latter values were determined by dividing the amount of material in the wash solution by the total amount in the wash solution plus the washed solids. The data indicated that 25% of the Al, 21% of the Cr, 67% of the P, 23% of the Ba, and 22% of the U were removed by washing the B-101 sludge with dilute NaOH. Most (88%) of the Na was removed from the B-101 solids by washing with dilute NaOH, with the washed solids containing 5.7 wt% Na. No other nonradioactive component was significantly removed by the dilute hydroxide washing process.

Table 2.4 also presents the concentration of the nonradioactive components in the as-received B-101 sludge. These values were determined by summing the amount of each component in the combined wash solution and the washed solids and dividing by the total amount of sludge treated (50.15 g). The relative concentrations of the various components differ considerably from the estimates given by Agnew (1997). The relative concentrations given by Agnew for Al, Bi, Cr, P, and Si were 0.6, 0.1, 0.01, 0.6, and 0.2 grams per gram of Fe, respectively. The corresponding values determined in this test were 0.4, 0.001, 0.03, 0.03, and 0.2. Thus, there appeared to be less Bi and P in the sample examined than would be expected from the historical tank data.

Table 2.5 presents the concentrations of some important radioactive B-101 sludge components in the washed solids and in the dilute hydroxide wash solution. The table also lists the total activity of each component present in each processing stream and the percentage of each component removed by the dilute hydroxide washing (as determined by the summation method). The transuranic (TRU) behavior is reflected in the total alpha activity data. As expected, little if any TRUs dissolved during the dilute hydroxide washing process. Less than 25% of the ^{60}Co dissolved during the dilute hydroxide washing. A substantial percentage (46%) of the ^{137}Cs was removed from the B-101 sludge sample during the dilute hydroxide wash. Technetium was below the detection limit (as indicated in Table 2.5) in both the wash solution and the washed solids.

If the combined dilute hydroxide wash solution were converted directly to a glass LLW form,(a) the resulting waste form would contain < 14 nCi TRU/g, < 0.21 Ci ^{90}Sr/m^3, 308 Ci ^{137}Cs/m^3, and < 0.04 Ci ^{99}Tc/m^3. Thus, the immobilized LLW from washing the B-101 sludge might exceed the U.S. Nuclear Regulatory Commission (NRC) Class A limits for TRU (< 10 nCi/g), ^{90}Sr (< 0.04 Ci/m^3), and ^{137}Cs (< 1 Ci/m^3), but it would be within the Class C limits of < 100 nCi/g), < 7000 Ci/m^3), and < 4600 Ci/m^3 for TRU, ^{90}Sr, and ^{137}Cs, respectively.

Table 2.4. Results of Dilute Hydroxide Washing of the B-101 Sludge Sample: Nonradioactive Components

	Combined Wash Solution		Washed Solids		Amount	Conc. in As-Received
Component	µg/mL	µg	µg/g	µg	Removed, %	Sample, µg/g(a)
Al	473	375089	82615	1148348	25	30378
Ba	0.74	583	140	1946	23	50
Bi	< 0.02	< 16	277	3844	< 0.4	77
Ca	< 0.1	< 79	2658	36947	< 0.2	737
Cr	30.7	24329	6461	89803	21	2276
Fe	1.76	1396	229885	3195402	0.04	63745
Mg	< 1.0	< 793	2299	31954	< 2.4	637
Mn	< 0.1	< 79	43103	599138	< 0.01	11947
Na	9680	6066940	57471	798851	88(b)	137000(b)
P	275	218075	7902	109842	67	6539
Si	< 10	< 7930	50287	698994	< 1.1	13938
Sr	< 0.005	< 4	173	2408	< 0.2	48
U	26.51	21025	5415	75272	22	1920
Zn	< 0.1	< 79	473	6571	< 1.2	131
Zr	< 1.0	< 793	3161	43937	< 1.8	876

(a) Concentration on a wet-weight basis. This was determined by summing the quantities in the combined wash solution and the washed solids and dividing by the total amount of as-received sludge treated (50.15 g).

(b) The value for Na has been adjusted for the 1609300 µg Na added as NaOH in the washing process.

(a) For this determination, it was assumed that the LLW glass form will contain 20 wt% Na_2O, and the density of the glass would be 2.7 MT/m^3.

Table 2.5. Results of Dilute Hydroxide Washing of the B-101 Sludge Sample: Radioactive Components

	Combined Wash Solution		Washed Solids		Amount	Conc. in As-Received
Component	μCi/mL	μCi	μCi/g	μCi	Removed, %	Sample, μCi/g(a)
Total Alpha	< 8.99E-04	< 6.48E-02	1.82E+01	2.53E+02	< 0.03	5.06E+00
Pu Alpha	< 4.50E-04	<3.24E-02	1.12E+01	1.56E+02	< 0.02	3.11E+00
^{241}Am(b)	< 4.49E-04	< 3.24E-02	6.99E+00	9.71E+01	< 0.03	1.94E+00
^{137}Cs	7.46E+00	5.37E+03	4.52E+02	6.29E+03	46	2.33E+02
^{60}Co	< 4.88E-03	< 3.52E+00	7.46E-01	1.04E+01	< 25	0.277 > x > 0.207
^{90}Sr	< 2.30E-03	< 1.66E+00	7.37E+03	1.03E+05	< 0.002	2.04E+03
^{99}Tc	< 8.77E-04	<6.32E+00	< 5.71E-01	<7.94E+00		<1.71E-01

(a) Concentration on a wet-weight basis. This was determined by summing the quantities in the combined wash solution and the washed solids and dividing by the total amount of sludge treated (50.15 g).

(b) Determined by gamma spectroscopy.

2.2.2 Caustic Leaching of B-101 Sludge

Table 2.6 summarizes the amounts of Al, Cr, Na, P, and Si removed from the washed B-101 solids under the various leaching conditions; the values given represent those obtained after 168 h of leaching. The values were obtained in two different ways. First, the quantities of a given component found in the leaching and final rinse solutions were summed, and that quantity was divided by the total found in those two solutions plus the residual solids (this will be referred to as the "summation method"). In the second method, the concentration of each component in the solids was normalized to the concentration of Fe (giving grams of component per grams of Fe). Since Fe was not significantly removed by caustic leaching, the normalized concentration values in the leached solids could be compared to those in the dilute hydroxide-washed solids. The latter method will be referred to as the "Fe normalization" method. The impetus for using the Fe normalization method was low mass recoveries obtained in the BX-112 test using the summation method (see Section 4.2). For B-101, agreement between these two methods is generally good. Table 2.7 presents the actual concentrations of the various components in the leaching and washing solutions and in the leached solids. The mass recovery for each component is presented in Table 2.7 as well.

Caustic leaching for 168 h removed ~45% of the Al from the dilute hydroxide-washed solids; in all cases, 45% to 50% of the Al was removed. Figure 2.1 shows the Al concentrations as a function of time, and Figure 2.2 shows the percent of the Al removed as a function of time. The latter values were obtained by applying the following formula:

$$\%R_t = \frac{\%R_{tot} C_t}{C_{168}} \tag{2.1}$$

where $\%R_t$ is the percent removed at time t, $\%R_{tot}$ is the total percent removed after 168 h, C_t is the concentration at time t, and C_{168} is the concentration at 168 h. Aluminum dissolution was rapid with the Al concentrations reaching >80% of their final values within the first 5 h of leaching. Aluminum removal at 3 M NaOH was slightly better than at 1 M NaOH, but increasing the temperature from 60°C to 100°C did not result in significant improvement. These results indicate that leaching the B-101 sludge with 1 M NaOH at 60°C is nearly as effective at removing Al as leaching with 3 M NaOH at 100°C.

Table 2.7. Concentrations of Key B-101 Sludge Components in Caustic Leaching Solutions and in the Caustic Leached Solids

	Washed Solids		5 h	24 h	72 h	168 h		Final Wash Solution		Leached Solids		Mass Recovery,
Component	µg/g	µg(a)	µg/mL	µg/mL	µg/mL	µg/mL	µg(b)	µg/mL	µg(c)	µg/g	µg(d)	%
						1 M NaOH, 60°C						
	Wt. Washed Solids in Sample, g:		2.76					Vol. Leach Soln., mL:			43	
	Wt. Leached Solids, g:		2.34					Vol. Final Wash Soln., mL:			30.3	
Al	82615	228017	1600	2,000	2,000	1,900	81700	308	9332	54,506	127495	96
Ba	140	386	0.7	<0.6	<0.6	0.6	28	0.1	2.2	166	388	108
Bi	277	763	<0.2	<0.2	<0.2	< 0.2	< 9	< 0.02	< 1	306	716	95 > x > 93
Ca	2658	7336	<1	<1	10	< 1	< 43	0.2	7	3270	7650	105
Cr	6461	17831	57	84	117	129	5562	22	675	4622	10812	96
Fe	229885	634483	10	14	10	10	430	4	133	264,535	618774	98
Mg	2299	6345	<10	<10	<10	< 10	< 430	<1	0	2580	6035	102>x>95
Mn	43103	118966	<1	<1	<1	< 1	< 43	0.6	17	47238	110495	93
Na	57471	158621	31000	30000	31000	29000	1247000	4730	143319	72674	169993	N/A
P	7902	21810	250	280	320	320	13760	53	1600	4360	10200	117
Si	50287	138793	170	<100	<100	< 100	< 4300	10	300	76308	178492	130
Sr	173	478	<0.05	<0.05	<0.05	< 0.05	< 2	< 0.01	< 0.2	213	497	104
U	5415	14946	199	185	154	107	4617	14	426	3331	7792	86
Zn	473	1305	78	<1	<1	< 1	< 43	< 0.1	< 3	612	1432	110
Zr	3161	8724	<10	<10	<10	< 10	< 430	4	133	3,307	7735	95 > x >90
						3 M NaOH, 60°C						
	Wt. Washed Solids in Sample, g:		2.77					Vol. Leach Soln., mL:			39.7	
	Wt. Leached Solids, g:		2.39					Vol. Final Wash Soln., mL:			30.4	
Al	82615	228843	2,400	2,400	2,700	2,600	103220	440	13376	46,898	112058	100
Ba	140	388	<0.6	0.9	0.6	1.3	52	0.1	2.9	162	387	114
Bi	277	766	<0.2	<0.2	<0.2	< 0.2	< 8	< 0.02	< 1	298	713	93
Ca	2658	7363	10	<1	10	13	516	22	669	2954	7059	112
Cr	6461	17896	71	91	125	152	6030	23	690	4579	10940	99

(a) Mass of each component in the aliquot treated under the indicated conditions. This was determined from analysis of the washed solids (aliquot B101-A0).

(b) Mass of each component in the caustic leaching solution.

(c) Mass of each component in the final washing solution.

(d) Mass of each component in the leached solids.

	Washed Solids		5 h	24 h	72 h	168 h		Final Wash Solution		Leached Solids		Mass
Component	µg/g	µg[(a)]	µg/mL	µg/mL	µg/mL	µg/mL	µg[(b)]	µg/mL	µg[(c)]	µg/g	µg[(d)]	Recovery, %
Fe	229885	636782	<10	<10	11	23	913	7	217	268833	642350	101
Mg	2299	6368	<10	<10	<10	< 10	< 397	21	635	2585	6176	107
Mn	43103	119397	<1	<1	<1	< 1	< 40	1.1	33	48375	115588	97
Na	57471	159195	78000	77000	80000	80000	3176000	14300	434720	95273	227646	N/A
P	7902	21889	330	370	400	420	16674	37	1137	2216	5294	106
Si	50287	139296	350	230	270	250	9925	42	1271	74963	179117	137
Sr	173	480	<0.05	<0.05	<0.05	< 0.05	< 2	< 0.01	< 0.2	190	453	95
U	5415	15000	170	167	123	100	3975	13.7	416	2698	6446	72
Zn	473	1310	2.8	2.4	4.6	3.6	142	2.1	64	1014	2423	201
Zr	3161	8756	<10	<10	<10	< 10	< 397	< 1	< 30	3323	7941	96 > x > 90

1 M NaOH, 100°C

Wt. Washed Solids in Sample, g: 2.79

Wt. Leached Solids, g: 2.46

Vol. Leach Soln., mL: 41.8

Vol. Final Wash Soln., mL: 28

Al	82615	230496	2000	2200	2000	2300	96140	308	8624	50798	125167	100
Ba	140	391	<0.6	<0.6	0.7	0.9	37	0.1	2.5	189	466	129
Bi	277	772	<0.2	<0.2	<0.2	< 0.2	< 8	< 0.02	< 0.6	311	766	99
Ca	2658	7416	<1	<1	<1	< 1	< 42	< 0.1	< 3	2830	6974	94
Cr	6461	18025	92	128	157	156	6533	20	561	4474	11023	101
Fe	229885	641379	<10	<10	<10	< 10	< 418	< 1	< 28	275762	679478	106
Mg	2299	6414	<10	<10	<10	< 10	< 418	< 1	< 28	2322	5722	96 > x >89
Mn	43103	120259	<1	<1	<1	< 1	< 42	< 0.1	< 3	50798	125167	104
Na	57471	160345	22000	24000	24000	24000	1003200	3630	101640	83454	205631	N/A
P	7902	22047	280	340	340	320	13376	42	1170	4717	11623	119
Si	50287	140302	<100	<100	<100	< 100	< 4180	18	493	79826	196691	140
Sr	173	483	<0.05	<0.05	<0.05	< 0.05	< 2	< 0.01	< 0.1	247	609	127
U	5415	15109	166	126	71	66	2751	7.1	198	4396	10832	91
Zn	473	1319	<1	<1	<1	< 1	< 42	< 0.1	< 3	539	1329	101
Zr	3161	8819	<10	<10	<10	< 10	< 418	< 1	< 28	3991	9835	112

	Washed Solids		5 h	24 h	72 h	168 h		Final Wash Solution		Leached Solids		Mass Recovery,
Component	µg/g	µg[(a)]	µg/mL	µg/mL	µg/mL	µg/mL	µg[(b)]	µg/mL	µg[(c)]	µg/g	µg[(d)]	%
						3 M NaOH, 100°C						
	Wt. Washed Solids in Sample, g:		2.61					Vol. Leach Soln., mL:		40.5		
	Wt. Leached Solids, g:		2.2					Vol. Final Wash Soln., mL:		33		
Al	82615	215625	2400	2600	2500	2600	105300	374	12342	54018	118630	110
Ba	140	365	0.8	1.1	1.0	1.6	66	0.1	4	178	390	126
Bi	277	722	<0.2	<0.2	<0.2	< 0.2	< 8	< 0.02	< 0.7	289	635	88
Ca	2658	6938	10	10	10	19	770	< 0.1	< 3	3030	6655	107
Cr	6461	16862	98	135	153	176	7122	23	748	3853	8461	97
Fe	229885	600000	14	16	15	16	648	5	174	264163	580129	97
Mg	2299	6000	<10	<10	<10	< 10	< 405	< 1	< 33	2668	5859	105>x>97
Mn	43103	112500	<1	<1	<1	< 1	< 41	1	36	47431	104163	93
Na	57471	150000	74000	77000	79000	80000	3240000	12100	399300	108366	237983	N/A
P	7902	20625	430	460	510	540	21870	72	2360	2108	4629	140
Si	50287	131250	230	180	200	160	6480	35	1162	68511	150457	120
Sr	173	452	<0.05	<0.05	<0.05	< 0.05	< 2	< 0.01	< 0.2	205	450	100
U	5415	14134	157	132	84	55	2218	6.3	209	3360	7378	69
Zn	473	1234	3	3	3	11	431	0.1	3	1152	2530	240
Zr	3161	8250	<10	<10	<10	< 10	< 405	< 1	< 33	3129	6872	89 > x >83

(a) Mass of each component in the aliquot treated under the indicated conditions. This was determined from analysis of the washed solids (aliquot B101-A0).

(b) Mass of each component in the caustic leaching solution.

(c) Mass of each component in the final washing solution.

(d) Mass of each component in the leached solids.

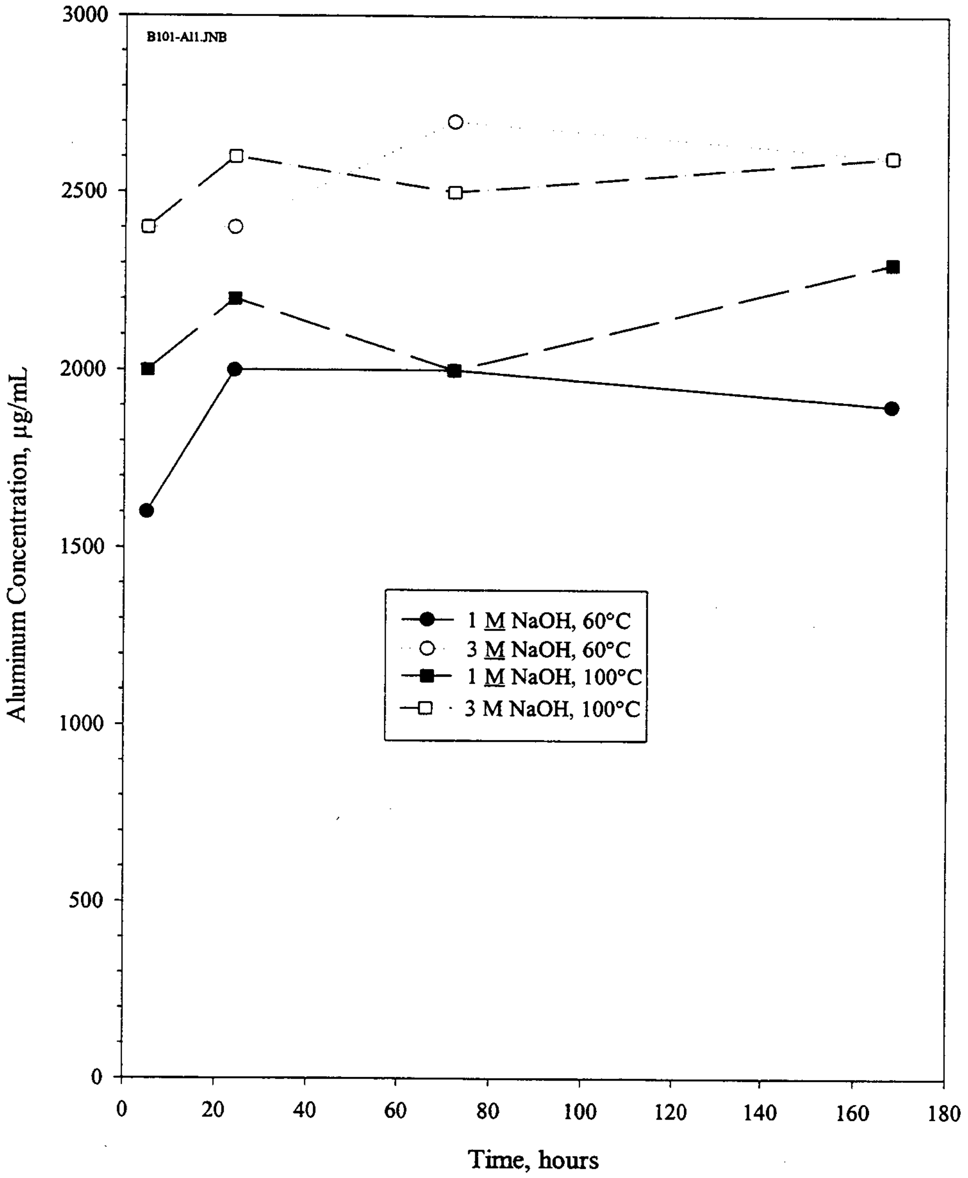

Figure 2.1. Aluminum Concentration as a Function of Time During the Caustic Leaching of Tank B-101 Sludge

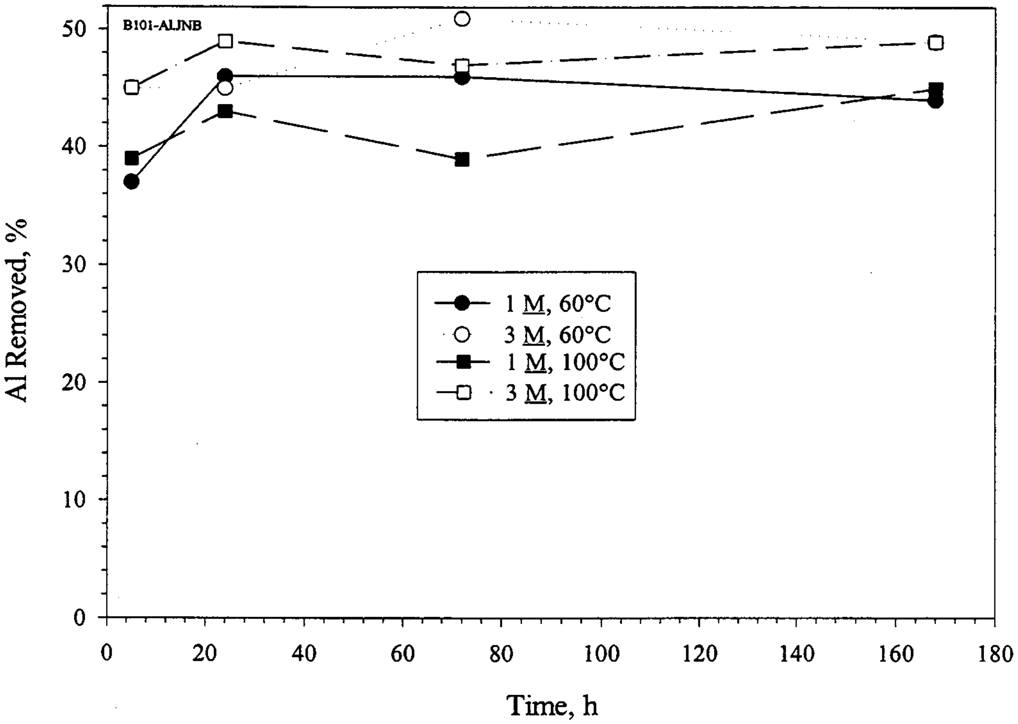

Figure 2.2. Aluminum Removal From the Dilute Hydroxide-Washed B-101 Sludge Solids as a Function of Time

In all cases examined for the B-101 sample, the amount of Na in the caustic-leached solids was greater than that in the washed-solids treated. This fact is reflected in the negative percent removed values for Na in Table 2.6. The residual Na is greater for the aliquots leached with 3 M NaOH leaching experiments than for those leached with 1 M NaOH, suggesting that the relatively large Na residuals were due to incomplete removal of NaOH during the final washing steps.

Phosphorus removal at 3 M NaOH was better than at 1 M NaOH, but increasing the temperature from 60 to 100°C did not result in significant improvements. Treatment with 1 M NaOH removed ~60% of the P from the dilute hydroxide-washed B-101 solids while treatment with 3 M NaOH removed ~80% of the P. Thus, when coupled with the 67% removed by dilute hydroxide washing (Table 2.4), greater than 90% of the P was removed from the B-101 sludge sample by leaching with 3 M NaOH at 100°C. The solution data (Table 2.7) indicate that phosphate metathesis increased slightly with time.

Table 2.8 summarizes the removal of some important radionuclides from the washed B-101 solids under the various leaching conditions. Table 2.9 presents the actual concentrations of the various radioactive components in the leaching and washing solutions and in the leached solids. The mass recovery for each component is presented in Table 2.9 as well. As was the case with the dilute hydroxide wash, little TRU, Sr, or Co dissolution occurred during the caustic leaching steps. The cumulative ^{137}Cs removal achieved by dilute hydroxide washing and caustic leaching of the B-101 sample was approximately 60 to 70%. Technetium-99 was not detected in the initial wash solution, the washed solids, the caustic leach solutions, or the caustic-leached solid.

Estimating the radionuclide content of LLW glass (20 wt% Na_2O; 2.7 MT/m^3) produced from the combined wash and leach solutions indicates that the TRU content would be < 40 nCi/g. The ^{90}Sr content would be 0.5 to 0.8 Ci/m^3 and the ^{137}Cs content would be 375 to 540 Ci/m^3. These are all within the Class C LLW limits, but exceed the Class A limits.

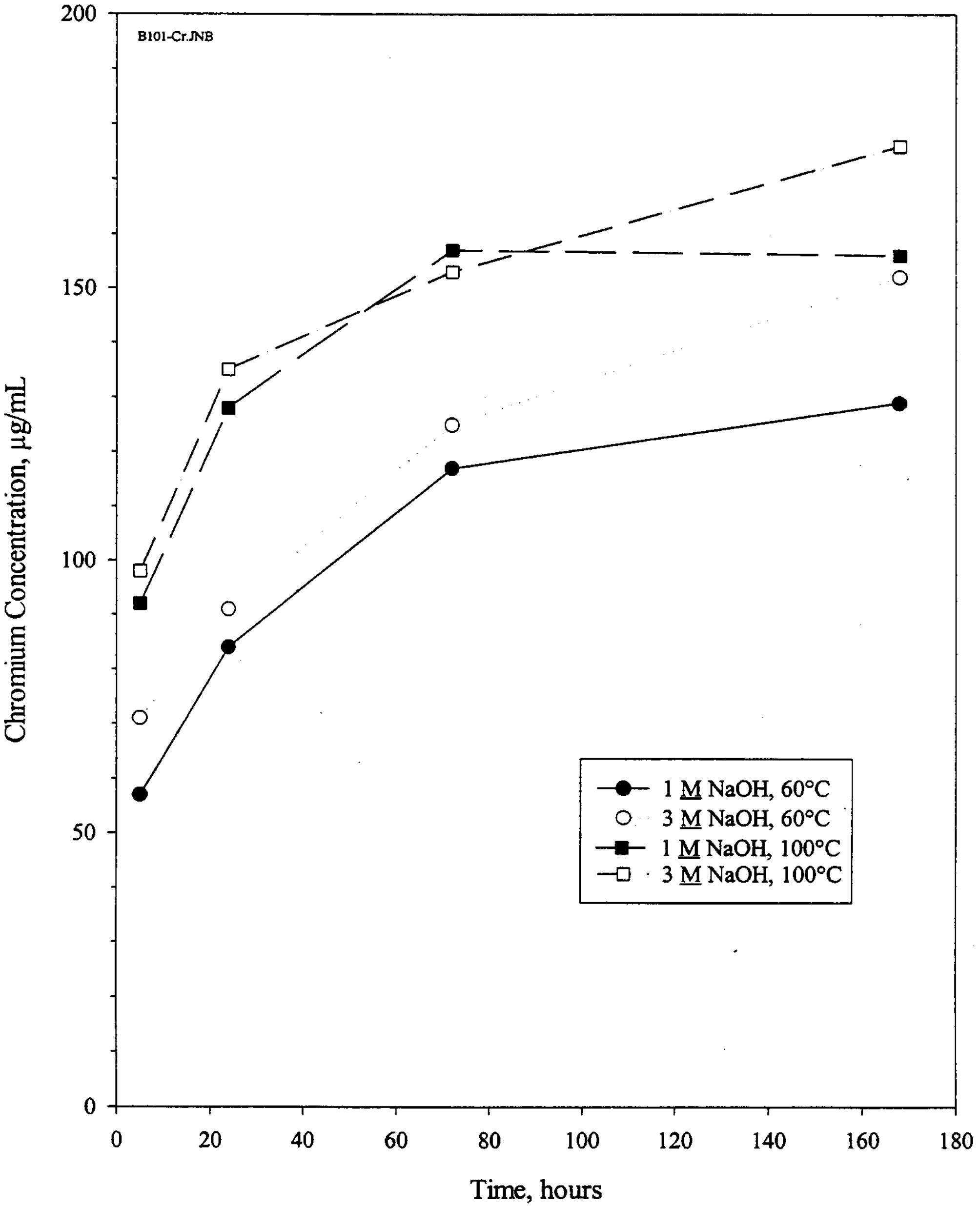

Figure 2.3. Chromium Concentration as a Function of Time During the Caustic Leaching of Tank B-101 Sludge

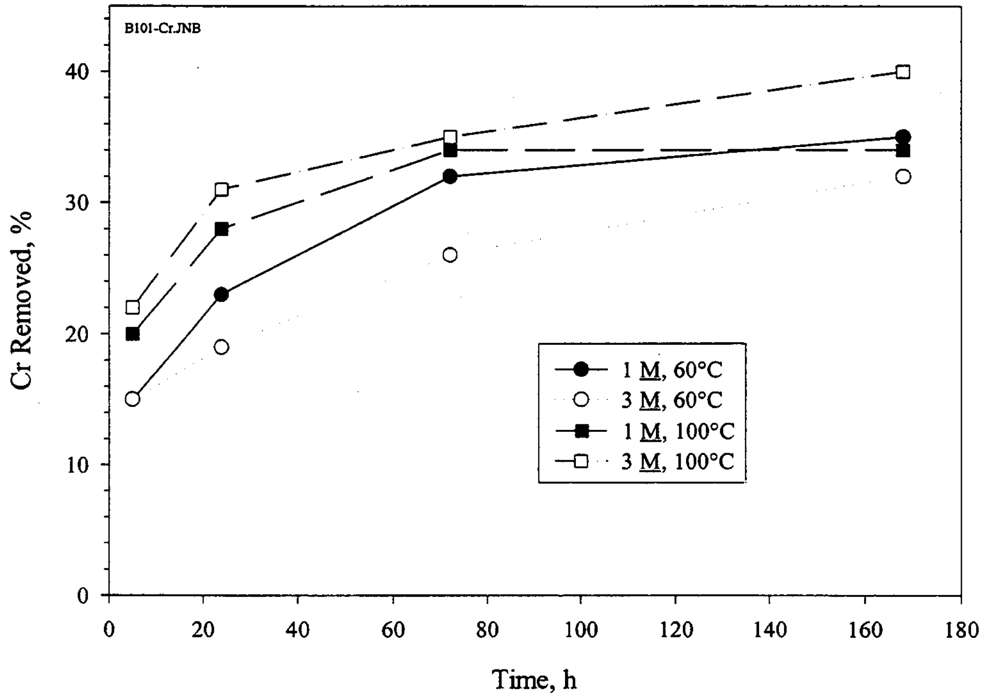

Figure 2.4. Chromium Removal From the Dilute Hydroxide-Washed B-101 Sludge Solids as a Function of Time

Table 2.8. Caustic Leaching Results for Key Radioactive B-101 Sludge Components

Component	Removed, %[(a)] 1 M NaOH	3 M NaOH
	Temperature = 60°C	
Total Alpha	<1 (<1)	<1 (<1)
^{90}Sr	<1 (<1)	<1 (<1)
^{137}Cs	27 (63)	28 (62)
	Temperature = 100°C	
Total Alpha	<1 (<1)	<1 (<1)
^{90}Sr	<1 (<1)	<1 (<1)
^{137}Cs	27 (61)	48 (72)

(a) Amount of material removed from the dilute hydroxide-washed solids; the values were obtained by the summation method (see Table 2.6, footnote a). The values in parentheses are the cumulative removals achieved by dilute hydroxide washing and caustic leaching.

