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Caustic Leaching of Sludges from Selected Hanford Tanks

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Chemical Technology Division

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AES	Atomic Emission Spectroscopy
DOE	Department of Energy
HLW	High Level Radioactive Waste
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
LANL	Los Alamos National Laboratory
LLW	Low-Level Radioactive Waste
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
REDOX	Reduction-Oxidation Process
TRU	Transuranium

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ABSTRACT

Fourteen separate experiments were performed to characterize the caustic leaching behavior of six different Hanford sludges. Six tests were performed with sludge from tank S-104, two tests on SX-113, one test on C-105, one test on C-107, three tests on C-104, and one test on S-101. The test variables were leaching time, leaching temperature, sodium hydroxide concentration in the leach solution, volume of the leaching solution, and mass of the sludge in a batch.

Sludge S-104 is a REDOX waste characterized by average aluminum concentration and high chromium concentration. It was leached with sodium hydroxide solutions ranging in concentration from 3.8 to 6.33 *M* for durations ranging from 4 to 126 h. More than 95% of the chromium and cesium was removed under all of the conditions tested. Removal of aluminum improved with increased caustic concentration and increased leaching time, ranging from 20 to 96% removal. Temperature was varied over a range of 67 to 80 °C, and the percentage of metals removed from the sludge increased with increasing temperature.

Sludge SX-113 is also a REDOX waste characterized as a low aluminum–, low chromium–bearing sludge. Increasing both leaching time and temperature increased the quantities of aluminum, chromium, and cesium removed from the SX-113 sludge with 6.33 *M* NaOH. Removal of aluminum ranged from 51 to 79%; removal of chromium ranged from 53 to 66%; and removal of cesium ranged from 60 to 86%.

Waste in tank C-105 contains high concentrations of aluminum. Approximately 97% of the aluminum and 71% of the chromium were removed from sludge C-105 with 6.33 *M* NaOH at 70 °C in 22 h. About 76% of the cesium was also removed. Similar conditions resulted in the removal of 82% of the aluminum, 70% of the chromium, and 73% of the cesium from sludge C-107, a waste with a high phosphorus concentration.

Leaching tests with sludge C-104 were performed at a sodium hydroxide concentration of 4 *M* and leaching times of 63–65 h. The sludge is high in phosphorus, with moderate concentrations of aluminum and chromium. As operating temperature was increased from 50 to 93 °C, the amount of aluminum removed increased from 29 to 90% and chromium removal increased from 40 to 74%. Removal of cesium also increased with temperature.

Sludge S-101, a waste with a high chromium concentration, was leached with 4 *M* NaOH at 93 °C for 65 h. About 98% of the aluminum, 86% of the chromium, and 99% of the cesium were removed from the sludge.

These results are compared with the results of related tests performed at Los Alamos National Laboratory and Pacific Northwest National Laboratory. In general, any advantages of using higher concentrations of sodium hydroxide can be achieved by increasing the leaching time and temperature, and thereby avoid the disadvantage of handling the additional sodium hydroxide. Differences in results are attributed to differences in leaching procedures, difficulties in chemical analysis, and inhomogeneity of the sludge samples. Additional tests are needed to optimize the caustic leaching parameters.

If it is accepted that these results are applicable to all of the sludge in the six tanks tested (i.e., that these were representative samples), then up to 680 metric tons of aluminum and 20 metric tons of chromium could be removed from the sludge alone by caustic leaching. Significant quantities of other components would also be removed. Therefore, these materials would not have to be included in high-level waste storage. Conditions for optimum removal and separation, especially from transuranium components, still need to be determined.

1. INTRODUCTION

1.1 THE WASTE REDUCTION PROBLEM

Production operations at many Department of Energy (DOE) sites throughout the United States have resulted in enormous quantities of radioactive and hazardous wastes which are stored in underground tanks. Most of this waste was produced by the processing of irradiated nuclear fuel to recover uranium and plutonium, and small amounts of waste were produced during research and development activities and during production of isotopes for special (e.g., medical) purposes.

The high-level radioactive waste (HLW) from irradiated fuel processing operations was an acidic aqueous liquid containing the fission products, some of which were highly radioactive, with large amounts of other chemicals added during processing. It also contained small amounts of the actinides, including the transuranium (TRU) elements up through curium. To permit storage of these materials in mild steel tanks, which would otherwise corrode or dissolve in acidic conditions, the waste was neutralized with a base, primarily sodium hydroxide. The addition of sodium hydroxide raised the pH of the solution (to ≥ 12) and precipitated many of the waste components, creating a sludge. Evaporation of the water to reduce the waste volume resulted in additional precipitation. These processes resulted in wastes comprised of three distinct phases: (1) a high-pH, nitrate-bearing supernatant, (2) a precipitated, actinides-bearing sludge, and (3) an intermediate layer of saltcake. The radioactive components represent only a small fraction of the waste.

If the waste were vitrified without any pretreatment, the resulting glass would be characterized as transuranic HLW and require disposal in a deep geologic repository. The cost of such an option would be prohibitive. Partitioning of the waste into a large low-level radioactive waste (LLW) fraction and a small HLW fraction can greatly reduce disposal costs. The LLW fraction would qualify for near-surface disposal following immobilization (vitrification or grouting), and only the smaller HLW

fraction would be vitrified and stored in a deep geologic repository. Large savings in the overall disposal costs would be realized.

1.2 ENHANCED SLUDGE WASHING

The waste sludges contain high concentrations of nonradioactive materials, such as aluminum, chromium, and phosphates, that can significantly increase the volume of the final HLW form requiring disposal. There is increasing emphasis on removing these materials using Enhanced Sludge Washing, a process taking advantage of the solubilities of these materials under very caustic conditions to partition the radioactive and nonradioactive components. The behavior of some of the components, such as chromium and phosphate, is also important to vitrification processes. If the nonradioactive components could be preferentially solubilized, then the volume of the remaining radioactive waste to be treated and/or stored would be significantly reduced. The optimum conditions for appropriate partitioning of the sludge components have not been determined.

Aluminum is present in the Hanford tank sludges in large quantities. Caustic leaching of the sludge is expected to solubilize the aluminum by converting it to sodium aluminate (Lumetta et al., 1996); in the case of boehmite,

$$AlOOH(s) + NaOH(aq) \rightarrow NaAlO_2(aq) + H_2O \qquad (1\text{-}1)$$

and in the case of gibbsite,

$$Al(OH)_3(s) + NaOH(aq) \rightarrow NaAlO_2(aq) + 2H_2O \qquad (1\text{-}2)$$

Metal phosphates in the sludges are expected to react with sodium hydroxide to form soluble sodium orthophosphate (Lumetta et al. 1996 and Lumetta et al. 1997a and 1997b). For example,

$$FePO_4(s) + 3NaOH(aq) \rightarrow Fe(OH)_3(s) + Na_3PO_4(aq) \qquad (1\text{-}3)$$

Chromium may be converted to the soluble tetrahydroxochromium(III) anion under conditions of high hydroxide concentration (Lumetta et al., 1996 and Lumetta et al., 1997a and 1997b). That is,

$$Cr(OH)_3(s) + NaOH(aq) \rightarrow Na[Cr(OH)_4](aq) \quad . \qquad (1\text{-}4)$$

The relatively poor chromium dissolution of some sludges has led to the study of the alkaline oxidative leaching of sludge to convert the chromium to chromate to improve the dissolution (Rapko et al., 1997).

1.3 OBJECTIVES OF STUDY

The objective of this project was to measure the caustic dissolution behavior of sludge components from selected Hanford waste tank sludge samples under different conditions. The dissolution of aluminum, chromium, and other constituents of actual sludge samples in aqueous sodium hydroxide solution was evaluated using various values of temperature, sodium hydroxide concentration, volume of caustic solution per unit mass of sludge (liquid:solids ratio), and leaching time.

2. DESCRIPTION OF EXPERIMENTS

2.1 PARAMETERS OF THE ENHANCED SLUDGE WASHING PROCESS

The proposed enhanced sludge washing baseline pretreatment would retrieve the sludge by mixing with inhibited water, leach the sludge with caustic, and wash the residue with additional inhibited water to remove all of the leachate solution. The inhibited water contains 0.01 *M* sodium hydroxide and 0.01 *M* sodium nitrite. In the initial tests conducted by Lumetta et al. (1996), the sludge was leached with 3 *M* NaOH for 5 h at 100°C. This was expected to remove significant quantities of the aluminum, phosphorus, and chromium. Additional tests by Lumetta et al. (1997b) have been conducted using sequential leach steps and longer leaching times. However, the optimum sodium hydroxide concentration, leach time, leach temperature, and caustic/sludge ratio have not been determined for maximum removal of these components.

2.2 SLUDGE SAMPLES

Samples of sludges from several Hanford tanks were obtained directly from Westinghouse Hanford/Pacific Northwest National Laboratory (PNNL). Other samples were the same samples that were provided to Los Alamos National Laboratory (LANL), and portions were then shipped from LANL to the Oak Ridge National Laboratory (ORNL).

Six sludge samples were selected for these leaching studies. The origin of the samples (specific tank), the type of waste believed to be included in the tank, the total amount of sludge in each tank, and the masses of some of the components of special interest are shown in Table 2.1. Sludges S-101 and S-104 have a high chromium concentration; C-104 and C-107 are high in phosphorus; and C-105 is high in aluminum. Over 8,000,000 kg of sludge is present in these six tanks, containing over 700,000 kg of aluminum and 23,000 kg of chromium.

2.3 EXPERIMENTAL PROCEDURES

The leaching experiments were conducted in hot cell A in Building 4501 at ORNL. The cell was cleaned prior to use to minimize any cross contamination. The low contamination level allowed entry into the cell to install and service the equipment. To contain spills, most of the equipment was placed in a large stainless steel tray on a raised platform. Whenever possible, the controls for the equipment were positioned outside the hot cell.

A calibrated Mettler PM4000 top-loading balance with a glass cover was used to weigh the samples. A mixing apparatus was designed and built to leach samples of sludge at temperatures up to 95°C (Figs. 2.1 and 2.2). The design allowed high-temperature leaching of up to three sludge samples simultaneously. The centrifuge tubes containing the sludge and leachant were placed in a Teflon holder inside a stainless steel vessel, which was sealed by compressing a Viton gasket between the lip of the vessel and a stainless steel lid. The Teflon holder positioned the centrifuge tubes inside the vessel in a way that prevented direct contact of the tubes with the steel vessel. During a test, about

Table 2.1. Inventory and some characteristics of sludges that were tested

Tank	Waste type	Total mass (kg)	Al mass (kg)	Cr mass (kg)	P mass (kg)	U mass (kg)	Cs-137 (Ci)
C-104[a]	PCW, Zr CW	1.34×10^6	7.29×10^4	1.18×10^3	1.76×10^4	4.34×10^4	8.51×10^4
C-105[a]	TBP, Sr	8.80×10^5	1.49×10^5	4.10×10^2	3.29×10^3	1.37×10^4	1.61×10^5
C-107[a]	$BiPO_4$ 1C, CW	1.35×10^6	6.39×10^4	4.29×10^2	6.66×10^4	1.43×10^4	4.59×10^4
S-101[a]	REDOX, EB	2.67×10^6	2.37×10^5	1.39×10^4	1.18×10^4	1.38×10^4	3.57×10^5
S-104[b]	REDOX	1.66×10^6	1.96×10^5	7.14×10^3		1.10×10^4	1.05×10^5
SX-113[a]	REDOX	1.38×10^5	1.59×10^3	8.50×10^0		1.90×10^1	3.42×10^3

Key: PCW= PUREX aluminum waste
Zr CW= zircaloy cladding waste
TBP= waste from tributyl phosphate uranium recovery
Sr = sludge wash waste from strontium extraction process
$BiPO_4$ 1C= bismuth phosphate first-cycle decontamination waste
CW = cladding waste
REDOX= reduction-oxidation process waste
EB = evaporator bottoms

[a] Source: Colton, N. G., *Status Report: Pretreatment Chemistry Evaluation FY 1997 — Wash and Leach Factors for the Single-shell Tank Waste Inventory*, PNNL-11646, Battelle, Pacific Northwest National Laboratory, August 1997.

[b] Source: Colton, N. G., *Status Report: Pretreatment Chemistry Evaluation — Wash and Leach Factors for the Single-shell Tank Waste Inventory*, PNNL-11290, Battelle, Pacific Northwest National Laboratory, September 1996.

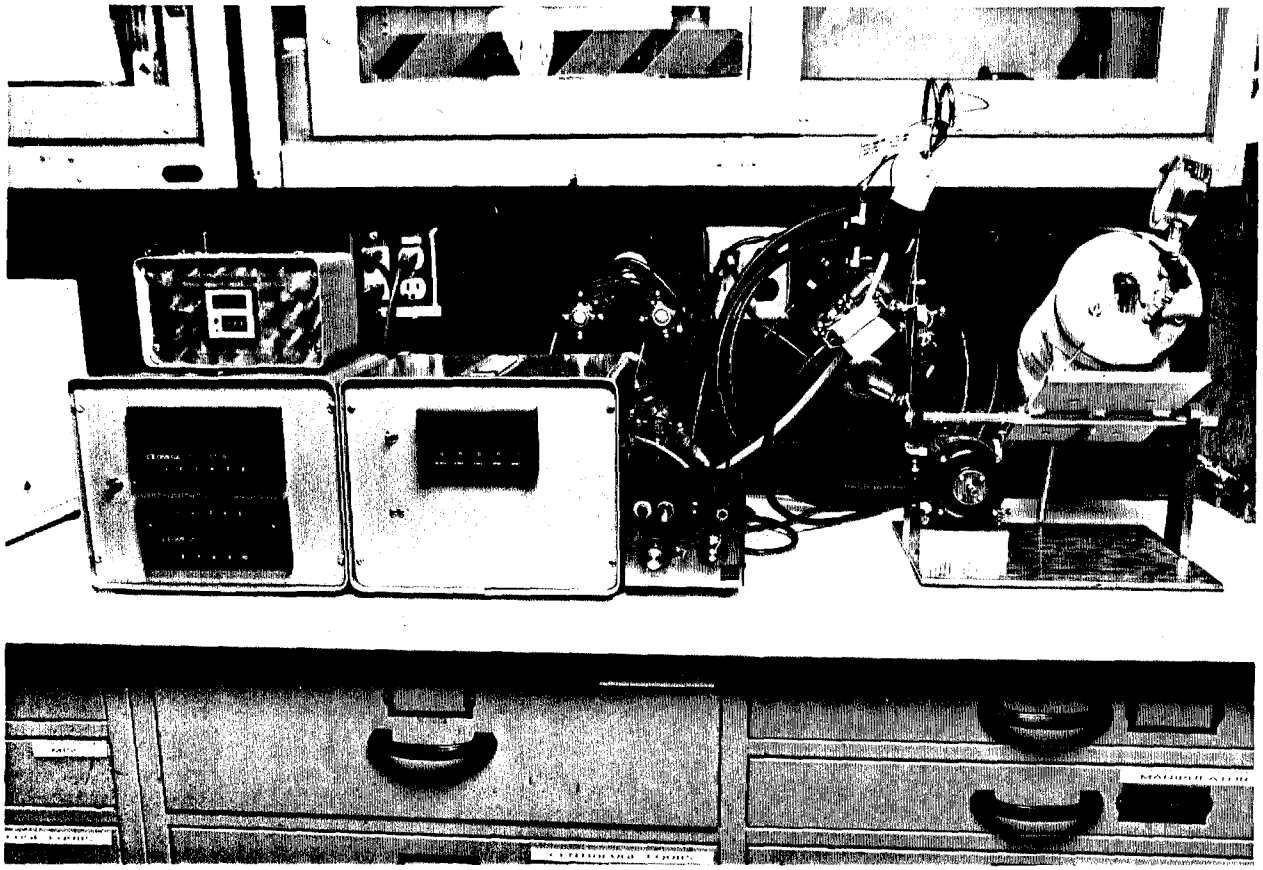

Fig. 2.1. Sludge leaching equipment featuring temperature monitor and controller and controlled-temperature mixer.

