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Characterization and Leaching Study of Sludge from Melton Valley Storage Tank W-25

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DEPARTMENT OF ENERGY

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Chemical Technology Division

CHARACTERIZATION AND LEACHING STUDY OF SLUDGE FROM MELTON VALLEY STORAGE TANK W-25

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EXECUTIVE SUMMARY

Bench-scale batch tests have been conducted with sludge from the Melton Valley Storage Tank (MVST) Facility at Oak Ridge National Laboratory (ORNL) to evaluate separation processes for use in a comprehensive sludge-processing flow sheet for concentrating the radionuclides and reducing the volumes of storage tank wastes for final disposal. This report discusses the hot cell apparatus, the characterization of the sludge, and the results obtained from a variety of basic and acidic leaching tests of samples of sludge.

Approximately 5 L of sludge/supernate from MVST W-25 was retrieved and transferred to a stainless steel tank for mixing and storage in a hot cell. Samples were centrifuged to separate the sludge liquid and the sludge solids. Air-dried samples of sludge were analyzed to determine the concentrations of radionuclides, other metals, and anions. Based upon the air-dried weight, about 41% of the centrifuged, wet sludge solids was water. The major alpha-, gamma-, and beta-emitting radionuclides in the centrifuged, wet sludge solids were ^{137}Cs, ^{60}Co, ^{154}Eu, ^{241}Am, ^{244}Cm, ^{90}Sr, Pu, U, and Th. The other major metals (in addition to the U and Th) and the anions were Na, Ca, Al, K, Mg, NO_3^-, CO_3^{2-}, OH^-, and O^{2-}. The organic carbon content was 3.0 ± 1.0%. The pH was 13.

Caustic Leaching of the Sludge

Samples of centrifuged, wet sludge solids were rinsed and leached with various concentrations of NaOH, ranging from 0.1 to 6.4 *M* at ambient temperature and at 75 and 95°C. About 93% of the ^{137}Cs in the centrifuged, wet sludge solids was bound in the solids and could not be solubilized by basic leaching at temperatures from ambient to 75°C. However, the solubility of the ^{137}Cs was enhanced by heating the sludge to 95°C. In one of the tests, about 42% of the ^{137}Cs was removed by leaching with 6.3 *M* NaOH at 95°C.

Most of the ^{137}Cs that was solubilized by the caustic rinses or caustic leaches at ambient temperature appeared to be a constituent of the interstitial sludge liquid that remained after centrifugation. The major metals and anions removed from the sludge by rinsing with 0.16 *M* NaOH at ambient temperature were Na (65%), K (81%), NO_3^- (88%), and Cl^- (51%).

The solubility of ^{137}Cs was enhanced by caustic leaching of the sludge at 95°C. Increasing the mixing time and the concentration of the caustic also enhanced the ^{137}Cs solubility. The removal of sodium from the sludge increased up to 91% by caustic leaching with 6.3 *M* NaOH at 95°C. The solubility of sodium was much less (only 15%) when the sludge was heated with 3.2 *M* NaOH at 75°C. With the exception of zinc, there was little difference in the solubility of the other sludge constituents when the sludge was leached with caustic at 75°C or at ambient temperature.

Acidic Leaching of the Sludge

Samples of centrifuged, wet sludge solids were leached with various concentrations of nitric acid, ranging from 0.5 to 6 *M* HNO_3 at ambient temperature. Removing the ^{137}Cs from the W-25 sludge with nitric acid was difficult. About 13% of the ^{137}Cs was removed in 16 h with 3.0 *M* HNO_3. Only 22% of the ^{137}Cs was removed in 117 h using 6.0 *M* HNO_3. Leaching of the sludge solids with a sequence of 0.5 *M*, 3.0 *M*, 3.0 *M*, and 6.0 *M* HNO_3 solutions for a total time of 578 h removed 84% of the ^{137}Cs.

Pretreatment of the centrifuged, wet sludge solids with strong caustic enhanced the removal of ^{137}Cs with a nitric acid leachant. Leaching the sludge at ambient temperature, first with 3.1 *M* NaOH (144 h) and 6.4 *M* NaOH (144 h) and then with 6.0 *M* HNO_3 (117 h), removed 55% of the ^{137}Cs. When the sludge was not first leached with caustic, only 22% of the ^{137}Cs was removed for the same mixing time and temperature. Heating the sludge at 95°C—and leaching with 3.2 *M* NaOH (4 h) and 6.3 *M* NaOH (4 h) and then with 6.0 *M* HNO_3 (185 h)—removed about 81% of the ^{137}Cs. Of this percentage, about half was removed with the caustic leaches.