Table 2.9. Concentrations of Key Radioactive B-101 Sludge Components in Caustic Leaching Solutions and in the Caustic Leached Solids

Component	Washed Solids		Leach Solution		Final Wash Solution		Leached Solids		Mass Recovery, %
	µCi/g	µCi	µCi/mL	µCi	µCi/mL	µCi	µCi/g	µCi	
				1 M NaOH, 60°C					
	Wt. Washed Solids in Sample, g:		2.76			Vol. Leach Soln., mL:		43	
	Wt. Leached Solids, g:		2.34			Vol. Final Wash Soln., mL:		30.3	
Total Alpha	1.82E+01	5.02E+01	<6.46E-04	<2.78E-02	<5.39E-04	<1.63E-02	1.94E+01	4.54E+01	90
Pu Alpha	1.12E+01	3.09E+01	<1.85E-04	<7.97E-03	<9.00E-05	<2.73E-03	1.27E+01	2.96E+01	95
^{241}Am (gamma)	6.99E+00	1.93E+01	<4.61E-04	<1.98E-02	<4.49E-04	<1.36E-02	6.75E+00	1.58E+01	82
^{137}Cs	4.52E+02	1.25E+03	6.61E+00	2.84E+02	8.41E-01	2.55E+01	3.54E+02	8.28E+02	91
^{60}Co	7.46E-01	2.06E+00	<5.02E-03	<2.16E-01	<4.88E-03	<1.48E-01	8.77E-01	2.05E+00	100<x<117
^{90}Sr	7.37E+03	2.04E+04	3.63E-02	1.56E+00	<1.16E-03	<3.50E-02	6.59E+03	1.54E+04	75
^{99}Tc	<5.71E-01	<1.58E+00	<4.51E-04	<1.94E-02	<4.39E-04	<1.33E-02	<5.78E-01	<1.35E+00	
				3 M NaOH, 60°C					
	Wt. Washed Solids in Sample, g:		2.77			Vol. Leach Soln., mL:		39.7	
	Wt. Leached Solids, g:		2.39			Vol. Final Wash Soln., mL:		30.4	
Total Alpha	1.82E+01	5.04E+01	<7.21E-04	<2.86E-02	<5.39E-04	<1.64E-02	1.96E+01	4.69E+01	93
Pu Alpha	1.12E+01	3.11E+01	<2.07E-04	<8.20E-03	<9.00E-05	<2.74E-03	1.12E+01	2.68E+01	86
^{241}Am (gamma)	6.99E+00	1.94E+01	<5.14E-04	<2.04E-02	<4.49E-04	<1.36E-02	8.40E+00	2.01E+01	104
^{137}Cs	4.52E+02	1.25E+03	7.47E+00	2.96E+02	1.22E+00	3.72E+01	3.68E+02	8.79E+02	97
^{60}Co	7.46E-01	2.07E+00	<5.59E-03	<2.22E-01	<4.88E-03	<1.48E-01	8.85E-01	2.12E+00	102<x<120
^{90}Sr	7.37E+03	2.04E+04	1.33E-01	5.29E+00	<1.16E-03	<3.51E-02	6.79E+03	1.62E+04	79
^{99}Tc	<5.71E-01	<1.58E+00	<5.03E-04	<2.00E-02	<4.39E-04	<1.33E-02	<5.87E-01	<1.40E+00	
				1 M NaOH, 100°C					
	Wt. Washed Solids in Sample, g:		2.79			Vol. Leach Soln., mL:		41.8	
	Wt. Leached Solids, g:		2.46			Vol. Final Wash Soln., mL:		28	
Total Alpha	1.82E+01	5.08E+01	<6.46E-04	<2.70E-02	<5.39E-04	<1.51E-02	2.05E+01	5.05E+01	100
Pu Alpha	1.12E+01	3.13E+01	<1.85E-04	<7.75E-03	<9.00E-05	<2.52E-03	1.13E+01	2.78E+01	89
^{241}Am (gamma)	6.99E+00	1.95E+01	<4.61E-04	<1.93E-02	<4.49E-04	<1.26E-02	9.23E+00	2.27E+01	118
^{137}Cs	4.52E+02	1.26E+03	7.66E+00	3.20E+02	9.26E-01	2.59E+01	3.71E+02	9.15E+02	101
^{60}Co	7.46E-01	2.08E+00	<5.02E-03	<2.10E-01	<4.88E-03	<1.37E-01	7.53E-01	1.86E+00	89<x<106
^{90}Sr	7.37E+03	2.06E+04	1.92E-02	8.02E-01	<1.16E-03	<3.23E-02	7.49E+03	1.85E+04	90
^{99}Tc	<5.71E-01	<1.59E+00	<4.51E-04	<1.88E-02	<4.39E-04	<1.23E-02	<5.77E-01	<1.42E+00	

	Washed Solids		Leach Solution		Final Wash Solution		Leached Solids		Mass
Component	µCi/g	µCi	µCi/mL	µCi	µCi/mL	µCi	µCi/g	µCi	Recovery, %
				3 M NaOH, 100°C					
	Wt. Washed Solids in Sample, g:		2.61			Vol. Leach Soln., mL:		40.5	
	Wt. Leached Solids, g:		2.2			Vol. Final Wash Soln., mL:		33	
Total Alpha	1.82E+01	4.75E+01	<7.21E-04	<2.92E-02	<5.39E-04	< 1.78E-02	1.69E+01	3.70E+01	78
Pu Alpha	1.12E+01	2.93E+01	<2.07E-04	<8.37E-03	<9.00E-05	2.97E-03	1.13E+01	2.49E+01	85
^{241}Am (gamma)	6.99E+00	1.82E+01	<5.14E-04	<2.08E-02	<4.49E-04	< 1.48E-02	5.52E+00	1.21E+01	67
^{137}Cs	4.52E+02	1.18E+03	1.17E+01	4.75E+02	1.42E+00	4.70E+01	2.61E+02	5.74E+02	93
^{60}Co	7.46E-01	1.95E+00	<5.59E-03	<2.27E-01	<4.88E-03	<1.61E-01	8.28E-01	1.82E+00	93<x<114
^{90}Sr	7.37E+03	1.92E+04	8.25E-02	3.34E+00	<1.16E-03	<3.81E-02	5.67E+03	1.25E+04	65
^{99}Tc	<5.71E-01	<1.49E+00	<5.03E-04	<2.04E-02	<4.39E-04	<1.45E-02	<5.24E-01	<1.15E+00	

Table 2.10 shows the concentration of waste oxides in the dilute hydroxide-washed and in the leached[(a)] B-101 solids, and the concentrations of waste-derived components that would result from vitrifying these solids at 25 wt% waste oxide loading (WOL), excluding oxides of Na and Si. The oxide concentrations in the washed and leached solids were determined by converting the elemental concentrations listed in Tables 2.4 (washed solids) and 2.7 (leached solids) to the corresponding oxide concentrations. The oxide concentrations in the IHLW were determined according to the following formula:

$$[C_x]_{IHLW} = WOL \bullet \left(\frac{C_x}{\sum_i C_i} \right) \tag{2.1}$$

where $[C_x]_{IHLW}$ is the concentration of component x oxide (wt%) in the IHLW, C_x is the concentration of component x oxide in the washed or leached solids, and ΣC_i is the sum of the concentration of all the component oxides in the washed or leached solids (excluding Na_2O and SiO_2).

Assuming upper limits of 15, 0.5, and 3.0 wt% for Al, Cr, and P oxides, respectively, in the IHLW, a 25 wt% WOL could be achieved with the B-101 solids after either simple washing or caustic leaching. The mass (W_{IHLW}) of IHLW glass produced at 25 wt% WOL from 1 g of the washed solids can be calculated as follows.

$$W_{IHLW} = 100 \bullet \frac{\sum_i C_i}{WOL} \tag{2.2}$$

Likewise, the mass of IHLW glass produced at 25 wt% WOL from the leached solids derived from 1 g of washed solids can be determined as follows:

$$W_{IHLW} = 100 \bullet \frac{W_L}{W_W} \bullet \frac{\sum_i C_i}{WOL} \tag{2.3}$$

where W_L is the weight of the leached solids obtained by leaching W_W grams of washed solids. In the case considered here, $W_L = 2.20$ g and $W_W = 2.61$ g (see Table 2.7). At 25 wt% WOL, the quantity of IHLW after simple washing would be 2.40 g IHLW/g dry washed solids. Upon caustic leaching, this quantity would decrease to 1.97. Thus, caustic leaching would result in an ~20% decrease in the IHLW glass volume for the B-101 waste compared to dilute hydroxide washing.

(a) For this analysis, we considered only the case where the solids were leached with 3 M NaOH for 168 h at 100°C.

Table 2.10. Estimated Concentrations of Waste-Derived Components in the IHLW Glass From B-101 Waste

	Washed Solids		Leached Solids (3 M NaOH/100°C/168 h)	
Component	g oxide/g solids	Conc. in IHLW, wt%(a)	g oxide/g solids	Conc. in IHLW, wt%(a)
Al_2O_3	0.1561	6.5	0.1021	4.4
BaO	0.0002	0.01	0.0002	0.0
Bi_2O_3	0.0003	0.01	0.0003	0.0
CaO	0.0037	0.2	0.0042	0.2
Cr_2O_3	0.0094	0.4	0.0056	0.2
Fe_2O_3	0.3287	13.7	0.3778	16.2
MgO	0.0038	0.2	0.0044	0.2
MnO_2	0.0682	2.8	0.0751	3.2
Na_2O	0.0775	3.2	0.1451	6.2
P_2O_5	0.0181	0.8	0.0048	0.2
SiO_2	0.1076	4.5	0.1466	6.3
SrO	0.0002	0.01	0.0002	0.0
UO_3	0.0065	0.3	0.0040	0.2
ZnO	0.0006	0.02	0.0014	0.1
ZrO_2	0.0043	0.2	0.0042	0.2

(a) Based on 25 wt% waste oxide loading (excluding Na_2O and SiO_2).

3.0 Tank BX-110 Test

3.1 BX-110 Experimental

The BX-110 sludge sample used was a composite mixture of three segments from Core #198. The composite sample was prepared at the Hanford 222-S laboratory and shipped to PNNL in January 1998.

Initial Wash: A 75.86-g portion of the BX-110 composite sample was placed in a 200-mL plastic centrifuge bottle labeled as "BX110-Wash." Sodium hydroxide solution (0.1 M) was added to give a total volume of 200 mL. The mixture was stirred overnight, then centrifuged for 15 minutes at 1,200 G. The centrifuged liquid was decanted to a 1-L plastic bottle labeled as "BX110-Wash-Solution." The BX110-Wash was again filled to the 200-mL mark with fresh 0.1 M NaOH. The mixture was stirred for 30 minutes, then centrifuged for 15 minutes at 1,200 G. Again, the centrifuged liquid was decanted to the BX110-Wash-Solution. This washing procedure was repeated for a total of four wash cycles. The wash solutions were yellow, but became progressively less so, and the final wash solution was colorless. Unlike the BX-112 sludge (see Section 4.1), the final wash solution was clear after the 15-minute centrifuge period. The volume of the combined wash solution was 717 mL.

Division of the Washed Solids: The washed BX-110 sludge was diluted to a volume of 75 mL with deionized water and stirred to homogenize. Aliquots (~5 g) were distributed between six 60-mL high-density polyethylene (HDPE) bottles (labeled as BX110-1, -2, -3, -4, -5, and -6, respectively). In addition, an approximately 10-g aliquot was placed into a 20-mL glass vial (BX110-8) for analysis. A 0.53-g aliquot was taken from BX110-8 and placed into another glass vial (BX110-8A) for microscopic analysis. Sample BX110-8 was dried at 105°C yielding 1.185 g of dried solids; this corresponded to 12.4 wt% washed solids in the homogenized slurry. Based on this value, the amount of washed solids in each of the other bottles was determined (Table 3.1).

Leaching: Table 3.2 summarizes the leaching conditions for each aliquot of the washed BX-110 solids. The amount of NaOH needed for each reaction vessel was determined by assuming that 1) each mole of Al consumes one mole of hydroxide, 2) each mole of Cr consumes one mole of hydroxide, and 3) each mole of phosphate consumes three moles of hydroxide. The estimated Al, Cr, and P concentrations in the as-received sludge were obtained from Schreiber and Tran (1996) (*Tank Characterization Report for Single-Shell Tank 241-BX-110*, WHC-SD-WM-ER-566, Westinghouse Hanford Company, Richland, Washington). These estimates were 25,500 µg Al/g, 794 µg Cr/g, and 24,700 µg P/g; these values are based on wet sludge solids. The appropriate amounts of 10 M NaOH and water were added to each reaction vessel to give the desired NaOH concentration and 10 mL of leachate per gram of as-received sludge. Based on the solubility of gibbsite at 60°C, it was estimated that this volume of leaching solution was sufficient to avoid Al saturation if all the Al dissolved.

Table 3.1. Weight of BX-110 Waste in Each Vial

Bottle #	Wt. BX-110 Sample, g[(a)]	Wt. Washed Solids, g[(b)]
BX110-1	4.79	0.594
BX110-2	4.62	0.573
BX110-3	4.88	0.605
BX110-4	4.87	0.604
BX110-5	4.88	0.605
BX110-6	4.89	0.606
BX110-8	9.51	1.185
BX110-8A	0.53	0.066

(a) Weight of as-received (wet) sludge.
(b) Weight of washed sludge solids on a dry-weight basis.

Table 3.2. Leaching Conditions for Each Aliquot of BX-110 Solids

Bottle #	[NaOH], M[(a,b)]	T, °C
BX110-1	1.2	60
BX110-2	3.2	60
BX110-3	1.2	80
BX110-4	3.1	80
BX110-5	1.2	95[(c)]
BX110-6	3.2	95[(c)]

(a) Concentrations determined by titration with standard HCl after leaching for 168 h.
(b) 10 mL per gram of untreated sample.
(c) The test plan originally indicated samples BX110-5 and -6 would be leached at 100°C, but for the particular heating apparatus used, the over-temperature shut-off device was triggered when the reaction mixture was heated to 100°C. The thermocouple for the over-temperature device was placed between the reaction vessel and the Al heating block. When the temperature in the reaction vessel approached 100°C, the temperature just outside the vessel exceeded 105°C. So to prevent damage to the reaction vessel, the reaction temperature was lowered to 95°C.

The liquid level was marked on each reaction vessel, and each vessel was closed with a cap equipped with a tube-condenser. The vessels were placed in an Al heating block at the appropriate temperature and the contents were stirred with a magnetic stirrer. Evaporation was minimal over several hours; occasionally, deionized water was added to bring the liquid level up to its original position. The leachates were sampled at intervals of 5, 24, 72, and 168 h. For each sampling, the stirrer was stopped, and the solids settled at temperature. The upper portion of the solution was typically clear enough to sample within 30 min. The transfer pipette and the syringe filter assembly (0.2-µm nylon membrane) were preheated by inserting in a boiling water bath. These were then used to filter ~2 mL of the leachate solution. A 1-mL aliquot of the filtered solution was immediately acidified with 15 mL of 0.3 M HNO_3. The remaining filtered solution was added back to the reaction vessel, and the leaching was continued. After the final sampling, two aliquots of the filtered leachate were taken and titrated with standard HCl to determine the free hydroxide concentration.

At the end of the leaching procedure, the reaction vessels were transferred directly from the heating block to a centrifuge and centrifuged for 5 min. The vessel was then placed back in the heating block to minimize cooling while the solution was transferred to a clean bottle. In all cases, a small amount of floating white solids was present.[a] A pipette was used to draw off the solution between the centrifuged solids and the floating solids. The leached solids were washed three successive times with 15-mL portions of 0.1 M NaOH, then were dried at 105°C. For each wash step, the wash mixture was stirred for a minimum of 30 minutes, centrifuged, and then the wash liquid was decanted. Table 3.3 gives the weights of the leached solids and the weight reductions achieved after 168 h of leaching.

Spectrophotometric Determination of Chromate: Aliquots of the filtered leachate and wash solutions were appropriately diluted with 0.1 M NaOH. The ultraviolet/visible (UV/vis) spectra of the resulting solutions were recorded using a Spectral 400 Series CCD Array UV-Vis Spectrophotometer (Spectral Instruments, Tucson, Arizona) equipped with a 1-cm pathlength fiber optic probe. The absorbance at 372 nm was compared to a calibration line generated by measuring the absorbance for a series of chromate standard solutions.

Table 3.3. Weight of the Leached BX-110 Solids

Bottle #	Wt. Leached Solids, g	Wt. Reduction, %[a]
BX110-1	0.094	84
BX110-2	0.058	90
BX110-3	0.084	86
BX110-4	0.062	90
BX110-5	0.079	87
BX110-6	0.051	92

(a) Weight reduction with respect to the dry weight of washed solids treated, which was achieved after 168 h of leaching.

3.2 BX-110 Results

The next two sections describe dilute hydroxide washing and caustic leaching of BX-110 sludge.

3.2.1 Dilute Hydroxide Washing of BX-110 Sludge

Table 3.4 presents the concentrations of some important nonradioactive BX-110 sludge components in the dilute-hydroxide wash solution and in the washed solids. The table also lists the total mass of each component in each processing stream (wash solution or washed solids) and the amount of each component removed by the dilute hydroxide washing in terms of percent. The data indicated that 4% of the Al, 23% of the Cr, 97% of the P, and 29% of the Si were removed by washing the as-received BX-110 sludge sample with dilute NaOH. Ninety-nine percent of the Na was removed by dilute hydroxide washing with the washed solids containing only 1.3 wt% Na. No other nonradioactive components were significantly removed by the dilute hydroxide wash.

Table 3.4 also presents the concentration of the nonradioactive components in the as-received BX-110 sludge sample. These values were determined by summing the amount of each component in the combined wash solution and the washed solids and dividing by the total amount of sample treated (75.86 g). The relative concentrations of the various components differ considerably from the estimates given by Schreiber and Tran (1996). In particular, relatively less Fe appeared to be in the sample

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(a) It is now believed that these floating solids are due to leaching of plasticizers from the HDPE bottles. Similar solids were observed when water was heated in such bottles under similar conditions.

examined than would be expected from the historical tank estimate. The relative concentrations given by Schreiber and Tran for Al, Bi, Cr, P, and Si were 1.6, 0.7, 0.05, 1.6, and 0.1 grams per gram of Fe, respectively. The corresponding values determined in this test were 13.0, 2.2, 0.5, 7.6, and 1.0.

Table 3.4. Results of Dilute Hydroxide Washing of BX-110 Sludge Sample: Nonradioactive Components(a)

Component	Wash Solution		Washed Solids		Amount Removed, %	Conc. in As-Received Sample, µg/g[b]
	µg/mL	µg	µg/g	µg		
Al	134	96078	247500	2472773	4	33863
Bi	(3)	(1793)	42650	426116	0	5641
Cr	31.4	22514	7665	76581	23	1306
Fe	< 0.13	< 90	19750	197322	0	2602
Mg	< 0.50	< 359	(865)	(8642)	< 4	(119)
Na[c]	21900	15702300	13375	133630	99	--
P	2020	1448340	4505	45009	97	19686
Pb	< 0.50	< 359	(770)	(7693)	< 4	(106)
Si	82.5	59153	14850	148366	29	2736
Sr	< 0.08	< 54	(150)	(1499)	< 3	(20)
Zn	< 0.25	< 179	(305)	(3047)	< 6	(43)

(a) Values in parentheses near detection limit.

(b) Concentration on a wet-weight basis. This was determined by summing the quantities in the wash solution and the washed solids and dividing by the total amount of sample treated (75.86 g).

(c) The percent removal value for Na includes Na added as NaOH in the washing process.

Table 3.5 presents the concentrations of some important radioactive BX-110 sludge components in the washed solids and in the dilute hydroxide wash solution. The table also lists the total activity of each component present in each processing stream and the amount of each component removed by the dilute hydroxide washing (as determined by the summation method). The TRU behavior is reflected in the total alpha activity data. Information regarding ^{241}Am is usually also obtained from the gamma spectroscopic analyses, but for this set of samples, ^{241}Am was below the detection limit (as indicated in Table 3.5). As expected, only a small amount of TRUs was removed during the dilute hydroxide washing process. However, a measurable quantity of ^{90}Sr was removed during the dilute hydroxide washing, with 6% of the ^{90}Sr being found in the washing solution. Most (80%) of the ^{137}Cs was removed from the BX-110 sludge sample during the dilute hydroxide wash. Likewise, ^{99}Tc was largely removed, which would be consistent with the presence of this element as a soluble species such as pertechnetate.

If the dilute hydroxide wash solution were converted directly to a glass LLW form,[a] the primary radionuclide content of that waste form would be 0.20 nCi TRU/g, 0.12 Ci ^{90}Sr/m^3, 46 Ci ^{137}Cs/m^3, and 0.04 Ci ^{99}Tc/m^3. This waste form would meet the NRC Class A limit for TRU (< 10 nCi/g) and ^{99}Tc (< 0.3 Ci/m^3), but would exceed the Class A limits for ^{90}Sr and ^{137}Cs (0.04 Ci/m^3 and 1 Ci/m^3, respectively). However, the ^{90}Sr and ^{137}Cs levels would be within the Class C LLW limits of 7,000 Ci/m^3 and 4,600 Ci/m^3, respectively.

(a) For this determination, it was assumed that the LLW glass form will contain 20 wt% Na$_2$O, and the density of the glass would be 2.7 MT/m^3.

Table 3.5. Results of Dilute Hydroxide Washing of BX-110 Sludge Sample: Radioactive Components

	Wash Solution		Washed Solids		Amount	Conc. in As-Received
Component	µCi/mL	µCi	µCi/g	µCi	Removed, %	Sample, µCi/g(a)
Total Alpha	< 3.00E-05	< 2.15E-02	2.13E-01	2.13E+00	< 1	2.83E-02
^{90}Sr	6.51E-03	4.67E+00	7.15E+00	7.14E+01	6	1.00E+00
^{60}Co	< 4.00E-05	< 2.87E-02	1.10E-02	1.10E-01	< 21	1.83E-03
^{137}Cs	2.51E+00	1.80E+03	4.39E+01	4.39E+02	80	2.95E+01
^{241}Am	< 3.00E-03	< 2.15E+00	< 5.00E-02	< 5.00E-01	--	< 3.49E-02
^{154}Eu	< 2.00E-04	< 1.43E-01	< 2.00E-02	< 2.00E-01	--	< 4.52E-03
^{99}Tc	1.97E-03	1.41E+00	2.29E-02	2.29E-01	86	2.16E-02

(a) Concentration on a wet-weight basis. This was determined by summing the quantities in the wash solution and the washed solids and dividing by the total amount of sample treated (75.86 g).

3.2.2 Caustic Leaching of BX-110 Sludge

Table 3.6 summarizes the amounts of Al, Cr, Na, P, and Si removed from the washed BX-110 solids under the various leaching conditions. Again, values obtained by both the summation and Fe normalization methods are presented. Agreement between these two methods is generally good. Table 3.7 presents the actual concentrations of the various components in the leaching and washing solutions and in the leached solids. The mass recovery for each component is presented in Table 3.7 as well.

Caustic leaching effectively removed Al from the dilute hydroxide-washed solids; in every case, ≥ 95% of the Al was removed after leaching for 168 h. Figure 3.1 shows the Al concentrations as a function of time, and Figure 3.2 shows the percent of the Al removed as a function of time. As expected, the Al concentration generally increased with time. This is especially evident for samples leached with 1 M NaOH. When leached with 3 M NaOH, Al dissolution was rapid with the Al concentrations reaching >90% of their final values within the first 5 h of leaching. These results indicate that, provided sufficient time is allowed, leaching the BX-110 sludge with 1 M NaOH at 60°C is as effective at removing Al as leaching with 3 M NaOH at 95°C.

Table 3.6 indicates that Cr removal increases with increasing NaOH concentration, although such increases are less noticeable at the higher temperatures. Likewise, increasing the temperature increases Cr removal from the BX-110 sludge. Table 3.7 and Figures 3.3 and 3.4 indicate that Cr removal is highly time dependent. From the figures, it is clear that Cr removal for 3 M NaOH at 60°C is very similar to that achieved at 1 M NaOH at 80°C. Likewise, the Cr removal is similar for 3 M NaOH at 80°C and 1 M at 95°C.

As has been seen with leaching tests for other Hanford sludges, the dissolved Cr is essentially all in the +6 oxidation state. Table 3.8 compares the chromate concentrations, (determine by UV/Vis spectrophotometry) with the total Cr concentrations (determined by inductively coupled plasma/atomic emission spectroscopy [ICP/AES]). The Cr(VI) concentrations are generally the same as the total Cr concentrations, within experimental error. There are two exceptions. First, the measured Cr(VI) concentration in the initial wash solution is significantly higher than the total Cr concentration determined by ICP/AES. This was likely due to interference from nitrite ion in the spectrophotometric measurement. Second, the Cr(VI) concentration is 23% less than the total Cr concentration in the leach solution obtained at 1 M NaOH at 60°C. This might indicate that some Cr(III) was present in that solution. The presence of Cr(III) in solution at 60°C would be consistent with the increased stability of alkaline Cr(III) solutions at lower temperatures (Lumetta et al. 1997). Close inspection of the absorption spectrum of the 1 M NaOH/60°C leaching solution revealed two bands not seen previously in the other sludge leaching solutions. These bands are centered at 553 nm and 706 nm. The presence of two bands is consistent with Cr(III), but the absorption maxima are different than seen when $Cr(OH)_3$ is dissolved in 3 M NaOH solution (419 nm and 596 nm; Lumetta et al. 1997). The exact nature of this species is unknown. This species is present to some extent in all of the BX-110 caustic leaching solutions. The absorbance for this species is very weak and, based on the ICP/AES data, would represent a very small fraction of the Cr present in solution (if it is a Cr-containing species).

As might be expected for an inhomogeneous system such as tank sludge, the Cr dissolution kinetics is complex. Plots of [Cr] versus time (Figure 3.2), ln[Cr] versus time, and 1/[Cr] versus time were not linear, indicating the Cr dissolution was neither zero, first, or second order. Because of this, it was not possible to determine the rate constants for the Cr dissolution.

Table 3.6. Caustic Leaching Results for Key Nonradioactive BX-110 Sludge Components: Amounts Removed from the Dilute Hydroxide-Washed Solids After Leaching for 168 h

	1 M NaOH		3 M NaOH	
Component	Summation Method,%(a)	Fe Normalization Method, %(b)	Summation Method,%(a)	Fe Normalization Method, %(b)
	Temperature = 60°C			
Al	95 (95)	94	99 (99)	99
Cr	49 (61)	38	77 (82)	74
Na(c)	50 (>99)	43	76 (> 99)	72
P	95 (100)	96	97 (100)	96
Si	26 (47)	33	73 (81)	73
	Temperature = 80°C			
Al	98 (98)	97	97 (97)	96
Cr	74 (80)	72	88 (91)	82
Na(c)	61 (>99)	59	53 (> 99)	31
P	97 (100)	96	97 (100)	96
Si	43 (60)	44	59 (71)	25
	Temperature = 95°C			
Al	99 (99)	99	99 (99)	98
Cr	87 (90)	90	93 (95)	92
Na(c)	70 (>99)	72	78 (>99)	68
P	97 (100)	98	98 (100)	98
Si	47 (62)	80	72 (80)	67

(a) Value obtained by summing the quantity of each component found in the leaching and final washing solutions and dividing by the total found in the leaching and washing solutions plus the residual solids. The values in parentheses are the cumulative removals achieved by dilute hydroxide washing and caustic leaching.

(b) Value obtained by normalizing the concentrations of each component to the Fe concentration and comparing the normalized values in the caustic- leached solids to those for the dilute hydroxide-washed solids.

(c) Because of the amount of Na added as NaOH during the leaching procedure, it was impossible to determine how much Na was actually removed from the sludge solids. The values reported were determined by comparing the amount of Na in the solids before and after the caustic leaching treatment.

Table 3.7. Concentrations of Key BX-110 Sludge Components in Caustic Leaching Solutions and in the Caustic Leached Solids[a]

	Washed Solids		5 h	24 h	72 h	168 h		Final Wash Solution		Leached Solids		Mass Recovery
Component	µg/g	µg[a]	µg/mL	µg/mL	µg/mL	µg/mL	µg[b]	µg/mL	µg[c]	µg/g	µg[d]	%
						1 M NaOH 60°C						
	Wt. Washed Solids in Sample g:			0.594				Vol. Leach Soln. mL:			35.2	
	Wt. Leached Solids g:			0.094				Vol. Final Wash Soln. mL:			48.6	
Al	247500	147015	1892	2712	3325	3529	124236	529	25698	77000	7238	107
Bi	42650	25334	27	26	23	23	798	< 3	< 156	201000	18894	78
Cr	7665	4553	8	16	29	57	2012	7	344	25700	2416	105
Fe	19750	11732	(3.2)	(2.9)	(1.9)	(1.9)	(68.4)	< 0.8	< 39	108000	10152	87
Mg	(865)	(514)	< 1.6	< 3.2	< 3.2	< 3.2	< 113	< 3.2	< 156	2420	227	--
Na	13375	7945	31370	30666	32119	32056	1128378	6905	335563	42400	3986	N/A
P	4505	2676	49	48	47	49	1727	5	251	(1100)	(103)	78
Pb	(770)	457	(3.2)	< 0.2	< 0.2	< 0.2	< 7	< 3	< 156	3160	297	--
Si	14850	8821	103	(82.3)	(66.2)	(51.8)	(1823.6)	< 1	< 49	54000	5076	79
Sr	(150)	(89)	< 0.25	< 0.5	< 0.5	< 0.5	< 17	< 0.5	< 24	767	72	> 83
U	< 3846	< 2285	< 2	< 4	< 4	< 4	< 2253	< 4	< 3110	(11000)	(1034)	--
Zn	(305)	181	(1.5)	(1.9)	(2.1)	(2.1)	(74.1)	< 1.6	< 78	881	83	--
Zr	< 96	< 57	< 0.80	< 1.6	< 1.6	< 1.6	< 56.0	< 1.6	< 78	926	87	--
						3 M NaOH 60°C						
	Wt. Washed Solids in Sample g:			0.573				Vol. Leach Soln. mL:			37.8	
	Wt. Leached Solids g:			0.058				Vol. Final Wash Soln. mL:			43.5	
Al	247500	141818	3299	3458	3546	3529	133412	243	10557	24200	1404	103
Bi	42650	24438	105	95	87	78	2956	< 3.2	< 139	259000	15022	74
Cr	7665	4392	20	35	57	80	3042	(5.8)	(253)	16900	980	97
Fe	19750	11317	13	15	10	9	335	< 0.8	< 35	162000	9396	86

(a) Mass of each component in the aliquot treated under the indicated conditions. This was determined from analysis of the washed solids (aliquot BX110-8).

(b) Mass of each component in the caustic leaching solution.

(c) Mass of each component in the final washing solution.

(d) Mass of each component in the leached solids.