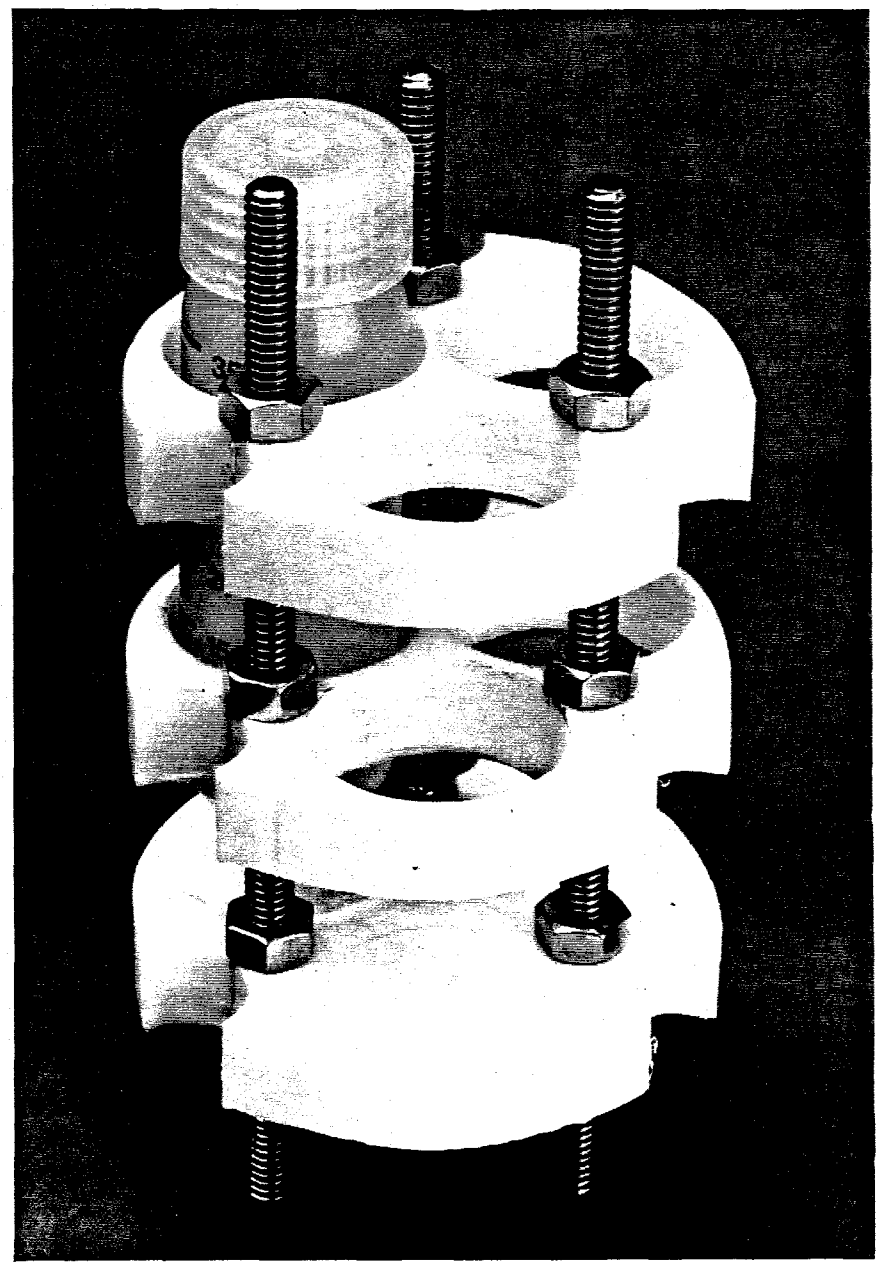

Fig. 2.2. Up to three samples could be processed simultaneously using this sample tube holder.

half of the volume of the free space in the steel vessel was filled with deionized water to improve heat transfer and temperature control. The temperature inside the vessel was measured with a calibrated J-type thermocouple, which also served as the control measurement. The vessel was placed in a well-insulated aluminum tube furnace, which was heated with heating tape. Calibrated thermocouples were taped directly to the outside surface of the furnace at three different locations. Two of the thermocouples were monitored with an OMEGA temperature indicator; the other thermocouple was connected to an OMEGA high-temperature controller (Model CN-375) and temperature indicator. The furnace assembly was attached to an oscillating mixer that rocked the assembly from −45° to +45° from the horizontal plane at ~8 cycles per minute. The centrifuge tubes containing the sludge and leachate were removed from the vessel after the temperature of the heating vessel reached room temperature.

After mixing, the samples were centrifuged for 15–20 min at 2500 rpm (~1500 × gravity) using an International Equipment Company Centra-GP8 tabletop centrifuge to separate the sludge solids from wash and leach solutions. The solutions were removed from the centrifuged sludge solids using a specially designed vacuum decantation apparatus. Following the leaching step, the centrifuged, wet sludge residues were rinsed three times with inhibited water, using ~15 mL of inhibited water for each rinse. A vortex mixer was used to suspend and mix the solids. The residues were again recovered by centrifugation. An ORION Research digital pH meter and an ORION 8103 Ross combination electrode were used for pH measurements.

2.4 ANALYSIS OF SAMPLES

Analytical methods were similar to those described in Appendix B of a report by Sears et al. (1990) and a report by Keller et al. (1996) and are briefly summarized here. Samples of sludge solids were solubilized by microwave-assisted digestion with nitric acid, based on SW-846 Method 3051, *Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils*. This method is considered by regulatory agencies to be a total digestion for metals and radionuclides. However, it gave poor

results for silicon. A simple nitric acid treatment will not dissolve most siliceous materials. Consequently, the residue was assumed to be silicon dioxide, and the silicon was determined gravimetrically.

The leachates and wash solutions were filtered and digested by the SW-846 Method 3015, *Microwave Assisted Acid Digestion of Aqueous Samples and Extracts.* The leachates and wash solutions were analyzed by the following methods: gross alpha and alpha pulse, gross beta, and gamma spectrometry for radionuclides; inductively coupled plasma atomic emission spectroscopy (ICP-AES) for metals; and ion chromatography for anions. In some samples, bismuth and antimony were determined by Method 7000A, *Atomic Absorption Methods*. The analytical error for the metal measurements depends upon the analytical method, the concentration level, and the matrix. ICP-AES is a multielement measurement technique designed for the best average performance for all elements and is not optimized for any single component.

The common inorganic anions were measured by ion chromatography (IC) with a Dionex Model 4500i system. The complex precipitation chemistry of the sludge complicates the measurement of total anions. The primary sludge anion data was based on a water leach, which represented the sum of the anions in the interstitial liquid and the water-soluble anions from the solids. The standard radiochemical methods for radioactive waste characterization are EPA Method 600/900.0, *Gross Alpha and Beta Radioactivity in Drinking Water,* and EPA Method 600/901.1, *Gamma Emitting Radionuclides in Drinking Water.* EPA Method 901.1 was used to determine Am-241, Co-60, Cs-134, Cs-137, Eu-152, Eu-154, and Eu-155. Gross beta measurements were made by liquid scintillation counting. In some cases, gross alpha activity was measured and plutonium isotopes were determined by alpha spectrometry after a radiochemical separation.

The moisture content of solids was determined by drying the samples in an oven at 110°C. Hydroxide concentrations were determined by titration with 0.1 *N* HCl using phenolphthalein indicator.

3. DATA REDUCTION METHODOLOGY

3.1 PARTITIONING BETWEEN PHASES

The caustic leaching studies described in this report are empirical in nature. They were intended to ascertain the extent of the solubility of sludge components under specific conditions. Because the time required to establish an equilibrium was unknown, one could not be sure when the leaching process was complete. As a scoping study, it was sufficient to vary the process conditions (including leaching time) and analyze the products. How each component partitioned between the phases was then quantified.

3.2 MATERIAL BALANCES

The data obtained by experiment consisted of the initial mass of the sludge sample, the mass of the residue, the initial and final volumes (or mass and density) of both the leaching and rinsing solutions, and a chemical analysis of the components in each of these four analytes. The percentage of each component removed (e.g., solubilized) from the sludge can be calculated from these data by more than one method. In one method the difference between the quantity of material in the original sludge and that in the residue is the amount removed. The percentage removed is then

$$w_i = \frac{m_0 C_{0,i} - m_R C_{R,i}}{m_0 C_{0,i}} \times 100 , \qquad (3\text{-}1)$$

where

w_i = the percentage of species i removed from the sludge by weight;

m_0 = mass of original sludge sample, g;

m_R = mass of sludge residue, g;

$C_{0,i}$ = concentration of component i in original sludge, μg/g;

$C_{R,i}$ = concentration of component i in the sludge residue, μg/g; and

i = the i*th* species.

This method is referred to as "based on residual."

Another method supposes that the amount of material removed from the sludge is that which appears in the leachate and rinse solutions. The percentage removed is then

$$w_i' = \frac{V_L C_{L,i} + V_W C_{W,i}}{m_0 C_{0,i}} \times 100 , \qquad (3\text{-}2)$$

where

w_i' = the percentage of species i removed from the sludge by weight (leachate and rinse basis);

V_L = volume (mass) of leachate solution, mL (g);

V_W = volume (mass) of wash or rinse solution, mL (g);

$C_{L,i}$ = concentration of component i in the leachate, μg/mL (μg/g); and

$C_{W,i}$ = concentration of component i in the wash solution, μg/mL (μg/g).

Alternate units are given in parenthesis because experimental measurements were made in both units.

An overall material balance was used to evaluate the chemical analyses; that is, the recovery of each species. The percentage recovery is expressed as

$$f_i = \frac{m_R C_{R,i} + V_L C_{L,i} + V_W C_{W,i}}{m_0 C_{0,i}} \times 100 . \qquad (3\text{-}3)$$

Values of f_i are 100 for a perfect material balance, <100 when the amount of i found in the original sludge is greater than the sum of the fractions into which it was partitioned, and >100 when the amount of i found in the original sludge is smaller than the sum of the fractions into which it was partitioned.

It is important to remember that Eqs. (3-1) through (3-3) are valid only if no solutes are introduced by the leaching or rinsing solutions. For example, a strong leaching solution of sodium hydroxide introduces sodium, and the equations must be modified to account for it. The primary interest is in those species, such as aluminum, chromium, phosphate, and a few others, that are not found in the processing solutions. Thus, the equations are adequate for evaluating the data.

3.3 PROPAGATION OF ERRORS

Difficulties in measuring the concentration of some species lead to questions regarding how sharply the solubility could be defined. Or, alternatively, how reproducible are the data expected to be?

In the experiments reported in this document, measuring the mass of a sample was easily done to within one part per thousand (0.1%). Measurements of sample volume and/or density also approached this accuracy. The largest errors occurred in measuring the concentration of species in the multicomponent mixtures. Errors in measured concentration were often in the 10% range and were sometimes larger for those species near the lower limit of detection. Therefore, to propagate the errors to the calculated results, it was assumed that the mass (or volume) measurements contained no error and that all of the error originated from the measurement of concentration. Methods to propagate measurement errors to calculated results are given in standard texts (e.g., Holman 1971).

Equation (3-1) was used to calculate the percentage of a species removed from the sludge based on residual analysis. The error in calculating this value was evaluated by

$$\sigma_{w,i} = \left[\left(\frac{m_R C_{R,i}}{m_0 C_{0,i}^2} \sigma_{0,i} \right)^2 + \left(\frac{m_R}{m_0 C_{0,i}} \sigma_{R,i} \right)^2 \right]^{1/2} \times 100 \ , \qquad (3\text{-}4)$$

where

$\sigma_{w,i}$ = error in calculated percentage removed, also expressed in percentage;

$\sigma_{0,i}$ = error in measurement of $C_{0,i}$, same units as $C_{0,i}$, and

$\sigma_{R,i}$ = error in measurement of $C_{R,i}$, same units as $C_{R,i}$.

Similarly, the errors in results calculated by Eq. (3-2) are given by

$$\sigma_{w',i} = \left[\left(\frac{V_L}{m_0 C_{0,i}}\sigma_{L,i}\right)^2 + \left(\frac{V_W}{m_0 C_{0,i}}\sigma_{W,i}\right)^2 + \left(\frac{(V_L C_{L,i} + V_W C_{W,i})}{m_0 C_{0,i}^2}\sigma_{0,i}\right)^2\right]^{1/2} \times 100 , \qquad (3\text{-}5)$$

where

$\sigma_{w',i}$ = error in calculated percentage removed (based on leachate and rinse), percentage;

$\sigma_{L,i}$ = error in measurement of $C_{L,i}$, same units as $C_{L,i}$; and

$\sigma_{W,i}$ = error in measurement of $C_{W,i}$, same units as $C_{W,i}$.

And finally, the errors in results calculated by Eq. (3-3) are given by

$$\sigma_{f,i} = \left[\left(\frac{m_R}{m_0 C_{0,i}}\sigma_{R,i}\right)^2 + \left(\frac{V_L}{m_0 C_{0,i}}\sigma_{L,i}\right)^2 + \left(\frac{V_W}{m_0 C_{0,i}}\sigma_{W,i}\right)^2 + \left(\frac{(m_R C_{R,i} + V_L C_{L,i} + V_W C_{W,i})}{m_0 C_{0,i}^2}\sigma_{0,i}\right)^2\right]^{1/2} \times 100 , \qquad (3\text{-}6)$$

where

$\sigma_{f,i}$ = error in calculated percentage recovery, percentage.

4. RESULTS AND DISCUSSION

Fourteen separate experiments were performed to characterize the leachability of the six different sludges listed in Table 2.1. Six tests were performed with sludge from tank S-104, two tests on SX-113, one test on C-105, one test on C-107, three tests on C-104, and one test on S-101. The leaching time, leaching temperature, sodium hydroxide concentration in the leach solution, volume of leaching solution, and mass of sludge utilized in the tests were varied. Table 4.1 summarizes the conditions at which each test was performed. The weight fraction of the sludge attributable to water is also given in the table. The large variation in water content of the different sludges is evident. The

Table 4.1. List of tests and experimental conditions

Test #	Tank sample	Sludge wt. (g)	NaOH concn. (*M*)	NaOH vol. (mL)	Temp. (°C)	Time (h)	Moisture (wt %)	Liquid:solids (mL/g)[a]
1	S-104	3.01	3.8	23	67	4	15.6	9
2	S-104	3.02	3.8	23	67	24	15.6	9
3	S-104	3.06	3.99	15	70	21	15.6	6
4	S-104	1.49	3.99	15	70	21	15.6	12
5	S-104	1.51	6.33	15	70	21	15.6	12
6	SX-113	1.46	6.33	15	70	21	47.9	20
7	C-105	1.51	6.33	15	70	22	4.7	10
8	C-107	4.37	6.33	15	70	22	46.3	6
9	S-104	1.10	6.33	30	80	126	15.6	32
10	SX-113	1.32	6.33	30	80	126	47.9	44
11	C-104	2.20	3.99	25	80	65	63.5	31
12	C-104	1.44	3.99	15	50	63	43.7	19
13	C-104	2.14	3.99	21	93	65	63.5	27
14	S-101	1.90	3.99	21	93	65	31.8	16

[a]Calculated on the basis of the mass of dry sludge: (NaOH volume)/[(mass wet sludge) (1 - % moisture/100)].

volume of solution used to leach the sludge sample and the mass of sludge sample are conveniently combined into the liquid-to-solid ratio, a scaled-parameter that is useful for process design calculations. Because of the variation in the moisture content among the sludges, the liquid:solids ratio was expressed on a dry solids basis, as shown in Table 4.1. Table 4.2 shows the mass of wet residual solids and the mass of the leachate and rinse solutions recovered in each test. The results of the leaching tests are organized by sample origin (i.e., tank name) in the following sections.

4.1 SLUDGE S-104

The primary metals found in sludge S-104 are sodium, aluminum, and uranium. Significant concentrations of chromium, iron and phosphorus are also present. (See original sludge analysis in Table 4.3.) Six separate enhanced sludge washing experiments were performed over a range of the operating parameters to ascertain how sludge S-104 would partition among the process streams. Comprehensive listings of the data and calculated results obtained on S-104 sludge are given in Tables 4.3 through 4.14. For a given experiment, the data are provided in one table and the calculated results are provided in the following table. The quantity of each partition or phase has already been given in Table 4.2. For example, the concentration of species measured in the original sludge, residue, leachate solution, and composite rinse solution for test #1 are given in Table 4.3. The estimated error (standard deviation) in each of these measurements is also listed in the table. Table 4.4 gives the corresponding calculated percentage of each species removed from the sludge and the estimated error in the result. For the purpose of calculation, concentrations below the detectable limit were set to zero.

To illustrate some of the considerations in interpretation of the data and results, discussion of test #1 is useful. Based on the analysis of the residual solids, 98.0% ± 0.1% of the chromium is removed from sludge S-104 by leaching with 9 mL of 3.8 *M* NaOH per gram of dry solids at 67°C for 4 h. Analysis of the leachate and rinse solutions indicate that 112.8% ± 1.3% of the chromium is removed. A recovery of 114.8% ± 1.3% indicates that the chromium material balance is adequate.

Table 4.2. Amount of sludge used, and amount of residue and liquid solutions recovered in each test

Test #	Tank sample	Sludge[a] (g)	Residue[a] (g)	Leachate (g)	Leachate density (g/mL)	Rinse (g)	Rinse density (g/mL)
1	S-104	3.01	3.57	27.18	1.267	44.24	1.110
2	S-104	3.02	3.29	27.10	1.273	44.17	1.109
3	S-104	3.06	6.82	19.12	1.189	55.12	1.009
4	S-104	1.49	4.12	18.46	1.166	57.18	1.005
5	S-104	1.51	2.33	21.96	1.230	44.10	1.0
6	SX-113	1.46	1.03	20.15	1.236	45.24	1.004
7	C-105	1.51	0.53	18.79	1.238	45.99	0.999
8	C-107	4.37	2.13	25.92	1.222	44.42	1.016
9	S-104	1.10	0.45	36.35	1.236	42.69	1.001
10	SX-113	1.32	0.73	35.34	1.230	45.59	1.006
11	C-104	2.20	2.18	28.72	1.162	48.42	1.004
12	C-104	1.44	1.57	16.50	1.154	45.54	1.008
13	C-104	2.14	1.69	21.55	1.168	45.93	1.002
14	S-101	1.90	0.42	21.92	1.182	47.10	0.998

[a]Mass of centrifuged wet solids following decantation of liquids.