Fairly large percentages of ^{60}Co (50.3%), ^{90}Sr (57.8%), Ca (68.3%), Mg (71.1%), Ni (29.6%), and U (27.3) were solubilized when a sample of centrifuged, wet sludge was leached (68-h mixing) with nitric acid to a pH of 6.6. In a similar test in which the final pH was 7.6, no ^{60}Co, ^{90}Sr, or U was solubilized. The dissolution behavior of ^{60}Co and ^{90}Sr suggests that they were probably present in the sludge as hydroxides. Both cobalt and strontium begin to precipitate above pH 6.8. Uranium precipitates in the pH range 3.2 to 4.2; however, in a carbonate-bicarbonate system, uranium is somewhat solubilized, forming carbonate complexes. At pH 7 the predominant controlling species is $UO_2(CO_3)_2^{2-}$.

Leachants of ~6.0 *M* HNO_3 that also contained 1.0 *M* and 1.9 *M* hydrofluoric acid enhanced the removal of the ^{137}Cs from the centrifuged, wet sludge solids; between 82 and 89% was removed.

Only 56 to 60% of the plutonium was removed from the centrifuged sludge solids by leaching with 6.0 *M* HNO_3. Leaching the sludge with mild or strong caustic at ambient temperature before leaching it with nitric acid had no effect on the leachability of the plutonium. However, 91% of the plutonium was solubilized with 6.0 *M* HNO_3 (185 h) from sludge residue obtained from a sample of sludge that was first heated at 95°C and leached with 3.2 *M* NaOH for 4 h and then leached with 6.3 *M* NaOH for 4 h at 95°C. The insoluble fraction of the plutonium in the sludge was probably metathesized to the hydroxide or some other acid-soluble form by heating the sludge with strong caustic.

Addition of hydrofluoric acid to the nitric acid leachant enhanced the removal of the plutonium from the sludge. Leaching with 5.6 *M* HNO_3 and 1.9 *M* HF effectively removed all (~97%) of the plutonium. In the presence of the strong concentrations of fluoride ions, the fraction of the plutonium that was nitric acid insoluble may have formed soluble PuF_2^{2+} and PuF_3^{+} complexes. This behavior is very concentration dependent. At higher plutonium concentrations, PuF_3 and PuF_4 can be precipitated from acid solutions by addition of excess HF.

The use of hydrofluoric acid with the nitric acid leachant decreased the solubility of thorium because of the formation of acid-insoluble ThF_4. Without the hydrofluoric acid, the nitric acid leaches removed most of the thorium. The thorium in the sludge is probably present as thorium hydroxide. Both the HNO_3 and the HNO_3 plus HF leachants removed most of the Sr, Co, Eu, Cm, Am, and U. These elements are also probably present as hydroxides.

Based upon the initial and the final air-dried weights of samples of sludge solids that were leached in nitric acid at ambient temperature, between 63 and 82% of the solids were dissolved. The average was about 73%. An average of 31% of the sludge solids was removed by the high-temperature caustic leaches. Different concentrations of the caustic leachant did not significantly affect the dissolution.

Because of the high carbonate content of the sludge (11.5% of the air-dried sludge weight), much care had to be given to nitric acid additions because of carbon dioxide evolution. One kilogram of centrifuged, wet sludge solids can liberate 27.4 L of carbon dioxide. Consequently, adding nitric acid to tank W-25 would have to be done slowly with extreme care, and good mixing of the sludge would be needed.

Gelation in Sludge Leachates

Gel formation proved to be one of the biggest problems associated with nitric acid leaching of the sludge. The gel formation was time dependent, and gels were found in most of the centrifuged, wet sludge solids and many of the leachates. Delayed gelation also occurred in many of the filtered acidic leachates and some of the acidic rinses. In one of the tests in which the sludge was leached for about 19 h with 3.0 M HNO_3, a thin gel coating was observed on the wall of the container 3 days after leaching. However, it took about 2 to 3 weeks for the gel to form at the liquid-air interface, thicken, and stabilize. In most of the tests, longer times were normally required for the gels to form, thicken, and stabilize. The gels are postulated to be some form of amorphous silica precipitated from silicic acid. No gels formed in the caustic leachates.