Component	Washed Solids µg/g	Washed Solids µg$^{(a)}$	5 h µg/mL	24 h µg/mL	72 h µg/mL	168 h µg/mL	168 h µg$^{(b)}$	Final Wash Solution µg/mL	Final Wash Solution µg$^{(c)}$	Leached Solids µg/g	Leached Solids µg$^{(d)}$	Mass Recovery %
Mg	(865)	(496)	< 1.6	< 3.2	< 3.2	< 3.2	< 121	< 3.2	< 139	3570	207	--
Na	13375	7664	77616	75467	80141	77874	2943633	7588	330096	31400	1821	N/A
P	4505	2581	49	53	48	50	1891	< 3.2	< 139	(920)	53	81
Pb	(770)	441	(5.50	(5.7)	(4.9)	(5.3)	(202)	< 3.2	< 139	2880	167	--
Si	14850	8509	153	(150.3)	(142.5)	(134.4)	(5079)	< 1	< 44	33000	1914	83
Sr	(150)	(86)	< 0.24	< 0.5	< 0.5	< 0.5	< 19	< 0.5	< 21	1210	70	128
U	< 3846	< 2204	< 32	< 64	< 64	< 64	< 2419	< 64	< 2784	(13000)	(754)	--
Zn	(305)	175	(2.1)	(2.6)	(2.6)	(2.8)	(104)	< 1.6	< 70	940	55	--
Zr	< 96	< 55	< 0.8	< 1.6	< 1.6	< 1.6	< 60	< 1.6	< 70	820	48	--

<u>1 M NaOH 80°C</u>

Wt. Washed Solids in Sample g: 0.605
Wt. Leached Solids g: 0.084
Vol. Leach Soln. mL: 40.5
Vol. Final Wash Soln. mL: 44

Al	247500	149738	2849	3189	3444	3481	140974	204	8981	43400	3646	103
Bi	42650	25803	< 2	< 2	< 2	< 2	< 65	< 2	< 70	239000	20076	78
Cr	7665	4637	16	36	59	79	3180	4.67	205	14500	1218	99
Fe	19750	11949	(3.6)	(3.4)	(2.6)	(2.6)	(105)	< 0.4	< 18	131000	11004	93
Mg	(865)	(523)	< 2	< 2	< 2	< 2	< 65	< 2	< 70	2910	244	--
Na	13375	8092	28333	28980	31532	31247	1265491	3694	162518	37150	3121	N/A
P	4505	2726	46	49	48	50	2039	(2.27)	(100)	(730)	(61)	81
Pb	(770)	466	(3.2)	(5.0)	(2.7)	(5.8)	236	< 2	< 70	2990	251	--
Si	14850	8984	(77.7)	(58.3)	(46.9)	(41.1)	(1665)	(42.12)	(1853)	55500	4662	91
Sr	(150)	(91)	< 0.25	< 0.25	< 0.25	< 0.25	< 10	< 0.25	< 11	948	80	111
U	< 3846	< 2327	< 32	< 32	< 32	< 32	< 1296	< 32	< 1408	(12000)	1008	--
Zn	(305)	185	(1.8)	(1.9)	(2.1)	(2.3)	(92)	< 0.8	< 35	936	79	--
Zr	< 96	< 58	< 0.8	< 0.8	< 0.8	< 0.8	< 32	< 0.8	< 35	1130	95	--

Component	Washed Solids		5 h	24 h	72 h	168 h		Final Wash Solution		Leached Solids		Mass Recovery %
	µg/g	µg(a)	µg/mL	µg/mL	µg/mL	µg/mL	µg(b)	µg/mL	µg(c)	µg/g	µg(d)	

3 M NaOH 80°C

Wt. Washed Solids in Sample g: 0.604
Wt. Leached Solids g: 0.062
Vol. Leach Soln. mL: 42
Vol. Final Wash Soln. mL: 44.9

Component	µg/g	µg(a)	µg/mL	µg/mL	µg/mL	µg/mL	µg(b)	µg/mL	µg(c)	µg/g	µg(d)	Mass Recovery %
Al	247500	149490	3254	3657	3283	3303	138716	202	9081	62700	3887	101
Bi	42650	25761	130	129	95	66	2761	(1.6)	(73)	226000	14012	65
Cr	7665	4630	31	68	82	88	3713	5	240	8460	525	97
Fe	19750	11929	14	13	11	8	345	< 0.4	< 18	130000	8060	71
Mg	(865)	(522)	< 2	< 2	< 2	< 2	< 67	< 2	< 72	2930	182	--
Na	13375	8079	72855	75237	72927	74474	3127908	6100	273884	60700	3763	N/A
P	4505	2721	51	51	46	48	2013	(2.3)	(102)	(1100)	(68)	80
Pb	(770)	465	(7.0)	(6.6)	(5.8)	(7.0)	(292)	< 2	< 72	2980	185	--
Si	14850	8969	139	144	123	119	4977	(32.4)	(1453)	72400	4489	122
Sr	(150)	(91)	< 0.25	< 0.25	< 0.25	< 0.25	< 11	< 0.25	< 11	936	58	88
U	< 3846	< 2323	(37.2)	< 32	< 32	< 32	< 1344	< 32	< 1437	(12000)	(744)	--
Zn	(305)	184	(2.3)	(2.9)	(2.7)	(2.9)	(122)	< 0.8	< 36	840	52	--
Zr	< 96	< 58	< 0.8	< 0.8	< 0.8	< 0.8	< 34	< 0.8	< 36	970	60	--

1 M NaOH 95°C

Wt. Washed Solids in Sample g: 0.605
Wt. Leached Solids g: 0.079
Vol. Leach Soln. mL: 35.4
Vol. Final Wash Soln. mL: 49.5

Component	µg/g	µg(a)	µg/mL	µg/mL	µg/mL	µg/mL	µg(b)	µg/mL	µg(c)	µg/g	µg(d)	Mass Recovery %
Al	247500	149738	3335	3394	3578	3321	117563	453	22401	14100	1114	94
Bi	42650	25803	< 2	< 2	< 2	< 2	< 57	< 2	< 79	240000	18960	74
Cr	7665	4637	27	56	83	87	3097	12	602	6790	536	91
Fe	19750	11949	4.65	(3.9)	(3.4)	(2.9)	(103)	< 0.4	< 20	163000	12877	109
Mg	(865)	(523)	< 2	< 2	< 2	< 2	< 57	< 2	< 79	3040	240	--
Na	13375	8092	30923	31350	33513	30456	1078142	5953	294661	30650	2421	N/A
P	4505	2726	49	49	51	47	1669	(5.4)	(265)	(690)	(55)	73
Pb	(770)	466	(4.2)	(4.8)	(4.4)	(4.1)	(143)	< 2	< 79	2170	171	--
Si	14850	8984	(74.5)	(53.3)	(45.3)	(37.3)	(1319)	(8.9)	(442)	24900	1967	41
Sr	(150)	(91)	< 0.25	< 0.25	< 0.25	< 0.25	< 9	< 0.25	< 12	1240	98	131
U	< 3846	< 2327	< 32	< 32	< 32	< 32	< 1133	< 32	< 1584	(11000)	(869)	--
Zn	(305)	185	(1.9)	(2.3)	(2.4)	(2.3)	(80)	< 0.8	< 40	730	58	--

	Washed Solids		5 h	24 h	72 h	168 h		Final Wash Solution		Leached Solids		Mass Recovery
Component	µg/g	µg(a)	µg/mL	µg/mL	µg/mL	µg/mL	µg(b)	µg/mL	µg(c)	µg/g	µg(d)	%
Zr	< 96	< 58	< 0.8	< 0.8	< 0.8	< 0.8	< 28	< 0.8	< 40	880	70	--

3 M NaOH 95°C

Wt. Washed Solids in Sample g:	0.606	Vol. Leach Soln. mL:	36.8
Wt. Leached Solids g:	0.051	Vol. Final Wash Soln. mL:	46

Al	247500	149985	3301	3483	3548	3532	129963	254	11700	30200	1540	95
Bi	42650	25846	160	121	90	75	2772	< 2	< 74	249000	12699	60
Cr	7665	4645	45	86	95	96	3547	7	336	5380	274	90
Fe	19750	11969	18	14	12	11	395	< 0.4	< 18	159000	8109	71
Mg	(865)	(524)	< 2	< 2	< 2	< 2	< 59	< 2	< 74	2900	148	53
Na	13375	8105	70221	73062	76302	73062	2688682	7290	335340	35750	1823	N/A
P	4505	2730	51	49	51	51	1878	(2.9)	(134)	(760)	(39)	75
Pb	(770)	467	(8.4)	(6.6)	(7.1)	(7.3)	(268)	< 2	< 74	1980	101	95
Si	14850	8999	139	134	129	122	4501	(13.3)	(611)	39500	2015	79
Sr	(150)	(91)	< 0.25	< 0.25	< 0.25	< 0.25	< 9	< 0.25	< 12	1200	61	90
U	< 3846	< 2331	(35.6)	< 32	< 32	< 32	< 1178	< 32	< 1472	(10000)	(510)	--
Zn	(305)	185	(2.6)	(2.9)	(3.2)	(3.2)	(119)	< 0.8	< 37	530	27	--
Zr	< 96	< 58	< 0.8	< 0.8	< 0.8	< 0.8	< 29	< 0.8	< 37	1220	62	--

(a) Values in parentheses are near the detection limit.

(b) Mass of each component in the aliquot treated under the indicated conditions. This was determined from analysis of the washed solids (aliquot BX110-8).

(c) Mass of each component in the caustic leaching solution.

(d) Mass of each component in the final washing solution.

(e) Mass of each component in the leached solids.

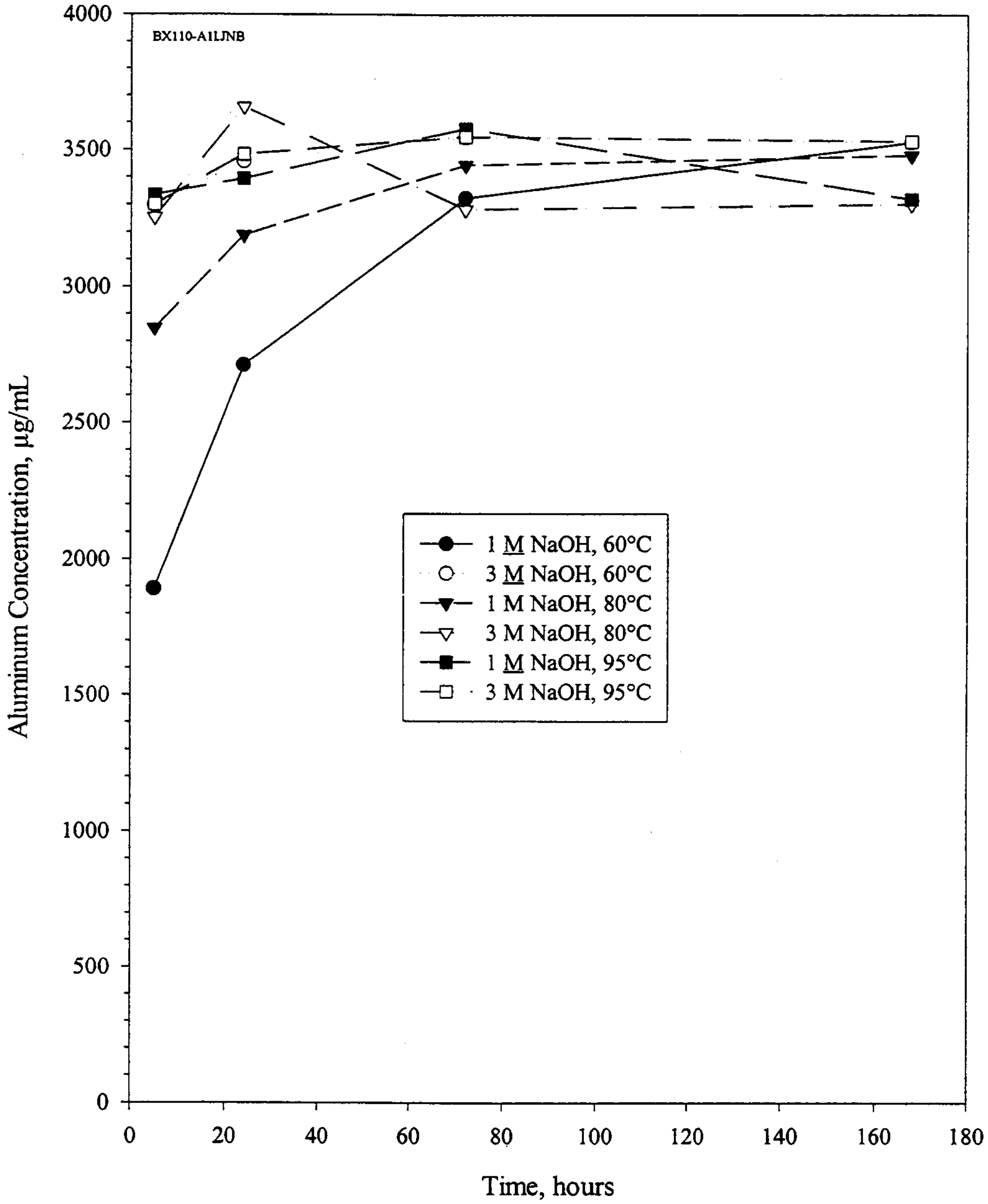

Figure 3.1. Aluminum Concentration as a Function of Time During the Caustic Leaching of Tank BX-110 Sludge

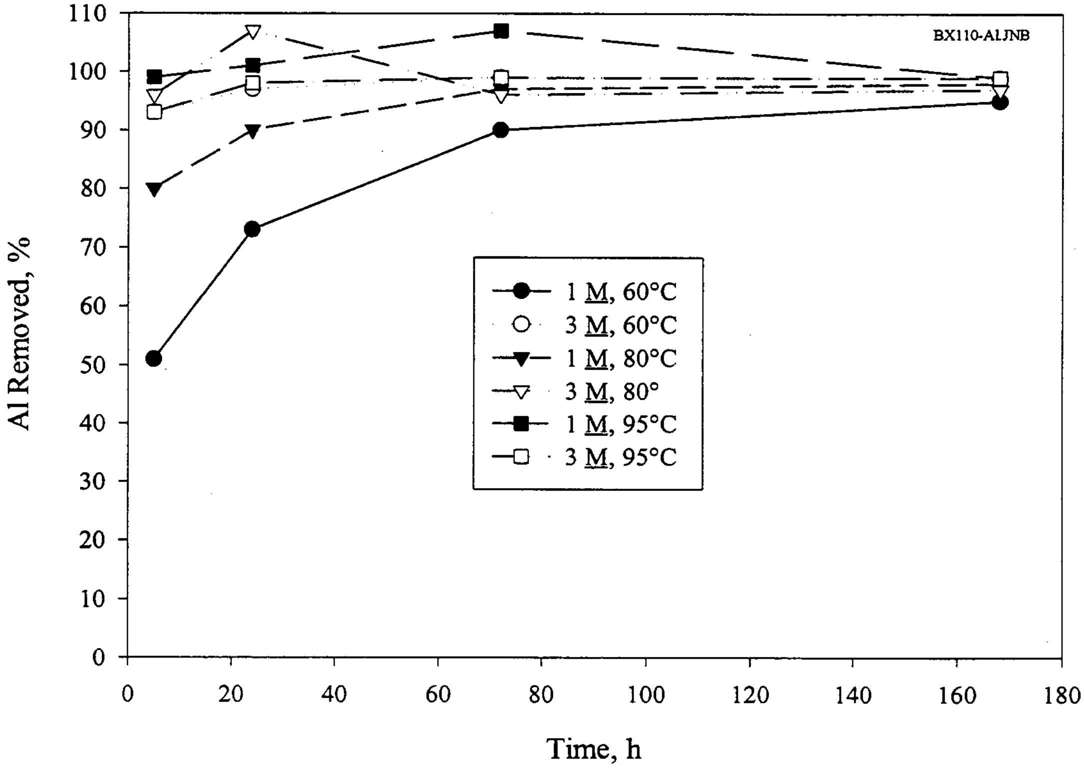

Figure 3.2. Aluminum Removal From the Dilute Hydroxide-Washed BX-110 Sludge Solids as a Function of Time

The results for Na are difficult to interpret. Based on the ICP/AES analyses, the residual Na in the caustic-leached solids generally ranged from ~30% to ~50% of what was present in the dilute hydroxide-washed solids. However, in all cases, the amount of residual Na was less than what would be expected based on the amount of interstitial 0.1 M NaOH present after the final washing step. Because of experimental uncertainties introduced by the presence of Na in the KOH flux, the significance of this discrepancy is unknown. The amount of Na in the flux was relatively large compared to the amount of Na in the solids. Indeed, in some cases, it represented as much as 63% of the total Na in the analyte solution. Although the Na concentrations in the solids were corrected for the contribution of the Na in the flux, this adjustment could introduce significant error into the results. In any case, the matter is relatively unimportant because the low Na content of the leached sludge would contribute only ~2 wt% Na_2O to the HLW glass made from this sludge (assuming 25 wt% oxide loading).

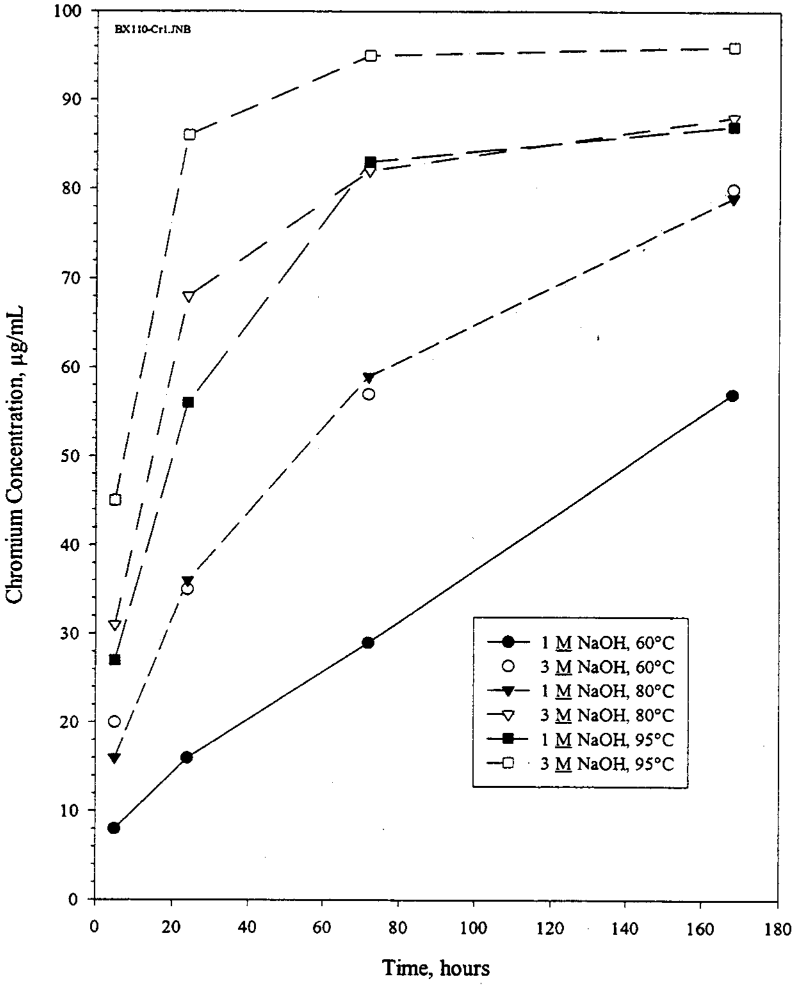

Figure 3.3. Chromium Concentration as a Function of Time During the Caustic Leaching of Tank BX-110 Sludge

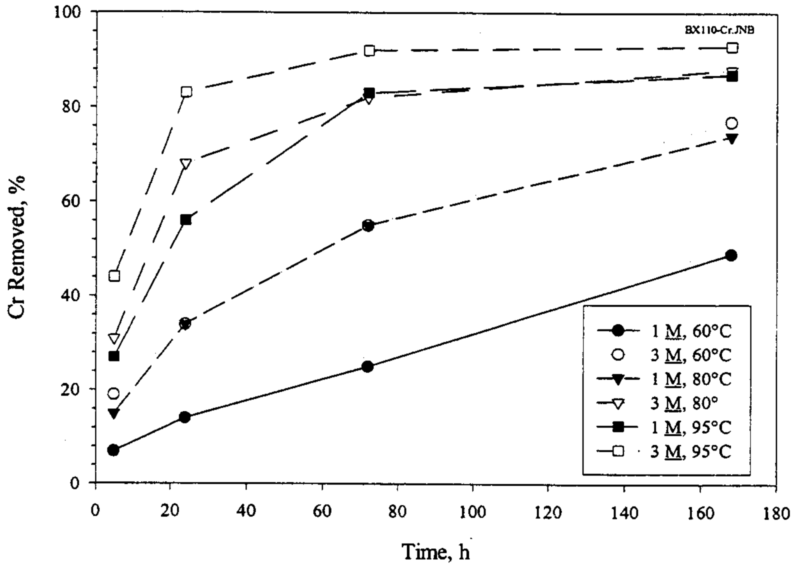

Figure 3.4. Chromium Removal From the Dilute Hydroxide-Washed BX-110 Sludge Solids as a Function of Time

Table 3.8. Chromate and Total Chromium Concentrations in the BX-110 Wash and Leach Solutions

Solution	Cr(VI), μg/mL[(a)]	Total Cr, μg/mL[(b)]
Initial Wash	40	31
BX110-1, Leach	44	57
BX110-1, Wash	6	7
BX110-2, Leach	79	80
BX110-2, Wash	5	6
BX110-3, Leach	79	79
BX110-3, Wash	4	5
BX110-4, Leach	95	88
BX110-4, Wash	5	5
BX110-5, Leach	95	87
BX110-5, Wash	12	12
BX110-6, Leach	106	96
BX110-6, Wash	7	7

(a) Determined spectrophotometrically.
(b) Determined by ICP/AES.

Caustic leaching removed ≥95% of the P from the dilute hydroxide-washed BX-110 solids, even under the mildest caustic leaching conditions examined (1 M NaOH, 60°C). Thus, when coupled with the 97% removed by dilute hydroxide washing (Table 3.4), greater than 99% of the P was removed from the BX-110 sludge sample. The solution data (Table 3.7) indicate that phosphate metathesis was rapid; it was essentially complete within the first 5 hours of leaching.

Transmission electron microscopy (TEM) was used to analyze samples of the dilute hydroxide-washed BX-110 solids and the solids remaining after leaching with 3 M NaOH at 95°C for 168 h. The TEM analysis indicated that a large fraction of the washed BX-110 solids consisted of gibbsite. This material was completely removed by caustic leaching, largely accounting for the 99% Al removal achieved. The remaining Al in the leached solids was present primarily as a crystalline aluminosilicate phase, $H_4(Si,Al)_{12}O_{24}$. Other crystalline phases identified in the leached BX-110 solids were $Bi_6O_{13}.xH_2O$, FeOOH, $MgSiO_3$, $Bi_2Fe_4O_9$, and Bi metals. In addition, an amorphous iron bismuth silicate material was also a major species present in the leached solids.

Table 3.9 summarizes the removal of some important radionuclides from the washed BX-110 solids under the various leaching conditions.[a] Table 3.10 presents the actual concentrations of the various radioactive components in the leaching and washing solutions and in the leached solids. The mass recovery for each component is presented in Table 3.10 as well. Only a small amount of TRU dissolved during the caustic leaching steps, but some ^{90}Sr did dissolve. Consistent with results from other Hanford sludges (Lumetta et al. 1997), caustic leaching liberated most of the ^{137}Cs from the BX-110 dilute-hydroxide washed sludge solids. Estimating the radionuclide content of LLW glass (20 wt% Na_2O; 2.7 MT/m^3) produced from the combined wash and leach solutions indicates that the highest TRU content would be found for the case where the sludge was leached with 3 M NaOH at 95°C. The TRU concentration in the resulting LLW form would be ~1 nCi/g. The ^{90}Sr content would be ~0.2 Ci/m^3, and the ^{137}Cs content would be ~50 Ci/m^3. These are all within the Class C LLW limits (but exceed the Class A limits for ^{90}Sr and ^{137}Cs).

Table 3.11 shows the concentration of waste oxides in the dilute hydroxide-washed and in the leached[b] BX-110 solids and the concentrations of waste-derived components that would result from vitrifying these solids at 25 wt% WOL, excluding oxides of Na and Si. The oxide concentrations in the washed and leached solids were determined by converting the elemental concentrations listed in Tables 3.4 (washed solids) and 3.7 (leached solids) to the corresponding oxide concentrations. The oxide concentrations in the IHLW were determined according to equation 2.1.

Assuming upper limits of 15, 0.5, and 3.0 wt% for Al, Cr, and P oxides, respectively, in the IHLW, a 25 wt% WOL would not be achievable for the dilute hydroxide-washed BX-110 solids. The Al oxide concentration would exceed the 15 wt% limit, and the Cr oxide concentration would be near the 0.5 wt% limit. On the other hand, 25 wt% WOL should be easily achievable for the caustic-leached BX-110 solids. Setting the upper limit for Al_2O_3 in the IHLW as 15 wt%, the maximum WOL that could be achieved for the washed BX-110 solids would be 18.2 wt%. At this WOL, application of equation 2.2 indicates that 3.12 g IHLW would be produced per gram of dry washed BX-110 solids. As calculated by equation 2.3, 0.19 g of IHLW glass would be produced at 25 wt% WOL from the leached solids derived from 1 g of washed BX-110 solids. Thus, a reduction in IHLW of 94% could be achieved by caustic leaching the BX-110 solids.

(a) Reliable data for ^{99}Tc could not be obtained because of the low levels of this radionuclide.

(b) For this analysis, we considered only the case where the solids were leached with 3 M NaOH for 168 h at 95°C.

Table 3.9. Caustic Leaching Results for Key Radioactive BX-110 Sludge Components

Component	1 M NaOH	3 M NaOH
	Removed, %[(a)]	
	Temperature = 60°C	
Total Alpha	< 1 (< 2)	< 5 (< 6)
^{90}Sr	1 (7)	4 (10)
^{137}Cs	72 (94)	93 (99)
	Temperature = 80°C	
Total Alpha	< 1 (< 2)	< 12 (< 13)
^{90}Sr	2 (8)	4 (10)
^{137}Cs	81 (96)	97 (99)
	Temperature = 95°C	
Total Alpha	< 1 (< 2)	< 16 (< 17)
^{90}Sr	2 (8)	6 (12)
^{137}Cs	73 (95)	93 (99)

(a) Amount of material removed from the dilute hydroxide-washed solids; the values were obtained by the summation method (see Table 3.6, footnote a). The values in parentheses are the cumulative removals achieved by dilute hydroxide washing and caustic leaching.

Table 3.10. Concentrations of Key Radioactive BX-110 Sludge Components in Caustic Leaching Solutions and in the Caustic Leached Solids

	Washed Solids		Leach Solution		Final Wash Solution		Leached Solids		Mass
Component	µCi/g	µCi	µCi/mL	µCi	µCi/mL	µCi	µCi/g	µCi	Recovery, %
				1 M NaOH, 60°C					
	Wt. Washed Solids in Sample, g:		0.594			Vol. Leach Soln., mL:		35.2	
	Wt. Leached Solids, g:		0.094			Vol. Final Wash Soln., mL:		48.6	
Total Alpha	2.13E-01	1.27E-01	< 3.24E-05	< 1.14E-03	< 1.62E-05	< 7.86E-04	2.45E+00	2.30E-01	181
^{90}Sr	7.15E+00	4.25E+00	1.26E-03	4.44E-02	2.07E-04	1.01E-02	3.97E+01	3.73E+00	89
^{60}Co	1.10E-02	6.53E-03	< 4.86E-05	< 1.71E-03	< 6.47E-05	< 3.14E-03	4.93E-02	4.63E-03	145 > x > 71
^{137}Cs	4.39E+01	2.61E+01	3.59E-01	1.27E+01	5.37E-02	2.61E+00	6.41E+01	6.03E+00	82
				3 M NaOH, 60°C					
	Wt. Washed Solids in Sample, g:		0.573			Vol. Leach Soln., mL:		37.8	
	Wt. Leached Solids, g:		0.058			Vol. Final Wash Soln., mL:		43.5	
Total Alpha	2.13E-01	1.22E-01	1.02E-04	3.84E-03	< 3.24E-05	< 1.41E-03	1.61E+00	9.34E-02	80
^{90}Sr	7.15E+00	4.10E+00	3.43E-03	1.30E-01	2.48E-04	1.08E-02	5.90E+01	3.42E+00	87
^{60}Co	1.10E-02	6.30E-03	< 9.71E-05	< 3.67E-03	< 4.85E-05	< 2.11E-03	8.38E-02	4.86E-03	169 > x > 77
^{137}Cs	4.39E+01	2.52E+01	4.60E-01	1.74E+01	3.07E-02	1.34E+00	2.59E+01	1.50E+00	80
				1 M NaOH, 80°C					
	Wt. Washed Solids in Sample, g:		0.605			Vol. Leach Soln., mL:		40.5	
	Wt. Leached Solids, g:		0.084			Vol. Final Wash Soln., mL:		44	
Total Alpha	2.13E-01	1.29E-01	< 1.62E-05	< 6.56E-04	< 1.46E-05	< 6.42E-04	1.46E+00	1.23E-01	95
^{90}Sr	7.15E+00	4.33E+00	1.91E-03	7.74E-02	2.61E-04	1.15E-02	4.81E+01	4.04E+00	95
^{60}Co	1.10E-02	6.66E-03	< 9.71E-05	< 3.93E-03	< 6.48E-05	< 2.85E-03	7.04E-02	5.91E-03	191 > x > 89
^{137}Cs	4.39E+01	2.66E+01	3.59E-01	1.46E+01	7.73E-02	3.40E+00	4.92E+01	4.13E+00	83

	Washed Solids		Leach Solution		Final Wash Solution		Leached Solids		Mass
Component	µCi/g	µCi	µCi/mL	µCi	µCi/mL	µCi	µCi/g	µCi	Recovery, %
				3 M NaOH, 80°C					
	Wt. Washed Solids in Sample, g:		0.604			Vol. Leach Soln., mL:		42	
	Wt. Leached Solids, g:		0.062			Vol. Final Wash Soln., mL:		44.9	
Total Alpha	2.13E-01	1.29E-01	2.98E-04	1.25E-02	< 1.46E-05	< 6.54E-04	1.49E+00	9.24E-02	81
^{90}Sr	7.15E+00	4.32E+00	4.10E-03	1.72E-01	3.82E-04	1.71E-02	6.67E+01	4.14E+00	100
^{60}Co	1.10E-02	6.64E-03	< 9.71E-05	< 4.08E-03	< 6.47E-05	< 2.91E-03	9.02E-02	5.59E-03	189 > x > 84
^{137}Cs	4.39E+01	2.65E+01	4.55E-01	1.91E+01	5.45E-02	2.45E+00	9.52E+00	5.90E-01	84
				1 M NaOH, 95°C					
	Wt. Washed Solids in Sample, g:		0.605			Vol. Leach Soln., mL:		35.4	
	Wt. Leached Solids, g:		0.079			Vol. Final Wash Soln., mL:		49.5	
Total Alpha	2.13E-01	1.29E-01	< 1.46E-05	< 5.16E-04	< 1.46E-05	< 7.23E-04	1.43E+00	1.13E-01	88
^{90}Sr	7.15E+00	4.33E+00	1.47E-03	5.19E-02	2.71E-04	1.34E-02	4.79E+01	3.78E+00	89
^{60}Co	1.10E-02	6.66E-03	< 1.13E-04	< 4.01E-03	< 6.49E-05	< 3.21E-03	6.62E-02	5.23E-03	187 > x > 79
^{137}Cs	4.39E+01	2.66E+01	3.56E-01	1.26E+01	4.91E-02	2.43E+00	7.22E+01	5.70E+00	78
				3 M NaOH, 95°C					
	Wt. Washed Solids in Sample, g:		0.606			Vol. Leach Soln., mL:		36.8	
	Wt. Leached Solids, g:		0.051			Vol. Final Wash Soln., mL:		46	
Total Alpha	2.13E-01	1.29E-01	3.42E-04	1.26E-02	< 1.46E-05	< 6.71E-04	1.34E+00	6.83E-02	63
^{90}Sr	7.15E+00	4.33E+00	4.97E-03	1.83E-01	2.77E-04	1.27E-02	5.88E+01	3.00E+00	74
^{60}Co	1.10E-02	6.67E-03	< 4.86E-05	< 1.79E-03	< 4.86E-05	< 2.24E-03	8.41E-02	4.29E-03	125 > x > 64
^{137}Cs	4.39E+01	2.66E+01	4.92E-01	1.81E+01	3.34E-02	1.54E+00	2.87E+01	1.46E+00	79

Table 3.11. Estimated Concentrations of Waste-Derived Components in the IHLW Glass From BX-110 Waste

Component	Washed Solids		Leached Solids (3 M NaOH/95°C/168h)	
	g oxide/g solids	Conc. in IHLW, wt%[(a)]	g oxide/g solids	Conc. in IHLW, wt%[(a)]
Al_2O_3	0.4678	20.6	0.0571	2.5
BaO	0.0000	0.00	0.0000	0.0
Bi_2O_3	0.0476	2.10	0.2776	12.0
CaO	0.0000	0.0	0.0000	0.0
Cr_2O_3	0.0112	0.5	0.0079	0.3
Fe_2O_3	0.0282	1.2	0.2274	9.8
MgO	0.0014	0.1	0.0048	0.2
MnO_2	0.0000	0.0	0.0000	0.0
Na_2O	0.0180	0.8	0.0482	2.1
P_2O_5	0.0103	0.5	0.0017	0.1
SiO_2	0.0318	1.4	0.0845	3.7
SrO	0.0002	0.01	0.0014	0.1
UO_3	0.0000	0.0	0.0000	0.0
ZnO	0.0004	0.02	0.0007	0.0

(a) Based on 25 wt% waste oxide loading (excluding Na_2O and SiO_2).

4.0 Tank BX-112 Test

4.1 BX-112 Experimental

The BX-112 sludge sample used was a mixture of Segment 3 from Core #118 and Segment 1 from Core #119. The relative proportions of each of these segments are not accurately known, but the Core #118 Segment 3 provided most of the sample. Deionized water (100 mL) was added to the jar containing the Core #118 Segment 3 sample. After mixing, the slurried solids were transferred to a plastic 200-mL centrifuge bottle (labeled as "Washed BX112"). The mixture was centrifuged, and the supernatant solution was used to rinse out the Core #118 Segment 3 sample jar. This cycle was repeated four times to ensure maximum transfer of solids to the centrifuge bottle. After the last cycle, the centrifuged supernate was transferred to the Core #119 Segment 1 sample jar, and the process was repeated to transfer the solids from that jar into "Washed BX112." At this point, the centrifuge bottle was essentially full with ~100 mL of centrifuged solids and ~100 mL of liquid.

Using a magnetic stirrer, the mixture was homogenized. A 1-mL (1.452 g) aliquot of the slurry was transferred to a pre-weighed glass vial. The aliquot was dried at 105°C yielding 0.447 g of dry solids. Thus, the slurry was 69.2 wt% water and 30.8 wt% solids (insoluble solids plus dissolved solids). A total of 83.1 g of insoluble and dissolved solids was contained in the centrifuge bottle "Washed BX112." The dried aliquot, representing the dried untreated BX-112 waste material, was analyzed by ICP/AES and radiochemical methods.

Initial Wash: The contents of "Washed BX112" were stirred for 30 minutes, then centrifuged for 30 minutes at 1,200 G. The centrifuged liquid was decanted to a 1-L plastic bottle labeled as "BX112-Wash." "Washed BX112" was filled to the 200-mL mark with 0.1 M NaOH. The mixture was stirred for 30 minutes,(a) then centrifuged for 30 minutes at 1,200 G. Again, the centrifuged liquid was decanted to "BX112-Wash." This cycle was repeated until seven wash cycles had been completed. The wash solutions were yellow, but became progressively less so, and the final wash solution was colorless. Also, the final wash solution was very cloudy after the 30-minute centrifuge period, indicating that most of the soluble salts had been removed. The solution cleared after standing over 2 days; it was then transferred to "BX112-Wash." The volume of the combined wash solution was 734 mL.

Division of the Washed Solids: The washed BX-112 sludge was diluted to a volume of 200 mL with deionized water and stirred to homogenize. The slurry weight was 227.2 g, which contained 36.6 wt% (100 x 83.1g/227.2 g) of total (soluble plus insoluble) BX-112 solids. Aliquots (8-mL) were distributed between seven 60-mL HDPE bottles (labeled as BX112-1, -2, -3, -4, -5, -6, and -7, respectively) and one 25-mL glass vial (BX112-8). Drying aliquot BX112-8 to a constant weight at 105°C indicated that the slurry contained 17.0 wt% washed solids. Based on the weight of each aliquot and the weight percent values given above, the amount of untreated BX-112 solids (insoluble solids plus dissolved solids) and the amount of washed solids in each aliquot were determined (Table 4.1).