Table 4.3. Test #1 - concentrations of species in enhanced sludge washing process steps for S-104 sludge
(leach conditions: liquid:solids, 9 mL/g; NaOH, 3.8 *M*; temperature, 67°C; time, 4 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/mL)		Rinse (μg/mL)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	<0.593[a]	b	<1.51	b	<0.774	b	<0.0774	b
Al	140000	1480	77300	520	1200	15.8	162	10.9
Ba	29.8	0.552	18.4	0	<0.0084	b	<0.0084	b
Be	<0.0735	b	<0.187	b	<0.0096	b	<0.0096	b
Bi	66.8	6.89	73.3	11	0.54	0.48	<0.3	b
Ca	256	1.47	178	2.57	0.492	0.024	0.228	0.048
Cd	<1.01	b	<2.57	b	<0.132	b	<0.132	b
Co	<0.662	b	<1.69	b	<0.0864	b	<0.0864	b
Cr	3100	14.2	51.5	1.4	392	4.85	53.2	0.624
Cu	47.9	0.643	13	0.468	3.82	0.132	0.036	0.012
Fe	2480	28.3	1040	6.55	0.864	0.18	<0.0204	b
K	314	11.3	67.4	4.91	124	44.8	42.3	0.66
Mg	52.6	1.75	42.9	1.64	<0.118	b	<0.118	b
Mn	1990	10.1	772	5.38	<0.0096	b	<0.0096	b
Ni	77.3	1.29	49.6	1.64	<0.135	b	<0.135	b
P	2480	216	720	10.1	<0.6	b	<0.6	b
Sb	<10.1	b	<25.8	b	<1.32	b	<1.32	b
Si	134	1.1	204	1.4	56	1.21	7.39	0.168
Sr	580	2.02	355	0	0.102	0.012	<0.03	b
Th	2.67	0.827	<5.68	b	0.372	0.312	<0.291	b
Tl	<8.9	b	<22.7	b	<1.16	b	<1.16	b
U	8400	76.8	4450	17.6	1.57	0.672	<0.547	b
V	<0.188	b	<0.48	b	<0.0246	b	<0.0246	b
Zn	11.1	1.19	8.54	2.57	1.26	0.072	0.414	0.06
Br^-	<146	b	<502	b	<50	b	<5	b
Cl^-	2900	30	<502	b	281	2	74.9	6.8
F^-	<293	b	<502	b	<10	b	<10	b
NO_3^-	388000	9000	2030	650	23400	600	3600	51
PO_4^{3-}	<585	b	<2008	b	<20	b	<20	b
SO_4^{2-}	1770	220	<1004	b	187	4	30.6	4.5
Radiospecies	Bq/g		Bq/g		Bq/mL		Bq/mL	
Cs-137	2700000	100000	49000	1000	c	c	c	c
Eu-152	<1800	b	<1200	b	c	c	c	c
Eu-154	5900	1400	2900	1500	c	c	c	c
Eu-155	<6700	b	<3000	b	c	c	c	c
Gross-α	23000	1000	16000	2000	c	c	c	c
Gross-β	34000000	1000000	16000000	1000000	c	c	c	c

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.4. Test #1 - percentage of each species solubilized and percentage recovery for S-104 sludge
(leach conditions: liquid:solids, 9 mL/g; NaOH, 3.8 *M*; temperature, 67°C; time, 4 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	a	a	a	a	a	a
Al	34.51	0.82	7.64	0.15	73.13	0.90
Ba	26.77	1.36	0.00	0.00	73.23	1.36
Be	a	a	a	a	a	a
Bi	-30.15	23.70	5.76	5.16	135.91	24.58
Ca	17.53	1.28	2.55	0.26	85.02	1.31
Cd	a	a	a	a	a	a
Co	a	a	a	a	a	a
Cr	98.03	0.05	112.84	1.26	114.81	1.26
Cu	67.81	1.24	57.83	2.14	90.02	2.60
Fe	50.26	0.65	0.25	0.05	49.99	0.65
K	74.54	2.07	459.81	103.05	485.27	103.22
Mg	3.27	4.90	0.00	0.00	96.73	4.90
Mn	53.99	0.40	0.00	0.00	46.01	0.40
Ni	23.90	2.82	0.00	0.00	76.10	2.82
P	65.57	3.04	0.00	0.00	34.43	3.04
Sb	a	a	a	a	a	a
Si	-80.56	1.93	370.84	7.31	551.41	8.14
Sr	27.41	0.25	0.13	0.01	72.72	0.25
Th	100.00	0.00	99.29	88.77	99.29	88.77
Tl	a	a	a	a	a	a
U	37.17	0.63	0.13	0.06	62.97	0.63
V	a	a	a	a	a	a
Zn	8.75	29.15	130.28	16.36	221.53	37.29
Br^-	a	a	a	a	a	a
Cl^-	100.00	0.00	103.25	3.32	103.25	3.32
F^-	a	a	a	a	a	a
NO_3^-	99.38	0.20	55.26	1.70	55.89	1.72
PO_4^{3-}	a	a	a	a	a	a
SO_4^{2-}	100.00	0.00	98.18	12.76	98.18	12.76
Radiospecies						
Cs-137	97.85	0.09	b	b	2.15	0.09
Eu-152	a	a	a	a	a	a
Eu-154	41.70	33.18	b	b	58.30	33.18
Eu-155	a	a	a	a	a	a
Gross-α	17.49	10.92	b	b	82.51	10.92
Gross-β	44.19	3.86	b	b	55.81	3.86

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit.

[b]Measurement was not made.

Table 4.5. Test #2 - concentrations of species in enhanced sludge washing process steps for S-104 sludge
(leach conditions: liquid:solids, 9 mL/g; NaOH, 3.8 *M*; temperature, 67°C; time, 24 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/mL)		Rinse (μg/mL)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	<0.593[a]	b	<1.8	b	<0.0774	b	<0.0774	b
Al	140000	1480	63900	731	1870	12.1	292	10.9
Ba	29.8	0.552	16	0.278	<0.0084	b	<0.0084	b
Be	<0.0735	b	<0.223	b	<0.0096	b	<0.0096	b
Bi	66.8	6.89	71.7	14.2	<0.3	b	<0.3	b
Ca	256	1.47	186	1.67	0.36	0.012	0.198	0.024
Cd	<1.01	b	<3.06	b	<0.132	b	<0.132	b
Co	<0.662	b	<2.01	b	<0.0864	b	<0.0864	b
Cr	3100	14.2	43.2	0.557	382	3.64	52.8	0.372
Cu	47.9	0.643	8.77	0.278	3.52	0.024	0.066	0.012
Fe	2480	28.3	940	0.835	1.21	0.084	<0.0204	b
K	314	11.3	19.2	6.68	116	3.64	36.9	0.468
Mg	52.6	1.75	39.1	2.23	<0.118	b	<0.118	b
Mn	1990	10.1	754	0.557	<0.0096	b	<0.0096	b
Ni	77.3	1.29	46.4	1.39	<0.135	b	<0.135	b
P	2480	216	616	33.1	2.41	1.13	0.87	1.57
Sb	<10.1	b	<30.7	b	<1.32	b	<1.32	b
Si	134	1.1	262	5.57	46.7	0.612	6.43	0.072
Sr	580	2.02	271	2.23	0.072	0.012	<0.03	b
Th	2.67	0.827	<6.75	b	0.45	0.312	<0.291	b
Tl	<8.9	b	<27	b	<1.16	b	<1.16	b
U	8400	76.8	4160	7.52	0.894	0.348	<0.547	b
V	<0.188	b	<0.571	b	<0.0246	b	<0.0246	b
Zn	11.1	1.19	8.63	2.78	1.07	0.108	0.354	0.132
Br^-	<146	b	<300	b	<5	b	<5	b
Cl^-	2900	30	<300	b	142	2	74.8	4.2
F^-	<293	b	<300	b	<10	b	<10	b
NO_3^-	388000	9000	1190	130	5840	30	4330	60
PO_4^{3-}	<585	b	<1200	b	<20	b	<20	b
SO_4^{2-}	1770	220	<600	b	82.4	15.3	35.6	2.8
Radiospecies	Bq/g		Bq/g		Bq/mL		Bq/ml	
Cs-137	2700000	100000	49000	2000	c	c	c	c
Eu-152	<1800	b	<1400	b	c	c	c	c
Eu-154	5900	1400	2300	800	c	c	c	c
Eu-155	<6700	b	<3200	b	c	c	c	c
Gross-α	23000	1000	13000	2000	c	c	c	c
Gross-β	34000000	1000000	17000000	1000000	c	c	c	c

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.6. Test #2 - percentage of each species solubilized and percentage recovery for S-104 sludge
(leach conditions: liquid:solids, 9 mL/g; NaOH, 3.8 *M*; temperature, 67°C; time, 24 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	a	a	a	a	a	a
Al	50.28	0.77	12.17	0.18	61.89	0.88
Ba	41.51	1.49	0.00	0.00	58.49	1.49
Be	a	a	a	a	a	a
Bi	-16.93	26.11	0.00	0.00	116.93	26.11
Ca	20.85	0.84	2.01	0.13	81.16	0.86
Cd	a	a	a	a	a	a
Co	a	a	a	a	a	a
Cr	98.48	0.02	109.33	0.98	110.85	0.98
Cu	80.05	0.69	53.62	0.87	73.57	1.27
Fe	58.71	0.47	0.34	0.02	41.64	0.48
K	93.34	2.33	415.42	17.15	422.08	17.51
Mg	19.02	5.35	0.00	0.00	80.98	5.35
Mn	58.72	0.21	0.00	0.00	41.28	0.21
Ni	34.61	2.24	0.00	0.00	65.39	2.24
P	72.94	2.77	1.15	0.90	28.21	2.99
Sb	a	a	a	a	a	a
Si	-113.00	4.85	308.97	4.16	521.98	7.05
Sr	49.10	0.45	0.09	0.01	50.99	0.46
Th	100.00	0.00	118.81	90.22	118.81	90.22
Tl	a	a	a	a	a	a
U	46.05	0.50	0.08	0.03	54.03	0.50
V	a	a	a	a	a	a
Zn	15.30	28.76	110.02	20.79	194.72	38.38
Br^-	a	a	a	a	a	a
Cl^-	100.00	0.00	68.54	2.09	68.54	2.09
F^-	a	a	a	a	a	a
NO_3^-	99.67	0.04	25.33	0.62	25.66	0.63
PO_4^{3-}	a	a	a	a	a	a
SO_4^{2-}	100.00	0.00	59.35	9.79	59.35	9.79
Radiospecies						
Cs-137	98.02	0.11	b	b	1.98	0.11
Eu-152	a	a	a	a	a	a
Eu-154	57.53	17.88	b	b	42.47	17.88
Eu-155	a	a	a	a	a	a
Gross-α	38.42	9.84	b	b	61.58	9.84
Gross-β	45.53	3.58	b	b	54.47	3.58

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit.

[b]Measurement was not made.

Table 4.7. Test #3 - concentrations of species in enhanced sludge washing process steps for S-104 sludge
(leach conditions: liquid:solids, 6 mL/g; NaOH, 4 *M*; temperature, 70°C; time, 21 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/mL)		Rinse (μg/mL)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	<0.593[a]	b	<2.89	b	<0.0387	b	<0.0387	b
Al	140000	1480	50000	404	2750	3.03	68.8	7.88
Ba	29.8	0.552	17.7	0	0.009	0	0.006	0
Be	<0.0735	b	<0.358	b	<0.0048	b	<0.0048	b
Bi	66.8	6.89	88.4	14.8	0.405	0.336	0.423	0.06
Ca	256	1.47	161	1.34	0.834	0	<0.0234	b
Cd	<1.01	b	<4.92	b	<0.066	b	<0.066	b
Co	<0.662	b	<3.22	b	<0.0432	b	<0.0432	b
Cr	3100	14.2	35.8	0.895	543	3.64	13.5	0.066
Cu	47.9	0.643	15.7	0	5.67	0.048	0.024	0.006
Fe	2480	28.3	907	4.92	1.38	0.012	<0.0102	b
K	314	11.3	<15.5	b	142	3.03	4.93	0.09
Mg	52.6	1.75	32.7	1.79	<0.0591	b	<0.0591	b
Mn	1990	10.1	762	3.58	<0.0048	b	<0.0048	b
Ni	77.3	1.29	41.2	1.79	<0.0675	b	<0.0675	b
P	2480	216	620	37.6	1.12	0.426	1.59	0.42
Sb	<10.1	b	<49.3	b	<0.661	b	<0.661	b
Si	134	1.1	545	13	68.4	0.816	6.99	0.114
Sr	580	2.02	216	3.58	0.063	0	<0.015	b
Th	2.67	0.827	<10.9	b	0.6	0.06	<0.146	b
Tl	<8.9	b	<43.4	b	<0.581	b	<0.581	b
U	8400	76.8	3180	41.2	<0.273	b	<0.273	b
V	<0.188	b	1.79	0	<0.0123	b	0.048	0.006
Zn	11.1	1.19	<6.6	b	1.08	0.084	<0.0885	b
Br^-	<146	b	<7.9	b	<50	b	<5	b
Cl^-	2900	30	<9	b	330	10	17.6	5.8
F^-	<293	b	<7.9	b	<5	b	<5	b
NO_3^-	388000	9000	433	46	24700	200	1010	20
PO_4^{3-}	<585	b	<15.8	b	<10	b	<10	b
SO_4^{2-}	1770	220	199	7	332	2	21.5	1.1

Radiospecies	Bq/g		Bq/g		Bq/mL		Bq/mL	
Co-60	c	c	<900	b	<60	b	<100	b
Cs-137	2700000	100000	61000	3000	450000	10000	12000	1000
Eu-152	<1800	b	c	c	c	c	c	c
Eu-154	5900	1400	3400	1100	c	c	c	c
Pu-238	380	c	184	c	c	c	c	c
Pu-239/240	19600	c	7810	c	c	c	c	c
Pu-242	64	c	9.6	c	c	c	c	c
Pu-all	20000	2000	8000	1300	<.2	b	0.28	0.64
Gross-α	23000	1000	11000	3000	2.5	9	5	18
Gross-β	34000000	1000000	12000000	1000000	520000	10000	13000	1000

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.8. Test #3 - percentage of each species solubilized and percentage recovery for S-104 sludge
(leach conditions: liquid:solids, 6 mL/g; NaOH, 4 *M*; temperature, 70°C; time, 21 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	a	a	a	a	a	a
Al	20.40	1.06	11.20	0.16	90.80	1.16
Ba	-32.38	2.45	0.52	0.01	132.90	2.46
Be	a	a	a	a	a	a
Bi	-194.94	58.00	14.50	3.43	309.44	58.88
Ca	-40.17	1.42	1.71	0.01	141.88	1.42
Cd	a	a	a	a	a	a
Co	a	a	a	a	a	a
Cr	97.43	0.07	99.82	0.77	102.40	0.78
Cu	26.95	0.98	63.10	1.02	136.15	1.92
Fe	18.49	1.03	0.29	0.00	81.80	1.03
K	100.00	0.00	265.68	10.83	265.68	10.83
Mg	-38.56	8.88	0.00	0.00	138.56	8.88
Mn	14.66	0.59	0.00	0.00	85.34	0.59
Ni	-18.79	5.53	0.00	0.00	118.79	5.53
P	44.28	5.91	1.38	0.34	57.10	6.02
Sb	a	a	a	a	a	a
Si	-806.47	22.87	361.40	4.62	1267.87	24.26
Sr	17.00	1.41	0.06	0.00	83.06	1.41
Th	100.00	0.00	118.09	38.44	118.09	38.44
Tl	a	a	a	a	a	a
U	15.63	1.34	0.00	0.00	84.37	1.34
V	a	a	a	a	a	a
Zn	100.00	0.00	51.13	6.77	51.13	6.77
Br^-	a	a	a	a	a	a
Cl^-	100.00	0.00	70.64	4.07	70.64	4.07
F^-	a	a	a	a	a	a
NO_3^-	99.75	0.03	38.10	0.93	38.35	0.93
PO_4^{3-}	a	a	a	a	a	a
SO_4^{2-}	74.94	3.24	120.26	15.00	145.32	18.13
Radiospecies						
Co-60	a	a	a	a	a	a
Cs-137	94.96	0.31	95.52	4.09	100.55	4.26
Eu-152	a	a	a	a	a	a
Eu-154	-28.44	51.53	b	b	128.44	51.53
Pu-238	-7.92	0.00	b	b	107.92	0.00
Pu-239/240	11.19	0.00	b	b	88.81	0.00
Pu-242	66.57	0.00	b	b	33.43	0.00
Pu-all	10.85	17.01	0.03	0.06	89.18	17.01
Gross-α	-6.59	29.44	0.45	1.41	107.04	29.47
Gross-β	21.34	6.95	8.72	0.30	87.38	7.04

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

[b]Measurement was not made.

Table 4.9. Test #4 - concentrations of species in enhanced sludge washing process steps for S-104 sludge
(leach conditions: liquid:solids, 12 mL/g; NaOH, 4 *M*; temperature, 70°C; time, 21 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/mL)		Rinse (μg/mL)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	<0.593[a]	b	<2.88	b	<0.0387	b	<0.0387	b
Al	140000	1480	40100	152	1620	9.09	33.8	0.336
Ba	29.8	0.552	15	0	0.009	0	0.006	0
Be	<0.0735	b	<0.358	b	<0.0048	b	<0.0048	b
Bi	66.8	6.89	52.1	4.47	0.534	0.192	0.666	0.288
Ca	256	1.47	118	1.34	0.903	0.018	0.027	0.006
Cd	<1.01	b	<4.92	b	<0.066	b	<0.066	b
Co	<0.662	b	<3.22	b	<0.0432	b	<0.0432	b
Cr	3100	14.2	26.8	1.34	258	1.21	4.34	0.036
Cu	47.9	0.643	13.2	0.447	2.4	0.006	0.015	0.006
Fe	2480	28.3	783	6.26	1.36	0.012	<0.0102	b
K	314	11.3	<15.5	b	109	7.27	4.27	0.264
Mg	52.6	1.75	26.6	3.13	<0.0591	b	<0.0591	b
Mn	1990	10.1	642	5.36	<0.0048	b	<0.0048	b
Ni	77.3	1.29	33.5	2.24	<0.0675	b	<0.0675	b
P	2480	216	516	15.6	<0.3	b	0.903	0.666
Sb	<10.1	b	<49.2	b	<0.661	b	<0.0661	b
Si	134	1.1	683	8.49	59.7	0.726	6.39	0.132
Sr	580	2.02	182	3.58	0.069	0	<0.015	b
Th	2.67	0.827	<10.8	b	0.405	0.108	<0.146	b
Tl	<8.9	b	<43.3	b	<0.581	b	<0.581	b
U	8400	76.8	2670	20.6	<0.273	b	<0.273	b
V	<0.188	b	1.12	1.34	<0.0123	b	0.042	0
Zn	11.1	1.19	<6.59	b	0.627	0.036	<0.0885	b
Br^-	<146	b	<9.85	b	<50	b	<5	b
Cl^-	2900	30	<9.85	b	224	1	7.5	0.57
F^-	<293	b	<9.85	b	<5	b	<5	b
NO_3^-	388000	9000	230	8	17500	200	337	34
PO_4^{3-}	<585	b	<19.7	b	<10	b	<10	b
SO_4^{2-}	1770	220	56.8	13.1	190	15	16.4	1.3
Radiospecies	Bq/g		Bq/g		Bq/mL		Bq/mL	
Co-60	c	c	<700	b	<40	b	<40	b
Cs-137	2700000	100000	34000	2000	230000	10000	4400	300
Eu-154	5900	1400	1600	600	c	c	c	c
Pu-238	380	c	136	c	c	c	c	c
Pu-239/240	19600	c	6650	c	c	c	c	c
Pu-242	64	c	13	c	c	c	c	c
Pu-all	20000	2000	6800	1200	0.025	0.004	0.03	0.41
Gross-α	23000	1000	9500	2700	<4	b	<7	b
Gross-β	34000000	1000000	9700000	100000	260000	10000	4500	100