Gel formation in the leachates or sludge solids as the result of acidic treatment of sludge would be an unacceptable problem because it could (1) prevent mixing, (2) prevent pumping, (3) retard separations, (4) coat surfaces, and (5) clog filters. Understanding the chemistry of gel formation and the steps needed to prevent its formation is essential.

1. INTRODUCTION

1.1 Overview of Task

One of the greatest challenges facing the Department of Energy (DOE) is the remediation of the 100 million gallons of high-level and low-level radioactive waste in the underground storage tanks at its Hanford, Savannah River, Oak Ridge, Idaho, and Fernald sites. Because of the magnitude of the problem and the extreme expense involved, DOE is in the process of developing technologies and strategies to minimize the amount of wastes requiring long-term disposal and storage.[1–5] Separation and concentration of the radioactive components will result in a larger fraction of the waste not requiring storage as high-level waste (HLW). The HLW is to be vitrified as glass logs and stored in canisters. Each canister is estimated to cost about $1 million. About 200,000 canisters would be needed at Hanford if the waste were not treated.

Bench-scale batch tests in a hot cell have been conducted with sludge from the Melton Valley Storage Tank (MVST) Facility at Oak Ridge National Laboratory (ORNL) to evaluate separation processes for use in a comprehensive sludge-processing flow sheet for concentrating the radionuclides and reducing the volumes of storage tank wastes for final disposal. This report discusses the hot cell apparatus, the characterization of the sludge, and the results obtained from a variety of basic and acidic leaching tests of samples of sludge.

Relatively large samples of sludge (60 to 80 g) were tested to minimize sample variation. At the start of the program, it was very difficult to obtain large quantities of sludge at Hanford. The Environmental Management Office of Technology Development felt that larger-scale demonstration of techniques was needed to prove the system could work with larger samples. Also, before this study, most of the work had been conducted on simulated waste, not actual tank waste. Simulants are by definition a stand-in and many times do not represent the complex chemistry involved in waste that has been exposed to aggressive chemicals and radiation for decades. Initial batch tests with actual MVST W-25 sludge revealed some surprises, such as the low solubility of cesium and the formation of gels in the leachates.

One of the goals of this work with actual sludge was to assist Hanford in evaluating treatment options and to help serve as a means of integrating the capabilities of the entire DOE complex in solving sludge problems. The collaboration that evolved from this work proved to be very useful and was subsequently applied to Hanford sludge studies. Presently the DOE team consists of technical input from Hanford, Oak Ridge, Los Alamos National Laboratory (LANL), Argonne National Laboratory (ANL), West Valley, Savannah River, and DOE headquarters staff.

Prior to this work, ORNL did not have a processing plan for the MVST tank waste, and this information was requested by Waste Operations at ORNL. The experimental evaluation of the MVST W-25 sludge has resulted in a better understanding of the capabilities of chemical treatment. The current approach is to privatize this effort, and results from the experiments in this report should prove useful in the treatment of the waste.

1.2 Etiology of MVST Sludge

ORNL served as the pilot plant for the Hanford production facility during the 1940s. As a result, the waste contained in the ORNL storage tanks has similarities to waste found at other sites; however, it typically has only 1 to 10% as much radioactivity. It is estimated that there are about 4.9 million liters (1.3 million gallons) of legacy waste stored on-site at ORNL, containing about 130,000 Ci composed of ^{137}Cs, ^{90}Sr, and smaller amounts of other fission products. About 20% of this waste (~1 million liters) is transuranic (TRU) sludge. The liquid component is liquid low-level waste (LLLW). The wastes were originally acidic in nature but were neutralized using Na_2CO_3, NaOH, and/or CaO to permit them to be stored in tanks constructed of carbon steel or concrete (Gunite). In addition to the legacy waste, about 57,000 L of concentrated waste—which contains about 13,000 Ci, consisting primarily of cesium, strontium, and small amounts of other fission products—is generated annually. A significant portion of this volume consists of TRU sludge.[6]

There are 34 significant underground storage tanks at ORNL. Of these, there are 21 inactive tanks (no longer in use) and 13 active tanks. These tanks are located at four tank farms referred to as the Gunite and Associated Tanks (GAAT), Old Hydrofracture Facility (OHF), Bethel Valley Evaporator Services Tanks (BVESTs), and MVSTs. There are 12 inactive Gunite (644,000-L capacity each) and 4 inactive stainless steel tanks ($\geq$5800-L capacity each) at GAAT, 5 inactive carbon steel tanks (50,000- to 95,000-L capacity each) at OHF, 5 active stainless steel tanks (190,000-L capacity each) at BVEST, and 8 stainless steel tanks (190,000-L capacity each) at