Leaching: Table 4.2 summarizes the leaching conditions for each aliquot of BX-112 sludge. Aliquot BX112-8 was held for analysis. The amount of NaOH added to each reaction vessel was determined by assuming that 1) each mole of Al consumes one mole of hydroxide, 2) each mole of Cr consumes one mole of hydroxide, and 3) each mole of phosphate consumes 3 moles of hydroxide. The estimated Al, Cr, and P concentrations in the sludge solids were obtained from Winkelman (1996). These

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(a) It was necessary to alternately bang the container on the hood tray and vigorously shake it to get the stir bar to break loose from the centrifuged solids.

estimates were 37,500 µg Al/g, 3,555 µg Cr/g, and 53,200 µg P/g; these values are based on wet sludge solids. To each reaction vessel the appropriate amounts of 10 M NaOH and water were added to give the desired NaOH concentration and 15 mL of leachate per gram of untreated BX-112 solids (insoluble solids plus dissolved solids). Based on the solubility of gibbsite at 60°C, it was estimated that this volume of leaching solution was sufficient to avoid Al saturation if all the Al dissolved.

Table 4.1. Weight of BX-112 Solids in Each Vial

Bottle #	Wt. BX-112 Solids, g[(a)]	Wt. Washed Solids, g[(b)]
BX112-1	3.32	1.54
BX112-2	3.36	1.56
BX112-3	3.37	1.57
BX112-4	3.35	1.56
BX112-5	3.37	1.57
BX112-6	3.38	1.57
BX112-7	3.37	1.57
BX112-8	3.37	1.57

(a) Weight of untreated sample on a dry-weight basis.
(b) Weight of washed sludge solids on a dry-weight basis.

Table 4.2. Leaching Conditions for Each Aliquot of BX-112 Solids

Bottle #	[NaOH], M[(a,b)]	T, °C
BX112-1	1.1	60
BX112-2	2.9	60
BX112-3	1.3	80
BX112-4	3.4	80
BX112-5	1.1	100
BX112-6	3.4	100
BX112-7[(c)]	3	100

(a) Concentrations determined by titration with standard HCl after leaching for 168 h, except for BX112-7 (target concentration given for the latter).
(b) 15 mL per gram of untreated sample.
(c) Tiron® (5 g) was added.

For aliquot BX112-7, 4,5-dihydroxy-1,3-benzenedisulfonate (Tiron®) was added to the leaching mixture. This was done to further test the Fe leaching technology described recently (Lumetta 1997).

The liquid level was marked on each reaction vessel, and each vessel was closed with a cap equipped with a tube-condenser. The vessels were placed in an Al heating block at the appropriate temperature and stirred with a magnetic stirrer. Evaporation was minimal over several hours; occasionally, deionized water was added to bring the liquid level up to its original position. The leachates were sampled at intervals of 5, 24, 72, and 168 h.[(a)] For each sampling, the stirrer was stopped, and the solids settled at temperature. At 60 and 80°C, the solids settled rapidly, with the solution typically being clear within 30 min. At 100°C, the reaction mixtures were near boiling; bumping sometimes caused fine particles to be suspended. This was especially true for BX112-6. The transfer pipette and the syringe filter assembly (0.2-µm nylon membrane) were preheated by inserting in a boiling water bath. These were then used to filter ~2 mL of the leachate solution. A 1-mL aliquot of the filtered solution was immediately acidified with 15 mL of 0.3 M HNO_3. The remaining filtered solution was added back to the reaction vessel, and the leaching was continued. After the final sampling, two aliquots of the filtered leachate were taken and titrated with standard HCl to determine the free-hydroxide concentration.

While at temperature, the leachate solution was transferred from the settled solids. The settled solids were then rapidly centrifuged, and the centrifuged liquid was decanted and combined with the rest of the leachate solution. The leached solids were washed thrice with 15-mL portions of 0.1 M NaOH, then were dried at 105°C. For each wash step, the wash mixture was stirred for a minimum of 30 minutes, centrifuged, and then the wash liquid was decanted. Table 4.3 gives the weights of the leached solids and the weight reductions achieved after leaching for 168 h.

Table 4.3. Weight of the Leached BX-112 Solids

Bottle #	Wt. Leached Solids, g	Wt. Reduction, %[(a)]
BX112-1	0.727	53
BX112-2	0.676	57
BX112-3	0.752	52
BX112-4	0.719	54
BX112-5	0.752	52
BX112-6	0.706	55
BX112-7	0.460	71

(a) Weight reduction with respect to the dry weight of washed solids treated achieved after leaching for 168 h.

Spectrophotometric Determination of Chromate. Aliquots (0.5-mL) of the filtered leachate and wash solutions were diluted with 10 mL of 0.1 M NaOH. The UV/vis spectra of the resulting solutions were recorded using a Spectral 400 Series CCD Array UV-Vis Spectrophotometer (Spectral Instruments, Tucson, Arizona) equipped with a 1-cm pathlength fiber-optic probe. The absorbance at 372 nm was compared to a calibration line generated by measuring the absorbance for a series of chromate standard solutions.

4.2 BX-112 Results

The following sections describe the dilute hydroxide washing, caustic leaching, and Tiron® Leaching of BX-112 sludge.

[(a)] The 5-, 24-, and 72-h samplings were not done for the BX112-7 test.

4.2.1 Dilute Hydroxide Washing of BX-112 Sludge

Table 4.4 presents the concentrations of some important nonradioactive BX-112 sludge components in the untreated and washed BX-112 sample and in the dilute hydroxide wash solution. The table also lists the total mass of each component present in each processing stream (untreated sample, wash solution, or washed solids) and the amount of each component removed by the dilute hydroxide washing. The latter values were determined by dividing the amount of material in the wash solution by the total amount in the wash solution plus the washed solids.(a) This analysis of the data indicated that 5% of the Al, 19% of the Cr, and 24% of the P was removed by washing the BX-112 sludge sample with dilute NaOH. The amount of Na present in the washed solids was 63% less than that in the initial sample. A reliable value for the Ca concentration in the untreated solids could not be obtained because it was present at near the ICP/AES detection limit, but Ca was clearly identified in the washed solids. No Ca was detected in the wash solution, so it is not significantly removed by dilute NaOH washing.

Except for P, the mass recoveries for these elements were only about 80%.(b) Because of these low mass recoveries, the removal efficiencies reported in Table 4.4 might not be totally reliable. Table 4.5 presents an alternative analysis of the data. Iron is generally insoluble under alkaline conditions, so it can be assumed that it remains entirely in the solid phase. This assumption is supported by the ICP/AES analysis indicating only ~1 µg Fe/mL in the dilute hydroxide washing solution. The concentrations of each sludge component in the untreated and washed solids can be normalized against the Fe concentrations in those materials. The normalized concentrations in the untreated sample and washed solids can then be compared to determine the amount of each component removed. When analyzed in this manner, the data indicate that 6% of the Al and 18% of the Cr were removed by dilute hydroxide washing. These values are consistent with those reported in Table 4.4. However, the amount of Na and P removed are less than reported in Table 4.4. Table 4.5 also indicates some removal for elements that normally are insoluble in dilute NaOH (e.g., Bi, Mn, and Sr), but this might be attributed to analytical uncertainty, especially for Mn and Sr, which were present in low concentrations. Analysis of the wash solution indicated that the amounts of Bi, Mn, and Sr removed were well below 1% (see Table 4.4).

(a) Because NaOH was added during the washing steps, the percent of Na actually removed from the sludge solids could not be determined. Instead, the amount of Na in the washed solids was compared directly to the amount in the untreated solids; that is, the percent of Na removed was 100 – 100(6.06 g/16.45 g) = 63%.

(b) The mass recovery is defined as the total amount of a given element determined to be in the wash solution and the washed solids divided by the amount of that element determined to be in the initial sludge sample.

Table 4.4. Results of Dilute Hydroxide Washing of BX-112 Sludge: Nonradioactive Components[(a)]

Component	Untreated Sample		Wash Solution		Washed Solids		Amount Removed, %	Mass Recovery, %
	µg/g	µg	µg/mL	µg	µg/g	µg		
Al	38000	3157800	191	140194	63000	2431800	5	81
Bi	57100	4745010	(1.8)	(1321)	97000	3744200	< 0.04	79
Ca	(5600)	(465360)	< 1.25	< 918	7,520	290272	< 0.3	63
Cr	4020	334062	74	54316	5830	225038	19	84
Fe	30400	2526240	(1.0)	(734)	53800	2076680	< 0.04	82
Mn	623	51771	< 0.025	< 19	966	37288	< 0.06	72
Na	198000	16453800	18800	13799200	157000	6060200	63	N/A
P	55500	4612050	1450	1064300	85400	3296440	24	95
Si	23500	1952850	44	32443	35600	1374160	2	72
Sr	394	32741	< 0.07	< 52	664	25630	< 0.2	78
U	< 5140	< 427134	138	101292	< 5880	< 488628	< 10	--

(a) Values in parentheses are near the analytical detection limit.

Table 4.5. Results of Dilute Hydroxide Washing of BX-112 Sludge Normalized to the Iron Concentrations

Component	g/g Fe		Removed, %
	Untreated Sample	Washed Solids	
Al	1.25	1.17	6
Bi	1.88	1.80	4
Ca	0.18	0.14	24
Cr	0.13	0.11	18
Fe	1.00	1.00	0
Mn	0.020	0.018	12
Na	6.51	2.92	55
P	1.83	1.59	13
Si	0.77	0.66	14
Sr	0.013	0.012	5

Table 4.6 presents the concentrations of some important radioactive BX-112 sludge components in the untreated sample and washed solids and in the dilute hydroxide wash solution. The table also lists the total activity of each component present in each processing stream and the amount of each component removed by the dilute hydroxide washing. The mass recoveries were reasonable for all the radionuclides listed. The TRU behavior is reflected in the total alpha activity data, although information regarding ^{241}Am was also obtained from the gamma spectroscopic analyses. As expected, little removal of TRUs or ^{90}Sr occurred during the dilute hydroxide washing process. A relatively small percentage (31%) of the ^{137}Cs was removed from the BX-112 sludge sample during the dilute hydroxide wash. However ^{99}Tc was largely removed, which would be consistent with the presence of this element as a soluble species such as pertechnetate.

Table 4.6. Results of Dilute Hydroxide Washing of BX-112 Sludge: Radioactive Components

	Untreated Sample		Wash Solution		Washed Solids			
Component	µCi/g	µCi	µCi/mL	µCi	µCi/g	µCi	Amount Removed, %	Mass Recovery, %
Total Alpha	0.272	22.6	9.32E-05	0.068	0.597	23.0	0.3	102
^{90}Sr	20.4	1695	6.63E-03	4.87	38.8	1498	0.3	89
^{137}Cs	131	10886	4.47	3281	192	7411	30.7	98
^{241}Am	0.117	9.7	< 0.005	< 3.67	0.259	10.0	< 27	< 141, > 99
^{99}Tc	0.154	12.8	0.0196	14.4	0.014	0.6	96	117

If the dilute hydroxide wash solution were converted directly to a glass LLW form,[(a)] the primary radionuclide content of that waste form would be 0.73 nCi TRU/g, 0.14 Ci ^{90}Sr/m^3, 95 Ci ^{137}Cs/m^3, and 0.42 Ci ^{99}Tc/m^3. This waste form would meet the 10 nCi/g NRC Class A limit for TRU, but would exceed the Class A limits for ^{90}Sr, ^{137}Cs, and ^{99}Tc (0.04 Ci/m^3, 1 Ci/m^3, and 0.3 Ci/m^3, respectively). However, the ^{90}Sr, ^{137}Cs, and ^{99}Tc levels would be within the Class C LLW limits of 7,000 Ci/m^3, 4,600 Ci/m^3, and 3 Ci/m^3, respectively.

4.2.2 Caustic Leaching of BX-112 Sludge

Table 4.7 summarizes the amounts of Al, Cr, Na, P, and Si removed from the washed BX-112 solids under the various leaching conditions. The values were obtained by the summation method and by the Fe normalization technique discussed in Section 4.2.1. These two methods generally agree. Table 4.8 presents the actual concentrations of the various components in the leaching and washing solutions and in the leached solids. Table 4.8 also presents the mass recovery for each component.

(a) For this determination, it was assumed that the LLW glass form will contain 20 wt% Na_2O, and the density of the glass would be 2.7 MT/m^3.

Table 4.7. Caustic Leaching Results for Key Nonradioactive BX-112 Sludge Components: Amounts Removed from the Dilute Hydroxide-Washed Solids

	1 M NaOH		3 M NaOH	
Component	Summation Method,%(a)	Fe Normalization Method, %(b)	Summation Method,%(a)	Fe Normalization Method, %(b)
	Temperature = 60°C			
Al	62 (64)	67	68 (69)	75
Cr	52 (62)	52	70 (76)	71
Na(c)	75 (91)	80	78 (92)	83
P	99 (99)	99	99 (99)	99
Si	12 (14)	17	23 (25)	28
	Temperature = 80°C			
Al	54 (56)	59	63 (65)	69
Cr	85 (88)	84	86 (89)	85
Na(c)	76 (91)	80	78 (92)	82
P	99 (99)	99	99 (99)	99
Si	8 (10)	21	16 (18)	17
	Temperature = 100°C			
Al	51 (53)	57	59 (61)	59
Cr	83 (86)	83	82 (86)	79
Na(c)	66 (92)	82	56 (90)	71
P	98 (99)	98	99 (100)	--
Si	1 (4)	4	16 (18)	6

(a) Value obtained by summing the quantity of each component found in the leaching and washing solutions and dividing by the total found in the leaching and washing solutions plus the residual solids. The values in parentheses are the cumulative removals achieved by dilute hydroxide washing and caustic leaching.

(b) Value obtained by normalizing the concentrations of each component to the Fe concentration and comparing the normalized values in the caustic-leached solids to those for the dilute hydroxide-washed solids.

(c) Because of the amount of Na added as NaOH during the leaching procedure, it was impossible to determine how much Na was actually removed from the sludge solids. The values reported were determined by comparing the amount of Na in the solids before and after the caustic leaching treatment.

Table 4.8. Concentrations of Key BX-112 Sludge Components in Caustic Leaching Solutions and in the Caustic Leached Solids(a)

	Washed Solids		5 h	24 h	72 h	168 h		Final Wash Solution		Leached Solids		Mass
Component	µg/g	µg(a)	µg/mL	µg/mL	µg/mL	µg/mL	µg(b)	µg/mL	µg(c)	µg/g	µg(d)	Recovery, %
						1 M NaOH, 60°C						
	Wt. Washed Solids in Sample, g:				1.544			Vol. Leach Soln., mL:		40.4		
	Wt. Leached Solids, g:				0.727			Vol. Final Wash Soln., mL:		44.3		
Al	63000	97272	1718	1691	1525	1434	57915	167	7383	55310	40210	108
Ba	(69)	(107)	(0.2)	< 0.81	< 0.81	< 0.81	< 33	< 0.16	< 7	149	109	139 > x > 102
Bi	97000	149768	24	(14)	(31)	(12)	(503)	< 1.62	< 72	261393	190032	127
Ca	7520	11611	< 4.02	< 20	< 20	(26)	(1046)	(25.9)	(1147)	3523	2561	41
Cr	5830	9002	15	49	95	131	5275	14	633	7436	5406	126
Fe	53800	83067	6	(6.6)	(5.5)	(4.0)	(163)	(0.4)	(19)	142422	103541	125
Mg	(1200)	(1853)	< 1.61	< 8.05	< 8.07	< 8.09	< 327	< 1.62	< 72	1087	790	64 > x > 43
Mn	966	1492	(0.1)	< 0.40	< 0.40	< 0.40	< 16	< 0.08	< 4	505	367	25
Na	157000	242408	37741	39767	38252	37699	1523056	5938	263056	82364	59879	N/A
P	85400	131858	2827	3011	2873	2815	113739	291	12902	2643	1921	98
Pb	(290)	(448)	< 0.96	< 4.83	< 4.84	< 4.85	< 196	< 0.97	< 43	356	259	111 > x > 58
Si	35600	54966	496	309	215	159	6439	28	1254	78361	56968	118
Sr	664	1025	< 0.08	< 0.40	< 0.40	< 0.40	< 16	< 0.08	< 4	1642	1193	116
Zn	(480)	(741)	10	(11)	(11)	(10)	(418)	(0.6)	(27)	500	363	109
Zr	(270)	(417)	< 0.40	< 20	< 20	< 20	< 817	< 0.40	< 18	3352	2437	785 > x > 584
						3 M NaOH, 60°C						
	Wt. Washed Solids in Sample, g:				1.561			Vol. Leach Soln., mL:		42.7		
	Wt. Leached Solids, g:				0.676			Vol. Final Wash Soln., mL:		45		
Al	63000	98343	2192	2,082	1790	1415.8	60452.5	141.31	6359	47250	31,941	100
Ba	(69)	(108)	< 0.32	< 0.81	< 0.81	< 0.81	< 35	< 0.16	< 7.27	173	117	147 > x > 108
Bi	97000	151417	(11.12	(10.33)	< 8.07	(9.22)	(394)	(2.26)	(102)	279629	189,029	125
Ca	7520	11739	< 8.06	< 20.18	< 20.16	< 20.23	< 864	(22.61)	(1017)	3464	2,341	36 > x > 20
Cr	5830	9101	42	89	151	165	7,047	16	734	4952	3,347	122

(a) Mass of each component in the aliquot treated under the indicated conditions. This was determined from analysis of the washed solids (aliquot BX112-8).

(b) Mass of each component in the caustic leaching solution.

(c) Mass of each component in the final washing solution.

(d) Mass of each component in the leached solids.

	Washed Solids		5 h	24 h	72 h	168 h		Final Wash Solution		Leached Solids		Mass
Component	µg/g	µg(a)	µg/mL	µg/mL	µg/mL	µg/mL	µg(b)	µg/mL	µg(c)	µg/g	µg(d)	Recovery, %
Fe	53800	83982	23	20.18	(16.13	(11.33)	(484)	(0.47)	(21)	160836	108725	129
Mg	(1200)	(1873)	< 3.22	< 8.07	< 8.07	< 8.09	< 345	< 1.62	< 73	1014	686	59 > x > 37
Mn	966	1,508	(0.23	< 0.40	< 0.40	< 0.40	< 17	< 0.08	< 3.63	582	393	26
Na	157000	245077	85436	81668	84037	73943	3157349	8996	404800	78082	52784	N/A
P	85400	133309	2950	2954	3000	2605	111233	240.6	10829	1415	956	92
Pb	(290)	(453)	(2.90	< 4.84	< 4.84	< 4.85	< 207	< 0.97	< 43.61	(327)	(221)	104 > x > 49
Si	35600	55572	993	825	511	325	13887	37	1686	76748	51881	121
Sr	664	1,037	< 0.16	< 0.40	< 0.40	< 0.40	< 17	< 0.08	< 4	1895	1281	124
Zn	(480)	(749)	15.7	(15.8)	(15.8)	(13.9)	(594)	(0.73)	(33)	278	188	109
Zr	(270)	(421)	< 0.81	< 20.18	< 20.16	< 20.23	< 864	< 0.40	< 18.2	3857	2608	828 > x > 619
						1 M NaOH, 80°C						
		Wt. Washed Solids in Sample, g:			1.57			Vol. Leach Soln., mL:		36.3		
		Wt. Leached Solids, g:			0.752			Vol. Final Wash Soln., mL:		43.5		
Al	63000	98910	1,727	1,412	1,443	1,394	50,601	145	6,292	65028	48901	107
Ba	(69)	(108)	(4)	(0.97)	< 0.81	< 0.81	< 29	< 0.16	< 7	137	103	128 > x > 95
Bi	97000	152290	(18)	(9.38)	< 8.10	< 8.10	< 294	< 1.62	< 70	247511	186128	122
Ca	7520	11806	< 20	< 20	< 20	< 20	< 735	(12.30)	(535)	3282	2468	32 > x > 21
Cr	5830	9153	55	165	215	240	8,698	24	1,042	2334	1755	126
Fe	53800	84466	(12)	(6.95)	(6)	(4)	(159)	< 0.40	< 18	136610	102731	122
Mg	(1200)	(1884)	< 8	< 8	< 8.10	< 8.10	< 294	< 1.62	< 70	1049	788	61 > x > 42
Mn	966	1,517	< 0	< 0	< 0.41	< 0.40	< 15	< 0.08	< 4	493	371	24
Na	157000	246490	39,220	39,617	41,148	41,446	1,504,504	6,132	266,752	78135	58757	N/A
P	85400	134078	3,018	3,008	3,191	3,189	115,776	319	13,865	2536	1907	98
Pb	(290)	(455)	< 5	< 5	< 4.86	< 4.86	< 176	< 0.97	< 42	337	254	104 > x > 56
Si	35600	55892	358	131	129	109	3,961	18	781	71582	53829	105
Sr	664	1042	< 0	< 0	< 0.41	< 0.40	< 15	< 0.08	< 4	1568	1179	113
Zn	(480)	(754)	(12)	(16)	(10)	(8.3)	(300)	(0.39)	< 17	655	493	105
Zr	(270)	(424)	< 20	< 20	< 20	< 20	< 735	< 0.40	< 18	3267	2456	757 > x > 579

	Washed Solids		5 h	24 h	72 h	168 h		Final Wash Solution		Leached Solids		Mass
Component	µg/g	µg$^{(a)}$	µg/mL	µg/mL	µg/mL	µg/mL	µg$^{(b)}$	µg/mL	µg$^{(c)}$	µg/g	µg$^{(d)}$	Recovery, %
						<u>3 M NaOH, 80°C</u>						
		Wt. Washed Solids in Sample, g:			1.559			Vol. Leach Soln., mL:		39.8		
		Wt. Leached Solids, g:			0.719			Vol. Final Wash Soln., mL:		43.4		
Al	63000	98217	2039	1683	1492	1470	58508	104	4508	51078	36725	102
Ba	(69)	(108)	(0.99	< 0.81	< 0.81	< 0.81	< 32	< 0.16	< 7	(164)	(118)	146 > x > 109
Bi	97000	151223	(45.3)	(8.25)	< 8.1	< 8.1	< 322	< 1.6	< 70	258,584	185,922	123
Ca	7520	11724	< 20	< 20	< 20	< 20	< 805	(26)	(1124)	(2674)	(1922)	33 > x > 26
Cr	5830	9089	82.5	191	219	233	9,279	16.0	695	2259	1624	128
Fe	53800	83874	31.7	21.7	(15)	(12)	490	< 0.40	< 18	142860	102716	123
Mg	(1200)	(1871)	< 8.1	< 8.1	< 8.1	< 8.1	322	< 1.6	< 70	(758)	(545)	50 > x > 46
Mn	966	1506	< 0.97	< 0.40	< 0.41	< 0.40	< 16	< 0.08	< 4	527	379	25
Na	157000	244763	87048	89314	85536	88559	3524660	8025	348297	73824	53080	N/A
P	85400	133139	3,123	3,139	3,062	3,141	125006	210	9,129	2127	1529	102
Pb	(290)	(452)	< 4.9	< 4.9	< 4.9	< 4.9	< 193	< 4.9	< 211	(323)	(232)	141 > x > 51
Si	35600	55500	733	405	311	238	9,472	25	1,088	78613	56523	121
Sr	664	1035	< 0.40	< 0.40	< 0.41	< 0.40	< 16	< 0.40	< 18	1764	1268	126 > x > 123
Zn	(480)	(748)	17.0	(17)	(16)	(15)	(612)	(0.53)	(23)	(279)	(201)	112
Zr	(270)	(421)	< 20	< 20	< 20	< 20	< 805	< 20	< 878	3400	2445	981 > x > 580
						<u>1 M NaOH, 100°C</u>						
		Wt. Washed Solids in Sample, g:			1.566			Vol. Leach Soln., mL:		33.1		
		Wt. Leached Solids, g:			0.752			Vol. Final Wash Soln., mL:		48.1		
Al	63000	98658	1,431	1,293	1,323	1,268	41,986	207	9974	67400	50685	104
Ba	(69)	(108)	(1.0)	< 0.81	< 0.81	< 0.81	< 27	< 0.16	< 8	(150)	(113)	136 > x > 105
Bi	97000	151902	(12)	(9)	< 8.1	(9)	(284)	< 1.6	< 78	226000	169952	112
Ca	7520	11776	< 20	< 20	< 20	< 20	< 670	(23)	(1091)	6870	5166	59 > x > 44
Cr	5830	9130	95	165	209	220	7,293	35	1699	2500	1880	119
Fe	53800	84251	(9.4)	(6.5)	(4.9)	(4.1)	(134)	< 0.41	< 19	134000	100768	120
Mg	(1200)	(1879)	< 8.1	< 8.1	< 8.1	< 8.1	< 268	< 1.6	< 78	(1700)	(1278)	86 > x > 68
Mn	966	1513	< 0.40	< 0.40	< 0.40	< 0.49	< 16	< 0.1	< 4	927	697	46
Na	157000	245862	39180	36729	39504	38880	1286928	8051	387272	70900	53317	N/A
P	85400	133736	2,995	2,864	3,044	2,997	99201	492	23688	3270	2459	94
Pb	(290)	(454)	< 4.9	< 4.9	< 4.9	< 4.9	< 161	< 1.0	< 47	(440)	(331)	119 > x > 73
Si	35600	55750	138	136	95	(75)	(2467)	17	826	85400	64221	121
Sr	664	1040	< 0.40	< 0.40	< 0.40	< 0.41	< 13	< 0.08	< 4	1610	1211	116

	Washed Solids		5 h	24 h	72 h	168 h		Final Wash Solution		Leached Solids		Mass
Component	µg/g	µg$^{(a)}$	µg/mL	µg/mL	µg/mL	µg/mL	µg$^{(b)}$	µg/mL	µg$^{(c)}$	µg/g	µg$^{(d)}$	Recovery, %
Zn	(480)	(752)	(11)	(9)	(7)	(6)	(193)	(1)	(29)	807	607	110
Zr	(270)	(423)	< 20	< 20	< 20	< 20	< 670	< 0.4	< 19	1010	760	343 > x > 180
						3 M NaOH, 100°C						
		Wt. Washed Solids in Sample, g:			1.573			Vol. Leach Soln., mL:		33.9		
		Wt. Leached Solids, g:			0.706			Vol. Final Wash Soln., mL:		46.5		
Al	63000	99099	1,604	1,462	1,457	1,445	48,987	186	8,658	57,100	40,313	99
Ba	(69)	(109)	(0.9)	< 0.8	< 0.8	0.8	27	< 0.2	< 8	(140)	(99)	123 > x > 116
Bi	97000	152581	(11)	< 8.1	< 8.1	(11)	(384)	< 1.6	< 75	218,000	153,908	101
Ca	7520	11829	< 20	< 20	< 20	(34)	(1153)	(23)	(1054)	(5300)	(3742)	50
Cr	5830	9171	79	175	206	219	7414	28	1287	2670	1885	115
Fe	53800	84627	(27)	(21)	(18)	(16)	(527)	< 0.4	< 19	118000	83308	98
Mg	(1200)	(1888)	< 8.1	< 8.1	< 8.1	< 8.1	< 275	< 1.6	< 75	(1400)	(988)	71 > x > 52
Mn	966	1520	< 0.40	< 0.40	< 0.40	< 0.41	< 14	< 0.08	< 3.8	874	617	41
Na	157000	246961	82245	83379	87588	88452	2998523	13082	608291	98600	69612	N/A
P	85400	134334	2930	2963	3092	3143	106541	398	18520	(2400)	(1694)	94
Pb	(290)	(456)	< 4.9	< 4.9	< 4.9	< 4.9	< 165	< 1.0	< 45	(420)	(297)	111 > x > 65
Si	35600	55999	436	329	280	237	8,018	36	1671	73500	51891	110
Sr	664	1044	< 0.40	< 0.40	< 0.40	< 0.41	< 14	< 0.40	< 19	1440	1017	> 97
Zn	(480)	(755)	(16)	(15)	(14)	(14)	(472)	(1)	(59)	(310)	(219)	99
Zr	(270)	(425)	< 20	(2.4)	< 20	< 20	< 686	< 20	< 941	844	596	524 > x > 140

(a) Values in parentheses are near the analytical detection limit.
(b) Mass of each component in the aliquot treated under the indicated conditions. This was determined from analysis of the washed solids (aliquot BX112-8).
(c) Mass of each component in the caustic leaching solution.
(d) Mass of each component in the final washing solution.
(e) Mass of each component in the leached solids.

Aluminum removal from the dilute hydroxide-washed solids ranged from 50 to 75%. For the most part, the hydroxide concentration dependence is as expected. That is, Al removal improves with increasing hydroxide concentration, although the increases are small. Interestingly, Al removal decreased with increasing temperature—a trend contrary to what was expected. We hypothesize that this is due to the formation of aluminosilicate minerals. Two pieces of evidence support this hypothesis. First, the general trends for Si removal parallel those for Al. That is, the Si removal decreases with increasing temperature. Second, the Al and Si concentrations in the leach solutions both decrease over time (Table 4.8). This was observed for virtually all conditions examined. Figure 4.1 shows the Al concentrations as a function of time, and Figure 4.2 shows the percent of the Al removed as a function of time. The decrease in Al concentration occurred more rapidly at 80 and 100°C; the decreases seen at 60°C were more gradual. An increased rate of formation of aluminosilicates at the higher temperatures would explain these observations. In all cases investigated, the Si removal was poor, but it was especially so at 100°C. The Al/Si molar ratios in the leached solids were very similar for each leaching condition investigated. The average Al/Si molar ratio was 0.78, with a standard deviation of 0.1. TEM analysis of the BX-112 solids remaining after leaching with 3 M NaOH at 100°C for 168 h revealed the presence of aluminosilicate minerals (see below).

Table 4.7 indicates a marked improvement in Cr removal in going from 60 to 80°C, but no significant improvement in going from 80 to 100°C. Furthermore, at a given temperature, there was little difference in Cr removal when leaching with 1 M NaOH or 3 M NaOH. Table 4.8 and Figure 4.3 and 4.4 indicate that Cr removal is highly time dependent. As might be expected for an inhomogeneous system such as tank sludge, the Cr dissolution kinetics is complex. Plots of [Cr] versus time, ln[Cr] versus time, and 1/[Cr] versus time were not linear, indicating the Cr dissolution was neither zero, first, or second order. Because of this, it was not possible to determine the rate constants for the Cr dissolution. As has been seen with leaching tests for other Hanford sludges, the dissolved Cr is essentially all in the +6 oxidation state. Table 4.9 compares the chromate concentrations, (determine by UV/Vis spectrophotometry) with the total Cr concentrations (determined by ICP/AES). Except for the initial washing solution,(a) the Cr(VI) concentrations are the same as the total Cr concentrations, within experimental error.

Sodium removal from the dilute hydroxide washed BX-112 solids was generally ~80%, with total removals of ~90% for the combined washing/leaching process. The residual Na is due in part to NaOH remaining in the interstitial liquid after washing. Estimates of the Na in the residual solids contributed by NaOH in the interstitial liquid ranged from 7 to 45%. The remainder of the Na might be present in aluminosilicate minerals.

Phosphorus was essentially completely removed from the BX-112 sludge solids. One molar NaOH at 60°C is an adequately vigorous leaching condition to achieve this level of P removal. The solution data (Table 4.8) indicate that phosphate metathesis is rapid; it is essentially complete within the first 5 hours of leaching.

(a) The errantly high chromate concentration found in the initial wash solution was likely due to interference by nitrite ion.