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.10. Test #4 - percentage of each species solubilized and percentage recovery for S-104 sludge
(leach conditions: liquid:solids, 12 mL/g; NaOH, 4 *M*; temperature, 70°C; time, 21 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	a	a	a	a	a	a
Al	20.80	0.89	13.22	0.16	92.42	1.02
Ba	-39.18	2.58	1.09	0.02	140.27	2.60
Be	a	a	a	a	a	a
Bi	-115.66	28.93	46.55	17.41	262.21	36.80
Ca	-27.45	1.62	4.15	0.12	131.60	1.64
Cd	a	a	a	a	a	a
Co	a	a	a	a	a	a
Cr	97.61	0.12	93.76	0.60	96.15	0.62
Cu	23.80	2.78	54.43	0.88	130.63	3.16
Fe	12.70	1.22	0.58	0.01	87.88	1.22
K	100.00	0.00	420.70	29.06	420.70	29.06
Mg	-39.83	17.10	0.00	0.00	139.83	17.10
Mn	10.79	0.87	0.00	0.00	89.21	0.87
Ni	-19.83	8.26	0.00	0.00	119.83	8.26
P	42.47	5.30	1.39	1.03	58.92	5.51
Sb	a	a	a	a	a	a
Si	-1309.38	20.99	655.34	8.73	2064.72	25.33
Sr	13.23	1.73	0.13	0.00	86.89	1.73
Th	100.00	0.00	161.15	65.87	161.15	65.87
Tl	a	a	a	a	a	a
U	12.11	1.05	0.00	0.00	87.89	1.05
V	a	a	a	a	a	a
Zn	100.00	0.00	60.01	7.30	60.01	7.30
Br^-	a	a	a	a	a	a
Cl^-	100.00	0.00	91.93	1.27	91.93	1.27
F^-	a	a	a	a	a	a
NO_3^-	99.84	0.01	51.23	1.35	51.40	1.35
PO_4^{3-}	a	a	a	a	a	a
SO_4^{2-}	91.13	2.32	149.41	20.83	158.28	21.91
Radiospecies						
Co-60	a	a	a	a	a	a
Cs-137	96.52	0.24	96.72	5.34	100.20	5.43
Eu-154	25.01	33.28	b	b	74.99	33.28
Pu-238	1.04	0.00	b	b	98.96	0.00
Pu-239/240	6.18	0.00	b	b	93.82	0.00
Pu-242	43.83	0.00	b	b	56.17	0.00
Pu-all	5.99	19.07	0.01	0.08	94.02	19.07
Gross-α	-14.21	32.84	0.00	0.00	114.21	32.84
Gross-β	21.11	2.46	8.63	0.40	87.52	2.72

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

[b]Measurement was not made.

Table 4.11. Test #5 - concentrations of species in enhanced sludge washing process steps for S-104 sludge
(leach conditions: liquid:solids, 12 mL/g; NaOH, 6.33 *M*; temperature, 70°C; time, 21 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/g)		Rinse (μg/g)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	<0.593[a]	b	3.76	0.429	<0.411	b	<0.507	b
Al	140000	1480	66600	191	1340	18.5	46.7	0.507
Ba	29.8	0.552	28.8	0	<0.0411	b	<0.0507	b
Be	<0.0735	b	<0.107	b	<0.0206	b	<0.0254	b
Bi	66.8	6.89	50.9	3.65	<8.22	b	<10.1	b
Ca	256	1.47	199	0	3.25	0.123	1.14	0.101
Cd	<1.01	b	<2.15	b	<0.411	b	<0.507	b
Co	<0.662	b	2.58	3	<0.39	b	<0.482	b
Cr	3100	14.2	58.8	0.644	170	2.14	6.24	0.0507
Cu	47.9	0.643	20900	49.6	59.6	1.07	1.77	0.152
Fe	2480	28.3	1590	9.44	3.97	0.123	0.761	0.0507
K	314	11.3	<10.7	b	59	1.44	2.66	1.37
Mg	52.6	1.75	24.7	3	<0.514	b	<0.634	b
Mn	1990	10.1	1280	5.58	0.0822	0	<0.0254	b
Ni	77.3	1.29	71.8	1.72	<0.411	b	<0.507	b
P	2480	216	822	19.7	<2.06	b	<2.54	b
Sb	<10.1	b	<21.5	b	<4.11	b	<5.07	b
Si	134	1.1	6900	0	61.2	1.56	36.8	0.406
Sr	580	2.02	359	2.36	0.164	0	<0.127	b
Th	2.67	0.827	140	4.08	<1.03	b	<1.27	b
U	8400	76.8	5030	59	<2.06	b	<2.54	b
V	<0.188	b	<1.07	b	<0.206	b	<0.254	b
Zn	11.1	1.19	28.9	7.94	1.01	0.288	<0.761	b
Radiospecies	Bq/g		Bq/g		Bq/g		Bq/g	
Co-60	c	c	190	30	<6	b	<1	b
Cs-137	2700000	100000	54000	1000	160000	10000	5100	0
Eu-152	<1800	b	<140	b	<21	b	<4	b
Eu-154	5900	1400	3100	200	<39	b	<3	b
Eu-155	<6700	b	<560	b	<110	b	<11	b
Pu-238	380	c	220	10	c	c	c	c
Pu-239/240	19600	c	8300	300	c	c	c	c
Pu-all	20000	2000	8500	300	2.9	2.6	0.4	1.4
Gross-α	23000	1000	17000	2000	1.4	4.7	0	0.5
Gross-β	34000000	1000000	19000000	1000000	200000	10000	6000	100

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.12. Test #5 - percentage of each species solubilized and percentage recovery for S-104 sludge
(leach conditions: liquid:solids, 12 mL/g; NaOH, 6.33 *M*; temperature, 70°C; time, 21 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	a	a	a	a	a	a
Al	26.60	0.80	14.89	0.25	88.30	0.98
Ba	-49.13	2.76	0.00	0.00	149.13	2.76
Be	a	a	a	a	a	a
Bi	-17.58	14.77	0.00	0.00	117.58	14.77
Ca	-19.95	0.69	31.47	1.36	151.42	1.60
Cd	a	a	a	a	a	a
Co	a	a	a	a	a	a
Cr	97.07	0.03	85.63	1.08	88.56	1.08
Cu	-67227.07	917.80	1917.45	42.47	69244.53	943.76
Fe	1.07	1.27	3.22	0.10	102.15	1.31
K	100.00	0.00	298.00	17.94	298.00	17.94
Mg	27.54	9.12	0.00	0.00	72.46	9.12
Mn	0.75	0.66	0.06	0.00	99.31	0.66
Ni	-43.33	4.18	0.00	0.00	143.33	4.18
P	48.86	4.62	0.00	0.00	51.14	4.62
Sb	a	a	a	a	a	a
Si	-7845.54	65.22	1466.26	22.58	9411.80	79.59
Sr	4.49	0.71	0.41	0.00	95.92	0.71
Th	-7990.88	2517.12	0.00	0.00	8090.88	2517.12
U	7.60	1.37	0.00	0.00	92.40	1.37
V	a	a	a	a	a	a
Zn	-301.75	118.48	132.33	40.31	534.08	129.94
Radiospecies						
Co-60	a	a	a	a	a	a
Cs-137	96.91	0.13	91.70	6.37	94.78	6.43
Eu-152	a	a	a	a	a	a
Eu-154	18.92	19.94	0.00	0.00	81.08	19.94
Eu-155	a	a	a	a	a	a
Pu-238	10.67	4.06	b	b	89.33	4.06
Pu-239/240	34.66	2.36	b	b	65.34	2.36
Pu-all	34.42	6.95	0.27	0.28	65.85	6.99
Gross-α	-14.05	14.30	0.09	0.30	114.14	14.31
Gross-β	13.77	5.20	9.07	0.50	95.30	5.35

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

[b]Measurement was not made.

Table 4.13. Test #9 - concentrations of species in enhanced sludge washing process steps for S-104 sludge
(leach conditions: liquid:solids, 32 mL/g; NaOH, 6.33 *M*; temperature, 80°C; time, 126 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/g)		Rinse (μg/g)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	<0.593[a]	b	<2.20	b	<0.0804	b	<0.103	b
Al	140000	1480	12600	125	3830	25.2	45.5	4.55
Ba	29.8	0.552	99	0.44	<0.00804	b	<0.0103	b
Be	<0.0735	b	<0.11	b	<0.00402	b	<0.00513	b
Bi	66.8	6.89	2.18	0.198	<0.0603	b	<0.0257	b
Ca	256	1.47	599	1.32	<0.0322	b	0.395	0.0395
Cd	<1.01	b	<2.20	b	<0.0804	b	<0.103	b
Co	<0.662	b	4.95	0.88	<0.0764	b	<0.0975	b
Cr	3100	14.2	68	0.44	84.4	2.44	1.03	0.103
Cu	47.9	0.643	27.4	0.88	<0.0161	b	0.133	0.0133
Fe	2480	28.3	3040	9.24	23.4	0.346	0.149	0.0149
K	314	11.3	<11.0	b	182	7.24	0.903	0.215
Mg	52.6	1.75	191	5.28	<0.100	b	<0.128	b
Mn	1990	10.1	4460	13.9	0.0723	0	<0.00513	b
Ni	77.3	1.29	268	13.9	<0.0804	b	<0.103	b
P	2480	216	224	64.9	0.655	1.3	<0.513	b
Sb	<10.1	b	<22.0	b	<0.804	b	<0.0257	b
Si	134	1.1	4900	0	c	c	c	c
Sr	580	2.02	1160	13.9	1.58	0.0402	<0.0257	b
Th	2.67	0.827	<231.	b	0.354	0.498	<0.257	b
U	8400	76.8	19900	240	0.599	0.402	<0.513	b
V	<0.188	b	<1.10	b	0.113	0.0161	<0.0513	b
Zn	11.1	1.19	15.1	2.42	<0.121	b	<0.154	b
Radiospecies	Bq/g		Bq/g		Bq/g		Bq/g	
Co-60	c	c	c	c	6.28	0	15.1	0
Cs-137	2700000	100000	150000	10000	86000	1000	980	80
Eu-152	<1800	b	c	c	<170	b	<31	b
Eu-154	5900	1400	c	c	<120	b	<67	b
Eu-155	<6700	b	c	c	<410	b	<49	b
Pu-238	380	c	1200	100	c	c	c	c
Pu-239/240	19600	c	43000	1000	c	c	c	c
Gross-α	23000	1000	57000	3000	<1.60	b		
Gross-β	34000000	1000000	64000000	1000000	180000	10000	1200	100

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.14. Test #9 - percentage of each species solubilized and percentage recovery for S-104 sludge
(leach conditions: liquid:solids, 32 mL/g; NaOH, 6.33 *M*; temperature, 80°C; time, 126 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	a	a	a	a	a	a
Al	96.32	0.05	91.66	1.14	95.35	1.18
Ba	-35.91	2.59	0.00	0.00	135.91	2.59
Be	a	a	a	a	a	a
Bi	98.66	0.18	0.00	0.00	1.34	0.18
Ca	4.28	0.59	5.99	0.60	101.71	0.86
Cd	a	a	a	a	a	a
Co	a	a	a	a	a	a
Cr	99.10	0.01	91.26	2.64	92.16	2.64
Cu	76.60	0.81	10.78	1.09	34.18	1.39
Fe	49.85	0.59	31.41	0.58	81.56	1.05
K	100.00	0.00	1926.53	103.05	1926.53	103.05
Mg	-48.55	6.43	0.00	0.00	148.55	6.43
Mn	8.31	0.55	0.12	0.00	91.81	0.55
Ni	-41.83	7.73	0.00	0.00	141.83	7.73
P	96.30	1.12	0.87	1.73	4.57	2.07
Sb	a	a	a	a	a	a
Si	-1395.93	12.28	0.00	0.00	1495.93	12.28
Sr	18.18	1.02	9.00	0.23	90.82	1.06
Th	100.00	0.00	438.13	631.12	438.13	631.12
U	3.08	1.47	0.24	0.16	97.15	1.48
V	a	a	a	a	a	a
Zn	44.35	10.73	0.00	0.00	55.65	10.73
Radiospecies						
Co-60	a	a	a	a	a	a
Cs-137	97.73	0.17	106.66	4.14	108.94	4.22
Eu-152	a	a	a	a	a	a
Eu-154	b	b	b	b	b	b
Eu-155	a	a	a	a	a	a
Pu-238	-29.19	10.77	b	b	129.19	10.77
Pu-239/240	10.25	2.09	b	b	89.75	2.09
Gross-α	-1.38	6.92	0.00	0.00	101.38	6.92
Gross-β	22.99	2.56	17.63	1.10	94.64	3.18

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.
[b]Measurement was not made.

It is also consistent with the expected behavior of chromium in this system. Examination of results on aluminum show that, based on residual solids, 34.5% ± 0.8% of it was removed while the analysis of the leachate and rinse shows a 7.6% ± 0.2% removal. Recovery of 73.1% ± 0.9% of the aluminum indicates only a fair material balance. Results on phosphorus are disappointing because analysis of the solid residue indicates 65.6% ± 3.0% removal, while the analysis on the leachate and rinse solutions indicates 0% removal. This occurred because phosphorus was below the detectable limit in the process liquids and led to a calculated recovery of 34.4% ± 3.0%. One possible cause of the absence of phosphorus in the liquid is that it may have precipitated from solution between the time the solids and liquids were separated and the time that an aliquot was withdrawn for analysis. This is partly corroborated by the relatively low errors propagated to the calculated results. If the estimated errors in the analysis are taken as correct, the estimated errors in the calculated results are too small to account for the missing material. The possibility of precipitation led to a change in procedure wherein the entire amount of both phases, beginning with test #5, was analyzed.

Poor material balances are not always indicative of a precipitation problem but could be an artifact of the small concentration of a given species in the original sludge. For example, the dilution factors were such that the lower limit of detection of thorium in the residue (Table 4.3) was greater than the concentration in the original sludge. The rules for computation, as already discussed, resulted in a value indicating complete removal of thorium from the sludge. However, based on the analysis of the process liquids, the percent removal could have ranged from 10.5 to 188%. This uncertainty is reflected in the percent recovery, 99.3% ± 88.8%. Because thorium is insoluble in alkali solutions, a high percentage removal was not expected. Conflicts between measured and expected values could also result if the measured concentration of thorium in the original sludge were lower than the actual concentration. Suppose thorium exists in the sludge as thorium hypophosphate ($ThP_2O_6 \cdot 11H_2O$), which is insoluble in either alkali or acidic solutions. The data on S-104 indicate that phosphorus, at

2480 μg/g, is present in great excess compared with thorium, at 2.67 μg/g. As an acid-insoluble form, the thorium could remain with the insoluble residue (assumed to be silicon dioxide) and fail to report for analysis by ICP-AES.

Generally the errors in the data and in the results are small for the more abundant constituents. Large errors occur where the analyte is near the detection level or where experimental difficulties, such as precipitation, may have occurred. Changing the experimental method to analyze the entire leachate solution, rather than a small aliquot, seems to have mitigated the latter problem. The reader may notice that the concentration of a given material is occasionally greater in the residue than in the original sludge, for example, uranium in Table 4.13. This means that other constituents were preferentially removed, and those that were not removed became a greater fraction of the total remaining mass.

To simplify the analysis of the effect of operational parameters on the leaching process, a subset of the more important sludge constituents was selected. Aluminum, chromium, and phosphorus were selected because these constituents strongly influence the quantities of glass that will be produced to immobilize the waste. Uranium and cesium were included to ascertain how these components partition between the solid and liquid phases, which has implications on the cleanup and recycle of the enhanced sludge washing solutions.

The operating conditions for each of the six tests on sludge S-104 and the percentage of selected constituents removed from the sludge are summarized in Table 4.15. Values of percentage removed are those based on the analysis of the residue. It was thought that these values would give the more consistent results because the untreated sludge and the sludge residue were analyzed using the same methodology. As shown in Table 4.15, chromium and cesium were readily removed from the sludge, with >95% removal under all conditions tested. Comparing test #1 with test #2 indicates that aluminum removal increased with increased leaching time. Tests #3 and #4 show no increase in

Table 4.15. Summary of effects of operating parameters on caustic leaching of S-104 sludge

Test	Liquid: solids (mL/g)	NaOH (*M*)	T (°C)	Time (h)	% Removal				
					Al	Cr	P	U	Cs-137
1	9	3.8	67	4	34.5	98.0	65.6	37.2	97.9
2	9	3.8	67	24	50.3	98.5	72.8	46.1	98.0
3	6	3.99	70	21	20.4	97.4	44.3	15.6	95.0
4	12	3.99	70	21	20.8	97.6	42.5	12.1	96.5
5	12	6.33	70	21	26.6	97.1	48.9	7.60	96.9
9	32	6.33	80	126	96.3	99.1	96.3	3.08	97.7

aluminum removal with increased liquid:solids ratio. Increasing the caustic concentration in test #5 slightly increased the amount of aluminum removed compared with test #4. In test #9, where all four variables of liquid:solids ratio, caustic concentration, temperature, and time were largest, a great increase in the percentage of aluminum removed was observed. To visualize these effects, the data in Table 4.15 were smoothed using an inverse distance method (Ulrich et al., 1995) to generate three-dimensional mesh plots. Fig. 4.1 illustrates the effect of caustic concentration and temperature without regard to the other parameters. The caustic concentration, in the range between 3.8 and 6.4 *M*, has little effect on the percentage of aluminum removed from the sludge. However, the temperature is shown to have a large effect. In Fig. 4.2, the percentage of aluminum removed from the sludge is plotted as a function of liquid:solids ratio and temperature, without regard to the other two parameters. This plot shows that both liquid:solids ratio and temperature strongly affect the percentage of aluminum removed from the sludge. One must bear in mind that these plots do not model physical chemistry but are merely convenient for showing trends. There is the temptation to conclude that aluminum removal is solubility limited. However, the test done at both the high temperature and high liquid:solids ratio also happens to be the test having the long leaching time (126 h), perhaps indicating that the process is reaction rate limited.