MVST. Currently, there are 1.5 million liters of waste at GAAT (12.4% sludge), 0.16 million liters of waste at OHF (14.6% sludge), 1.13 million liters of waste at BVEST (13.0% sludge), and 1.59 million liters of waste at MVST (40.5% sludge). About 64% of all the sludge waste stored underground at ORNL is at MVST.[6,7]

The Gunite tanks were built in 1943 as part of the Manhattan Project and were used to contain and treat radioactive liquids until the tanks were removed from service in the early 1970s. The Gunite process, in which portland cement and sand mixture is sprayed over a wire mesh and reinforcing rod frame, was used to construct these tanks. From 1981 to 1983, most of the sludge (~90%) was removed from these tanks by using a process called sluicing, which removed the waste with a water stream. In the process, a 2.5% bentonite and water mixture was impinged on the sludge to resuspend the solids and retard settling while the slurry was pumped to the MVSTs. Based on the volumes of liquid used in the slucing operation, it is estimated that ~140 tons of bentonite was injected into the Gunite tanks. Inspection of the Gunite tanks after the slucing operation showed that the walls were damaged and that the steel reinforcing bars were visible. It is likely that some of the cement and sand material was sluiced into the MVSTs along with the sludge.[8,9]

Sludge transferred from the Gunite tanks to the MVSTs was mixed with grout and injected into the shale (hydrofracture) beneath the Oak Ridge reservation. However, portions of these sludges are likely to have settled in these tanks and are part of the current sludge inventory at MVST Facility. The MVSTs were built to serve as both storage tanks and feed tanks for the hydrofracture facility.[6,7]

Unlike the tanks at GAAT and OHF, the tanks at MVST and BVEST are "double-containment" tanks and meet U.S. Environmental Protection Agency (EPA) requirements for underground storage tanks. As was pointed out previously, there are eight 190,000-L storage tanks at the MVST Facility at ORNL (Fig. 1). The horizontal stainless steel tanks are 3.7 m in diam by 18.3 m long and are located underground in reinforced concrete vaults with stainless steel liners (Fig. 2). These tanks contain alkaline evaporator concentrates from various past and present research and development (R&D) activities such as (1) process recovery of transuranium elements from fuels from the High Flux Isotopes Reactor and other reactors; (2) process development and purification studies using fission products and actinides; (3) fuel reprocessing studies such as the PUREX, THOREX, and TRUEX separation processes; (4) fission product release studies with high-

Fig. 1. Melton Valley Storage Tank Facility.