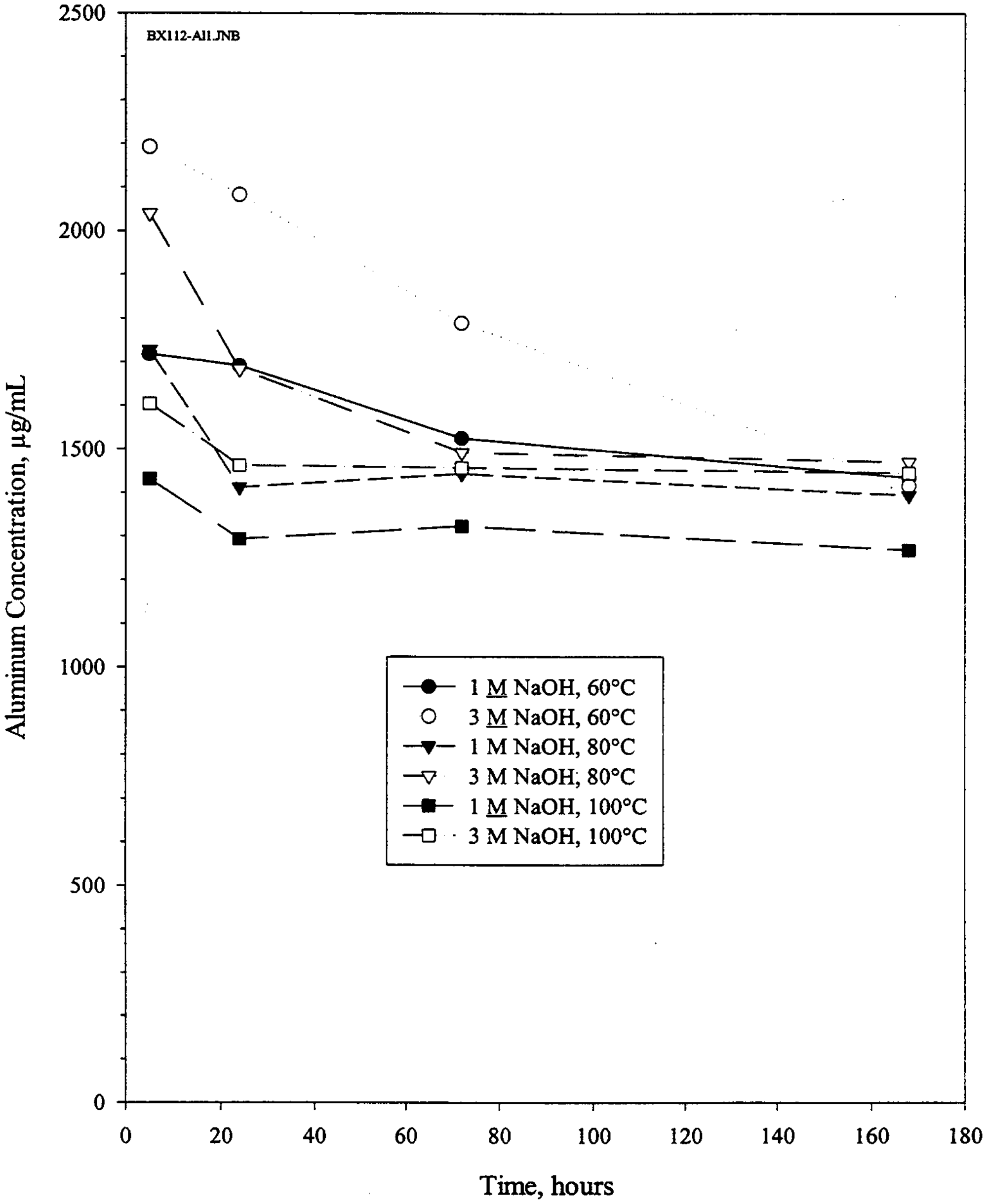

Figure 4.1. Aluminum Concentration as a Function of Time During the Caustic Leaching of Tank BX-112 Sludge

TEM was used to analyze samples of the dilute hydroxide-washed BX-112 solids and the solids remaining after leaching with 3 M NaOH at 100°C for 168 h. The TEM analysis indicated that the washed BX-112 solids were considerably different than the washed BX-110 solids. The washed BX-112 solids contained significant concentrations of sodium and aluminum phosphates. These phases were completely removed by the caustic leaching process, accounting for virtually complete P removal and the initial rapid Al dissolution. The leached solids consisted primarily of sodium aluminosilicate minerals, iron hydroxide, and Bi metal. Bismuth metal was also observed in the leached BX-110 solids.

Table 4.10 summarizes the removal of some important radionuclides from the washed BX-112 solids under the various leaching conditions.[a] Table 4.11 presents the actual concentrations of the various radioactive components in the leaching and washing solutions and in the leached solids. Table 4.11 also presents the mass recovery for each radioactive component. As was the case with the dilute hydroxide wash, little TRU or ^{90}Sr was removed during the caustic leaching steps. However, caustic leaching liberated nearly all the ^{137}Cs from the BX-112 sludge solids. Estimating the radionuclide content of LLW glass (20 wt% Na_2O; 2.7 MT/m^3) produced from the combined wash and leach solutions indicates that the highest TRU content would be found for the case where the sludge was leached with 3 M NaOH at 80°C. The TRU concentration in the resulting LLW form would be ~6 nCi/g. The ^{90}Sr content would be ~0.2 Ci/m^3, and the ^{137}Cs content would be ~200 Ci/m^3. These are all within the Class C LLW limits.

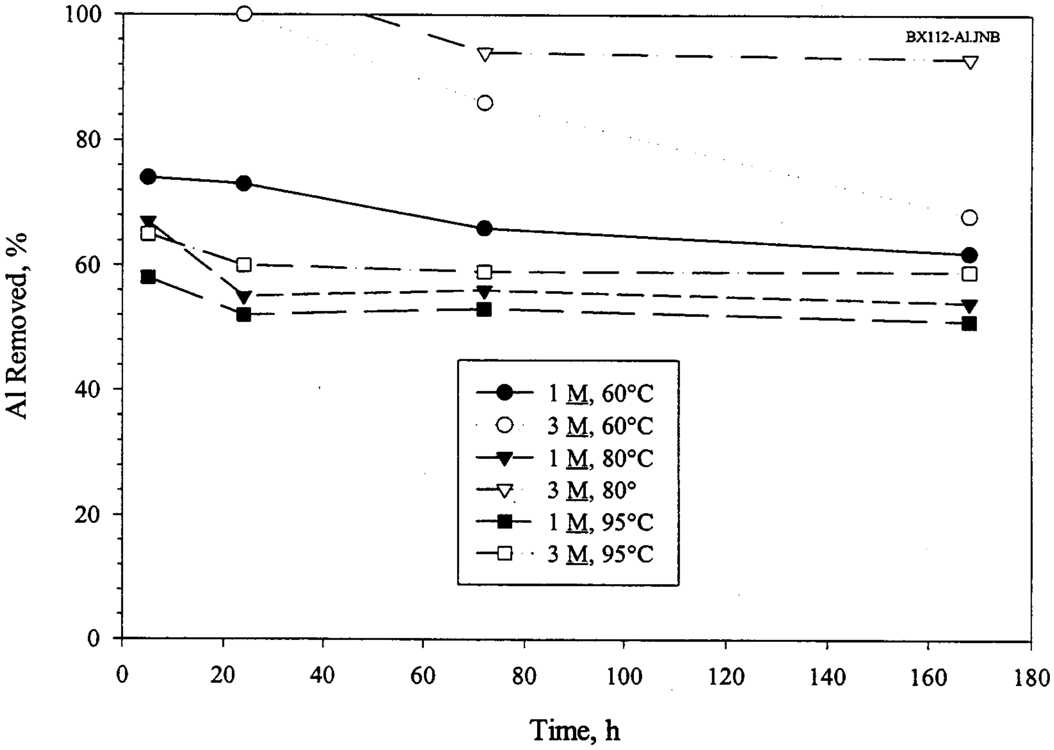

Figure 4.2. Aluminum Removal from the Dilute Hydroxide-Washed BX-112 Sludge Solids as a Function of Time

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(a) Reliable data for ^{99}Tc could not be obtained because of the low levels of this radionuclide.

Table 4.9. Chromate and Total Chromium Concentrations in the BX-112 Wash and Leach Solutions

Solution	Cr(VI), μg/mL[a]	Total Cr, μg/mL[b]
Initial Wash	108	74
BX112-1, Leach	129	131
BX112-1, Wash	11	14
BX112-2, Leach	166	165
BX112-2, Wash	13	16
BX112-3, Leach	219	240
BX112-3, Wash	20	24
BX112-4, Leach	213	233
BX112-4, Wash	12	16
BX112-5, Leach	225	220
BX112-5, Wash	35	35
BX112-6, Leach	212	219
BX112-6, Wash	25	28

(a) Determined spectrophotometrically.
(b) Determined by ICP/AES.

Table 4.12 shows the concentration of waste oxides in the dilute hydroxide-washed and in the leached[a] BX-112 solids and the concentrations of waste-derived components that would result from vitrifying these solids at 25 wt% WOL, excluding oxides of Na and Si. The oxide concentrations in the washed and leached solids were determined by converting the elemental concentrations listed in Tables 4.4 (washed solids) and 4.8 (leached solids) to the corresponding oxide concentrations. The oxide concentrations in the IHLW were determined according to equation 2.1.

Assuming upper limits of 15, 0.5, and 3.0 wt% for Al, Cr, and P oxides, respectively, in the IHLW, a 25 wt% WOL would not be achievable for the dilute hydroxide-washed BX-112 solids because of the high P_2O_5 content. On the other hand, 25 wt% WOL should be easily achievable for the caustic-leached BX-112 solids. Setting the upper limit for P_2O_5 in the IHLW as 3 wt%, the maximum WOL that could be achieved for the washed BX-112 solids would be 8.0 wt%. At this WOL, application of equation 2.2 indicates that 6.51 g IHLW would be produced per gram of dry-washed BX-112 solids. As calculated by equation 2.3, 0.97 g of IHLW glass would be produced at 25 wt% WOL from the leached solids derived from 1 g of washed BX-112 solids. Thus, a reduction in IHLW of 85% could be achieved by caustic leaching the BX-110 solids.

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[a] For this analysis, we considered only the case where the solids were leached with 3 M NaOH for 168 h at 100°C.

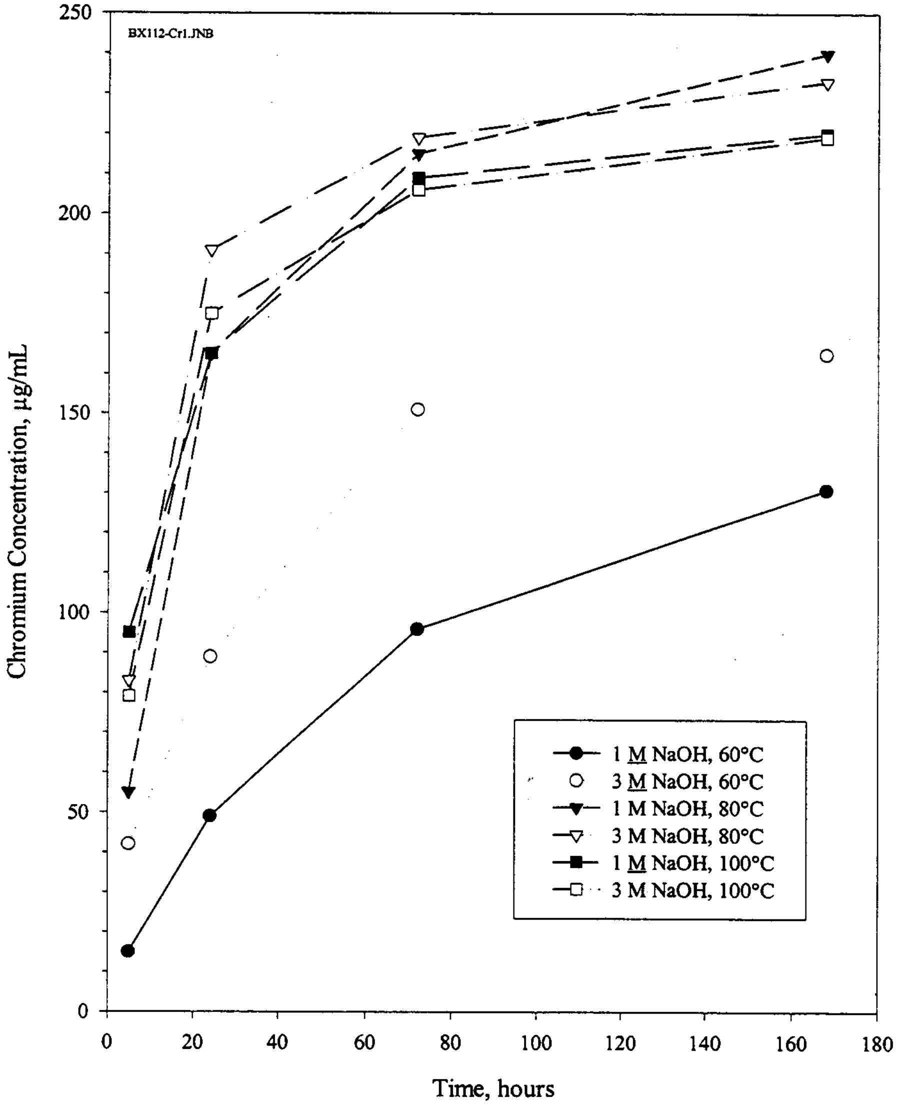

Figure 4.3. Chromium Concentration as a Function of Time During the Caustic Leaching of Tank BX-112 Sludge

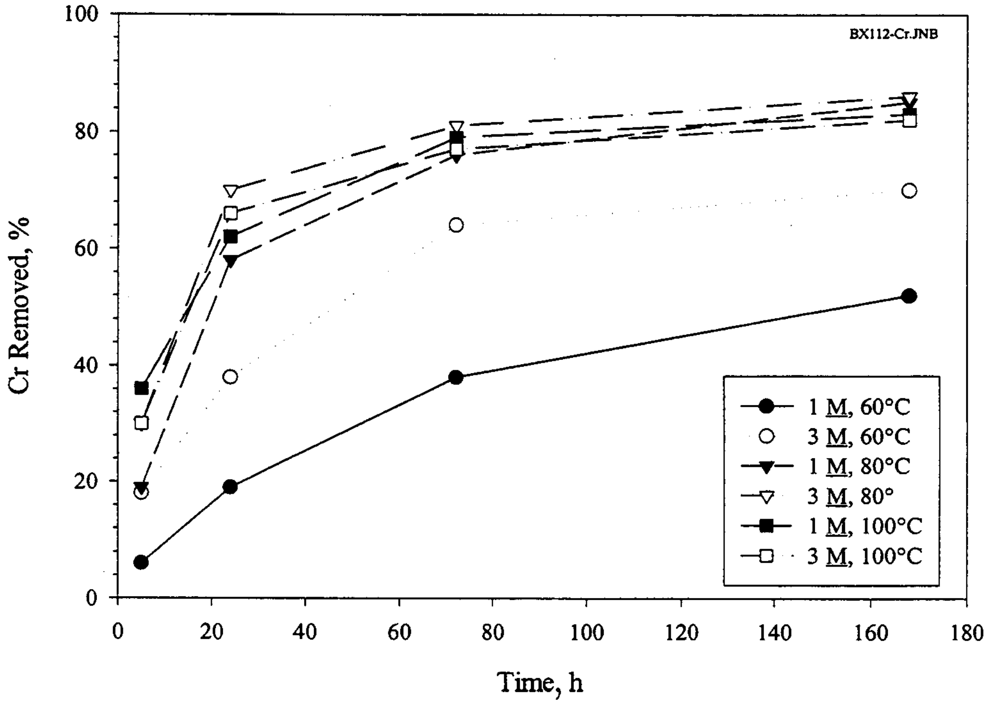

Figure 4.4. Chromium Removal From the Dilute Hydroxide-Washed BX-112 Sludge Solids as a Function of Time

4.2.3 Tiron® Leaching of BX-112 Sludge

Table 4.13 summarizes the results of leaching BX-112 sludge with 3 M NaOH and Tiron® (the Tiron®-to-Fe molar ratio was ~30 in this test). The purpose of this test was to determine if Fe could also be removed from the sludge by alkaline leaching methods. Previous tests with Hanford Tank U-110 sludge suggested that Tiron® was a promising reagent to do this (Lumetta 1997). Indeed, this method removed 99% of the Fe from the BX-112 sludge. Unfortunately, the TRU component of the waste was also dissolved. This amount of TRU dissolution is unacceptable because additional processing would be required to remove the TRU from the LLW stream. As catechols are known to strongly bind to actinide ions, the dissolution of TRU is not that surprising.

In the previous Tiron® leaching test (with U-110 sludge), TRU dissolution was low. However, there were significant differences in the leaching procedure between the U-110 and BX-112 tests. For the U-110 test, the sludge was first leached with 3 M NaOH, then the caustic-leached solids were treated with Tiron® at pH 13 and ambient temperature. In the BX-112 test, the caustic and Tiron® leaching steps were combined into a single step, and this step was conducted at 100°C. Perhaps performing the Tiron® leaching step at pH 13 and ambient temperature is necessary to avoid TRU dissolution, although Fe dissolution also appears to be somewhat less effective under those conditions.

Interestingly, all of the Cr was removed in the Tiron® leaching process. Approximately 90% of the Cr was removed in the previously conducted Tiron® leaching test performed on U-110 sludge. One possible explanation for this result is that the Cr not removed in the usual caustic leaching process is tied up with Fe in the sludge solids. Dissolution of the Fe would have exposed the Cr to the leaching solution where it was either oxidized to Cr(VI) or was complexed by Tiron® to form a soluble complex. Alternatively, it is possible that Tiron® complexed Cr(III) before it was oxidized to Cr(VI). It is not known which mechanism was responsible for the additional Cr dissolution.

Table 4.10. Caustic Leaching Results for Key Radioactive BX-112 Sludge Components

Component	1 M NaOH	3 M NaOH
	Removed, %(a)	
	Temperature = 60°C	
Total Alpha	< 1 (< 1)	< 1 (< 1)
^{90}Sr	< 1 (< 1)	< 1 (< 1)
^{137}Cs	96 (98)	93 (99)
	Temperature = 80°C	
Total Alpha	< 1 (< 1)	8 (< 9)
^{90}Sr	< 1 (< 1)	< 1 (< 1)
^{137}Cs	97 (98)	98 (99)
	Temperature = 100°C	
Total Alpha	< 1 (< 1)	5 (5)
^{90}Sr	< 1 (< 1)	< 1 (< 1)
^{137}Cs	95 (97)	98 (99)

(a) Amount of material removed from the dilute hydroxide-washed solids; the values were obtained by the summation method (see Table 3.6, footnote a).

(b) The values in parentheses are the cumulative removals achieved by dilute hydroxide washing and caustic leaching.

Table 4.11. Concentrations of Key Radioactive BX-112 Sludge Components in Caustic Leaching Solutions and in the Caustic Leached Solids

	Washed Solids		Leach Solution		Final Wash Solution		Leached Solids		Mass Recovery,	Removed from Washed	Total Removal Wash+Leach,
Component	µCi/g	µCi	µCi/mL	µCi	µCi/mL	µCi	µCi/g	µCi	%	Solids,%	%
					1 M NaOH, 60°C						
	Wt. Washed Solids in Sample, g: 1.544 Wt. Leached Solids, g: 0.727 Vol. Leach Soln., mL: 40.4						Vol. Final Wash Soln., mL: 44.3 Vol. Diss. Sludge Soln., mL: 25.7				
Total Alpha	0.597	0.922	< 6.47E-05	< 2.61E-03	< 4.85E-05	< 2.15E-03	1.28	0.931	> 99	< 1	< 1
^{90}Sr	38.8	59.9	< 4.85E-03	< 1.96E-01	< 8.09E-04	< 3.58E-02	86.9	63.2	> 99	0	< 1
^{137}Cs	192	296	6.71	271	0.76	34	15.2	11.1	107	96	98
^{241}Am	0.259	0.400	< 4.85E-03	< 1.96E-01	< 1.62E-03	< 7.17E-02	0.463	0.336	> 84	< 44	< 59
					3 M NaOH, 60°C						
	Wt. Washed Solids in Sample, g: 1.561 Wt. Leached Solids, g: 0.676 Vol. Leach Soln., mL: 42.7						Vol. Final Wash Soln., mL: 45 Vol. Diss. Sludge Soln., mL: 27.9				
Total Alpha	0.597	0.932	< 8.77E-05	< 3.74E-03	< 6.46E-05	< 2.91E-03	1.45	0.983	> 99	1	< 1
^{90}Sr	38.8	60.6	6.57E-03	2.80E-01	< 8.08E-04	< 3.63E-02	94.8	64.1	> 99	0	< 1
^{137}Cs	192	300	6.21	265	0.59	27	6.9	4.7	99	98	99
^{241}Am	0.259	0.404	< 8.09E-03	< 3.45E-01	< 3.23E-03	< 1.45E-01	0.412	0.278	> 99	< 64	< 74
					1 M NaOH, 80°C						
	Wt. Washed Solids in Sample, g: 1.57 Wt. Leached Solids, g: 0.752 Vol. Leach Soln., mL: 36.3						Vol. Final Wash Soln., mL: 43.5 Vol. Diss. Sludge Soln., mL: 23.4				
Total Alpha	0.597	0.937	8.89E-05	3.23E-03	< 6.47E-05	< 2.82E-03	1.70	1.281	> 99	0	< 1
^{90}Sr	38.8	60.9	< 4.86E-03	< 1.76E-01	< 8.09E-04	< 3.52E-02	85.2	64.1	> 99	0	< 1
^{137}Cs	192	301	7.66	278	0.74	32	13.8	10.4	106	97	98
^{241}Am	0.259	0.407	< 6.48E-03	< 2.35E-01	< 1.62E-03	< 7.04E-02	0.420	0.316	> 77	< 49	< 63

Component	Washed Solids µCi/g	Washed Solids µCi	Leach Solution µCi/mL	Leach Solution µCi	Final Wash Solution µCi/mL	Final Wash Solution µCi	Leached Solids µCi/g	Leached Solids µCi	Mass Recovery, %	Removed from Washed Solids,%	Total Removal Wash+Leach, %
					3 M NaOH, 80°C						
		Wt. Washed Solids in Sample, g: 1.559					Vol. Final Wash Soln., mL: 43.4				
		Wt. Leached Solids, g: 0.719					Vol. Diss. Sludge Soln., mL: 17.7				
		Vol. Leach Soln., mL: 39.8									
Total Alpha	0.597	0.931	2.36E-03	9.41E-02	< 6.47E-05	< 2.81E-03	1.50	1.076	> 99	8	< 9
^{90}Sr	38.8	60.5	4.32E-03	1.72E-01	< 8.09E-04	< 3.51E-02	92.2	66.3	> 99	0	< 1
^{137}Cs	192	299	7.46	297	0.47	21	7.8	5.6	108	98	99
^{241}Am	0.259	0.404	< 8.10E-03	< 3.22E-01	< 3.24E-03	< 1.40E-01	0.471	0.339	> 83	< 58	< 69
					1 M NaOH, 100°C						
		Wt. Washed Solids in Sample, g: 1.566					Vol. Leach Soln., mL: 33.1				
		Wt. Leached Solids, g: 0.752					Vol. Final Wash Soln., mL: 48.1				
Total Alpha	0.597	0.935	1.09E-04	3.59E-03	< 6.48E-05	< 3.12E-03	1.07	0.805	> 86	< 1	< 1
^{90}Sr	38.8	60.8	3.65E-03	1.21E-01	< 8.10E-04	< 3.90E-02	89.4	67.2	> 99	0	< 1
^{137}Cs	192	301	7.16	237	1.13	54	18.8	14.138	102	95	97
^{241}Am	0.259	0.406	< 6.48E-03	< 2.14E-01	< 3.24E-03	< 1.56E-01	0.414	0.311	> 77	< 54	< 67
					3 M NaOH, 100°C						
		Wt. Washed Solids in Sample, g: 1.573					Vol. Leach Soln., mL: 33.9				
		Wt. Leached Solids, g: 0.706					Vol. Final Wash Soln., mL: 46.5				
Total Alpha	0.597	0.939	1.13E-03	3.82E-02	< 6.48E-05	< 3.01E-03	1.08	0.762	> 81	5	< 5
^{90}Sr	38.8	61.0	4.23E-03	1.43E-01	< 8.10E-04	< 3.76E-02	85.9	60.6	> 99	0	< 1
^{137}Cs	192	302	7.60	258	0.91	42	9.4	6.608	102	98	99
^{241}Am	0.259	0.407	< 6.48E-03	< 2.20E-01	< 3.24E-03	< 1.51E-01	0.443	0.313	> 76	< 54	< 67

Table 4.12. Estimated Concentrations of Waste-Derived Components in the IHLW Glass From BX-112 Waste

Component	Washed Solids		Leached Solids (3 M NaOH/100°C/168h)	
	g oxide/g solids	Conc. in IHLW, wt%[a]	g oxide/g solids	Conc. in IHLW, wt%[a]
Al_2O_3	0.1191	5.7	0.1079	5.0
Bi_2O_3	0.1082	5.19	0.2431	11.3
CaO	0.0105	0.5	0.0074	0.3
Cr_2O_3	0.0085	0.4	0.0039	0.2
Fe_2O_3	0.0769	3.7	0.1687	7.8
MgO	0.0000	0.0	0.0000	0.0
MnO_2	0.0015	0.1	0.0014	0.1
Na_2O	0.2116	10.2	0.1329	6.2
P_2O_5	0.1957	9.4	0.0055	0.3
SiO_2	0.0762	3.7	0.1573	7.3
SrO	0.0008	0.04	0.0017	0.1

(a) Based on 25 wt% waste oxide loading (excluding Na_2O and SiO_2).

Table 4.13. Results of the Tiron® Leaching of BX-112 Sludge(a)

	Washed Solids		Leaching Solution		Final Wash Solution		Leached Solids		Mass	Removed from Washed
Component	µg/g	µg(b)	µg/mL	µg(c)	µg/mL	µg(d)	µg/g	µg(e)	Recovery, %	Solids, %
Al	63000	98847	1137	51485	96	4365	93300	42918	100	57
Bi	97000	152193	835	37844	70	3196	260000	119600	106	26
Cr	5830	9147	220	9974	18	836	(80)	(37)	118	100
Fe	53800	84412	1943	88009	161	7362	2450	1127	114	99
Na	157000	246333	84188	3813716	9212	420993	91800	42228	N/A	83
P	85400	133993	2623	118812	214	9766	3050	1403	97	99
Si	35600	55856	196	8874	21	969	111000	51060	109	16
Sr	664	1041.82	< 0.03	< 1.13	< 0.01	< 0.23	2180	1003	96	< 4
	µCi/g	µCi	µCi/mL	µCi	µCi/mL	µCi	µCi/g	µCi		
Total Alpha	0.597	0.937	3.17E-02	1.44E+00	2.48E-03	1.13E-01	0.09	0.039	> 99	98
^{90}Sr	38.8	60.9	1.93E-02	8.73E-01	2.01E-03	9.17E-02	118.0	54.280	91	2
^{137}Cs	192	301	6.44	292	0.52	24	4.3	1.955	105	99
^{241}Am	0.259	0.406	< 6.48E-03	< 2.93E-01	< 3.24E-03	< 1.48E-01	< 0.100	< 0.046	--	--

(a) Values in parentheses are near the analytical detection limit.

(b) Mass of each component in the aliquot treated under the indicated conditions. This was determined from analysis of the washed solids (aliquot BX112-8).

(c) Mass of each component in the caustic leaching solution.

(d) Mass of each component in the final washing solution.

5.0 Tank C-102 Test

5.1 C-102 Experimental

The C-102 sludge sample used was a composite mixture (from jars 6364 and 6365) prepared at the 222-S laboratory and shipped to LANL in January 1998. It should be noted that this sample was obtained as an auger sample (taken in August 1995) rather than a core sample, so it represents only the top portion of the sludge in Tank C-102. The sample was a dry greenish-brown powder.

Initial Wash: A 25.55-g portion of the C-102 composite sample was placed in a 225-mL plastic centrifuge bottle labeled as "C-102." Fifty milliliters of 0.1 M NaOH was added to the bottle. The mixture was stirred 30 min at ambient temperature, a 2-mL portion of the slurry was removed for ICP/AES and radiochemical analyses, and the remainder (representing 24.75 g sludge) was centrifuged for 15 min at 1,200 G. The centrifuged liquid was decanted to a 1-L plastic bottle labeled as "C-102-Wash-Solution." Another 100-mL of fresh 0.1 M NaOH was added to C-102. The mixture was stirred for 30 min, then centrifuged for 15 min at 1,200 G. Again, the centrifuged liquid was decanted to C-102-Wash-Solution. This washing procedure was repeated for a total of three wash cycles. The initial wash solutions were pale yellow, and the final wash solution was colorless. The volume of the combined wash solution was 224 mL (231.5 g of solution/[1.0329g/mL]).

Division of the Washed Solids: The washed C-102 sludge was diluted by adding 1 mL deionized water per gram of original sludge (25 mL) and stirred for 30 min to homogenize. Aliquots (~15 g) were distributed between five 125-mL polymethylpentene (PMP) bottles (labeled as C102-A0, A1, A2, A3, and A4, respectively). The method for dividing the slurry was to use a 10-mL pipette with a tip that had been trimmed so that the opening was large enough to accommodate the thick and granular nature of the slurry. While the slurry was stirred, 5 mL were removed successively into the five tared containers. This process was continued until all the slurry had been dispensed. Uniform dispensing of the slurry was made difficult by formation of dense chunks that formed during the dilute hydroxide wash, and some of the sludge had to be dispensed using a spatula to distribute the solids as uniformly as possible. Heterogeneous sampling can be a problem when comparing data generated from two or more sludge-slurry portions. Assuming an even distribution of sludge in the slurry, the amount of C-102 sludge solids estimated (from the measured slurry weights) to be in each vial is given in Table 5.1. Sample C102-A0 was dried at 105°C yielding 3.2032 g of dried solids; this corresponded to 68.2 wt% washed solids per gram of sludge. Based on this value, the amount of washed solids in each of the bottles was calculated (Table 5.1).

Leaching: Table 5.2 summarizes the leaching conditions for each aliquot of C-102 sludge. The amount of NaOH needed to yield the desired final NaOH concentration in each reaction vessel was determined by assuming that 1) each mole of Al consumes one mole of hydroxide, 2) each mole of Cr consumes one mole of hydroxide, and 3) each mole of phosphate consumes three moles of hydroxide. The estimated Al, Cr, and P concentrations in the as-received sludge were obtained from Agnew (1997). These estimates were 90,300 μg Al/g, 92 μg Cr/g, and 255 μg P/g. The appropriate amounts of 10 M NaOH and water were added to each reaction vessel to give the desired NaOH concentration. The amounts of as-received sludge sample in each reaction mixture were as follows: 17.7 wt% for the 1 M NaOH/60°C test, 9.5 wt% for the 3 M NaOH/60°C test, 24.8 wt% for the 1 M NaOH/100°C test, and 15.4 wt% for the 3 M NaOH/100°C test.

Table 5.1. Weight of C-102 Solids in Each Bottle

Bottle #	Wt. C-102 Sample, g[a]	Wt. Washed Solids, g[b]
C-102-A0	4.69	3.20
C-102-A1	4.74	3.24
C-102-A2	5.19	3.54
C-102-A3	4.81	3.28
C-102-A4	4.42	3.01

(a) Weight of as-received untreated sample.
(b) Weight of washed sludge solids on a dry-weight basis.

Table 5.2. Leaching Conditions For Each Aliquot of C-102 Solids

Bottle #	[NaOH], M[a]	T, °C	Solution Volume, mL
C-102-A1	1.1	60	18
C-102-A2	1.0	100	13
C-102-A3	2.9	60	40
C-102-A4	2.9	100	19

(a) Concentration determined by titration with standard HCl immediately after NaOH addition.

Each slurry was mixed for 5 min, then allowed to settle for 5 min. A 0.1-mL aliquot of the supernatant liquid was removed for free-hydroxide determination. If the [OH^-] was not within 0.2 M of the target value, appropriate adjustments were made with deionized water and/or 10 M NaOH, as needed. The liquid level was marked on each reaction vessel, and each vessel was closed with a cap equipped with a tube-condenser. The vessels were placed in an Al heating block at the appropriate temperature and stirred with a magnetic stirrer. Evaporation was minimal over several hours; occasionally, deionized water was added to bring the liquid level up to its original position. The leachates were sampled after 5 h and again after 72 h. For the 5-h sampling event, the stirrer was stopped, and the solids settled at temperature. The upper portion of the solution was typically clear enough to sample within 30 min. The transfer pipette and the syringe filter assembly (0.2-µm PVDF membrane) were preheated by inserting in a boiling water bath. These were then used to filter ~2.5 mL of the leachate solution. A 2-mL aliquot of the filtered solution was immediately acidified with 1.5 mL of 16 M HNO_3 and diluted with 16.5 mL deionized water. The remaining filtered solution was added back to the reaction vessel, and the leaching was continued.

After the leaching steps were completed, the reaction vessels were removed from the heating block, allowed to cool to ambient temperature, and then centrifuged for 15 min. A pipette was used to draw off the solution above the centrifuged solids. The leached solids were washed successively with three 10-mL portions of 0.01 M NaOH/0.01 M $NaNO_2$, then were dried at 105°C. Table 5.3 gives the weights of the leached solids and the weight reductions achieved after leaching for 72 h.

Table 5.3. Weight of the Leached C-102 Solids

Bottle #	Wt. Leached Solids, g	Wt. Reduction, %[(a)]
C-102-A1	2.682	17
C-102-A2	2.938	17
C-102-A3	1.395	58
C-102-A4	1.266	58

(a) Weight reduction with respect to the dry weight of washed solids treated achieved after leaching for 72 h.