Removal of phosphorus seemed to coincide with that of aluminum. Plotting the percentage of phosphorus removed as a function of the percentage of aluminum removed, as shown in Fig. 4.3, illustrates the trend. Removal of uranium seems to vary inversely with caustic concentration, removal being the highest at the lowest caustic concentration (3.8 *M*) tested.

Sludge S-104 has also been studied by Rapko et al. (1995) and Lumetta et al. (1997b). The concentrations of selected components measured in dry, untreated sludge in those studies are compared with the present study in Table 4.16. The analyses agree to within about 25% on aluminum, chromium, uranium, cesium-137, and plutonium-239/240. However, there is a great discrepancy in

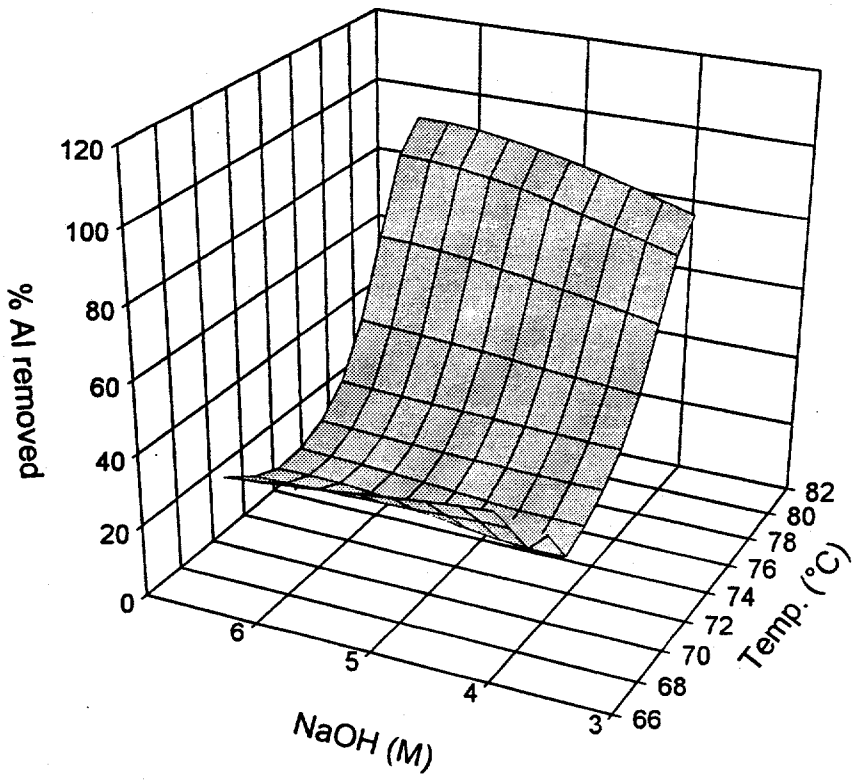

Fig. 4.1. The percentage of aluminum removed from S-104 sludge as a function of temperature and caustic concentration.

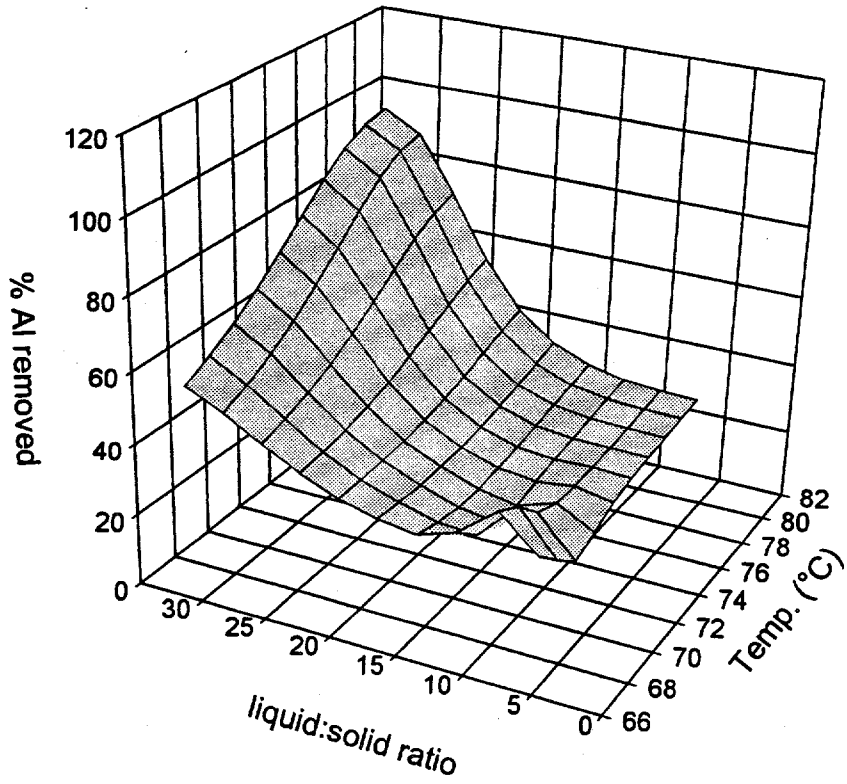

Fig. 4.2. The percentage of aluminum removed from S-104 sludge as a function of temperature and liquid-to-solids ratio.

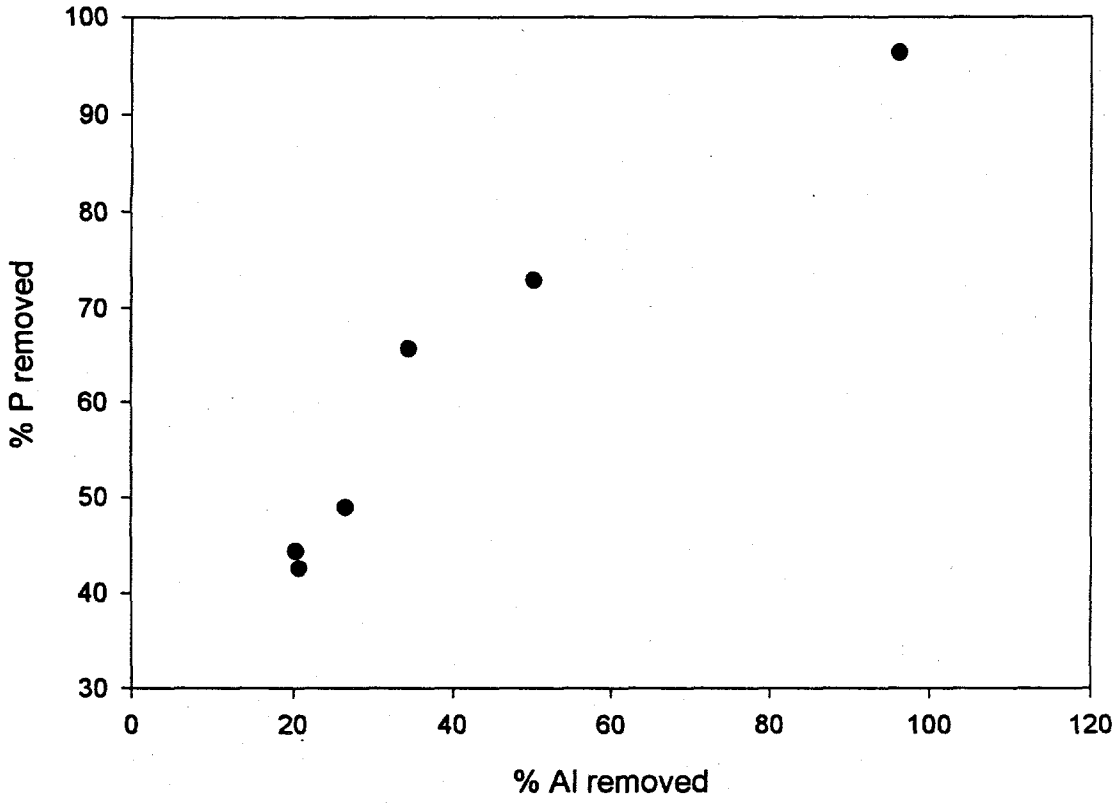

Fig. 4.3. Phosphorus follows aluminum removal for S-104 sludge.

the results for phosphorus. The amount of each of these materials removed from the sludge by the different researchers is compared in Table 4.17. Chromium and cesium were readily removed from the sludge under all process conditions evaluated. Removal of aluminum varied appreciably; as little as 20% was removed in 21 h at 70°C using 4 *M* NaOH, but nearly all was removed in 75 h when the temperature was increased to 80°C or more at sodium hydroxide concentrations between 3 and 6 *M*. Removal of uranium and plutonium was higher than expected, which is a consequence of having selected the analysis of the residue for computing percentage removal. Returning to the data tables, the analysis of the leachate solution indicates that neither uranium nor plutonium were removed from the sludge by caustic leaching. This is consistent with the known solubility of uranium and plutonium in caustic solutions. Except for tests #1 and #2, the values associated with gross-alpha analysis confirm that plutonium was not removed.

4.2 SLUDGE SX-113

Two tests were performed on sludge samples from tank SX-113. Analyses of this sludge, as shown in Table 4.18, indicate that it has relatively low aluminum, chromium, and phosphorus content. However, iron and silicon are quite abundant. Analytical data describing the samples taken from the two tests are given in Tables 4.18 and 4.20, and the associated calculated results are given in Tables 4.19 and 4.21, respectively.

Table 4.22 summarizes the effect of the two different leaching conditions on the removal of aluminum, chromium, phosphorus, uranium, and cesium from sludge SX-113. At a fixed sodium hydroxide concentration, a combined increase in the liquid:solids ratio, leaching time, and leaching temperature increased the percentage of constituents leached from the sludge. The recovery of chromium was low, 53 to 66%, but there was only a small amount of it in the sludge initially. The high phosphorus removal (92%) in test #10 was probably not real since the recovery was only 11%. A large fraction of the uranium was removed, but there was only a small quantity of it in the sludge

Table 4.16. Concentration of selected constituents in dry, untreated S-104 sludge determined by different researchers

Species	Unit of measure	PNNL[a]	PNNL[b]	ORNL[c]
Al	μg/g	150000.	153000.	166000.
Cr	μg/g	4700.	4470.	3670.
P	μg/g	<200.	17.	2940.
U	μg/g	10100.	9360.	9950.
Cs-137	μCi/g	91.6		86.5
Pu-239/240	μCi/g	0.545		0.628

[a]Rapko et al., PNL-10712 (1995).
[b]Lumetta et al., PNNL-11636 (1997b).
[c]This work.

Table 4.17. Comparison of percentage of selected species removed from S-104 sludge by different researchers

	% Removed			
Species	PNNL[a]	PNNL[b]	ORNL[c]	ORNL[d]
Al	38	99	21	96
Cr	97	99	97	99
P			44	96
U	0	0	12	3
Cs	98		97	98
Pu			6	10

[a]Rapko et al., PNL-10712 (1995); 10 *M* NaOH for 5 h, 3 *M* NaOH for 5 h, 100°C, 1:1 ≤ liquid:solid ≤ 2:1.
[b]Lumetta et al., PNNL-11636 (1997b); 3 *M* NaOH, 75 h, 100°C, liquid:solids of 10:1.
[c]This work; 4 *M* NaOH, 21 h, 70°C, and liquid:solids of 12:1.
[d]This work; 6 *M* NaOH, 126 h, 80°C, and liquid:solids of 32:1.

Table 4.18. Test #6 - concentrations of species in enhanced sludge washing process steps for SX-113 sludge
(leach conditions: liquid:solids, 20 mL/g; NaOH, 6.33 *M*; temperature, 70°C; time, 21 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/g)		Rinse (μg/g)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	<2.44[a]	b	<4.85	0.429	<0.409	b	<0.417	b
Al	7320	52.7	5080	191	307	11.2	10	0.209
Ba	20.5	0.244	33.7	0	<0.0409	b	<0.0417	b
Be	<0.122	b	<0.243	b	<0.0205	b	<0.0209	b
Bi	60.9	10.5	<97.1	3.65	<8.18	b	<8.34	b
Ca	1770	11.7	1830	0	1.37	0.0818	0.876	0.0417
Cd	<2.44	b	<4.85	b	<0.409	b	<0.417	b
Co	<2.32	b	<4.61	3	<0.389	b	<0.396	b
Cr	57.1	0.488	38.1	0.644	0.716	0.0818	<0.104	b
Cu	13.4	0.732	18.2	49.6	9.9	3.89	1.94	0.167
Fe	10400	26.4	13100	9.44	91.4	0.0818	1.69	0.125
K	85.9	1.95	42	0	22	1.39	3.75	1.67
Mg	1580	20.3	2330	3	<0.511	b	<0.521	b
Mn	234	1.22	325	5.58	0.777	0.245	<0.0209	b
Ni	5.12	1.22	15.3	1.72	<0.409	b	<0.417	b
P	3890	39.3	4820	19.7	33.3	4.99	<2.09	b
Sb	<24.4	b	<48.5	b	<4.09	b	<4.17	b
Si	220000	0	22000	0	488	2.7	425	1.17
Sr	15.3	0	21.1	2.36	<0.102	b	<0.104	b
Th	10.9	4.64	<12.1	4.08	<1.02	b	<1.04	b
U	94.6	13.9	<24.3	59	5.89	1.43	<2.09	b
V	123	1.22	30.8	0	7.98	0.0409	0.25	0.0417
Zn	218	2.93	36.9	7.94	4.23	0.818	<0.626	b
Radiospecies	Bq/g		Bq/g		Bq/g		Bq/g	
Co-60	<42	b	34	30	<1	b	<1	b
Cs-137	840000	10000	480000	1000	38000	1000	2400	100
Eu-152	<120	b	<70	b	<6	b	<4	b
Eu-154	<260	b	340	200	<8	b	<3	b
Eu-155	<650	b	<540	b	<37	b	<7	b
Pu-238	70	4	40	10	1	0.3	c	c
Pu-239/240	2300	200	2000	300	31	8	c	c
Pu-all	2400	200	2000	300	32	8	0.3	1.1
Gross-α	2700	300	2600	2000	33	14	0.28	0.56
Gross-β	3000000	100000	3200000	1000000	46000	1000	3000	100

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.

[b]No standard deviation for values below the detectable limit.

[c]Not measured.

Table 4.19. Test #6 - percentage of each species solubilized and percentage recovery for SX-113 sludge
(leach conditions: liquid:solids, 20 mL/g; NaOH, 6.33 *M*; temperature, 70°C; time, 21 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	a	a	a	a	a	a
Al	51.04	1.87	62.12	2.16	111.08	2.91
Ba	-15.97	1.38	0.00	0.00	115.97	1.38
Be	a	a	a	a	a	a
Bi	100.00	4.23	0.00	0.00	0.00	4.23
Ca	27.06	0.48	2.60	0.10	75.54	0.51
Cd	a	a	a	a	a	a
Co	a	a	a	a	a	a
Cr	52.93	0.89	17.31	1.98	64.38	2.20
Cu	4.18	261.19	1468.26	410.42	1564.08	487.34
Fe	11.14	0.23	12.63	0.05	101.50	0.27
K	65.51	0.78	488.74	65.20	523.24	65.34
Mg	-4.04	1.34	0.00	0.00	104.04	1.34
Mn	2.02	1.76	4.58	1.45	102.57	2.28
Ni	-110.82	55.54	0.00	0.00	210.82	55.54
P	12.59	0.95	11.81	1.77	99.23	2.07
Sb	a	a	a	a	a	a
Si	92.95	0.00	9.05	0.02	16.10	0.02
Sr	2.71	10.88	0.00	0.00	97.29	10.88
Th	100.00	26.41	0.00	0.00	0.00	26.41
U	100.00	44.00	85.93	24.39	85.93	50.31
V	82.33	0.18	95.84	1.49	113.50	1.61
Zn	88.06	2.57	26.78	5.19	38.72	5.80
Radiospecies						
Co-60	a	a	a	a	a	a
Cs-137	59.69	0.49	71.29	1.89	111.60	2.15
Eu-152	a	a	a	a	a	a
Eu-154	a	a	a	a	a	a
Eu-155	a	a	a	a	a	a
Pu-238	59.69	10.34	19.72	6.02	60.03	12.18
Pu-239/240	38.65	10.64	18.60	5.07	79.95	12.49
Pu-all	41.21	10.09	18.79	5.06	77.58	11.95
Gross-α	32.06	52.80	17.19	7.43	85.12	53.59
Gross-β	24.75	23.65	24.26	0.94	99.51	23.75

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

Table 4.20. Test #10 - concentrations of species in enhanced sludge washing process steps for SX-113 sludge
(leach conditions: liquid:solids, 44 mL/g; NaOH, 6.33 *M*; temperature, 80°C; time, 126 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/g)		Rinse (μg/g)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	<2.44[a]	b	<1.36	b	<0.0844	b	<0.0986	b
Al	7320	52.7	2820	48.6	215	11.9	6.61	0.661
Ba	20.5	0.244	37.1	0.136	0.0169	0	<0.00986	b
Be	<0.122	b	<0.068	b	<0.00422	b	<0.00493	b
Bi	60.9	10.5	<1.02	b	<0.0633	b	<0.0247	b
Ca	1770	11.7	2470	14.3	0.477	0.0338	0.463	0.463
Cd	<2.44	b	<1.36	b	<0.0844	b	<0.0986	b
Co	<2.32	b	1.63	0.952	<0.0802	b	<0.0937	b
Cr	57.1	0.488	35.6	0.136	0.397	0.0169	0.0394	0.00986
Cu	13.4	0.732	5.3	0.272	0.228	0.00844	0.296	0.0296
Fe	10400	26.4	13400	14.3	66.9	0.852	0.478	0.0478
K	85.9	1.95	44.5	0.68	127	7.97	1.14	0.237
Mg	1580	20.3	2610	25.7	0.122	0.118	<0.123	b
Mn	234	1.22	289	0.544	0.57	0.00844	<0.00493	b
Ni	5.12	1.22	9.04	0.816	<0.0844	b	<0.0986	b
P	3890	39.3	581	36.4	4.04	0.996	<0.493	b
Sb	<24.4	b	59.4	85	<0.844	b	<0.0247	b
Si	220000	0	18000	0	c	c	c	c
Sr	15.3	0	21.5	0.408	0.0422	0	<0.0247	b
Th	10.9	4.64	<3.4	b	<0.211	b	<0.247	b
U	94.6	13.9	11.8	4.22	2.27	0.0338	<0.493	b
V	123	1.22	7.62	0.136	4	0.0253	0.163	0.0163
Zn	218	2.93	31.1	1.9	1.61	0.203	<0.148	b
Radiospecies	Bq/g		Bq/g		Bq/g		Bq/g	
Co-60	<42	b			7.5	0	15.3	0
Cs-137	840000	10000	210000	10000	37000	1000	870	50
Eu-152	<120	b	c	c	<170	b	<52	b
Eu-154	<260	b	c	c	<150	b	<46	b
Eu-155	<650	b	c	c	<270	b	<32	b
Pu-238	70	4	100	10	c	c	c	c
Pu-239/240	2300	200	2300	100	c	c	c	c
Pu-all	2400	200	c	c	c	c	c	c
Gross-α	2700	300	2900	500	27	13	c	c
Gross-β	3000000	100000	2900000	100000	32000	1000	1100	100

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.

[b]No standard deviation for values below the detectable limit.

[c]Not measured.

Table 4.21. Test #10 - percentage of each species solubilized and percentage recovery for SX-113 sludge
(leach conditions: liquid:solids, 44 mL/g; NaOH, 6.33 *M*; temperature, 80°C; time, 126 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	a	a	a	a	a	a
Al	78.69	0.40	81.75	4.40	103.06	4.44
Ba	-0.08	1.25	2.21	0.03	102.29	1.27
Be	a	a	a	a	a	a
Bi	100.00	0.00	0.00	0.00	0.00	0.00
Ca	22.83	0.68	1.62	0.90	78.80	1.14
Cd	a	a	a	a	a	a
Co	a	a	a	a	a	a
Cr	65.52	0.32	21.00	1.01	55.48	1.11
Cu	78.13	1.64	121.85	10.26	143.72	11.13
Fe	28.74	0.20	17.38	0.22	88.64	0.32
K	71.35	0.78	4004.09	264.68	4032.74	264.91
Mg	8.64	1.48	0.21	0.20	91.56	1.49
Mn	31.70	0.38	6.52	0.10	74.82	0.42
Ni	2.36	24.88	0.00	0.00	97.64	24.88
P	91.74	0.52	2.78	0.69	11.04	0.87
Sb	a	a	a	a	a	a
Si	95.48	0.00	0.00	0.00	4.52	0.00
Sr	22.29	1.47	7.38	0.00	85.10	1.47
Th	100.00	0.00	0.00	0.00	0.00	0.00
U	93.10	2.67	64.24	9.49	71.14	10.78
V	96.57	0.07	91.64	1.16	95.07	1.19
Zn	92.11	0.49	19.77	2.51	27.66	2.57
Radiospecies						
Co-60	a	a	a	a	a	a
Cs-137	86.17	0.68	121.50	3.51	135.33	3.64
Eu-152	a	a	a	a	a	a
Eu-154	a	a	a	a	a	a
Eu-155	a	a	a	a	a	a
Pu-238	21.00	9.10	b	b	79.00	9.10
Pu-239/240	44.70	5.38	b	b	55.30	5.38
Pu-all	b	b	b	b	0.00	0.00
Gross-α	40.60	12.18	26.77	13.23	86.17	19.05
Gross-β	46.54	2.56	29.82	1.34	83.28	3.45

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

[b]Measurement was not made.

initially. Uranyl hydroxide [$UO_2(OH)_2$] is known to be soluble in alkali carbonate solutions. If the sludge contained a significant concentration of, for instance, sodium carbonate, the uranium could be solubilized when the caustic leaching solution was added. Alternatively, if the sludge contained uranyl sodium carbonate ($UO_2CO_3 \cdot 2NaCO_3$), which is slightly soluble, it would enter solution when exposed to the relatively large volume of aqueous caustic solution. Thorium and bismuth were apparently removed from the sludge as indicated in Tables 4.19 and 4.21, but this is an artifact of the lower limits of detection in both the residue and leachate. About half of the plutonium was also removed from the sludge, which appears to be confirmed by the gross-alpha measurement.

Concentrations of selected species in the untreated sludge measured by Temer and Villarreal (1997) are compared to the present analysis in Table 4.23. The widest variation occurs in the determination of phosphorus. Analysis of the aluminum content varied by 50%, but results for chromium, uranium, cesium-137, and plutonium-239/240 were comparable. Table 4.24 presents the percentage of each species, from the same subset, removed from the sludge under various conditions. Except for chromium and plutonium, our experiment at 80 °C and ~6 *M* NaOH and the tests performed by Temer and Villarreal (1997) at 100 °C and ~3 *M* NaOH removed similar percentages of the sludge components.

4.3 SLUDGE C-105

One test was performed with sludge C-105 in which the material was leached with 6.33 *M* NaOH at 70 °C for 22 h. Results of the analysis of the sludge and each "phase" into which the sludge was partitioned are given in Table 4.25. As shown in the table, the relative concentrations of aluminum, silicon, uranium, and plutonium are high in this sludge. The concentrations of iron and phosphorus are low. The percentages of each species removed from the sludge were calculated from the analytical data and are given in Table 4.26. Approximately 97% of the aluminum, 71% of the

Table 4.22. Effect of operating parameters on caustic leaching behavior of SX-113 sludge

Test	Liquid: solids (mL/g)	NaOH (*M*)	T (°C)	Time (h)	% Removal				
					Al	Cr	P	U	Cs
6	20	6.33	70	21	51.0	52.9	12.6	100.	59.7
10	44	6.33	80	126	78.7	65.5	91.7	93.1	86.2

Table 4.23. Concentration of selected constituents in dry, untreated SX-113 sludge determined by different researchers

Species	Unit of measure	LANL[a]	ORNL[b]
Al	μg/g	21200.	14000.
Cr	μg/g	113.	110.
P	μg/g	<68.4	7470.
U	μg/g	253.	182.
Cs-137	μCi/g	45.5	43.6
Pu-239/240	μCi/g	0.108	0.12

[a]Temer and Villarreal, LAUR 97-2889 (1997).
[b]This work.

Table 4.24. Comparison of percentage of selected species removed from SX-113 sludge by different researchers

Species	% Removed		
	LANL[a]	ORNL[b]	ORNL[c]
Al	89	51	79
Cr	40	53	66
P	85	13	92
U	88	100	93
Cs	88	60	86
Pu	0	39	45

[a]Temer and Villarreal, LAUR 97-2889 (1997); first leach 2.3 *M* NaOH, 5 h, 100°C, 5 wt % solids; second leach 3.0 *M* NaOH, 5 h, 100°C, 1 wt % solids.
[b]This work; 6.33 *M* NaOH, 21 h, 70°C, and liquid:solids of 20:1.
[c]This work; 6.33 *M* NaOH, 126 h, 80°C, and liquid:solids of 44:1.

Table 4.25. Test #7 - concentrations of species in enhanced sludge washing process steps for C-105 sludge
(leach conditions: liquid:solids, 10 mL/g; NaOH, 6.33 *M*; temperature, 70°C; time, 22 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/g)		Rinse (μg/g)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	8.87	0.199	<20.8[a]	b	<0.0902	b	<0.102	b
Al	247000	503	18700	116	18100	75.6	160	0.672
Ba	27.4	0.199	75.7	0.377	0.0496	0.0631	<0.0102	b
Be	<0.0997	b	<0.0943	b	<0.00451	b	<0.00509	b
Bi	381	8.57	1180	11.1	0.334	2.08	5.26	4.03
Ca	919	6.78	1130	5.28	1.25	0.153	7.61	0.336
Cd	3.49	1.2	4.62	1.89	0.126	0.0722	<0.102	b
Co	4.09	0.797	13.3	0.189	<0.0857	b	<0.0967	b
Cr	405	3.19	332	0.755	28.2	0	0.229	0.0102
Cu	703	4.78	1590	16.6	17.8	0.226	<0.0204	b
Fe	4020	20.1	9990	31.1	19.4	5.85	0.336	0
K	447	1.4	31.3	1.89	<45.6	b	2.56	0.143
Mg	31.2	2.59	41.5	4.15	<11.4	b	<0.127	b
Mn	1480	0	3800	10.4	0.293	0.334	<0.00509	b
Ni	1450	161	4440	35.3	0.505	0.658	<0.102	b
P	3590	4070	640	334	320	66.5	1.3	0.906
Sb	<19.9	b	<18.9	b	<91.1	b	<1.02	b
Si	15000	0	22000	0	c	c	c	c
Sr	95.6	0.399	318	2.08	0.0361	0.0271	<0.0255	b
Th	319	3.39	992	8.68	0.537	0.559	<0.255	b
U	12400	1030	38500	232	7.22	2.45	<0.509	b
V	8.77	0.199	9.06	0.377	0.41	0.00902	<0.0509	b
Zn	206	2.59	108	1.51	5.78	0.0992	<0.153	b
Radiospecies	Bq/g		Bq/g		Bq/g		Bq/g	
Co-60	4600	1000	15000	2000	24.6	c	25.7	c
Cs-137	11000000	1000000	7600000	100000	684000	c	8000	c
Eu-152	<3700	b	<3800	b	c	c	c	c
Eu-154	<5500	b	17000	0	c	c	c	c
Eu-155	<15000	b	33000	0	c	c	c	c
Pu-238	1000	100	1400	100	c	c	c	c
Pu-239/240	43000	2000	110000	10000	c	c	c	c
Pu-all	44000	2000	110000	10000	c	c	c	c
Am-241	<30000	b	48000	0	c	c	c	c
Gross-α	49000	16000	160000	30000	14	14	1.4	1.4
Gross-β	32000000	1000000	63000000	1000000	840000	10000	9800	100

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.

[b]No standard deviation for values below the detectable limit.

[c]Not measured.

Table 4.26. Test #7 - percentage of each species solubilized and percentage recovery for C-105 sludge
(leach conditions: liquid:solids, 10 mL/g; NaOH, 6.33 *M*; temperature, 70°C; time, 22 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	100.00	0.00	0.00	0.00	0.00	0.00
Al	97.34	0.02	93.16	0.43	95.82	0.43
Ba	3.03	0.85	2.25	2.87	99.22	2.99
Be	a	a	a	a	a	a
Bi	-8.71	2.65	43.14	32.94	151.85	33.12
Ca	56.84	0.38	26.91	1.15	70.07	1.26
Cd	53.54	24.83	44.93	30.02	91.39	44.85
Co	-14.14	22.30	0.00	0.00	114.14	22.30
Cr	71.23	0.24	88.37	0.70	117.14	0.93
Cu	20.61	0.99	31.51	0.45	110.89	1.19
Fe	12.78	0.51	6.26	1.81	93.48	1.89
K	97.54	0.15	17.44	0.98	19.90	0.99
Mg	53.31	6.07	0.00	0.00	46.69	6.07
Mn	9.88	0.25	0.25	0.28	90.37	0.37
Ni	-7.48	11.96	0.43	0.57	107.91	12.03
P	93.74	7.81	112.02	129.08	118.28	136.10
Sb	a	a	a	a	a	a
Si	48.52	0.00	0.00[b]	0.00[b]	51.48	0.00
Sr	-16.75	0.91	0.47	0.35	117.22	0.97
Th	-9.15	1.50	2.09	2.18	111.24	2.66
U	-8.98	9.08	0.72	0.25	109.70	9.14
V	63.74	1.72	58.17	1.84	94.43	2.92
Zn	81.60	0.35	34.91	0.74	53.32	0.94
Radiospecies						
Co-60	-14.45	29.19	23.67	5.15	138.13	33.68
Cs-137	75.75	2.23	79.59	7.24	103.84	9.45
Eu-152	a	a	a	a	a	a
Eu-154	a	a	a	a	a	a
Eu-155	a	a	a	a	a	a
Pu-238	50.86	6.04	b	b	49.14	6.04
Pu-239/240	10.21	9.17	b	b	89.79	9.17
Pu-all	12.25	8.92	b	b	87.75	8.92
Am-241	a	a	a	a	a	a
Gross-α	-14.61	43.15	0.44	0.39	115.05	43.28
Gross-β	30.90	2.42	33.60	1.46	102.70	3.41

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

[b]Measurement was not made.

chromium, 94% of the phosphorus, and 76% of the cesium were removed from the sludge. None of the uranium was removed. Values of recovery for these species indicate that the data are reliable.

Temer and Villarreal (1997) also analyzed and performed a caustic leaching test on this sludge. Their analysis of selected components of the sludge are compared with those of the present study in Table 4.27. There is good agreement between the two analyses for aluminum, chromium, cesium, and plutonium. Phosphorus and uranium showed significant differences. In their study, Temer and Villarreal (1997) leached sludge C-105 with ~3 *M* NaOH at 100 °C. In this work, ~6 *M* NaOH at 70 °C was used, and the liquid:solids ratio was lower. Although the conditions varied considerably, and the initial analyses were different in some cases, the percentages of aluminum, phosphorus, and uranium leached from the sludge were about the same, as shown in Table 4.28. The percentages of chromium and cesium leached from the sludge were slightly lower at the conditions of the present study. The gross-alpha measurements did not confirm that plutonium was leached from the sludge.

4.4 SLUDGE C-107

One enhanced sludge washing test was performed with a sample of C-107 sludge. Analysis of this sludge (Table 4.29) indicates that the primary constituents are aluminum, bismuth, iron, phosphorus, and silicon. Uranium is ~0.1 wt % of the wet sludge.

The measured concentrations of sludge components in the process streams are given in Table 4.29. Calculated values of the percentages of each species removed from the sludge and the percentage recovery are given in Table 4.30. Approximately 82% of the aluminum, 70% of the chromium, 94% of the phosphorus, and 73% of the cesium were removed from the sludge by leaching with 6.33 *M* NaOH at 70°C for 22 h. The extent to which uranium and plutonium were leached was 1% and 6%, respectively. The recovery of these six components was very good, providing a measure of confidence in the estimated fractions of each species removed from the sludge. Thorium was

Table 4.27. Concentration of selected constituents in dry, untreated C-105 sludge determined by different researchers

Species	Unit of measure	LANL[a]	ORNL[b]
Al	μg/g	272000.	276000.
Cr	μg/g	448.	452.
P	μg/g	2000.	4010.
U	μg/g	24900.	13800.
Cs-137	μCi/g	293.	332.
Pu-239/240	μCi/g	1.94	1.30

[a]Temer and Villarreal, LAUR 97-2889 (1997).
[b]This work.

Table 4.28. Comparison of percentage of selected species removed from C-105 sludge by different researchers

	% Removed	
Species	LANL[a]	ORNL[b]
Al	99	97
Cr	86	71
P	100	94
U	4	0
Cs	92	76
Pu	0	10

[a]Temer and Villarreal, LAUR 97-2889 (1997); first leach 2.6 *M* NaOH, 5 h, 100°C, 5 wt % solids; second leach 3.1 *M* NaOH, 5 h, 100°C, 1.6 wt % solids.
[b]This work; 6.33 *M* NaOH, 22 h, 70°C, and liquid:solids of 10:1.

Table 4.29. Test #8 - concentrations of species in enhanced sludge washing process steps for C-107 sludge
(leach conditions: liquid:solids, 6 mL/g; NaOH, 6.33 *M*; temperature, 70°C; time, 22 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/g)		Rinse (μg/g)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	7.04	0.515	373	2.96	<0.0838[a]	b	0.147	0
Al	56600	303	20900	144	7060	16.9	319	10.9
Ba	312	3.61	546	3.94	0.021	0.0168	<0.00978	b
Be	<0.0859	b	<0.0235	b	<0.00419	b	<0.00489	b
Bi	10500	245	20200	208	163	7.62	70.1	43.5
Ca	1090	21.6	1270	13.8	0.482	0.0335	65.7	3.95
Cd	43	1.03	75.5	0.704	<0.0838	b	<0.0978	b
Co	9.19	0	15.4	0.141	<0.0796	b	<0.0929	b
Cr	518	10.8	315	3.94	53.3	0.846	2.43	0.0293
Cu	90.4	0.859	98.2	0.704	3.79	0.0168	0.103	0.00978
Fe	37100	256	57400	232	13.1	0.846	0.171	0.00978
K	300	7.56	20.1	1.08	<42.3	b	4.8	0.372
Mg	290	10.8	503	10.8	<0.105	b	<0.122	b
Mn	1870	10.8	2990	17.7	0.0461	0.0754	<0.00489	b
Ni	3260	61.3	6140	65.1	<0.0838	b	<0.0978	b
P	14800	343	1870	437	474	67.7	1270	118
Sb	596	5.84	<98.6	b	<0.838	b	<0.978	b
Si	29000	0	75000	0	c	c	c	c
Sr	189	3.61	360	0.986	0.0461	0.0335	<0.0245	b
Th	532	7.9	554	36.5	1.21	0.251	<0.245	b
U	9660	112	19700	171	42.5	0.411	1.64	0.215
V	8.93	0.515	12.3	0.986	<0.0419	b	0.0831	0
Zn	137	9.79	115	0.704	9.03	0.0754	0.308	0.0685
Radiospecies	Bq/g		Bq/g		Bq/g		Bq/g	
Co-60	12000	1000	20000	4000	25.4	c	22.1	c
Cs-137	1600000	100000	900000	20000	175000	c	9180	c
Eu-152	<4000	b	<8800	b	c	c	c	c
Eu-154	94000	7000	170000	20000	c	c	c	c
Eu-155	79000	14000	170000	30000	c	c	c	c
Pu-238	11000	1000	22000	2000	c	c	c	c
Pu-239/240	51000	2000	98000	8000	c	c	c	c
Pu-all	62000	2000	120000	10000	c	c	c	c
Am-241	84000	22000	180000	70000	c	c	c	c
Gross-α	190000	30000	290000	60000	240	50	6	11
Gross-β	130000000	10000000	250000000	10000000	230000	10000	14000	1000