5.2 C-102 Results

The following sections describe dilute hydroxide washing and caustic leaching of C-102 sludge.

5.2.1 Dilute Hydroxide Washing of C-102 Sludge

Table 5.4 presents the concentrations of some important nonradioactive C-102 sludge components in the dilute hydroxide wash solution and in the washed solids. The table also lists the total mass of each component present in each processing stream (wash solution or washed solids) and the amount of each component removed by the dilute hydroxide washing in terms of percent. The data indicated that 74% of the Na and 25% of the P were removed by washing the C-102 sludge with dilute NaOH. The washed solids contained 2.6 wt% Na. No other nonradioactive component was significantly removed by the dilute hydroxide wash.

Table 5.4 also presents the concentrations of the nonradioactive components in the as-received C-102 sample. The relative concentrations of the various components differ considerably from the estimates given by Agnew (1997). In particular, there appeared to be much more Al, P, and Si in the sample examined than would be expected from the historical tank estimate. The relative concentrations given by Agnew for Al, P, and Si were 4.8, 0.01, and 0.0005 grams per gram of Fe, respectively. The corresponding values determined in this test were 14.9, 0.6, and 1.5. This discrepancy might be because the sample examined here represented only the top portion of the sludge layer in Tank C-102.

Table 5.5 presents the removal of nonradioactive B-201 sludge components during the dilute hydroxide wash as determined by the Fe normalization method. This analysis of the data indicates that 79% of the Na and 51% of the P were removed from the solids during the dilute hydroxide wash. The Na value agrees with the removal as expressed in Table 5.4, but the P value is much higher using the normalization method, and this could explain the low recovery for P observed in the material balance column on Table 5.4.

Table 5.4. Results of Dilute Hydroxide Washing of C-102 Sludge: Nonradioactive Components

Component	Untreated Sample		Wash Solution		Washed Solids		Amount Removed, %(a)	Mass Recovery
	µg/g	µg	µg/mL	µg	µg/g	µg		
Al	109542	2711153	53.35	11950	189297	3180186	0.4	118
Ba	40	998	<0.01	<2	56	947	< 0.2	95
Bi	17	416	<0.01	<2	22	373	<1	90
Ca	620	15351	<0.01	<2	948	15924	< 0.01	104
Cr	< 438	< 10845	<2.20	<493	<675	<11338		
Fe	7368	182352	1.25	279	11550	194042	0.1	107
Mg	299	7412	<0.22	<49	362	6077	< 0.008	83
Mn	12529	310102	0.07	16	18083	303790	0.01	98
Na(b)	72466	1973720	7968	1784922	26194	440067	74(c)	87(c)
P	4154	102807	77.8	17433	3166	53185	25	69
Si	11182	276755	4.40	986	16510	277373	0.4	101
Sr	21	515	0.01	2	31	516	0.5	101
U	46118	1141424	60.2	13482	60255	1012285	1	90
Zn	< 22	< 542	<0.11	<25	<33.74	<567		
Zr	64126	1587109	0.95	212	87225	1465380	0.01	92

(a) The value for % removed was determined by dividing the quantity in the wash solution by the sum of the quantities in the wash solution plus the washed solids.

(b) The value for Na in the untreated solids has been adjusted for the NaOH added in the sampling process.

(c) The value for Na has been adjusted for the 515200 µg Na added as NaOH in the washing process.

Table 5.5. Results of Dilute Hydroxide Washing of C-102 Sludge Normalized to the Iron Concentrations

	g/g Fe		
Component	Untreated Sample	Washed Solids	Removed %
Al	14.87	16.39	-10
Ba	0.0055	0.0049	11
Bi	0.0023	0.0019	16
Ca	0.084	0.082	3
Cr	< 0.06	< 0.06	--
Fe	1.00	1.00	0
Mg	0.041	0.031	23
Mn	1.70	1.57	8
Na	10.82	2.27	79
P	0.56	0.27	51
Si	1.52	1.43	6
Sr	0.0028	0.0027	6
U	6.26	5.22	17
Zn	< 0.003	< 0.003	--
Zr	8.70	7.55	13

Table 5.6 presents the concentrations of some important radioactive C-102 sludge components in the washed solids and in the dilute hydroxide wash solution. The table also lists the total activity of each component in each processing stream and the amount of each component removed by the dilute hydroxide washing (as determined by the summation method). Since Tc analyses on previous sludge samples examined at LANL has always yielded results below the detection limit and because of budget cuts in this program, Tc analyses were not performed for these samples. Cobalt-60 was below the detection limit in all solids and the wash solution. A ^{90}Sr analysis was performed, but because of poor data quality, no Sr results were reported. Normally the analyses would have been repeated, but because of the budget cut in this program, the analysis was not redone. As expected, little if any TRUs were removed during the dilute-hydroxide washing process. A significant portion (35%) of the ^{137}Cs was removed from the C-102 sludge solids during the dilute hydroxide wash. No other radioactive components were removed by the dilute hydroxide wash. The mass recovery was reasonable for ^{241}Am and ^{137}Cs, but was somewhat low for Pu.

Table 5.6. Results of Dilute Hydroxide Washing of C-102 Sludge: Radioactive Components

	Untreated Sample		Wash Solution		Washed Solids		Amount Removed,	Mass
Component	µCi/g	µCi	µCi/mL	µCi	µCi/g	µCi	%	Recovery
Pu Alpha(a)	3.01E+00	5.09E+01	< 2.35E-04	<5.27E-02	1.99E+00	3.36E+01	< 0.2	66
^{241}Am	4.57E+00	7.71E+01	< 1.44E-04	< 3.23E-0	3.91E+00	6.60E+01	<0.05	86
^{137}Cs	2.40E+01	4.06E+02	5.99E-01	1.34E+02	1.44E+01	2.43E+02	35	93

(a) Sum of ^{238}Pu, ^{239}Pu, and ^{240}Pu activity.

If the dilute hydroxide wash solution were converted directly to a glass LLW form (20 wt% Na_2O, 2.7 MT/m^3), the resulting waste would contain < 8 nCi TRU/g and 30 Ci ^{137}Cs/m^3. Since the ^{90}Sr data were not reliable, an assessment of this radionuclide could not be done. Nevertheless, it is likely that the waste would meet the NRC Class C classification.

5.2.2 Caustic Leaching of C-102 Sludge

Table 5.7 summarizes the amounts of Al, Na, P, and Si removed from the washed C-102 solids under the various leaching conditions (for this particular waste, Cr was below the analytical detection limits). Table 5.8 presents the actual concentrations of the various components in the leaching and washing solutions and in the leached solids. The mass recovery for each component is presented in Table 5.8 as well. Again, the data were analyzed using both the summation method and the Fe normalization method. Agreement between these two methods is generally good; one notable exception is Al removal at 1 M NaOH and 60°C. Also, the Si values are erratic. There appears to be considerable uncertainty associated with the Si analysis of the solids. No Si was detected in the leachates, so it can be concluded that Si removal was very low. The mass recoveries for many of the other components (e.g., Ca and Mg) were also poor; the results for these components should be viewed with caution. On the other hand, the mass recoveries for the major components of concern (Al and P) are reasonable.

For the C-102 sludge, there was clearly a benefit in increasing the NaOH concentration from 1 to 3 M. Leaching with 1 M NaOH removed ~20 to 30% of the Al from the dilute hydroxide-washed solids while leaching with 3 M NaOH removed ~95% of the Al. As expected, the Al concentration generally increased with time (Table 5.8). This is especially evident for samples leached with 3 M NaOH. For example, leaching with 3 M NaOH at 60°C removed 70% of the Al after 5 h, but leaching for an additional 67 h removed another 25%. Increasing the temperature from 60 to 100°C did not result in significant improvement in Al removal from the C-102 sludge. Indeed, leaching the C-102 sludge with 1 M NaOH at 100°C was not as effective at removing Al as leaching with 3 M NaOH at 60°C.

The amounts of Na in the leached solids were generally about the same as that in the washed sludge solids, indicating that caustic leaching did not result in any additional Na removal. Approximately 25% of the Na remained in the residual sludge after dilute caustic washing and caustic leaching (Table 5.7.). It was estimated that ~4.5% of the Na in the residue from the 1 M NaOH leaches and ~10% of the Na in the residue from the 3 M NaOH leaches was attributable to Na in the interstitial liquid.

Caustic leaching removed ~50% of the P from the dilute hydroxide-washed C-102 solids using any of the caustic leaching conditions examined. Slightly more P was removed with 3 M NaOH than with 1 M NaOH at the same temperature. Thus, when coupled with the 25% removed by dilute hydroxide washing (Table 5.4), approximately 60% of the P was removed from the C-102 sludge sample. The solution data (Table 5.8) indicate that phosphate metathesis increased slightly with time.

Table 5.9 summarizes the removal of TRU (total alpha) and ^{137}Cs from the washed C-102 solids under the various leaching conditions. Table 5.10 presents the actual concentrations of the various radioactive components in the leaching and washing solutions and in the leached solids. The mass recovery for each component is presented in Table 5.10 as well. As was the case with the dilute hydroxide wash, little TRU was removed during the caustic leaching steps. Removal of the ^{137}Cs from dilute hydroxide-washed C-102 solids during caustic leaching varied from ~25% for 1 M NaOH at 60°C to ~60% at the 3 M NaOH and 100°C. Estimating the radionuclide content of LLW glass (20 wt% Na_2O; 2.7 MT/m^3) produced from the combined wash and leach solutions indicates that the TRU content would be < 85 nCi/g, and the maximum ^{137}Cs content would be ~60 Ci/m^3.

Table 5.11 shows the concentration of waste oxides in the dilute hydroxide-washed and in the leached(a) C-102 solids and the concentrations of waste-derived components that would result from vitrifying these solids at 25 wt% WOL, excluding oxides of Na and Si. The oxide concentrations in the washed and leached solids were determined by converting the elemental concentrations listed in Tables 5.4 (washed solids) and 5.8 (leached solids) to the corresponding oxide concentrations. The oxide concentrations in the IHLW were determined according to equation 2.1.

Assuming upper limits of 15, 0.5, and 3.0 wt% for Al, Cr, and P oxides, respectively, in the IHLW, a 25 wt% WOL could be achieved with the C-102 solids after either simple washing or caustic leaching. The Cr and P oxide concentrations in the IHLW from the washed C-102 solids are well within the 0.5 and 3.0 wt% limits, but the Al oxide content is just within the 15 wt% limit. Again, the caustic leached solids can be easily immobilized at 25 wt% WOL under the assumptions used here. As calculated by equation 2.3, the quantity of IHLW after dilute hydroxide washing would be 2.41 g IHLW/g dry-washed solids. Upon caustic leaching, this quantity would decrease to 0.96. Thus, caustic leaching would result in an ~60% decrease in the IHLW glass volume for the C-102 waste compared to dilute hydroxide washing.

Table 5.7. Caustic Leaching Results for Key Nonradioactive C-102 Sludge Components: Amounts Removed from the Dilute Hydroxide-Washed Solids

Component	1 M NaOH		3 M NaOH	
	Summation Method,%(a)	Fe Normalization Method, %(b)	Summation Method,%(a)	Fe Normalization Method, %(b)
	Temperature = 60°C			
Al	27(27)	44	95(95)	94
Na(c)	0(74)	9	7(76)	9
P	47(60)	34	55(66)	42
Si	1(1)	-29	2(2)	-52
	Temperature = 100°C			
Al	20(20)	26	95(94)	94
Na(c)	13(77)	19	1(74)	8
P	41(56)	43	48(61)	36
Si	1(1)	-8	3(3)	42

(a) Value obtained by summing the quantity of each component found in the leaching and washing solutions and dividing by the total found in the leaching and washing solutions plus the residual solids. Numbers in parentheses are cumulative removals achieved by dilute hydroxide washing and caustic leaching.

(b) Value obtained by normalizing the concentrations of each component to the Fe concentration and comparing the normalized values in the caustic-leached solids to those for the dilute hydroxide-washed solids.

(c) Because of the amount of Na added as NaOH during the leaching procedure, the Na removal was based on the ratio of the solids before and after caustic leaching.

(a) For this analysis, we considered only the case where the solids were leached with 3 M NaOH for 72 h at 95°C.

Table 5.8. Concentrations of Key C-102 Sludge Components in Caustic Leaching Solutions and in the Caustic Leached Solids

Component	Washed Solids		5 h	72 h		Final Wash Solution		Leached Solids		Mass
	µg/g	µg[a]	µg/mL	µg/mL	µg[b]	µg/mL	µg[c]	µg/g	µg[d]	Recovery, %
				1 M NaOH, 60°C						
	Wt. Washed Solids in Sample, g: 3.23					Vol. Leach Soln., mL: 18.4				
	Wt. Leached Solids, g: 2.68					Vol. Final Wash Soln., mL: 30.3				
Al	189297	611429	5185	6273	115419	745	22344	139345	373891	84
Ba	56	182	< 0.08	< 0.08	< 1.48	< 0.01	<0.26	102	273	150
Bi	22	72	< 0.10	< 0.10	< 1.85	< 0.01	<0.33	30	81	113
Ca	948	3062	< 0.09	< 0.09	< 1.66	< 0.01	<0.30	1942	5210	170
Cr	<675	<2180	< 20	< 20	< 369	< 2	< 66	<627	<1683	N/A
Fe	11550	37307	< 2.0	< 2.0	< 36.9	< 0.2	< 6.6	15255	40931	110
Mg	362	1168	< 2.0	< 2.0	< 36.9	< 0.2	< 6.6	959	2574	220
Mn	18083	58407	< 0.20	< 0.20	< 3.69	< 0.02	<0.66	24912	66844	114
Na	26194	84608	23800	26270	483360	3771	113124	31318	84033	N/A
P	3166	10225	216	313	5752	28	833	2762	7410	137
Si	16510	53328	< 40	< 40	< 739	< 4	< 132	28151	75535	142
Sr	31	99	<0.10	<0.10	<1.85	<0.01	<0.33	45	122	123
U	60255	194624	19	15	285	2	54	69404	186225	96
Zn	< 34	< 109	< 1.0	< 1.0	< 18.5	< 0.1	< 3.3	54	144	132
Zr	87225	281737	< 2.0	< 2.0	< 36.9	< 0.2	< 6.6	106422	285551	101
				3 M NaOH, 60°C						
	Wt. Washed Solids in Sample, g: 3.28					Vol. Leach Soln., mL: 39.1				
	Wt. Leached Solids, g: 1.39					Vol. Final Wash Soln., mL: 30.2				
Al	189297	620894	12030	16260	635766	2066	62393	26042	36321	118
Ba	56	185	< 0.08	< 0.08	< 3.13	< 0.01	< 0.24	267	373	202

(a) Mass of each component in the aliquot treated under the indicated conditions. This was determined from analysis of the washed solids (aliquot C-102 A0).

(b) Mass of each component in the caustic leaching solution.

(c) Mass of each component in the final washing solution.

(d) Mass of each component in the leached solids.

Component	Washed Solids µg/g	Washed Solids µg(a)	5 h µg/mL	72 h µg/mL	72 h µg(b)	Final Wash Solution µg/mL	Final Wash Solution µg(c)	Leached Solids µg/g	Leached Solids µg(d)	Mass Recovery, %
Bi	22	73	< 0.10	< 0.10	< 3.91	< 0.01	< 0.30	40	56	77
Ca	948	3109	< 0.09	< 0.09	< 3.52	< 0.01	< 0.27	7208	10053	323
Cr	<675	<2214	<20	<20	<782	<2	<60	<712	<992	N/A
Fe	11550	37884	< 2.0	< 2.0	< 78.2	< 0.2	< 6.0	27903	38916	103
Mg	362	1186	< 2.0	< 2.0	< 78.2	< 0.2	< 6.0	5365	7483	631
Mn	18083	59311	< 0.20	< 0.20	< 7.82	< 0.02	< 0.60	36893	51455	87
Na	26194	85918	70420	72760	2844916	8760	264552	57208	79788	N/A
P	3166	10384	127	179	7003	16	492	4397	6133	131
Si	16510	54154	<40	<40	<1564	<4	<121	60356	84179	155
Sr	31	101	<0.10	<0.10	<3.91	<0.01	<0.30	142	197	196
U	60255	197637	24	19	740	2	73	103875	144875	74
Zn	< 34	< 111	1.1	1.1	43.4	< 0.1	< 3.0	78	109	141
Zr	87225	286098	< 2.0	< 2.0	< 78.2	< 0.2	< 6.0	149673	208749	73

1 M NaOH, 100°C

Wt. Washed Solids in Sample, g: 3.54
Wt. Leached Solids, g: 2.94
Vol. Leach Soln., mL: 12.3
Vol. Final Wash Soln., mL: 30

Al	189297	670111	8524	9406	115694	535	16059	180464	530202	99
Ba	56	199	< 0.08	< 0.08	< 0.98	< 0.01	< 0.24	64	189	95
Bi	22	78	< 0.10	< 0.10	< 1.23	< 0.01	< 0.30	20	58	74
Ca	948	3355	< 0.09	< 0.09	< 1.11	< 0.01	< 0.27	1675	4923	147
Cr	< 675	< 2389	< 20	< 20	< 246	< 2	< 60	< 662	< 1946	N/A
Fe	11550	40888	< 2.0	< 2.0	< 24.6	< 0.2	< 6.0	14901	43778	107
Mg	362	1280	< 2.0	< 2.0	< 24.6	< 0.2	< 6.0	517	1519	119
Mn	18083	64013	< 0.20	< 0.20	< 2.46	< 0.02	< 0.60	19298	56698	89
Na	26194	92729	22300	25240	310452	3600	108000	27424	80571	N/A
P	3166	11207	203	301	3700	35	1048	2315	6800	103
Si	16510	58447	< 40	< 40	< 492	< 4	< 120	22980	67516	116
Sr	31	109	< 0.10	< 0.10	< 1.23	< 0.01	< 0.30	41	120	110
U	60255	213303	15	13	160	1	38	48985	143917	68
Zn	< 34	< 119	< 1.0	< 1.0	< 12.3	< 0.1	< 3.0	< 33	< 97	N/A
Zr	87225	308776	< 2.0	< 2.0	< 24.6	< 0.2	< 6.0	73212	215097	70

Component	Washed Solids		5 h	72 h		Final Wash Solution		Leached Solids		Mass
	µg/g	µg$^{(a)}$	µg/mL	µg/mL	µg$^{(b)}$	µg/mL	µg$^{(c)}$	µg/g	µg$^{(d)}$	Recovery, %
				3 M NaOH, 100°C						
		Wt. Washed Solids in Sample, g: 3.01				Vol. Leach Soln., mL: 17.4				
		Wt. Leached Solids, g: 1.27				Vol. Final Wash Soln., mL: 30.1				
Al	189297	569783	24160	30620	532788	3356	101026	27600	34949	117
Ba	56	170	<0.08	<0.08	<1.39	<0.01	<0.24	194	246	145
Bi	22	67	<0.10	<0.10	<1.74	<0.01	<0.30	51	64	96
Ca	948	2853	<0.09	<0.09	<1.57	<0.01	<0.27	4571	5788	203
Cr	< 675	< 2031	<20	<20	<348	<2	<60	< 628	< 795	N/A
Fe	11550	34766	< 2.0	< 2.0	< 34.8	< 0.2	< 6.0	28482	36066	104
Mg	362	1089	< 2.0	< 2.0	< 34.8	< 0.2	< 6.0	2544	3221	296
Mn	18083	54429	<0.20	<0.20	<3.48	<0.02	<0.69	48725	61701	113
Na	26194	78845	71230	63470	1104378	7122	214375	59337	75138	N/A
P	3166	9529	242	294	5116	21	619	4957	6277	126
Si	16510	49696	<40	<40	<696	<4	<121	23766	30095	61
Sr	31	92	<0.10	<0.10	<1.74	<0.01	<0.30	85	108	117
U	60255	181368	25	18	307	2	57	128084	162193	90
Zn	< 34	< 102	3.3	2.0	< 35.1	< 0.1	< 3.0	207	262	258
Zr	87225	262547	< 2.0	< 2.0	< 34.8	< 0.2	< 6.0	165107	209075	80

(a) Mass of each component in the aliquot treated under the indicated conditions. This was determined from analysis of the washed solids (aliquot C-102 A0).

(b) Mass of each component in the caustic leaching solution.

(c) Mass of each component in the final washing solution.

(d) Mass of each component in the leached solids.

Table 5.9. Caustic Leaching Results for Key Radioactive C-102 Sludge Components

	Removed, %[a]	
	Temperature = 60°C	
Component	1 M NaOH	3 M NaOH
Total Alpha	<1(<1)	1(1)
^{137}Cs	24(51)	50(67)

	Temperature = 100°C	
Component	1 M NaOH	3 M NaOH
Total Alpha	2(2)	<1(<1)
^{137}Cs	44(64)	59(73)

(a) Amount of material removed from the dilute hydroxide-washed solids; the values were obtained by the summation method (see Table 5.7, footnote a)

Table 5.10. Concentrations of Key Radioactive C-102 Sludge Components in Caustic Leaching Solutions and in the Caustic Leached Solids

Component	Washed Solids		Leach Solution		Final Wash Solution		Leached Solids		Mass
	µCi/g	µCi	µCi/mL	µCi	µCi/mL	µCi	µCi/g	µCi	Recovery, %
				1 M NaOH, 60°C					
	Wt. Washed Solids in Sample, g:		3.23		Vol. Leach Soln., mL:		18.4		
	Wt. Leached Solids, g:		2.68		Vol. Final Wash Soln., mL:		30.3		
Total Alpha	5.90E+00	1.90E+01	<3.45E-03	<6.38E-02	<3.80E-04	<1.14E-02	7.89E+00	2.12E+01	112
Pu Alpha	1.99E+00	6.42E+00	<2.14E-03	<3.95E-02	<2.35E-04	<7.06E-03	2.20E+00	5.89E+00	93
^{241}Am (gamma)	3.91E+00	1.26E+01	<1.31E-03	<2.42E-02	<1.44E-04	<4.32E-03	5.70E+00	1.53E+01	121
^{137}Cs	1.44E+01	4.64E+01	4.28E-01	7.91E+00	1.06E-01	3.18E+00	1.30E+01	3.48E+01	99
				3 M NaOH, 60°C					
	Wt. Washed Solids in Sample, g:		3.28		Vol. Leach Soln., mL:		39.1		
	Wt. Leached Solids, g:		1.39		Vol. Final Wash Soln., mL:		30.2		
Total Alpha	5.90E+00	1.93E+01	<3.45E-03	<1.35E-01	<3.80E-04	<1.15E-02	1.52E+01	2.12E+01	111
Pu Alpha	1.99E+00	6.52E+00	<2.14E-03	<8.38E-02	<2.35E-04	<7.10E-03	7.20E+00	1.00E+01	155
^{241}Am (gamma)	3.91E+00	1.28E+01	<1.31E-03	<5.13E-02	<1.44E-04	<4.35E-03	8.02E+00	1.12E+01	88
^{137}Cs	1.44E+01	4.71E+01	5.64E-01	2.21E+01	6.65E-02	2.00E+00	1.74E+01	2.43E+01	103
				1 M NaOH, 100°C					
	Wt. Washed Solids in Sample, g:		3.54		Vol. Leach Soln., mL:		12.3		
	Wt. Leached Solids, g:		2.94		Vol. Final Wash Soln., mL:		30		
Total Alpha	5.90E+00	2.09E+01	<1.04E-02	<1.27E-01	<3.80E-04	<1.14E-02	2.91E+00	8.55E+00	42
Pu Alpha	1.99E+00	7.03E+00	<6.42E-03	<7.87E-02	<2.35E-04	<7.05E-03	1.59E+00	4.67E+00	68
^{241}Am (gamma)	3.91E+00	1.38E+01	<3.93E-03	<4.82E-02	<1.44E-04	<4.32E-03	1.32E+00	3.88E+00	28
^{137}Cs	1.44E+01	5.09E+01	9.18E-01	1.13E+01	1.54E-01	4.62E+00	6.95E+00	2.04E+01	71
				3 M NaOH, 100°C					
	Wt. Washed Solids in Sample, g:		3.01		Vol. Leach Soln., mL:		17.4		
	Wt. Leached Solids, g:		1.27		Vol. Final Wash Soln., mL:		30.1		
Total Alpha	5.90E+00	1.77E+01	<3.45E-03	<6.01E-02	<3.80E-04	< 1.14E-02	1.77E+01	2.24E+01	126
Pu Alpha	1.99E+00	5.98E+00	<2.14E-03	<3.73E-02	<2.35E-04	< 7.09E-03	8.99E+00	1.14E+01	191
^{241}Am (gamma)	3.91E+00	1.18E+01	<1.31E-03	<2.28E-02	<1.44E-04	< 4.34E-03	8.67E+00	1.10E+01	94
^{137}Cs	1.44E+01	4.33E+01	1.00E+00	1.74E+01	1.23E-01	3.69E+00	1.15E+01	1.46E+01	83

Table 5.11. Estimated Concentrations of Waste-Derived Components in the IHLW Glass From C-102 Waste

	Washed Solids		Leached Solids (3 M NaOH/100°C/168h)	
Component	g oxide/g solids	Conc. in IHLW, wt%[(a)]	g oxide/g solids	Conc. in IHLW, wt%[(a)]
Al_2O_3	0.3578	14.8	0.0522	2.3
BaO	0.0001	0.00	0.0002	0.0
Bi_2O_3	0.0000	0.00	0.0001	0.0
CaO	0.0013	0.1	0.0064	0.3
Cr_2O_3	0.0010	0.0	0.0009	0.0
Fe_2O_3	0.0165	0.7	0.0407	1.8
MgO	0.0006	0.0	0.0042	0.2
MnO_2	0.0286	1.2	0.0771	3.4
Na_2O	0.0353	1.5	0.0800	3.5
P_2O_5	0.0073	0.3	0.0114	0.5
SiO_2	0.0353	1.5	0.0509	2.2
SrO	0.0000	0.00	0.0001	0.0
UO_3	0.0724	3.0	0.1540	6.7
ZnO	0.0000	0.00	0.0003	0.0
ZrO_2	0.1178	4.9	0.2231	9.8

(a) Based on 25 wt% waste oxide loading (excluding Na_2O and SiO_2).

6.0 Tank S-101 Test

This section presents selected results from a test conducted at the Oak Ridge National Laboratory (ORNL) using a Tank S-101 sample. For further details regarding this test, see Hunt et al. (1998).

6.1 S-101 Experimental

The S-101 sludge sample used in this test was shipped by the Hanford 222-S laboratory to ORNL in March 1997. The 222-S laboratory number for this sample was S96T005965, and the jar number was 11720. This sample was a composite made from segments 5 through 9 of core number 137.

Initial Wash: A 110.61-g portion of the S-101 sludge sample was transferred to a 250-mL centrifuge bottle with the assistance of 103 g of 0.01 M NaOH/0.01 M $NaNO_2$. The mixture was agitated for 24 h at ambient temperature using an end-over-end mixer. The slurry was centrifuged at 4,500 G, the liquid was decanted, and the wet solids were then weighed. Three additional washes were conducted at ambient temperature, followed by two washes at 97°C as described in Table 6.1. The conductance and ^{137}Cs activity of each of these wash solutions are provided in Table 6.1. As can be seen from the table, the mass change between the fifth and sixth washes was minimal, so it was concluded that additional washes would have little effect.

Division of the Washed Solids: At this point, the washed S-101 sludge was diluted with 0.01 M NaOH/0.01 M $NaNO_2$, and the slurry was homogenized using a mechanical stirrer. While the slurry was mixed, 20 homogeneous samples were transferred into preweighed centrifuge tubes. Each tube was centrifuged, and the liquid was decanted. Table 6.2 lists the weights of each washed sludge-solids sample used. A 0.9245-g aliquot from one of the centrifuge tubes was transferred to a preweighed crucible and dried to a constant weight at 104°C. The final weight of the dried sludge was 0.2516 g, indicating the water content in this sample to be 72.8%. It was assumed that the each aliquot of washed sludge contained the same percentage of water. Therefore, this result was used to estimate the dry weight of each of the washed sludge samples, as shown in Table 6.2.

The decanted liquids from the final transfer steps were combined into a single 250-mL centrifuge tube. Then 10% of the decanted liquid from each of the wash steps and the transfer wash was removed to make a composite wash solution. This composite wash solution was filtered through a 0.45-μm syringe filter, then analyzed.

The density of the composite wash solution, the total volume of the wash solution, and the dry weight of the washed sludge sample were used to determine that the original sludge sample contained 30 wt % water-soluble solids, 21 wt % water-insoluble solids, and 49 wt % water. An earlier test at PNNL determined that the S-101 sludge sample contained 40 wt % water-soluble solids, 24 wt % water-insoluble solids, and 36 wt % water (Lumetta et al. 1997). These results are in good agreement. The ORNL result indicates that 59% of the S-101 waste solids are water-soluble, while the corresponding value from the PNNL test is 62%.

Table 6.1. Summary of Dilute-Hydroxide Washes For S-101 Sludge

Wash #	Temperature	Duration, h	Wt. Solution Added, g[(a)]	Mixing Method	Wt. of Wet Solids, g[(b)]	^{137}Cs in Wash Solution, µCi	Cumulative ^{137}Cs Removed, %	Solution Conductivity, millimho
1	Ambient	24	102.98	End over end	91.58	7.99E+03	62	625
2	Ambient	16	102.28	End over end	83.09	3.21E+03	87	274
3	Ambient	143	100.43	End over end	78.85	7.26E+02	93	122
4	Ambient	21	103.21	End over end	75.04	3.05E+02	95	55
5	97°C	> 1	120.73	Rocked	68.20	1.97E+02	97	26
6	97°C	> 1	119.10	Magnetic stir bar	66.78	1.28E+02	98	17

(a) The wash solution consisted of 0.01 M NaOH/0.01 M $NaNO_2$.

(b) Weight of the wet S-101 solids after decanting the washing liquid.

Table 6.2. Weights of Treated S-101 Sludge Samples

	Washed Solids		Leached Solids	
Sample ID	Measured Wet Wt., g	Estimated Dry Wt., g	Measured Wet Wt., g	Measured Dry Wt., g
S101-1-70-5	4.524	1.231	5.723	1.292
S101-1-70-24	4.537	1.236	4.907	(a)
S101-1-70-72	4.605	1.254	3.829	1.069
S101-1-70-168	4.980	1.356	3.809	1.015
S101-1-95-5	4.655	1.267	3.968	1.067
S101-1-95-24	4.692	1.277	2.920	1.072
S101-1-95-72	4.730	1.288	2.657	0.931
S101-1-95-168	5.082	1.384	2.303	0.842
S101-3-70-5	4.747	1.292	5.928	1.441
S101-3-70-24	4.771	1.299	5.825	1.440
S101-3-70-72	4.956	1.350	4.748	1.309
S101-3-70-168	6.827	1.859	5.621	1.311
S101-3-95-5	4.368	1.189	2.822	0.974
S101-3-95-24	4.439	1.209	1.898	0.801
S101-3-95-72	4.786	1.302	1.834	0.774
S101-3-95-168	4.996	1.359	1.431	0.576

(a) It is suspected that an error occurred during the drying procedure. The actual dried weight is probably between 1.20 and 1.25 g.

Leaching: The caustic leaching of the washed S-101 solids was conducted in a manner somewhat different from the other sludge samples in this report. In the other tests, a single aliquot was subjected to a given NaOH concentration and temperature, with the leachate solution being sampled at specific time intervals. In this case, individual aliquots were used for each time interval. Table 6.3 summarizes the leaching conditions for each aliquot of the washed S-101 sludge. Thermodynamic calculations were used to determine the amount of sodium hydroxide to be used in each test (Beahm et al. 1998). These calculations determined the amount of NaOH solution needed to yield a solution saturated in aluminate. Based on these calculations, the determined leaching conditions were as follows: 1) 20.0 mL of 1 M NaOH per gram of initial sludge solids at 70°C, 2) 9.9 mL of 1 M NaOH per gram of initial sludge solids at 100°C, 3) 5.7 mL of 3 M NaOH per gram of initial sludge solids at 70°C, and 4) 3.0 mL of 3 M NaOH per gram of initial sludge solids at 100°C. The calculated amounts of sodium hydroxide were increased by 50% in the actual experiments to compensate for uncertainties associated with the calculations. After each leaching step was completed, the sample was centrifuged for 3.5 min. The centrifuged liquid was then immediately decanted. The liquid was kept at the leaching temperature during sampling. The leached solids were washed three times with 25 mL of 0.01 M $NaNO_2$.

Table 6.3. Leaching Conditions for Each Aliquot of Washed S-101 Sludge

Sample ID	[NaOH], M[a]	Temp., °C	Duration, h	Wt. Leaching Solution Added, g	Liquid/Solids (mL/g)
S101-1-70-5	1	70	5	175.37	30
S101-1-70-24	1	70	24	176.00	30
S101-1-70-72	1	70	72	178.32	30
S101-1-70-168	1	70	168	193.08	30
S101-1-95-5	1	95	5	89.53	14.9
S101-1-95-24	1	95	24	90.01	14.9
S101-1-95-72	1	95	72	90.81	14.9
S101-1-95-168	1	95	168	97.40	14.9
S101-3-70-5	3	70	5	56.09	8.5
S101-3-70-24	3	70	24	56.23	8.5
S101-3-70-72	3	70	72	58.50	8.5
S101-3-70-168	3	70	168	80.28	8.5
S101-3-95-5	3	95	5	27.40	4.5
S101-3-95-24	3	95	24	27.86	4.5
S101-3-95-72	3	95	72	29.84	4.5
S101-3-95-168	3	95	168	31.35	4.5

(a) Initial NaOH concentration.

6.2 6.2 S-101 Results

The following sections describe dilute hydroxide washing and caustic leaching of S-101 sludge.

6.2.1 Dilute Hydroxide Washing of S-101 Sludge

Table 6.4 presents the concentrations of some important nonradioactive S-101 sludge components in the dilute hydroxide wash solution and in the washed solids. The table also lists the total mass of each component present in each processing stream (wash solution or washed solids) and the amount of each component removed by the dilute hydroxide washing in terms of percent. The data indicated that 11% of the Al, 46% of the Cr, and 98% of the Na were removed by washing the S-101 sample with dilute NaOH. These values agree well with those obtained in a previous S-101 sludge washing test (Table 6.5). The data for the P is somewhat difficult to interpret. The wash solution and washed solids were analyzed for phosphate ion by ion chromatography (IC) and for elemental phosphorus by inductively-coupled plasma/mass spectrometry (ICP/MS). The data from the two methods do not agree very well. For example, ICP/MS indicates the P concentration in the washed solids was 1,690 µg/g, whereas the IC analysis indicated the P concentration due to phosphate ion was 427 µg/g. The IC data indicated that 80% of the phosphate was removed whereas the ICP/MS data indicated that 55% of the P was removed. The former value is consistent with what was observed earlier at PNNL (Table 6.5), where the total elemental P was measured by ICP/AES. It is possible that a fraction of the P in the washed solids is in a form other than phosphate. Alternatively, some analytical error could have occurred in the analysis.

Table 6.4 also presents the concentration of the nonradioactive components in the as-received S-101 sample. These values were determined by summing the amount of each component in the wash solution and the washed solids and dividing by the total amount of sample treated (110.61g). The resulting concentration values are on a wet-weight basis; thus direct comparison to values obtained in previous S-101 sludge washing tests cannot be made. However, if normalized to the Fe concentration, the concentrations for Al, Cr, Na, and P agree reasonably well with the previous study. The concentrations found here were Al (62.7 g/g Fe), Cr (3.1 g/g Fe), Na (84.0 g/g Fe), and P (2.0 g/g Fe); the corresponding values found by Lumetta et al. (1997) were Al (68.4 g/g Fe), Cr (3.3 g/g Fe), Na (83.7 g/g Fe), and P (1.1 g/g Fe).

Table 6.4. Results of Dilute Hydroxide Washing of S-101 Sludge: Nonradioactive Components

Component	Untreated Sample, μg/g(a)	Wash Solution		Washed Solids		Amount Removed, %
		μg/mL	μg	μg/g	μg	
Ag	2.15E+00	2.00E-02	1.63E+01	2.49E+00	2.22E+02	7
Al	9.41E+04	1.40E+03	1.14E+06	1.04E+05	9.27E+06	11
Ba	3.36E+01	1.00E-02	8.13E+00	4.16E+01	3.71E+03	0.2
Ca	5.26E+02	< 3.20E-02	< 2.60E+01	6.53E+02	5.82E+04	< 0.04
Cr	4.67E+03	2.94E+02	2.39E+05	3.11E+03	2.77E+05	46
Cu	5.38E+01	1.34E-01	1.09E+02	6.55E+02	5.84E+03	2
Fe	1.50E+03	1.67E-01	1.36E+02	1.86E+03	1.66E+05	0
K	3.45E+03	4.78E+02	3.88E+05	< 4.04E+01	< 3.60E+03	> 99
Mg	1.07E+01	< 3.60E-02	< 2.90E+01	1.30E+01	1.16E+03	2
Mn	2.01E+03	< 1.20E-03	< 9.80E-01	2.49E+03	2.22E+05	0
Na	1.26E+05	1.62E+04(b)	1.32E+07	3.21E+03	2.86E+05	98
Ni	1.11E+02	< 8.00E-02	< 6.50E+01	1.37E+02	1.22E+04	1
P	3.02E+03	2.25E+02	1.83E+05	1.69E+03	1.51E+05	55
PO_4	5.21E+03	5.64E+02	4.59E+05	1.31E+03	1.17E+05	80
Sr	3.04E+02	< 1.10E-02	< 8.94E+00	3.77E+02	3.36E+04	< 0.03
SO_4	8.81E+03	1.12E+03	9.10E+05	7.27E+02	6.48E+04	93
Th	2.59E+01	7.88E-01	6.40E+02	2.49E+01	2.22E+03	22
U	6.50E+03	< 1.60E-01	< 1.30E+02	8.07E+03	7.19E+05	< 0.02
V	9.45E+00	4.88E-01	3.97E+02	7.27E+00	6.48E+02	38
Zn	1.91E+02	3.52E-01	2.86E+02	2.33E+02	2.08E+04	1

(a) Determined by the summation method; values are on a wet-weight basis.
(b) The value for Na has been adjusted for the Na added as NaOH and $NaNO_2$ in the washing process.

The conductance and ^{137}Cs activity of each of the decanted wash solutions were measured, and the results are presented in Table 6.1. As expected, the largest changes in conductance and ^{137}Cs activity occurred between the first and second washes, and the conductance and ^{137}Cs activity decreased as the weight of the washed solids decreased. In addition, changes in the conductance and ^{137}Cs activity decreased as the weight changes became smaller. Therefore, conductance and ^{137}Cs activity of the wash solutions can likely be used to determine when additional sludge washing steps will no longer be effective.

Table 6.5. Dilute Hydroxide Washing of S-101 Waste: Comparison to Previous Results

	Removed, %	
Component	This Study	Lumetta et al. 1997
Al	11	12
Cr	46	44
Na	98	97
P	55	87
^{137}Cs	98	97
^{99}Tc	> 99	97

Table 6.6 presents the concentrations of some important radioactive S-101 sludge components in the washed solids and in the dilute hydroxide wash solution. The table also lists the total activity of each component present in each processing stream and the amount of each component removed by the dilute hydroxide washing (as determined by the summation method).

Table 6.6. Results of Dilute Hydroxide Washing of S-101 Sludge: Radioactive Components

Component	Untreated Sample, µCi/g(a)	Wash Solution		Washed Solids		Amount Removed, %
		µCi/mL	µCi	µCi/g	µCi	
Total Alpha	2.20E+00	< 7.02E-05	< 5.70E-02	2.73E-01	2.43E+01	< 0.2
Total Beta	6.91E+02	1.70E+01	1.38E+04	7.02E+02	6.26E+04	18
^{241}Am	1.22E-01	< 2.32E+00	< 1.89E-03	1.51E-01	1.35E+01	< 0.01
^{244}Cm	0	(d)	(d)	5.72E-03	5.10E-01	--
^{60}Co	1.00E-02	< 4.05E-01	< 3.24E-04	1.24E-02	1.11E+00	< 0.03
^{137}Cs	1.12E+02	1.49E+01	1.21E+04	3.24E+00	2.89E+02	98
^{154}Eu	1.09E-01	< 1.16E+00	< 9.45E-04	1.35E-01	1.20E+01	< 0.01
^{155}Eu	4.78E-02	< 1.24E+00	< 9.99E-04	5.94E-02	5.29E+00	< 0.02
Pu(b)	1.96E-01	< 7.02E-05	< 5.70E-02	2.43E-01	2.17E+01	< 0.3
^{90}Sr	2.39E+02	1.89E-03	1.54E+00	2.97E+02	2.65E+04	0
^{99}Tc	1.25E-01	1.68E-02	1.37E+01	< 1.69E-03	< 1.51E-01	> 99

(a) Determined by the summation method; values are on a wet-weight basis.
(b) 2.3% ^{238}Pu and 97.8% $^{239+240}$Pu

The TRU behavior is reflected in the total alpha activity data. As expected, only small amounts of TRUs were removed during the dilute hydroxide washing process. A measurable quantity of ^{90}Sr was removed during the dilute hydroxide washing, but this was an insignificant fraction of the ^{90}Sr in the sludge. Nearly all (98%) of the ^{137}Cs was removed from the S-101 sample during the dilute hydroxide wash. Likewise, ^{99}Tc was largely removed, which would be consistent with the presence of this element as a soluble species such as pertechnetate. Again, these results were similar to previous results (Table 6.5).

If the dilute hydroxide wash solution were converted directly to a glass LLW form,(a) the primary radionuclide content of that waste form would be < 0.6 nCi TRU/g, 4.5 Ci ^{90}Sr/m^3, 360 Ci ^{137}Cs/m^3, and 0.4 Ci ^{99}Tc/m^3. This waste form would meet the NRC Class A limit for TRU (< 10 nCi/g), but would exceed the Class A limits for ^{90}Sr, ^{137}Cs, and ^{99}Tc (0.04, 1, and 0.3 Ci/m^3, respectively). However, the ^{90}Sr, ^{137}Cs, and ^{99}Tc levels would be within the Class C LLW limits of 7000, 4600, and 3 Ci/m^3, respectively.

6.2.2 Caustic Leaching of S-101 Sludge

Table 6.7 summarizes the amounts of Al, Cr, and Na removed from the washed S-101 solids under the various leaching conditions as well as the cumulative removals achieved by a combination of washing and caustic leaching. Only data for the samples leached for 168 h are presented in Table 6.7. Values obtained by both the summation and Fe normalization methods are presented. There are significant differences between these two methods, especially for Cr. The reason for this is unclear. Table 6.8 presents the actual concentrations of the various components in the leaching and washing solutions and in the leached solids. The mass recovery for each component is presented in Table 6.8 as well.

Caustic leaching removed about 60 to 90% of the Al from the dilute hydroxide-washed solids. Figure 6.1 shows the percent of the Al removed as a function of time. The slow Al dissolution is consistent with boehmite being the predominant Al-containing phase. Microscopy studies at PNNL showed this to be the case not only for S-101, but also for other reduction-oxidation (REDOX) sludges (Lumetta 1997). As would be expected for this type of waste, Al removal was best for 3 M NaOH at 95°C. The cumulative Al removal for these conditions was 90% after leaching for 168 h. This result was consistent with the 96% Al removal obtained at PNNL in FY 1997, when a total leaching time of 105 h was applied to S-101 sludge at 100°C. At a given temperature, Al dissolution was faster for the 3 M NaOH than for 1 M NaOH, but after 168 h of leaching, the total Al removed was similar at both concentrations. The shapes of the plots in Figure 6.2 suggest that additional Al dissolution would have occurred if leaching were conducted beyond 168 h.

The data in Table 6.2 indicate that for 3 of the 16 samples examined, the dry weight of the leached solids appeared to be greater than the dry weight of the washed solids. This appeared to be the case for the sample leached with 1 M NaOH at 70°C for 5 h, the sample leached with 3 M NaOH at 70°C for 5 h, and the sample leached with 3 M NaOH at 70°C for 24 h. The indicated increased mass might have been due to incomplete washing of NaOH from the interstitial liquid or perhaps to the formation of sodium aluminosilicate phases. If the latter is true, such phases must have been transient because mass decreases were observed after longer leaching times. Another possible explanation for this observation is simply experimental uncertainty.

Figure 6.2 shows the percent of the Cr removed as a function of time. Like with the other sludges examined, Cr removal from the S-101 solids is highly time dependent. This was also observed in the previous S-101 test at PNNL (Lumetta et al. 1997). After 168 h of leaching, the total Cr removed was similar when leached with 3 M NaOH at 70 or 95°C and with 1 M NaOH at 95°C. Chromium removal was markedly less efficient at 1 M NaOH/70°C. Again, plots of [Cr] versus time, ln[Cr] versus time, and 1/[Cr] versus time were not linear, indicating the Cr dissolution was neither zero, first, or second order. The 87% cumulative Cr removal achieved by leaching with 3 M NaOH at 95°C was comparable to the 89% removed in the previous S-101 test conducted at PNNL (Lumetta et al. 1997).

(a) For this determination, it was assumed that the LLW glass form will contain 20 wt% Na_2O, and the density of the glass would be 2.7 MT/m^3.

Caustic leaching resulted in only a modest improvement in Na removal. For the 3 M NaOH/95°C case, the amount of Na present in the residue was actually greater than in the washed solids treated (this is reflected in the negative percent removed value in Table 6.7). This was likely due to incomplete washing of NaOH from the leached solids.

The mass recoveries for phosphate were very low. For this reason, no values for the amount of P removed are given in Table 6.7. The low mass recovery for phosphate can be traced to the sample preparation method employed in this particular experiment. The leached solids were digested with HNO_3, and the resulting solution was analyzed by IC. There were some insoluble solids, and these might have contained phosphate-containing compounds, such as $Ca_3(PO_4)_2$. Previous caustic leaching tests with S-101 solids indicated a cumulative P removal of 97% (Lumetta et al. 1997).

Table 6.7. Caustic Leaching Results for Key Nonradioactive S-101 Sludge Components: Amounts Removed from the Dilute Hydroxide-Washed Solids

	1 M NaOH		3 M NaOH	
Component	Summation Method,%[(a)]	Fe Normalization Method, %[(b)]	Summation Method,%[(a)]	Fe Normalization Method, %[(b)]
		Temperature = 70°C		
Al	66 (70)	71	59 (63)	57
Cr	52 (74)	35	75 (86)	65
Na[(c)]	39 (99)	28	26 (99)	20
P	(d)	(d)	(d)	(d)
		Temperature = 95°C		
Al	87 (88)	75	89 (90)	70
Cr	71 (84)	32	76 (87)	21
Na[(c)]	21 (98)	-58	-99 (96)	-527
P	(d)	(d)	(d)	(d)

(a) Value obtained by summing the quantity of each component found in the leaching and washing solutions and dividing by the total found in the leaching and washing solutions plus the residual solids. The values in parentheses are the cumulative removals achieved by dilute hydroxide washing and caustic leaching.

(b) Value obtained by normalizing the concentrations of each component to the Fe concentration and comparing the normalized values in the caustic-leached solids to those for the dilute hydroxide-washed solids.

(c) Because of the amount of Na added as NaOH during the leaching procedure, it was impossible to determine how much Na was actually removed from the sludge solids. The values reported were determined by comparing the amount of Na in the solids before and after the caustic leaching treatment.

(d) Because of the low mass recovery for P, no values for this element are reported.

Table 6.9 presents the concentrations of the various radioactive components in the leaching and washing solutions and in the leached solids. The mass recovery for each component is presented in Table 6.9 as well. The data indicate that little TRU, Sr, or Co dissolved during the caustic leaching steps. Leaching with 1 or 3 M NaOH at 70°C removed 99% of the ^{137}Cs from the dilute hydroxide-washed S-101 solids. Interestingly, leaching at 95°C removed only ~80% of the ^{137}Cs from the dilute hydroxide-washed S-101 solids. Nevertheless, in all cases, the cumulative removal achieved by dilute hydroxide washing and caustic leaching of the S-101 sludge was >99%. Again, it should be mentioned that the leaching of ^{137}Cs from the solids is an undesirable feature of the sludge washing/caustic leaching process because it requires the subsequent removal of this isotope from the washing and leaching solutions. In the case of the S-101 sludge, the radionuclides dissolved during caustic leaching would not have much impact on the LLW up and beyond what would be dissolved in the dilute hydroxide washing (*vide supra*).

Table 6.10 shows the concentration of waste oxides in the dilute hydroxide-washed and in the leached[(a)] S-101 solids and the concentrations of waste-derived components that would result from vitrifying these solids at 25 wt% WOL, excluding oxides of Na and Si. The oxide concentrations in the washed and leached solids were determined by converting the elemental concentrations listed in Tables 6.6 (washed solids) and 6.8 (leached solids) to the corresponding oxide concentrations. The oxide concentrations in the IHLW were determined according to equation 2.1.

Assuming upper limits of 15, 0.5, and 3.0 wt% for Al, Cr, and P oxides, respectively, in the IHLW, a 25 wt% WOL would not be achievable for either the dilute hydroxide-washed or caustic-leached S-101 solids. In the case of the washed solids, the Al oxide concentration limit of 15 wt% is exceeded, and the Cr oxide content is borderline. Caustic leaching would bring the Al oxide content within 15 wt%, but the Cr oxide content would exceed 0.5 wt%. Setting the upper limit for Al_2O_3 in the IHLW as 15 wt%, the maximum WOL that could be achieved for the washed S-101 solids would be 17.0 wt%. At this WOL, application of equation 2.2 indicates that 1.31 g IHLW would be produced per gram of washed S-101 solids. Likewise, setting the upper limit for Cr_2O_3 in the IHLW as 0.5 wt%, the maximum WOL that could be achieved for the leached S-101 solids would be 15.2 wt%. At this WOL, application of equation 2.3 indicates that 0.23 g IHLW would be produced per gram of washed S-101 solids. Thus, a reduction in IHLW of 82% could be achieved by caustic leaching the S-101 solids. However, it is likely that oxidative leaching methods could reduce the Cr content of the leached solids (Rapko 1998). If the Cr could be removed, then ~0.14 g of IHLW glass would be produced at 25 wt% WOL from the leached solids derived from 1 g of washed S-101 solids. In the latter case, a total 89% reduction in the IHLW would be achieved.

(a) For this analysis, we considered only the case where the solids were leached with 3 M NaOH for 168 h at 95°C.

Table 6.8. Concentrations of Key S-101 Sludge Components in Caustic Leaching Solutions and in the Caustic Leached Solids

	Washed Solids(a)		5 h	24 h	72 h	168 h(a)		Final Wash Solution(a)		Leached Solids(a)		Mass Recovery, %(a)
Component	µg/g	µg	µg/mL	µg/mL	µg/mL	µg/mL	µg	µg/mL	µg	µg/g	µg	
						1 M NaOH at 70°C						
Ag	2.49E+00	1.24E+01	< 5.01E-03	< 5.01E-03	< 5.01E-03	< 5.01E-03	< 9.52E-01	< 5.01E-03	< 3.91E-01	3.05E+00	1.16E+01	> 94
Al	1.04E+05	5.18E+05	8.63E+01	5.01E+02	8.60E+02	1.26E+03	2.39E+05	4.49E+01	3.52E+03	3.32E+04	1.26E+05	71
Ba	4.16E+01	2.07E+02	< 1.67E-03	4.50E 2	4.50E 2	4.50E 2	8.53E+00	4.50E 2	3.53E+00	5.70E+01	2.17E+02	111
Ca	6.53E+02	3.25E+03	< 3.17E-02	< 3.17E-02	< 3.17E-02	< 3.17E-02	< 6.02E+00	< 3.17E-02	< 2.47E+00	5.98E+02	2.28E+03	70
Cr	3.11E+03	1.55E+04	7.59E+00	2.80E+01	3.96E+01	4.77E+01	9.04E+03	1.93E+00	1.51E+02	2.23E+03	8.49E+03	114
Cu	6.55E+01	3.26E+02	2.62E 1	6.55E 1	5.75E 1	5.25E 1	9.95E+01	5.00E 2	3.92E+00	7.00E+01	2.67E+02	114
Fe	1.86E+03	9.26E+03	2.09E 1	6.85E 1	1.31E+00	1.40E+00	2.65E+02	3.50E 2	2.75E+00	2.06E+03	7.85E+03	88
Mg	1.30E+01	6.47E+01	< 3.67E-02	< 3.67E-02	< 3.67E-02	< 3.67E-02	< 6.97E+00	< 3.67E-02	< 2.86E+00	2.24E+01	8.53E+01	132
Mn	2.49E+03	1.24E+04	< 1.67E-03	< 1.67E-03	< 1.67E-03	< 1.67E-03	< 3.17E-01	< 1.67E-03	< 1.30E-01	3.01E+03	1.15E+04	93
Na	3.21E+03	1.60E+04	2.21E+04	2.31E+04	2.28E+04	2.09E+04	3.96E+06	1.04E+03	8.16E+04	2.56E+03	9.75E+03	N/A
Ni	1.37E+02	6.82E+02	< 5.34E-02	< 5.34E-02	< 5.34E-02	< 5.34E-02	< 1.01E+01	< 5.34E-02	< 4.17E+00	1.95E+02	7.43E+02	109
PO_4	1.31E+03	6.52E+03	< 1.70E-01	1.82E+01	2.41E+01	2.10E+01	3.98E+03	1.95E+01	1.53E+03	< 7.81E+00	< 2.97E+01	85
SO_4	7.27E+02	3.62E+03	2.54E+00	< 1.70E-01	1.18E+01	< 1.70E-01	< 3.23E+01	< 1.70E-01	< 1.33E+01	< 7.81E+00	< 2.97E+01	1
Th	2.49E+01	1.24E+02	5.68E 1	1.19E+00	1.25E+00	1.24E+00	2.35E+02	< 2.45E-01	< 1.91E+01	< 2.07E+01	< 7.88E+01	> 64
U	8.07E+03	4.02E+04	< 1.60E-01	< 1.60E-01	< 1.60E-01	< 1.60E-01	< 3.04E+01	< 1.60E-01	< 1.25E+01	9.51E+03	3.62E+04	90
V	7.27E+00	3.62E+01	< 1.34E-02	1.20E 1	1.35E 1	1.55E 1	2.94E+01	9.00E 2	7.06E+00	< 6.25E-01	< 2.38E+00	101
Zn	2.33E+02	1.16E+03	5.91E 1	< 2.92E-01	< 2.92E-01	< 2.92E-01	< 5.55E+01	< 2.92E-01	< 2.28E+01	6.87E+01	2.62E+02	23
						3 M NaOH at 70°C						
Ag	2.49E+00	1.70E+01	< 5.01E-03	< 5.01E-03	< 5.01E-03	< 5.01E-03	< 3.21E-01	< 5.01E-03	< 4.01E-01	3.12E+00	1.75E+01	103
Al	1.04E+05	7.10E+05	3.34E+02	1.17E+03	1.17E+03	3.10E+03	3.62E+05	4.69E+02	3.76E+04	4.98E+04	2.80E+05	96
Ba	4.16E+01	2.84E+02	< 1.67E-03	4.50E 2	4.50E 2	4.50E 2	< 1.07E-01	< 1.67E-03	< 1.34E-01	5.36E+01	3.01E+02	106
Ca	6.53E+02	4.46E+03	< 3.17E-02	< 3.17E-02	< 3.17E-02	< 3.17E-02	< 2.03E+00	< 3.17E-02	< 2.54E+00	5.88E+02	3.31E+03	74
Cr	3.11E+03	2.12E+04	4.83E+01	1.33E+02	1.33E+02	2.01E+02	1.86E+04	2.30E+01	1.85E+03	1.19E+03	6.69E+03	128
Cu	6.55E+01	4.47E+02	2.06	6.13	6.13	4.76	5.07E+02	1.59E 1	1.28E+01	5.91E+01	3.32E+02	191
Fe	1.86E+03	1.27E+04	7.04E 1	3.02	3.02	7.04E+00	5.81E+01	1.69E 1	1.36E+01	2.19E+03	1.23E+04	97
Mg	1.30E+01	8.88E+01	< 3.67E-02	< 3.67E-02	< 3.67E-02	< 3.67E-02	< 2.35E+00	< 3.67E-02	< 2.94E+00	2.95E+01	1.66E+02	187

(a) Values reported for the aliquot leached for 168 h.

	Washed Solids[(a)]		5 h	24 h	72 h	168 h[(a)]		Final Wash Solution[(a)]		Leached Solids[(a)]		Mass
Component	µg/g	µg	µg/mL	µg/mL	µg/mL	µg/mL	µg	µg/mL	µg	µg/g	µg	Recovery, %[(a)]
Mn	2.49E+03	1.70E+04	< 1.67E-03	2.00E 2	2.00E 2	< 1.67E-03	< 1.07E-01	< 1.67E-03	< 1.34E-01	2.71E+03	1.52E+04	89
Na	3.21E+03	2.19E+04	6.13E+04	7.11E+04	7.11E+04	7.25E+04	4.34E+06	6.00E+03	4.81E+05	2.86E+03	1.61E+04	N/A
Ni	1.37E+02	9.35E+02	< 5.34E-02	< 5.34E-02	< 5.34E-02	< 5.34E-02	< 3.42E+00	< 5.34E-02	< 4.27E+00	1.22E+03	6.86E+03	734
PO_4	1.31E+03	8.94E+03	< 1.70E-01	2.03E+01	2.03E+01	2.76E+01	1.27E+03	< 1.70E-01	< 1.36E+01	< 7.81E+00	< 4.39E+01	14
SO_4	7.27E+02	4.96E+03	< 1.70E-01	< 1.70E-01	< 1.70E-01	< 1.70E-01	< 1.09E+01	< 1.70E-01	< 1.36E+01	< 7.81E+00	< 4.39E+01	1
Th	2.49E+01	1.70E+02	4.81E 1	1.93E+00	1.93E+00	1.95E+00	3.37E+01	< 2.45E-01	< 1.96E+01	25.2	142	103
U	8.07E+03	5.51E+04	< 1.60E-01	< 1.60E-01	< 1.60E-01	< 1.60E-01	< 1.02E+01	< 1.60E-01	< 1.28E+01	8.28E+03	4.65E+04	84
V	7.27E+00	4.96E+01	< 1.34E-02	1.55E 1	1.55E 1	1.75E 1	< 8.58E-01	< 1.34E-02	< 1.07E+00	< 6.25E-01	< 3.51E+00	7
Zn	2.33E+02	1.59E+03	< 2.92E-01	1.02	1.02	8.95E 1	203	< 2.92E-01	< 2.34E+01	1.45E+02	8.15E+02	64
						1 M NaOH at 95°C						
Ag	2.49E+00	1.27E+01	< 5.01E-03	< 5.01E-03	< 5.01E-03	< 5.01E-03	< 4.31E-01	< 5.01E-03	< 3.81E-01	6.06E+00	1.40E+01	110
Al	1.04E+05	5.29E+05	1.62E+03	2.64E+03	3.61E+03	4.95E+03	4.27E+05	7.53E+01	5.74E+03	2.84E+04	6.54E+04	94
Ba	4.16E+01	2.11E+02	< 1.67E-03	< 1.67E-03	2.90E 1	4.50E 2	3.89E+00	< 1.67E-03	< 1.27E-01	1.08E+02	2.49E+02	120
Ca	6.53E+02	3.32E+03	< 3.17E-02	< 3.17E-02	< 3.17E-02	< 3.17E-02	< 2.73E+00	< 3.17E-02	< 2.41E+00	0.00E+00	0.00E+00	0
Cr	3.11E+03	1.58E+04	4.21E+01	8.96E+01	1.18E+02	1.49E+02	1.29E+04	2.89E+00	2.20E+02	2.34E+03	5.39E+03	117
Cu	6.55E+01	3.33E+02	5.19E 1	5.66E 1	6.25E 1	7.35E 1	6.35E+01	< 3.34E-03	< 2.54E-01	1.46E+02	3.36E+02	120
Fe	1.86E+03	9.45E+03	1.37	2.62	1.41E+00	1.69E+00	1.46E+02	< 8.35E-03	< 6.35E-01	4.27E+03	9.83E+03	106
Mg	1.30E+01	6.61E+01	< 3.67E-02	< 3.67E-02	< 3.67E-02	< 3.67E-02	< 3.16E+00	< 3.67E-02	< 2.79E+00	5.61E+01	1.29E+02	195
Mn	2.49E+03	1.27E+04	< 1.67E-03	< 1.67E-03	< 1.67E-03	< 1.67E-03	< 1.44E-01	< 1.67E-03	< 1.27E-01	0.00E+00	0.00E+00	0
Na	3.21E+03	1.63E+04	2.01E+04	2.05E+04	2.17E+04	2.40E+04	2.07E+06	7.92E+02	6.04E+04	5.61E+03	1.29E+04	N/A
Ni	1.37E+02	6.96E+02	< 5.34E-02	< 5.34E-02	< 5.34E-02	< 5.34E-02	< 4.59E+00	< 5.34E-02	< 4.06E+00	3.54E+02	8.15E+02	117
PO_4	1.31E+03	6.66E+03	< 1.70E-01	< 1.70E-01	1.49E+01	1.74E+01	1.50E+03	< 1.70E-01	< 1.29E+01	< 7.81E+00	< 1.80E+01	23
SO_4	7.27E+02	3.69E+03	1.51E+00	1.54	1.17E+01	< 1.70E-01	< 1.46E+01	< 1.70E-01	< 1.29E+01	< 7.81E+00	< 1.80E+01	0
Th	2.49E+01	1.27E+02	5.63E 1	6.62E 1	1.58E+00	1.65E+00	1.42E+02	< 2.45E-01	< 1.86E+01	< 2.07E+01	< 4.77E+01	112
U	8.07E+03	4.10E+04	< 1.60E-01	< 1.60E-01	< 1.60E-01	< 1.60E-01	< 1.38E+01	< 1.60E-01	< 1.22E+01	1.61E+04	3.71E+04	90
V	7.27E+00	3.69E+01	< 1.34E-02	< 1.34E-02	1.85E 1	2.05E 1	1.77E+01	< 1.34E-02	< 1.02E+00	< 6.25E-01	< 1.44E+00	48
Zn	2.33E+02	1.18E+03	< 2.92E-01	< 2.92E-01	1.37	< 2.92E-01	< 2.51E+01	< 2.92E-01	< 2.22E+01	1.26E+02	2.90E+02	25

	Washed Solids(a)		5 h	24 h	72 h	168 h(a)		Final Wash Solution(a)		Leached Solids(a)		Mass Recovery, %(a)
Component	µg/g	µg	µg/mL	µg/mL	µg/mL	µg/mL	µg	µg/mL	µg	µg/g	µg	
3 M NaOH at 95°C												
Ag	2.49E+00	1.24E+01	< 5.01E-03	< 5.01E-03	< 5.01E-03	< 5.01E-03	< 1.50E-01	< 5.01E-03	< 3.91E-01	8.17E+00	1.17E+01	94
Al	1.04E+05	5.20E+05	4.67E+03	9.95E+03	1.09E+04	1.34E+04	4.05E+05	1.04E+02	8.09E+03	3.48E+04	4.98E+04	89
Ba	4.16E+01	2.08E+02	< 1.67E-03	< 1.67E-03	< 1.67E-03	< 1.67E-03	< 5.01E-02	< 1.67E-03	< 1.30E-01	1.49E+02	2.13E+02	102
Ca	6.53E+02	3.26E+03	< 3.17E-02	< 3.17E-02	< 3.17E-02	< 3.17E-02	< 9.51E-01	< 3.17E-02	< 2.47E+00	1.38E+03	1.98E+03	61
Cr	3.11E+03	1.55E+04	7.12E+01	2.35E+02	3.74E+02	4.07E+02	1.23E+04	3.28E+00	2.55E+02	2.73E+03	3.91E+03	106
Cu	6.55E+01	3.27E+02	5.23	4.48	3.7	4.18	1.26E+02	< 3.34E-03	< 2.61E-01	1.13E+02	1.62E+02	88
Fe	1.86E+03	9.29E+03	7.6	4.42	7.68E+00	2.35E+00	7.11E+01	< 8.35E-03	< 6.51E-01	5.94E+03	8.50E+03	92
Mg	1.30E+01	6.49E+01	< 3.67E-02	< 3.67E-02	< 3.67E-02	< 3.67E-02	< 1.10E+00	< 3.67E-02	< 2.86E+00	8.88E+01	1.27E+02	196
Mn	2.49E+03	1.24E+04	4.63E 2	< 1.67E-03	< 1.67E-03	< 1.67E-03	< 5.01E-02	< 1.67E-03	< 1.30E-01	8.27E+03	1.18E+04	95
Na	3.21E+03	1.60E+04	5.69E+04	6.72E+04	5.55E+04	5.95E+04	1.80E+06	9.81E+02	7.63E+04	2.23E+04	3.19E+04	N/A
Ni	1.37E+02	6.84E+02	< 5.34E-02	< 5.34E-02	< 5.34E-02	< 5.34E-02	< 1.60E+00	< 5.34E-02	< 4.17E+00	5.37E+02	7.69E+02	112
PO_4	1.31E+03	6.54E+03	< 1.70E-01	6.57E+00	1.63E+01	7.37E+00	2.23E+02	< 1.70E-01	< 1.33E+01	< 7.81E+00	< 1.12E+01	3
SO_4	7.27E+02	3.63E+03	< 1.70E-01	< 1.70E-01	< 1.70E-01	< 1.70E-01	< 5.10E+00	< 1.70E-01	< 1.33E+01	< 7.81E+00	< 1.12E+01	0
Th	2.49E+01	1.24E+02	1.56	1.10E+00	1.35E+00	1.25E+00	3.78E+01	< 2.45E-01	< 1.91E+01	59.5	85.2	99
U	8.07E+03	4.03E+04	< 1.60E-01	< 1.60E-01	< 1.60E-01	< 1.60E-01	< 4.80E+00	< 1.60E-01	< 1.25E+01	2.32E+04	3.32E+04	82
V	7.27E+00	3.63E+01	< 1.34E-02	< 1.34E-02	< 1.34E-02	< 1.34E-02	< 4.02E-01	< 1.34E-02	< 1.05E+00	< 6.25E-01	< 8.94E-01	2
Zn	2.33E+02	1.16E+03	< 2.92E-01	< 2.92E-01	< 2.92E-01	< 2.92E-01	< 8.76E+00	< 2.92E-01	< 2.28E+01	0.00E+00	0.00E+00	0

(a) Values reported for the aliquot leached for 168 h.