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.30. Test #8 - percentage of each species solubilized and percentage recovery for C-107 sludge
(leach conditions: liquid:solids, 6 mL/g; NaOH, 6.33 *M*; temperature, 70 °C; time, 22 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	-2482.46	190.02	21.22	1.55	2603.69	191.57
Al	82.00	0.16	79.71	0.50	97.71	0.60
Ba	14.70	1.16	0.04	0.03	85.34	1.16
Be	a	a	a	a	a	a
Bi	6.23	2.39	15.99	4.25	109.76	5.04
Ca	43.21	1.28	61.53	3.88	118.32	4.41
Cd	14.42	2.20	0.00	0.00	85.58	2.20
Co	18.32	0.75	0.00	0.00	81.68	0.75
Cr	70.36	0.72	65.80	1.68	95.44	2.24
Cu	47.05	0.63	26.03	0.29	78.97	0.86
Fe	24.59	0.60	0.21	0.01	75.63	0.60
K	96.73	0.19	16.26	1.33	19.53	1.36
Mg	15.46	3.63	0.00	0.00	84.54	3.63
Mn	22.07	0.64	0.01	0.02	77.95	0.65
Ni	8.20	1.98	0.00[b]	0.00[b]	91.80	1.98
P	93.84	1.45	106.22	8.89	112.38	9.05
Sb	100.00	0.00	0.00	0.00	0.00	0.00
Si	-26.06	0.00	0.00	0.00	126.06	0.00
Sr	7.16	1.79	0.14	0.11	92.99	1.80
Th	49.24	3.43	1.35	0.28	52.11	3.44
U	0.60	1.44	2.78	0.05	102.18	1.47
V	32.86	6.63	9.46	0.55	76.59	6.96
Zn	59.09	2.93	41.38	3.02	82.29	5.92
Radiospecies						
Co-60	-18.76	17.60	3.13	0.26	84.36	17.70
Cs-137	72.58	1.82	70.71	4.42	98.12	6.16
Eu-152	a	a	a	a	a	a
Eu-154	11.85	12.27	b	b	88.15	12.27
Eu-155	-4.89	26.23	b	b	104.89	26.23
Pu-238	2.52	12.53	b	b	97.48	12.53
Pu-239/240	6.34	8.48	b	b	93.66	8.48
Pu-all	5.66	8.43	b	b	94.34	8.43
Am-241	-4.45	48.97	b	b	104.45	48.97
Gross-a	25.61	19.36	0.78	0.21	75.18	19.44
Gross-b	6.27	8.13	1.16	0.10	94.89	8.21

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

[b]Measurement was not made.

probably not removed to 49% because the relatively low value of its recovery, 52%, could indicate that more thorium remained in the residue than was measured.

Concentrations of selected constituents in C-107 sludge as measured in this work and by other researchers [Temer and Villarreal (1996) and Lumetta et al. (1996)] are compared in Table 4.31. The wide variation in concentrations of the components determined at different laboratories may indicate that the samples were different as a consequence of the sludge within the tank being inhomogeneous. A comparison of the percentages of each constituent removed from the sludge by the different researchers is shown in Table 4.32. These numbers are generally consistent, except for uranium. The percentage removed is, by definition, scaled to the concentrations in the original sludge, so the variations in percentage removed can be attributed to the different leaching conditions employed. With leaching conditions ranging from 3 *M* to 6.33 *M* NaOH, 70 to 100°C, and 10 to 22 h, 63 to 82% of the aluminum, 48 to 70% of the chromium, 91 to 94% of the phosphorus, and 70 to 73% of the cesium were removed from the sludge.

4.5 SLUDGE C-104

C-104 sludge samples arrived at ORNL in two bottles. Sludge in one bottle contained a small piece of hard material resembling concrete; the remainder of the sludge was the typical slurry-like material and had a water content of 63.5 wt %. This sludge (without the "rock") was used in tests #11 and #13. Sludge in the other bottle was of the usual consistency and had a water content of 43.7 wt % and was used in test #12. Samples from each bottle were analyzed to determine whether the sludge was different. The analyses of the wet samples are given in Tables 4.33 and 4.35 as part of the enhanced sludge washing partitioning data. There are small differences in the concentrations of most species in the two samples (even on a dry basis, as shown later in Table 4.40). The major constituents of sludge C-104 are aluminum, iron, silicon, thorium, and uranium. Bismuth and phosphorus concentrations are low.

Table 4.31. Concentration of selected constituents in dry, untreated C-107 sludge determined by different researchers

Species	Unit of measure	LANL[a]	PNNL[b]	PNNL[c]	ORNL[d]
Al	μg/g	105000.	86800.	34400.	60500.
Cr	μg/g	706.	1250.	595.	553.
P	μg/g	36500.	9500.	11800.	15800.
U	μg/g	23500.	11100.	6450.	10300.
Cs-137	μCi/g	75.4	127.	57.4	46.2
Pu-239/240	μCi/g	2.90	5.77		1.47

[a]Temer and Villarreal, LAUR 96-2839 (1996).
[b]Lumetta et al., PNNL-11278 (1996).
[c]Brooks et al., Letter Report (September 1996).
[d]This work.

Table 4.32. Comparison of percentage of selected species removed from C-107 sludge by different researchers

	% Removed			
Species	LANL[a]	PNNL[b]	PNNL[c]	ORNL[d]
Al	76	78	63	82
Cr	68	48	64-67	70
P	94	94	91	94
U	22	22	31-34	1
Cs	73	70	71	73
Pu	0	2		6

[a]Temer and Villarreal, LAUR 96-2839 (1996); 3.0 *M* NaOH, 10 h, 100°C, 8 wt % solids.
[b]Lumetta et al., PNNL-11278 (1996); 3.0 *M* NaOH, 10 h, 100°C, 8 wt% solids.
[c]Brooks et al., Letter Report (September 1996); 1.2 *M* NaOH, 5 h, 100°C, 5.4 wt % solids; second leach 3.5 *M* NaOH, 5 h, 100°C, 5.8 wt% solids
[d]This work; 6.33 *M* NaOH, 22 h, 70°C, liquid:solids = 6:1.

As indicated above, three enhanced sludge washing tests were performed with C-104 sludge. In each of these tests the sodium hydroxide concentration was 4 *M* and the leaching time was ~64 h. The primary variables were temperature and liquid:solids ratio, which varied from 50 to 93 °C and from 19 to 31 mL/g, respectively. Concentrations measured in each process stream and calculated values of the percentage of each constituent removed from the sludge are given in Tables 4.33 through 4.38. The operating conditions and the percentages of selected constituents removed from the sludge in the three tests are summarized in Table 4.39. Data on the percentage of phosphorus removed from the sludge is useless. Difficulty in obtaining good values may have been caused by the initially low concentration of phosphorus in the sludge. The percentages of chromium, uranium, and cesium removed from the sludge increased in lock-step with operating temperature. The same trend was not seen with aluminum, presumably due to the poor recovery of aluminum in test #12 (80% versus >90% in the other two tests). Based on the analysis of the residue, about 23% of the thorium was removed from the sludge; but again the analysis of the leachate did not corroborate this.

The concentrations of selected constituents in C-104 sludge (on a dry basis) determined in this work are compared with measurements made by Temer and Villarreal (1997) in Table 4.40. The analysis of the sludge sample with low water content compares favorably with the results of Temer and Villarreal. With the exception of phosphorus, the high-water-content sample has higher concentrations of the metals in the selected subset. This seeming contradiction may be an artifact of too high a value for the water content which is used to adjust the concentrations to a dry basis.

The percentage of species removed from the sludge in these tests are compared to the findings of Temer and Villarreal (1997) in Table 4.41. Clearly, increasing the temperature from 50 °C to above 90 °C improves the removal of aluminum, chromium, and cesium. There is poor agreement on the removal of uranium.

Table 4.33. Test #11 - concentrations of species in enhanced sludge washing process steps for C-104 sludge
(leach conditions: liquid:solids, 31 mL/g; NaOH, 4 *M*; temperature, 80°C; time, 65 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/g)		Rinse (μg/g)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	<1.53[a]	b	<5.05	b	0.323	0.091	<0.103	b
Al	31700	3170	22800	2280	441	44.1	17.3	1.73
Ba	120	12	110	11	0.0319	0.0364	<0.0103	b
Be	34.1	3.41	10.3	1.03	1.25	0.125	<0.00517	b
Bi	27.7	11.8	23.7	4.97	<0.0228	b	<0.0259	b
Ca	1940	194	1510	151	0.0501	0.437	0.429	0.0429
Cd	1030	103	881	88.1	1.41	0.246	<0.103	b
Co	10.2	1.02	7.32	2.52	<0.0865	b	<0.0982	b
Cr	1130	113	462	46.2	31.7	3.17	1.21	0.121
Cu	31.9	3.36	21.4	2.14	0.168	0.0168	0.119	0.0207
Fe	21700	2170	17400	1740	7.56	4.71	0.719	0.3
K	643	64.3	107	10.7	96.6	9.66	12.8	1.28
Mg	387	48.7	303	30.3	<0.114	b	<0.129	b
Mn	4140	414	3340	334	0.601	0.956	0.0259	0.062
Ni	2090	209	1750	175	2.09	0.573	<0.103	b
P	77	104	233	400	231	36	3.47	3.47
Sb	4.22	4.58	0.853	0.165	<0.0228	b	<0.0259	b
Si	8500	0	56000	0	c	c	c	c
Sr	51.2	5.12	41.8	4.18	<0.0228	b	<0.0259	b
Th	11600	1160	8950	895	2.17	2.57	0.346	0.455
U	20200	2020	16900	3640	15.7	4.81	<0.517	b
V	4.58	0.458	<0.229	b	0.237	0.0237	<0.0517	b
Zn	62.6	6.26	40.1	4.01	0.805	0.0805	0.191	0.0517
Radiospecies	Bq/g		Bq/g		Bq/g		Bq/g	
Co-60	6100	3700	4200	1300	<310	b	<35	b
Cs-137	2700000	100000	970000	20000	110000	10000	4200	200
Eu-152	<4700	b	<6200	b	<950	b	<140	b
Eu-154	18000	8000	16000	5000	<410	b	<31	b
Eu-155	23000	25000	19000	11000	<970	b	<67	b
Pu-238	9300	100	6100	100	c	c	c	c
Pu-239/240	59000	1000	40000	1000	c	c	c	c
Pu-all	68000	1000	46000	1000	c	c	c	c
Am-241	86000	49000	110000	20000	<2000	b	<160	
Gross-α	210000	10000	170000	10000	c	c	c	c
Gross-β	30000000	1000000	21000000	1000000	120000	10000	4700	100

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.34. Test #11 - percentage of each species solubilized and percentage recovery for C-104 sludge (leach conditions: liquid:solids, 31 mL/g; NaOH, 4 *M*; temperature, 80°C; time, 65 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	a	a	a	a	a	a
Al	28.73	10.08	19.36	2.66	90.63	11.67
Ba	9.17	12.85	0.35	0.40	91.18	12.88
Be	70.07	4.23	47.85	6.77	77.78	9.61
Bi	15.22	40.26	0.00	0.00	84.78	40.26
Ca	22.87	10.91	0.52	0.30	77.65	10.95
Cd	15.24	11.99	1.79	0.36	86.54	12.12
Co	28.89	25.49	0.00	0.00	71.11	25.49
Cr	59.49	5.73	38.98	5.35	79.49	9.65
Cu	33.53	9.65	15.09	2.24	81.56	10.98
Fe	20.54	11.24	0.53	0.29	79.98	11.28
K	83.51	2.33	239.94	31.30	256.42	32.62
Mg	22.42	12.47	0.00	0.00	77.58	12.47
Mn	20.06	11.31	0.20	0.30	80.15	11.32
Ni	17.03	11.73	1.31	0.38	84.28	11.83
P	-199.85	654.97	4015.55	5458.73	4315.39	5883.85
Sb	79.97	22.08	0.00	0.00	20.03	22.08
Si	-552.83	0.00	b	b	652.83	0.00
Sr	19.10	11.44	0.00	0.00	80.90	11.44
Th	23.55	10.81	0.31	0.30	76.76	10.84
U	17.10	19.69	1.01	0.33	83.92	19.73
V	100.00	0.00	67.55	9.55	67.55	9.55
Zn	36.52	8.98	23.50	3.41	86.98	11.05
Radiospecies						
Co-60	31.77	46.46	0.00	0.00	68.23	46.46
Cs-137	64.40	1.51	56.61	5.27	92.21	5.97
Eu-152	a	a	a	a	a	a
Eu-154	11.92	47.86	0.00	0.00	88.08	47.86
Eu-155	18.14	100.81	0.00	0.00	81.86	100.81
Pu-238	35.00	1.27	b	b	65.00	1.27
Pu-239/240	32.82	2.03	b	b	67.18	2.03
Pu-all	32.97	1.76	b	b	67.03	1.76
Am-241	-26.74	75.80	0.00	0.00	126.74	75.80
Gross-α	19.78	6.07	b	b	80.22	6.07
Gross-β	30.64	4.03	5.57	0.47	74.93	4.16

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

[b]Measurement was not made.

Table 4.35. Test #12 - concentrations of species in enhanced sludge washing process steps for C-104 sludge
(leach conditions: liquid:solids, 19 mL/g; NaOH, 4 *M*; temperature, 50°C; time, 63 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/g)		Rinse (μg/g)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	60.7	6.07	183	18.3	1.34	0.134	<0.209[a]	b
Al	36000	3600	19900	1990	559	55.9	16.5	1.65
Ba	113	11.3	90.3	9.03	<0.0182	b	<0.0209	b
Be	33	3.3	12.2	1.22	1.26	0.126	<0.0104	b
Ca	2080	208	1410	141	1.23	0.123	1.65	0.165
Cd	952	95.2	712	71.2	1.88	0.188	0.282	0.188
Co	6.19	0.619	5.03	0.51	<0.173	b	<0.198	b
Cr	999	99.9	554	55.4	21.9	2.19	0.386	0.0418
Cu	69.9	6.99	43.3	4.33	0.2	0.02	0.647	0.0647
Fe	19000	1900	14600	1460	3.88	0.388	0.251	0.0251
K	621	62.1	157	15.7	139	13.9	17.5	1.75
Mg	292	29.2	225	22.5	0.228	0	0.261	0
Mn	3580	358	2860	286	<0.0091	b	0.0104	0
Ni	1890	189	1450	145	2.23	0.255	<0.209	b
P	2280	2280	2110	211	226	22.6	5.9	1.15
Si	16000	0	52000	0	c	c	c	c
Sr	46.7	47.2	46.6	43.1	<0.0455	b	<0.0522	b
Th	10800	1080	7470	747	<0.455	b	<0.522	b
U	16300	1630	13400	1340	11.5	1.15	<1.04	b
V	5.06	0.75	1.91	0.191	0.109	0.0182	<0.104	b
Zn	192	19.2	108	10.8	1.25	0.874	<0.313	b
Radiospecies	Bq/g		Bq/g		Bq/g		Bq/g	
Co-60	7400	1200	5000	600	110	30	3.7	1.9
Cs-137	2700000	100000	1300000	100000	110000	10000	3200	100
Eu-152	<3200	b	<1600	b	<75	b	<7.6	b
Eu-154	22000	3000	18000	2000	<52	b	<6.7	b
Eu-155	26000	9000	24000	5000	<31	b	<19	b
Am-241	150000	20000	130000	10000	<640	b	<38	b
Gross-α	260000	20000	220000	10000	c	c	c	c
Gross-β	31000000	1000000	24000000	1000000	140000	10000	4000	100

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.36. Test #12 - percentage of each species solubilized and percentage recovery for C-104 sludge
(leach conditions: liquid:solids, 19 mL/g; NaOH, 4 *M*; temperature, 50°C; time, 63 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	-228.70	46.49	25.30	3.58	354.00	48.37
Al	39.73	8.52	19.24	2.62	79.51	10.14
Ba	12.87	12.32	0.00	0.00	87.13	12.32
Be	59.69	5.70	43.75	6.19	84.06	10.30
Ca	26.09	10.45	3.19	0.41	77.09	10.68
Cd	18.46	11.53	3.20	0.74	84.74	11.78
Co	11.40	12.62	0.00	0.00	88.60	12.62
Cr	39.54	8.55	26.34	3.64	86.80	10.87
Cu	32.46	9.55	32.55	4.39	100.09	12.43
Fe	16.22	11.85	0.28	0.04	84.06	11.87
K	72.44	3.90	345.60	43.95	373.16	46.23
Mg	15.99	11.88	3.72	0.37	87.73	12.15
Mn	12.90	12.32	0.01	0.00	87.11	12.32
Ni	16.35	11.83	1.35	0.21	85.00	11.93
P	-0.90	101.40	121.76	122.30	222.66	223.18
Si	-254.34	0.00	a	a	354.34	0.00
Sr	-8.79	149.05	0.00	0.00	108.79	149.05
Th	24.59	10.66	0.00	0.00	75.41	10.66
U	10.37	12.68	0.81	0.11	90.44	12.73
V	58.85	7.36	24.68	5.51	65.84	11.36
Zn	38.67	8.67	7.46	5.27	68.79	10.59
Radiospecies						
Co-60	26.33	14.86	18.61	5.60	92.28	18.01
Cs-137	47.51	4.48	50.43	4.64	102.93	6.99
Eu-152	b	b	b	b	b	b
Eu-154	10.80	15.69	0.00	0.00	89.20	15.69
Eu-155	-0.64	40.66	0.00	0.00	100.64	40.66
Am-241	5.51	14.55	0.00	0.00	94.49	14.55
Gross-α	7.75	8.24	a	a	92.25	8.24
Gross-β	15.59	4.45	5.58	0.41	89.99	4.58

[a]Measurement was not made.