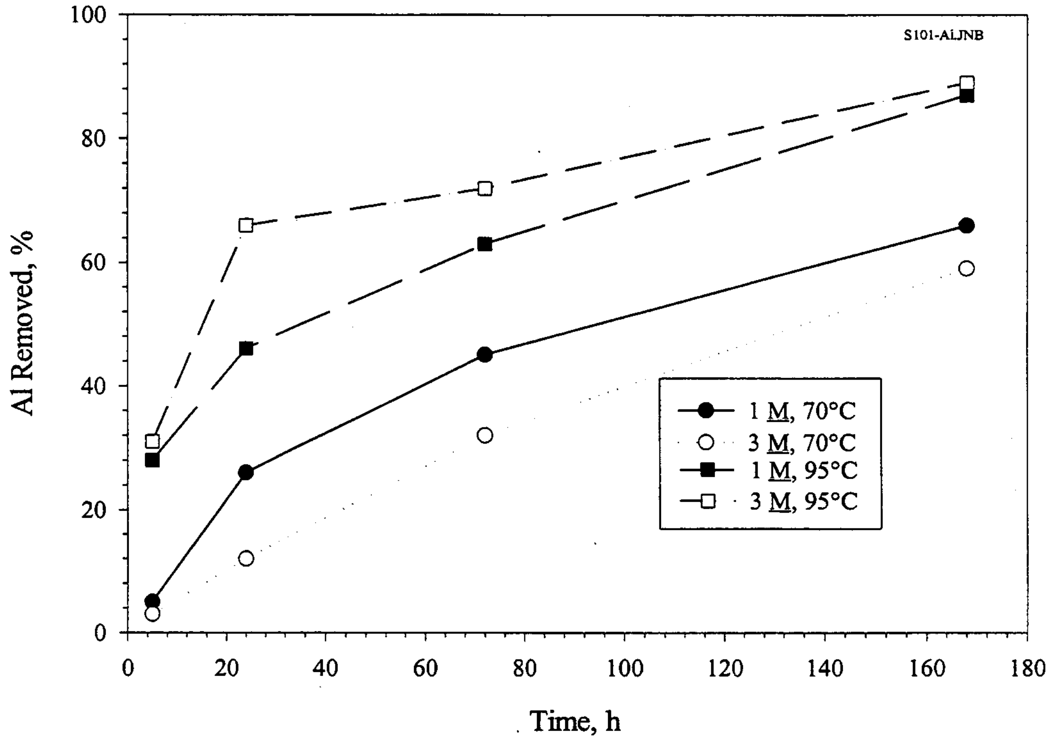

Figure 6.1. Aluminum Removal From the Dilute Hydroxide-Washed S-101 Sludge Solids as a Function of Time

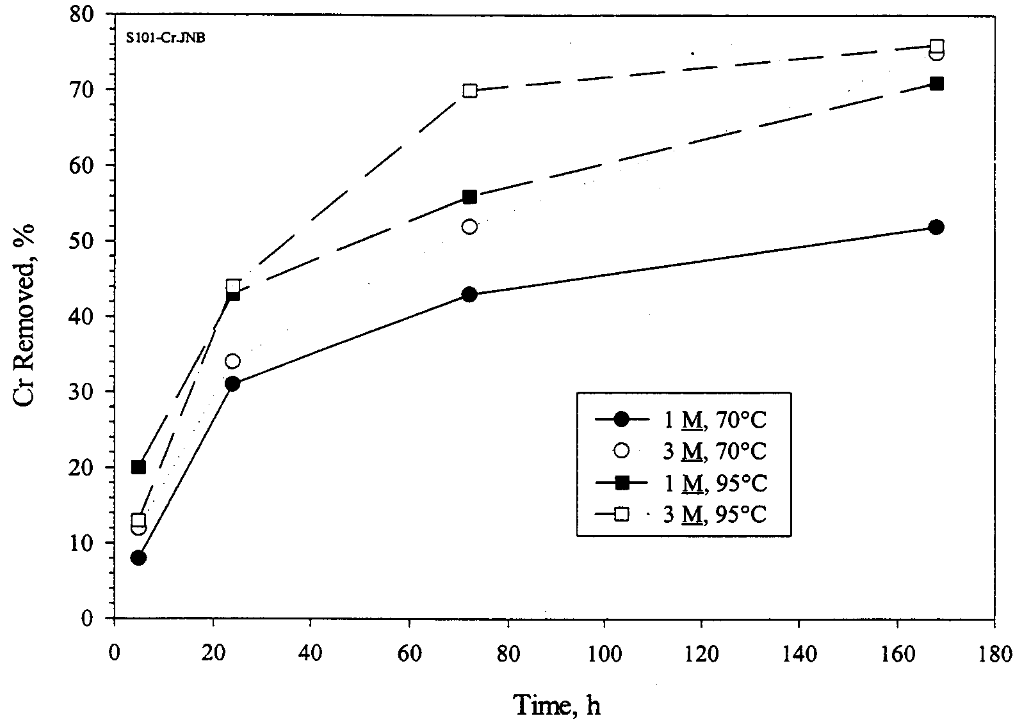

Figure 6.2. Chromium Removal From the Dilute Hydroxide-Washed S-101 Sludge Solids as a Function of Time

Table 6.9. Concentrations of Key S-101 Sludge Components in Caustic Leaching Solutions and in the Caustic Leached Solids

	Washed Solids(a)		5 h	24 h	72 h	168 h(a)		Final Wash Solution(a)		Leached Solids(a)		Mass Recovery, %(a)
Component	µCi/g	µCi	µCi/mL	µCi/mL	µCi/mL	µCi/mL	µCi	µCi/mL	µCi	µCi/g	µCi	
						1 M NaOH at 70°C						
Total Alpha	2.73E-01	1.36E+00	(b)	(b)	(b)	1.35E-04	2.57E-02	< 1.05E-04	< 8.37E-03	(b)	(b)	--
Total Beta	7.02E+02	3.50E+03	(b)	(b)	(b)	1.32E-01	2.51E+01	6.75E-03	5.40E-01	1.11E+03	4.22E+03	121
^{241}Am	1.51E-01	7.53E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	1.86E-01	7.10E-01	94
^{244}Cm	5.72E-03	2.85E-02	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{60}Co	1.24E-02	6.19E-02	(b)	(b)	(b)	(b)	(b)	(b)	(b)	1.54E-02	5.86E-02	95
^{137}Cs	3.24E+00	1.61E+01	9.72E-02	8.64E-03	7.56E-03	9.45E-02	1.78E+01	3.24E-03	2.54E-01	2.97E-02	1.13E-01	113
^{154}Eu	1.35E-01	6.72E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	2.11E-01	8.02E-01	119
^{155}Eu	5.94E-02	2.96E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	1.38E-01	5.24E-01	177
Pu(b)	2.43E-01	1.21E+00	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{90}Sr	2.97E+02	1.48E+03	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{99}Tc	< 1.69E-03	< 8.42E-03	< 1.51E-01	(b)	(b)	4.43E-05	3.81E-03	< 1.14E-05	< 9.12E-04	< 5.29E-04	< 2.01E-03	--
						3 M NaOH at 70°C						
Total Alpha	2.73E-01	1.86E+00	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
Total Beta	7.02E+02	4.79E+03	(b)	(b)	(b)	(b)	(b)	(b)	(b)	9.99E+02	5.62E+03	117
^{241}Am	1.51E-01	1.03E+00	(b)	(b)	(b)	(b)	(b)	(b)	(b)	2.05E-01	1.15E+00	112
^{244}Cm	5.72E-03	3.91E-02	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{60}Co	1.24E-02	8.48E-02	(b)	(b)	(b)	(b)	(b)	(b)	(b)	1.54E-02	8.65E-02	102
^{137}Cs	3.24E+00	2.21E+01	2.97E-01	2.97E-01	3.24E-01	3.51E-01	2.24E+01	3.24E-02	2.59E+00	6.75E-02	3.79E-01	115
^{154}Eu	1.35E-01	9.22E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	1.81E-01	1.02E+00	110

(a) Values reported for the aliquot leached for 168 h.
(b) Not Measured.

	Washed Solids$^{(a)}$		5 h	24 h	72 h	168 h$^{(a)}$		Final Wash Solution$^{(a)}$		Leached Solids$^{(a)}$		Mass Recovery, %$^{(a)}$
Component	µCi/g	µCi	µCi/mL	µCi/mL	µCi/mL	µCi/mL	µCi	µCi/mL	µCi	µCi/g	µCi	
^{155}Eu	5.94E-02	4.06E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	9.45E-02	5.31E-01	131
Pu$^{(b)}$	2.43E-01	1.66E+00	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{90}Sr	2.97E+02	2.03E+03	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{99}Tc	< 1.69E-03	< 1.15E-02	< 1.11E-04	(b)	(b)	< 2.58E-04	< 1.64E-04	< 1.14E-05	< 9.12E-04	< 5.29E-04	< 2.97E-03	--
1 M NaOH at 95°C												
Total Alpha	2.73E-01	1.39E+00	(b)	(b)	(b)	1.57E-04	1.35E-02	(b)	(b)	(b)	(b)	--
Total Beta	7.02E+02	3.57E+03	(b)	(b)	(b)	2.41E-01	2.08E+01	(b)	(b)	1.94E+03	4.48E+03	125
^{241}Am	1.51E-01	7.68E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	4.59E-01	1.06E+00	138
^{244}Cm	5.72E-03	2.91E-02	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{60}Co	1.24E-02	6.31E-02	(b)	(b)	(b)	(b)	(b)	(b)	(b)	2.97E-02	6.84E-02	108
^{137}Cs	3.24E+00	1.65E+01	1.73E-01	1.62E-01	1.46E-01	1.92E-01	1.65E+01	3.24E-03	2.46E-01	1.43E+00	3.30E+00	122
^{154}Eu	1.35E-01	6.86E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	4.05E-01	9.33E-01	136
^{155}Eu	5.94E-02	3.02E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	2.70E-01	6.22E-01	205
Pu$^{(b)}$	2.43E-01	1.23E+00	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{90}Sr	2.97E+02	1.51E+03	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{99}Tc	< 1.69E-03	< 8.59E-03	< 9.53E-05	< 1.16E-04	(b)	1.56E-04	1.35E-02	< 1.14E-05	< 8.66E-04	< 5.29E-04	< 1.22E-03	--
3 M NaOH at 95°C												
Total Alpha	2.73E-01	1.36E+00	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
Total Beta	7.02E+02	3.51E+03	(b)	(b)	(b)	(b)	(b)	(b)	(b)	2.70E+03	3.86E+03	110
^{241}Am	1.51E-01	7.55E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	5.94E-01	8.50E-01	113
^{244}Cm	5.72E-03	2.86E-02	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{60}Co	1.24E-02	6.21E-02	(b)	(b)	(b)	(b)	(b)	(b)	(b)	4.86E-02	6.95E-02	112
^{137}Cs	3.24E+00	1.62E+01	5.13E-01	4.86E-01	4.05E-01	4.05E-01	1.22E+01	5.13E-03	4.05E-01	2.30E+00	3.28E+00	98
^{154}Eu	1.35E-01	6.74E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	5.40E-01	7.73E-01	115

	Washed Solids(a)		5 h	24 h	72 h	168 h(a)		Final Wash Solution(a)		Leached Solids(a)		Mass
Component	µCi/g	µCi	µCi/mL	µCi/mL	µCi/mL	µCi/mL	µCi	µCi/mL	µCi	µCi/g	µCi	Recovery, %(a)
^{155}Eu	5.94E-02	2.97E-01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	4.32E-01	6.18E-01	208
Pu(b)	2.43E-01	1.21E+00	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{90}Sr	2.97E+02	1.48E+03	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	--
^{99}Tc	< 1.69E-03	< 8.44E-03	< 1.64E-04	< 2.94E-05	< 4.54E-05	< 4.13E-05	< 1.25E-04	< 1.14E-05	< 9.01E-04	< 5.29E-04	< 7.57E-04	--

(a) Values reported for the aliquot leached for 168 h.

(b) Not Measured.

Table 6.10. Estimated Concentrations of Waste-Derived Components in the IHLW Glass From S-101 Waste

	Washed Solids		Leached Solids (3 M NaOH/100°C/168h)	
Component	g oxide/g solids	Conc. in IHLW, wt%[a]	g oxide/g solids	Conc. in IHLW, wt%[a]
Al_2O_3	0.1966	22.0	0.0658	13.5
BaO	0.0000	0.01	0.0002	0.0
Bi_2O_3	0.0000	0.00	0.0000	0.0
CaO	0.0009	0.1	0.0019	0.4
Cr_2O_3	0.0045	0.5	0.0040	0.8
Fe_2O_3	0.0027	0.3	0.0085	1.7
MgO	0.0000	0.0	0.0001	0.0
MnO_2	0.0039	0.4	0.0131	2.7
Na_2O	0.0043	0.5	0.0301	6.2
P_2O_5	0.0039	0.4	0.0000	0.0
SiO_2[b]	0.0057	0.6	0.0180	3.7
SrO	0.0004	0.05	0.0000	0.0
UO_3	0.0097	1.1	0.0279	5.7
ZnO	0.0003	0.03	0.0000	0.0

(a) Based on 25 wt% waste oxide loading (excluding Na_2O and SiO_2).

(b) Values for SiO_2 taken from Lumetta et al. (1997).

7.0 Discussion

This section presents a general discussion of the key results from the parametric ESW tests conducted in FY 1998. Data from ESW tests conducted before FY 1998 are also discussed, as appropriate. This discussion summarizes the behaviors of the specific sludge components Al, Cr, P, Na, and radionuclides during washing and caustic leaching. The effects of caustic leaching on the amount of HLW glass required for immobilizing the wastes are also discussed.

7.1 Aluminum

As observed in previous sludge washing tests (Lumetta et al. 1997), washing with dilute NaOH was usually not very effective at removing Al. Aluminum removal was less than 10% for the BX-110, BX-112, or C-102 samples investigated. Slightly better Al removals were observed for B-101 (25%) and S-101 (11%) sludges, when washed with dilute hydroxide. The Al removed by dilute hydroxide washing was likely present in the samples as soluble aluminate, either in the interstitial liquid or the dried salts. As expected, improved Al removal was achieved by caustic leaching for all the sludges examined.

The behavior of Al-containing phases in the caustic leaching process can be discussed in terms of four classifications:

- Phases that dissolve rapidly under the process conditions
- Phases that dissolve slowly under the process conditions
- Phases that do not completely dissolve under the process conditions
- Phases that precipitate during processing

Tank BX-110 sludge exemplifies the first type of behavior. Figure 3.1 shows that when this sludge is leached with 3 M NaOH at 95°C, the Al concentration in solution at 5 h of leaching is >90% of the final concentration at 168 h of leaching. Similar behavior is seen with Tank B-101 sludge when this sludge is leached with 3 M NaOH at 100°C (Figure 2.1). Thus, in these two sludges, there is one or more major Al-containing phases that dissolve rapidly in 3 M NaOH at ~100°C. The TEM examination of the dilute hydroxide-washed BX-110 solids indicated gibbsite to be a major Al-containing phase present. Gibbsite would be expected to dissolve readily under the caustic leaching conditions. Indeed, this phase was essentially completely removed from the BX-110 solids after leaching with 3 M NaOH at 100°C for 168h. The remaining Al-containing phases dissolve slowly, if at all, under these conditions. TEM examination of the leached BX-110 solids indicated the crystalline aluminosilicate mineral, $H_4(Si,Al)_{12}O_{24}$, to be one of the major Al-containing phases remaining. Aluminosilicates are generally difficult to dissolve. There are some differences in the Al behavior for the BX-110 and B-101 sludges. For the BX-110 sludge, rapid Al dissolution is seen at 3 M NaOH, regardless of the temperature from 60 to 95°C. When leached with 1 M NaOH, the rate of Al dissolution increases with increasing temperature, but the extent of Al dissolution after 168 h is similar to that at 3 M NaOH (Figure 3.1). In contrast, for B-101 the amount of Al dissolved is always greater at 3 M NaOH than at 1 M NaOH (Figure 2.1) within the time frame of these tests.

Tank S-101 sludge exemplifies the second type of behavior. Microscopy studies conducted in FY 1997 indicated the predominant Al-containing species in the S-101 sludge solids is boehmite (Lumetta et al. 1997). Boehmite dissolves slowly under conditions similar to those employed here (Weber 1982). Indeed, for the S-101 sludge, Al dissolves relatively slowly, even at 95°C (Figure 6.2). It is likely that additional Al would be removed by leaching for a longer period of time, especially if the leaching is done at lower temperatures. Aluminum has also been found to dissolve slowly in other REDOX sludges (S-104 and S-111; Lumetta et al. 1997).

All the sludges examined in these parametric ESW tests had Al in the residual solids, even after leaching at the harshest conditions (3 M NaOH/100°C). In most cases, the plots of Al concentration versus time indicate that leaching for longer times would not cause more Al to dissolve. This is evidence for the third type of behavior—Al phases that do not dissolve under the process conditions. Microscopy studies done previously indicated that the phases that are difficult to dissolve are generally aluminosilicates (Lumetta et al. 1998).

Comparison of the Al behavior for BX-110 sludge to that for BX-112 sludge illustrates the difficulties in extrapolating results between tanks with similar waste types. Both of these tanks contain the same primary and secondary wastes (Table 1.1), yet the Al behavior is markedly different for each. For BX-110, the Al concentration generally increases with time until a constant concentration is reached (Figure 3.1). However, for BX-112 (Figure 4.1), the Al concentration decreases with time, indicating that some of the Al rapidly dissolves (first type of behavior listed above), but then subsequently forms an insoluble phase and precipitates (fourth type of behavior listed above). As was discussed in Section 4.0, this behavior might be due to the formation of aluminosilicates. The TEM analyses of the dilute hydroxide-washed BX-112 solids and the solids remaining after leaching with 3 M NaOH at 100°C for 168 h support this hypothesis. The washed BX-112 solids contained a significant concentration of aluminum phosphate. This phase would be expected to dissolve rapidly in 3 M NaOH at 100°C; this is consistent with the observed Al behavior. Furthermore, the TEM analysis indicated the leached BX-112 solids contained sodium aluminosilicate minerals, whereas such phases were not seen in the TEM images before leaching.

The weights of the leached S-101 solids suggest that additional phases may have formed under specific conditions. For example, when the dilute hydroxide-washed S-101 solids were leached with 1 or 3 M NaOH for 5 h at 70°C, a slight increase in the mass of the solids was observed. This suggests that another phase might have formed under these conditions. However, unlike for the BX-110 sludge, this phase appeared to dissolve again upon further leaching. Also, analyses of the S-101 leaching solutions indicate a steady increase in the Al concentrations (Figure 6.1), so it is unclear if transient solid sodium aluminosilicates formed in the S-101 leaching tests.

7.2 Chromium

For the sludges examined in FY 1998, the behavior of Cr during dilute hydroxide washing was consistent with observations made in previous sludge washing tests (Lumetta et al. 1997). Namely, approximately 20 to 30% of the Cr was usually removed by washing with 0.1 M NaOH. For the S-101 sludge, a somewhat larger fraction (46%) of the Cr was removed by dilute hydroxide washing, but again, this was consistent with previous results. The Cr removed by such washing was likely present in the samples as soluble chromate ion, either in the interstitial liquid or the dried salts. Spectrophotometric examination of the washing solutions indicated the removed Cr to be chromate ion. Like Al, additional Cr was removed by caustic leaching.

Chromium removal from the washed sludge solids by caustic leaching is dependent on time, temperature, and hydroxide concentration. All the parametric tests clearly indicate that Cr removal increases with increasing leaching time, although the kinetics do not fit simple zero-, first-, or second-order reaction models. Generally, increasing temperature leads to more rapid Cr removal. However, in the case of BX-112 sludge, there is little difference between leaching at 80 or 100°C (Figure 4.4). Likewise, the rate of Cr removal increases as the hydroxide concentration increases, but the differences between 1 and 3 M NaOH are diminished at higher temperature.

As has been previously observed (Lumetta et al. 1997), the Cr present in the sludge washing and leaching solutions is predominantly Cr(VI) (see Tables 3.8 and 4.9). Thus, the mechanism of Cr removal during the ESW process appears to involve oxidation of Cr(III) to Cr(VI). This oxidation is likely due to the presence of adventitious oxygen present in the system. Recent studies conducted at PNNL have indicated that O_2 is capable of oxidizing a significant fraction of the Cr(III) in Hanford sludges to Cr(VI) under highly alkaline conditions (Rapko 1998). This reaction proceeds according to the following equation:

$$4Cr(OH)_3 + 3O_2 + 8OH^- \rightarrow 4CrO_4^{2-} + 10H_2O \tag{7.1}$$

According to this equation, oxidation of Cr(III) with O_2 is favored by high hydroxide concentration.

7.3 Phosphorus

For the sludges examined in FY 1998, washing with dilute hydroxide had variable effectiveness at removing P. The removals for the B-101, BX-110, BX-112, C-102, and S-101 samples were 67, 97, 24, 25, and 55%, respectively. Again, the difference in behavior for BX-110 and BX-112 is significant, since these tanks are supposed to contain similar wastes. The subsequent caustic leaching of the washed solids was generally effective at removing the remaining P; this was especially true for BX-110, BX-112, and S-101 sludges.

In most cases, P removal from the dilute hydroxide-washed sludge solids by caustic leaching was rapid. For example, phosphate metathesis was essentially complete within 5 h in the leaching of the washed BX-110 and BX-112 solids. Phosphorus removal from the washed B-101 and C-102 solids did display a mild time-dependence, but in most cases was nearly complete within 24 h. Thus, for the sludges examined here, P removal will probably not be the rate-limiting step in the pretreatment process.

7.4 Sodium

The minimum sludge pretreatment that would be applied at Hanford is dilute hydroxide washing. The primary 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.

Lumetta et al. (1997) summarized Na removal by dilute hydroxide washing for Hanford sludges examined before FY 1998. The previous tests indicated Na removal from the samples investigated was almost always greater than 70% and was greater than 90% for over half of the tanks examined. Similar results were obtained in the FY 1998 tests. Dilute hydroxide washing removed 88, 99, 63, 87, and 98% of the Na from the B-101, BX-110, BX-112, C-102, and S-101 samples, respectively. As was the case with Al and P, the difference in Na behavior for BX-110 and BX-112 is significant, since these tanks are supposed to contain similar wastes. *Clearly, caution should be exercised when extrapolating experimental results from one tank to another, even if the tanks contain similar wastes.*

7.5 Radionuclides

In general, only ^{137}Cs and ^{99}Tc are appreciably removed by the alkaline washing and leaching solutions. Consistent with previous results (Lumetta et al. 1997), ^{137}Cs removal by dilute hydroxide washing was nowhere near complete for most of the samples examined here. Dilute hydroxide washing removed 46, 80, 31, 35, and 98% of the ^{137}Cs from B-101, BX-110, BX-112, C-102, and S-101 samples, respectively. Caustic leaching generally improved the ^{137}Cs removal from the sludges. One possible explanation for this behavior is that some of 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. Alternatively, the Cs-containing phase is dissolved in the caustic leaching process.

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 (as well as from tank supernatant and dissolved salt cake solutions) before LLW immobilization. As discussed in the previous sections, the projected ^{137}Cs content for the LLW(a) resulting from the immobilization of the sludge washing/leaching solutions would range from ~50 to ~540 Ci/m^3. Although these values are below the NRC Class C LLW limit of 4,600 Ci/m^3, they are well above the proposed guideline of 3 Ci/m^3 for the immobilized LLW product from the proposed private processing facilities (DOE 1996).

For the tank sludges examined here, the projected TRU concentrations in the immobilized LLW fall below the 0.1 μCi/g limit for Class C LLW, but exceed the 0.01 μCi/g Class A LLW limit. 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. Thus, TRU and Sr removal would likely not be required for the washing and leaching solutions from processing the sludges examined here.

7.6 Impacts on HLW Glass Volume

Table 7.1 compares the reductions in the quantities of IHLW that can be expected from caustic leaching of the five tank wastes examined in FY 1998. It should be emphasized that these estimates are based on simple comparison (as discussed in the preceding sections); no consideration has been given to the effects of waste blending, glass formulation, or other factors that might further reduce the HLW glass volume.

The results are highly variable from tank-to-tank, with estimated IHLW reductions ranging from ~20% to ~95%. The components that control the IHLW quantity also vary from tank-to-tank and depend on the extent of processing (simple washing or caustic leaching). Nevertheless, it can be concluded that there is general benefit in caustic leaching. Except for B-101, > 50% reductions in the IHLW quantities can be achieved by caustic leaching for the wastes examined in this study.

(a) The LLW form is assumed to contain 20 wt% Na_2O and have a density of 2.7 MT/m^3.

Table 7.1. Impact of Caustic Leaching on HLW Glass Volume

Tank	IHLW Glass Reduction Due to Caustic Leaching, %[a]	Component Controlling IHLW Quantity[b]	
		Washed	Leached
B-101	20	WOL	WOL
BX-110	94	Al_2O_3	WOL
BX-112	85	P_2O_5	WOL
C-102	60	WOL	WOL
S-101	82	Al_2O_3	Cr_2O_3

(a) Relative to dilute-hydroxide washing.
(b) Controlling values assumed to be:
- 25 wt% WOL (excluding Na_2O and SiO_2)
- 15 wt% Al_2O_3
- 3 wt% P_2O_5
- 0.5 wt% Cr_2O_3

7.7 Conclusions

The results of the sludge washing and caustic leaching studies reported here indicate the importance of performing parametric leaching studies. The response of the various tank sludge samples to dilute hydroxide washing and caustic leaching is highly variable. This can be true even for tanks containing similar waste types (e.g., BX-110 and BX-112).

Figure 7.2 illustrates this point. The figure summarizes Cr removal for the sludges examined. One consistent trend is that Cr removal increases with increasing leaching duration. But beyond that, trends are difficult to discern. Table 7.2 summarizes the effects of changing parameters on Cr removal. As can be seen, the effects are quite variable. Similar conclusions can be drawn regarding Al removal (Table 7.3).

Thus, before processing a particular batch of waste, parametric leaching tests should be performed. The data from the parametric leaching tests will allow the process engineers to choose the optimal processing conditions needed to achieve the process objectives. This will allow for conservation in NaOH (can use the minimum needed to achieve adequate removals) and energy (can operate at lowest temperature needed). Furthermore, the process objectives will likely be different for the various batches of waste processed. For example, Cr removal would not be much concern from C-102 sludge, as this waste contains very little Cr.

The radionuclide behavior in the tests reported here is consistent with previous sludge washing and caustic leaching tests. It is likely that ^{137}Cs (and perhaps ^{99}Tc) will need to be removed from the sludge washing/leaching solutions, but TRU and ^{90}Sr removal will generally not be needed.

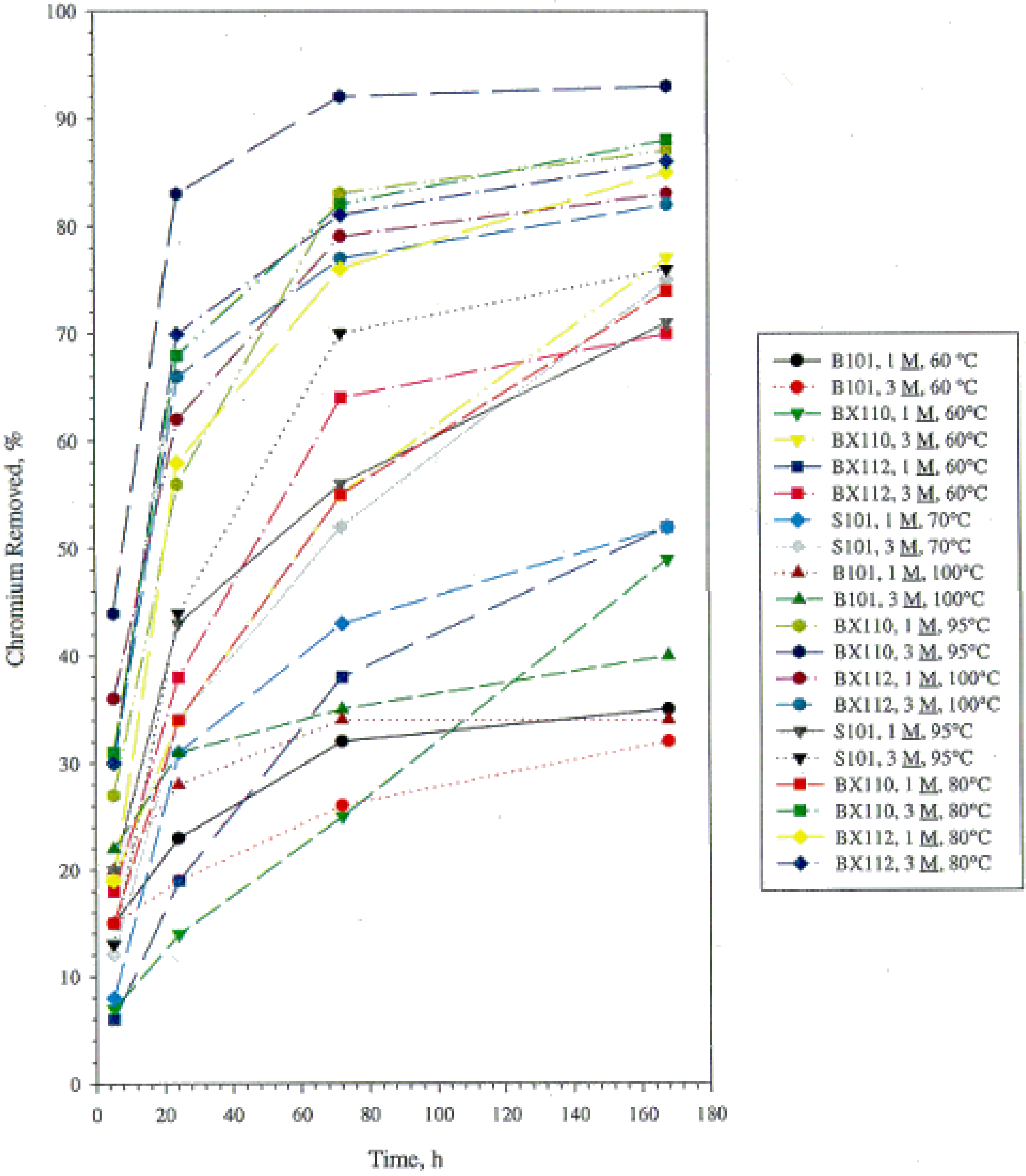

Figure 7.1. Summary of Chromium Removal from Dilute Hydroxide-Washed B-101, BX-110, BX-112, and S-101 Solids

Table 7.2. Effects of Changing Parameters on Chromium Removal

	Improved Chromium Removal?					
	Increase	Increase NaOH Concentration			Increase Temperature	
Tank	Time	60-70°C	80°C	95-100°C	1 M NaOH	3 M NaOH
B-101	Y	N	--	Y	N	N
BX-110	Y	Y	Y	Y	Y	Y
BX-112	Y	Y	N	N	Y/N(a)	Y/N(a)
S-101	Y	Y	--	Y	Y	Y (marginal)

(a) Increasing the temperature from 60 to 80°C resulted in improved Cr removal, but increasing the temperature from 80 to 100°C did not.

Table 7.3. Effects of Changing Parameters on Aluminum Removal

	Improved Aluminum Removal?					
	Increase	Increase NaOH Concentration			Increase Temperature	
Tank	Time	60-70°C	80°C	95-100°C	1 M NaOH	3 M NaOH
B-101	Y	Y	--	Y	N	N
BX-110	Y	Y	Y	N	Y	N
BX-112	N	Y	Y	Y	N	Y/N(a)
S-101	Y	Y	--	Y	Y	Y (marginal)

(a) Increasing the temperature from 60 to 80°C resulted in improved Al removal, but increasing the temperature from 80 to 95°C did not.

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