[b]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

Table 4.37. Test #13 - concentrations of species in enhanced sludge washing process steps for C-104 sludge
(leach conditions: liquid:solids, 27 mL/g; NaOH, 4 *M*; temperature, 93°C; time, 65 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/g)		Rinse (μg/g)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	<1.53[a]	b	354	35.4	0.637	0.0637	0.366	0.0366
Al	31700	3170	3920	392	2440	244	83.4	8.34
Ba	120	12	132	13.2	<0.0182	b	<0.0222	b
Be	34.1	3.41	21.5	2.15	1.97	0.197	<0.0111	b
Bi	27.7	11.8	95	33.7	<0.137	b	<0.166	b
Ca	1940	194	1960	196	3.81	0.381	4.79	0.479
Cd	1030	103	1080	108	1.85	0.473	0.355	0.421
Co	10.2	1.02	28.9	2.89	<0.173	b	<0.211	b
Cr	1130	113	378	37.8	62.8	6.28	2.15	0.215
Cu	31.9	3.36	85.1	8.51	0.228	0.0228	0.122	0.0222
Fe	21700	2170	21400	2140	2.94	0.294	<0.0443	b
K	643	64.3	106	10.6	136	13.6	6.93	0.693
Mg	387	48.7	<1.48	b	<0.228	b	<0.277	b
Mn	4140	414	5720	572	<0.455	b	<0.0554	b
Ni	2090	209	2150	215	2.26	0.291	0.421	0.244
P	77	104	141	14.1	227	22.7	<5.54	b
Sb	4.22	4.58	<0.888	b	<0.137	b	<0.166	b
Si	8500	0	13000	2600	c	c	c	c
Sr	51.2	5.12	61.2	6.12	<0.0455	b	<0.0554	b
Th	11600	1160	11400	1140	0.61	0.309	<0.554	b
U	20200	2020	19400	1940	13.4	1.34	<1.11	b
V	4.58	0.458	29	2.9	0.328	0.0728	<0.111	b
Zn	62.6	6.26	75.6	7.56	1.27	0.255	<0.332	b
Radiospecies	Bq/g		Bq/g		Bq/g		Bq/g	
Co-60	6100	3700	9000	2300	c	c	c	c
Cs-137	2700000	100000	760000	20000	210000	10000	7800	100
Eu-152	<4700	b	c	c	c	c	c	c
Eu-154	18000	8000	34000	8000	c	c	c	c
Eu-155	23000	25000	21000	12000	c	c	c	c
Pu-238	9300	100	16000	1000	c	c	c	c
Pu-239/240	59000	1000	94000	2000	c	c	c	c
Pu-all	c	c	110000	10000	c	c	c	c
Am-241	86000	49000	210000	30000	c	c	c	c
Gross-α	210000	10000	320000	10000	c	c	c	c
Gross-β	30000000	1000000	34000000	1000000	250000	10000	9300	100

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.38. Test #13 - percentage of each species solubilized and percentage recovery for C-104 sludge
(leach conditions: liquid:solids, 27 mL/g; NaOH, 4 *M*; temperature, 93°C; time, 65 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	a	a	a	a	a	a
Al	90.23	1.38	83.16	11.38	92.92	12.15
Ba	13.13	12.29	0.00	0.00	86.87	12.29
Be	50.21	7.04	58.18	8.23	107.97	13.24
Bi	-170.84	150.14	0.00	0.00	270.84	150.14
Ca	20.21	11.28	7.28	0.92	87.06	11.82
Cd	17.19	11.71	2.55	1.02	85.35	11.93
Co	-123.75	31.64	0.00	0.00	223.75	31.64
Cr	73.58	3.74	60.05	8.22	86.47	10.64
Cu	-110.67	30.60	15.41	2.32	226.08	31.84
Fe	22.12	11.01	0.14	0.02	78.02	11.02
K	86.98	1.84	236.12	31.88	249.14	32.88
Mg	100.00	0.00	0.00	0.00	0.00	0.00
Mn	-9.11	15.43	0.00	0.00	109.11	15.43
Ni	18.76	11.49	1.52	0.32	82.76	11.60
P	-44.61	195.85	2968.72	4020.67	3113.33	4215.50
Sb	100.00	0.00	0.00	0.00	0.00	0.00
Si	-20.78	24.16	b	b	120.78	24.16
Sr	5.60	13.35	0.00	0.00	94.40	13.35
Th	22.39	10.98	0.05	0.03	77.66	10.98
U	24.16	10.73	0.67	0.09	76.51	10.77
V	-400.04	70.72	72.12	17.56	572.16	77.65
Zn	4.63	13.49	20.43	4.58	115.80	15.55
Radiospecies						
Co-60	-16.52	76.69	b	b	116.52	76.69
Cs-137	77.77	1.01	84.52	4.87	106.75	5.47
Eu-152	a	a	a	a	a	a
Eu-154	-49.17	75.02	b	b	149.17	75.02
Eu-155	27.90	88.55	b	b	72.10	88.55
Pu-238	-35.87	8.62	b	b	135.87	8.62
Pu-239/240	-25.82	3.42	b	b	125.82	3.42
Pu-all	-27.75	11.76	b	b	127.75	11.76
Am-241	-92.84	113.27	b	b	192.84	113.27
Gross-α	-20.34	6.85	b	b	120.34	6.85
Gross-β	10.50	3.98	9.06	0.45	98.56	4.22

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

[b]Measurement was not made.

Table 4.39. Effect of operating parameters on caustic leaching of C-104 sludge

Test	Liquid:solid (mL/g)	NaOH (*M*)	T (°C)	Time (h)	% Removal			
					Al	Cr	U	Cs
11	31	3.99	80	65	28.7	59.5	17.1	64.4
12	19	3.99	50	63	39.7	39.5	10.4	47.5
13	27	3.99	93	65	90.2	73.6	24.2	77.8

Table 4.40. Concentration of selected constituents in dry, untreated C-104 sludge determined by different researchers

Species	Unit of measure	LANL[a]	ORNL[b]	ORNL[c]
Al	μg/g	63200.	86800.	63900.
Cr	μg/g	2280.	3100.	1770.
P	μg/g	6320.	211.	4050.
U	μg/g	30000.	55300.	29000.
Cs-137	μCi/g	174.	200.	130.
Pu-239/240	μCi/g	4.93	4.4	

[a]Temer and Villarreal, LAUR 97-2889 (1997).
[b]This work, high-water-content sample.
[c]This work, low-water-content sample.

Table 4.41. Comparison of percentage of selected species removed from C-104 sludge by different researchers

Species	% Removed		
	LANL[a]	ORNL[b]	ORNL[c]
Al	97	40	90
Cr	52	40	74
P	89		
U	4	10	24
Cs	100	48	78
Pu	0		

[a]Temer and Villarreal, LAUR 97-2889 (1997); first leach 2.7 *M* NaOH, 5 h, 100°C, 5 wt % solids; second leach 3.2 *M* NaOH, 5 h, 100°C, 1 wt % solids.
[b]This work; 3.99 *M* NaOH, 63 h, 50°C, and liquid:solids of 19:1.
[c]This work; 3.99 *M* NaOH, 65 h, 93°C, and liquid:solids of 27:1.

4.6 SLUDGE S-101

One experiment was performed to measure the effect of the enhanced sludge washing process on sludge from tank S-101. Analyses of the untreated sludge and the phases into which it partitioned are shown in Table 4.42. Major constituents in this sludge are aluminum, silicon, and uranium. The sludge was leached with 4 *M* NaOH at 93 °C with a liquid:solids ratio of 16 mL/g for 65 h. Calculated values of the percentage of each species leached from the sludge and total recovery of each species are listed in Table 4.43. About 98% of the aluminum and 99% of the cesium were leached from the sludge, and the excellent material balances (percentage recovery) indicate that these values are reliable. The data indicate that approximately 86% of the chromium, 26% of the uranium, and 19% of the plutonium were removed from the sludge, although the uncertainty is greater than that of the aluminum and cesium data.

The concentrations of selected species in sludge S-101 quantified in this work are compared with measurements made by Lumetta et al. (1997b) in Table 4.44. Agreement is quite good for aluminum, chromium, uranium, cesium-137, and plutonium-239/240. However, there is a great difference in the measured concentration of phosphorus. In their leaching study, Lumetta et al. (1997b) used a lower caustic concentration (~2.5 *M*) with a slightly higher temperature (100 °C) and about twice the leaching time (100 h) than was used in this study. The percentages of aluminum, chromium, and cesium-137 removed from the sludge in the two studies are similar, as shown in Table 4.45. There is significant disagreement in the measured behavior of uranium and plutonium-239/240. However, part of the difference may be attributable to the substantial standard deviations and slightly low recoveries estimated in the present study (Table 4.43).

Table 4.42. Test #14 - concentrations of species in enhanced sludge washing process steps for S-101 sludge
(leach conditions: liquid:solids, 16 mL/g; NaOH, 4 *M*; temperature, 93°C; time, 65 h)

	Original sludge (μg/g)		Residual (μg/g)		Leachate (μg/g)		Rinse (μg/g)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	9.04	0.904	24	2.4	0.186	0.0186	0.224	0.0224
Al	86300	8630	8760	876	7050	705	106	10.6
Ba	44.9	4.49	144	14.4	<0.0178[a]	b	<0.0213	b
Be	<0.171	b	<0.238	b	<0.00888	b	<0.0107	b
Bi	17.9	1.79	457	45.7	0.277	0.0277	<0.160	b
Ca	1330	133	1600	160	3.88	0.388	1.66	0.166
Cd	14.3	10.9	27.9	6.67	0.959	0.16	0.448	0.405
Co	4.94	0.495	16.7	1.67	<0.169	b	<0.203	b
Cr	3430	343	2220	222	365	36.5	5.85	0.585
Cu	52.6	5.26	77.4	7.74	2.91	0.291	0.128	0.0128
Fe	1830	183	5920	592	10.1	1.01	<0.0426	b
K	839	83.9	<23.8	b	162	16.2	4.82	0.482
Mg	31.7	3.17	67.4	15.2	<0.222	b	<0.267	b
Mn	1600	160	7330	733	<0.444	b	<0.0533	b
Ni	116	11.6	491	49.1	0.435	0.0888	0.267	0.533
P	<85.0	b	1680	168	20.3	2.03	<5.33	b
Sb	<2.56	b	<3.57	b	<0.133	b	<0.160	b
Si	9200	1840	29000	5800	c	c	c	c
Sr	404	40.4	1220	122	0.0799	0.00799	<0.0533	b
Th	240	24	824	82.4	<0.444	b	<0.533	b
U	7420	742	24700	2470	2.98	0.426	<1.07	b
V	9.73	0.973	22.4	2.24	0.408	0.0408	<0.107	b
Zn	205	20.5	154	15.4	0.506	0.0506	<0.320	b
Radiospecies	Bq/g		Bq/g		Bq/g		Bq/g	
Co-60	c	c	1500	700	c	c	c	c
Cs-137	3800000	100000	230000	10000	340000	10000	5400	100
Eu-152	c	c	c	c	c	c	c	c
Eu-154	c	c	17000	3000	c	c	c	c
Eu-155	c	c	9300	7300	c	c	c	c
Pu-238	260	20	840	30	c	c	c	c
Pu-239/240	9600	600	35000	1000	c	c	c	c
Pu-all	9800	600	35000	1000	c	c	c	c
Am-241	c	c	21000	18000	c	c	c	c
Gross-α	15000	1000	57000	3000	c	c	c	c
Gross-β	29000000	1000000	81000000	1000000	410000	10000	6400	100

[a]The symbol < indicates that the concentration was below the detectable limit given by the following numerical value.
[b]No standard deviation for values below the detectable limit.
[c]Not measured.

Table 4.43. Test #14 - percentage of each species solubilized and percentage recovery for S-101 sludge
(leach conditions: liquid:solids, 16 mL/g; NaOH, 4 *M*; temperature, 93°C; time, 65 h)

	Based on residue (%)		Based on leachate & rinse (%)		Recovery (%)	
Species	Value	Std deviation	Value	Std deviation	Value	Std deviation
Ag	41.31	8.30	85.16	10.77	143.85	16.87
Al	97.76	0.32	97.29	13.55	99.54	13.71
Ba	29.11	10.03	0.00	0.00	70.89	10.03
Be	a	a	a	a	a	a
Bi	-464.36	79.81	17.85	2.52	582.22	81.10
Ca	73.41	3.76	6.46	0.79	33.05	4.27
Cd	56.87	34.45	155.03	138.06	198.16	167.38
Co	25.27	10.58	0.00	0.00	74.73	10.58
Cr	85.69	2.02	127.00	17.67	141.30	18.78
Cu	67.47	4.60	69.86	9.48	102.39	12.51
Fe	28.49	10.11	6.37	0.90	77.88	10.59
K	100.00	0.00	237.00	32.56	237.00	32.56
Mg	53.00	11.59	0.00	0.00	47.00	11.59
Mn	-1.27	14.32	0.00	0.00	101.27	14.32
Ni	6.43	13.23	10.03	11.47	103.60	18.04
P	a	a	a	a	a	a
Sb	a	a	a	a	a	a
Si	30.32	19.71	0.00	0.00	69.68	19.71
Sr	33.25	9.44	0.23	0.03	66.98	9.46
Th	24.11	10.73	0.00	0.00	75.89	10.73
U	26.42	10.41	0.46	0.08	74.05	10.44
V	49.11	7.20	48.38	6.84	99.27	12.16
Zn	83.39	2.35	2.85	0.40	19.45	2.57
Radiospecies						
Co-60	a	a	a	a	a	a
Cs-137	98.66	0.07	106.75	4.14	108.09	4.16
Eu-152	a	a	a	a	a	a
Eu-154	a	a	a	a	a	a
Eu-155	a	a	a	a	a	a
Pu-238	28.58	6.06	b	b	71.42	6.06
Pu-239/240	19.41	5.54	b	b	80.59	5.54
Pu-all	21.05	5.33	b	b	78.95	5.33
Am-241	a	a	a	a	a	a
Gross-α	16.00	7.13	b	b	84.00	7.13
Gross-β	38.26	2.26	16.86	0.70	78.60	2.84

[a]Insufficient data for calculation; measured concentration in original sludge was below the detectable limit or was not measured.

[b]Measurement was not made.

Table 4.44. Concentration of selected constituents in dry, untreated S-101 sludge determined by different researchers

Species	Unit of measure	PNNL[a]	ORNL[b]
Al	μg/g	147000.	127000.
Cr	μg/g	7110.	5030.
P	μg/g	2300.	<125.
U	μg/g	9560.	10900.
Cs-137	μCi/g	138.	151.
Pu-239/240	μCi/g	0.48	0.38

[a]Lumetta et al., PNNL-11636 (1997b).
[b]This work.

Table 4.45. Comparison of percentage of selected species removed from S-101 sludge by different researchers

	% Removed	
Species	PNNL[a]	ORNL[b]
Al	96	98
Cr	89	86
P	97	
U	1	26
Cs	100	99
Pu	<4	19

[a]Lumetta et al., PNNL-11636 (1997b); first leach 2.5 *M* NaOH, 5 h, 100°C, 5 wt % solids; second leach 2.7 *M* NaOH, 100 h, 100°C, 1 wt % solids.
[b]This work; 3.99 *M* NaOH, 65 h, 93°C, and liquid:solids of 16:1.

5. SUMMARY AND RECOMMENDATIONS

5.1 SUMMARY

Fourteen separate experiments were performed to characterize the behavior of six different Hanford sludges under different caustic leaching conditions. Six tests were performed with sludge from tank S-104, two tests on SX-113, one test on C-105, one test on C-107, three tests on C-104, and one test on S-101. The test variables were leaching time, leaching temperature, sodium hydroxide concentration in the leach solution, volume of the leaching solution, and mass of the sludge.

Sludge S-104 was leached with sodium hydroxide solutions ranging in concentration from 3.8 to 6.33 *M* for durations ranging from 4 to 126 h. More than 95% of the chromium and cesium were removed under all of the conditions tested. Removal of aluminum improved with increased caustic concentration and increased leaching time, ranging from 20 to 96% removal. Temperature was varied over a range of 67 to 80°C, and the percentage of metals removed from the sludge increased with increasing temperature.

Increasing both leaching time and temperature increased the quantities of aluminum, chromium, and cesium removed from the SX-113 sludge with 6.33 *M* NaOH. Removal of aluminum ranged from 51 to 79%; removal of chromium ranged from 53 to 66%; and cesium removal ranged from 60 to 86%.

Approximately 97% of the aluminum and 71% of the chromium were removed from sludge C-105 with 6.33 *M* NaOH at 70°C in 22 h. About 76% of the cesium was also removed. Similar conditions resulted in the removal of 82% of the aluminum, 70% of the chromium, and 73% of the cesium from sludge C-107.

Leaching tests with sludge C-104 were performed at a sodium hydroxide concentration of 4 *M* and leaching times of 63–65 h. As operating temperature was increased from 50 to 93°C, the amount

of aluminum removed increased from 29 to 90% and chromium removal increased from 40 to 74%. Removal of cesium also increased with temperature.

Sludge S-101 was leached with 4 *M* NaOH at 93 °C for 65 h. About 98% of the aluminum, 86% of the chromium, and 99% of the cesium were removed from the sludge.

Analyses of the untreated sludges reported by various researchers were compared with the results obtained in this work. Generally there was good agreement on concentrations of aluminum, chromium, and cesium. One exception was sludge C-107, where there was considerable scatter in the data. There was uniform disagreement on the phosphorus concentration. It is postulated that some differences can be attributed to variations in the nonhomogeneous samples, but differences in phosphorus results appear to be an artifact of the analysis technique. Comparisons of the removal of selected metals from the sludge exhibited about the same level of agreement.

5.2 RECOMMENDATIONS

Planned parametric studies of the effect of caustic concentration, liquid:solids ratio, and temperature on the enhanced sludge washing process should also evaluate the effect of leaching time. The data presented in this report can aid in selecting conditions and duration of the process.

Because sludge samples from one tank may be distributed to more than one researcher, it is recommended that a large sample be collected and homogenized with strong mechanical agitation prior to distribution of aliquots. This would eliminate the concern that some differences in results could occur because of sample inhomogeneity.

The chemical analyses of sludges and process streams continue to be a problem and need to be improved. The methods to analyze phosphorus should be reviewed to determine the cause of the large differences reported by various workers.

6. REFERENCES

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