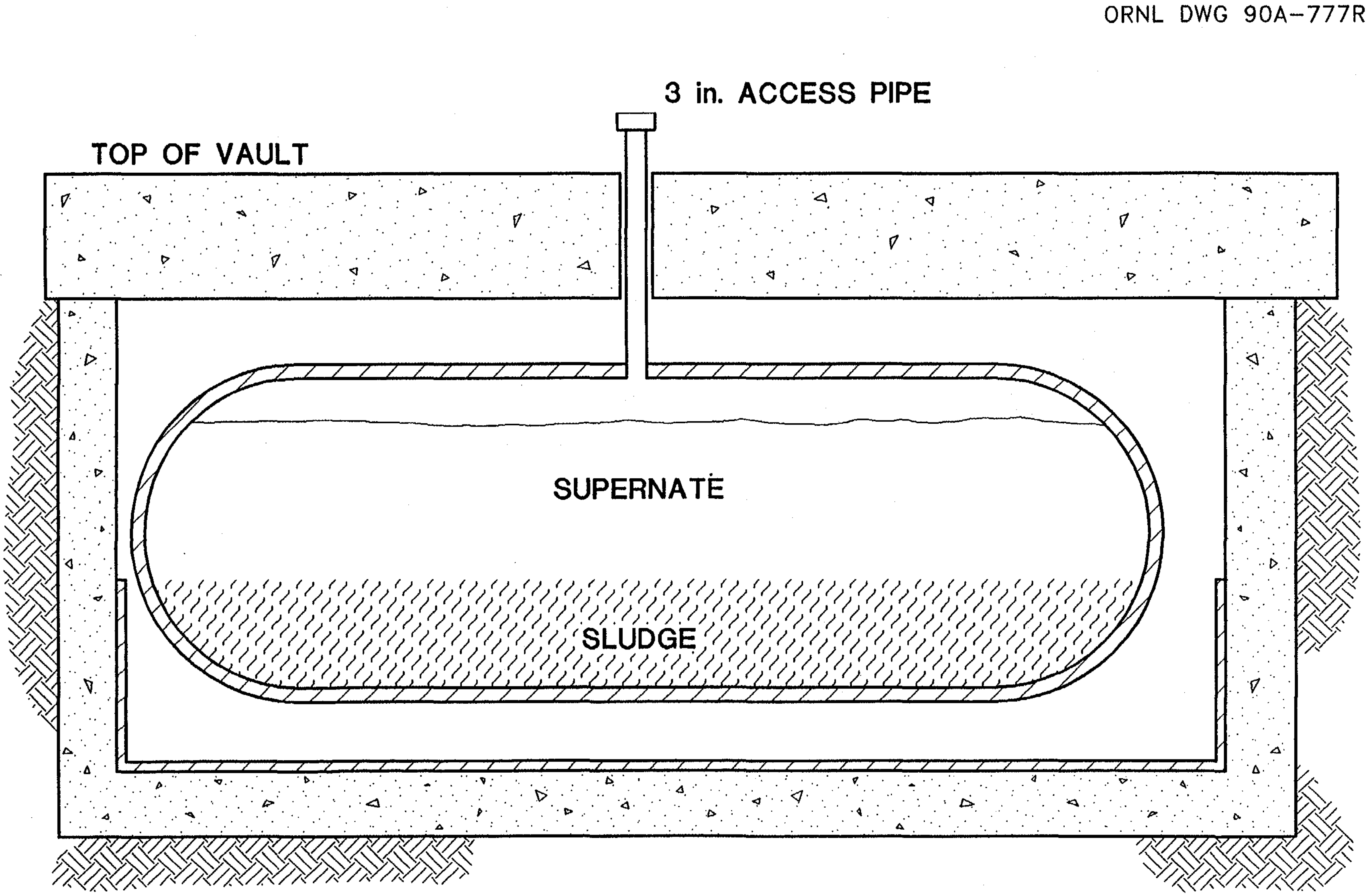

Fig. 2. Configuration of Melton Valley Storage Tanks.

burnup light-water reactor fuels; (5) tracer studies using radioactive isotopes; and (6) hot cell and decontamination activities. These tanks also contain some sludge residue from the Gunite tanks. Many of these waste streams were acidic and were made basic with NaOH in collection tanks or in the evaporator feed tanks prior to being concentrated in the Low-Level Waste Evaporator. Many of the metals therein, including the actinides and lanthanides, were precipitated as hydroxides when the solutions were made basic. However, certain elements—such as some of the transition metals that tend to form complexes, along with portions of the alkali metals—remained in solution. Concentrating these solutions likely resulted in the formation of insoluble solids of alkali aluminosilicates.

The evaporator concentrates were stored in four 190,000-L hold tanks near the evaporator. Approximately every 2 years, portions of these concentrates were pumped about 2 miles to the MVSTs through a 2-in. stainless steel pipe. Since there are no mixers in these tanks, the sludges are not homogeneous. The sludges and supernatants in the tanks at the MVST Facility were characterized in studies by Sears et al.[10] in 1989 and by Keller et al. in 1996.[11]

During September and December of 1988, about 180,000 L of waste was removed from tanks W-29 and W-30. In May of 1989 these tanks were refilled with waste from tanks W-25 and W-26. Tanks W-25 and W-26 were refilled in May and August of 1989 by waste transfers from the BVESTs.[10]

2. MVST W-25 SLUDGE CHARACTERISTICS

2.1 Tank Sampling

Samples of sludge (~250 mL each) were retrieved at different depths of the sludge layer in tank W-25 at the MVST Facility in April 1993 (Fig. 3). The sludge layer in this tank was about 1.7 m deep. Figure 4 is a photograph that shows chemical operators removing one of the sludge samples via an access pipe that penetrated the tank from the vault roof (Fig. 2). The bottom-opening sludge sampler (~51 cm long), shown in Fig. 5, was attached to the end of a long stainless steel segmented tube. Samples were collected at successively lower layers (3 samples per vertical core), and this process was repeated four times. To obtain a denser, composite sludge mixture, the samples at the

Fig. 3. Sample of sludge collected from MVST W-25.

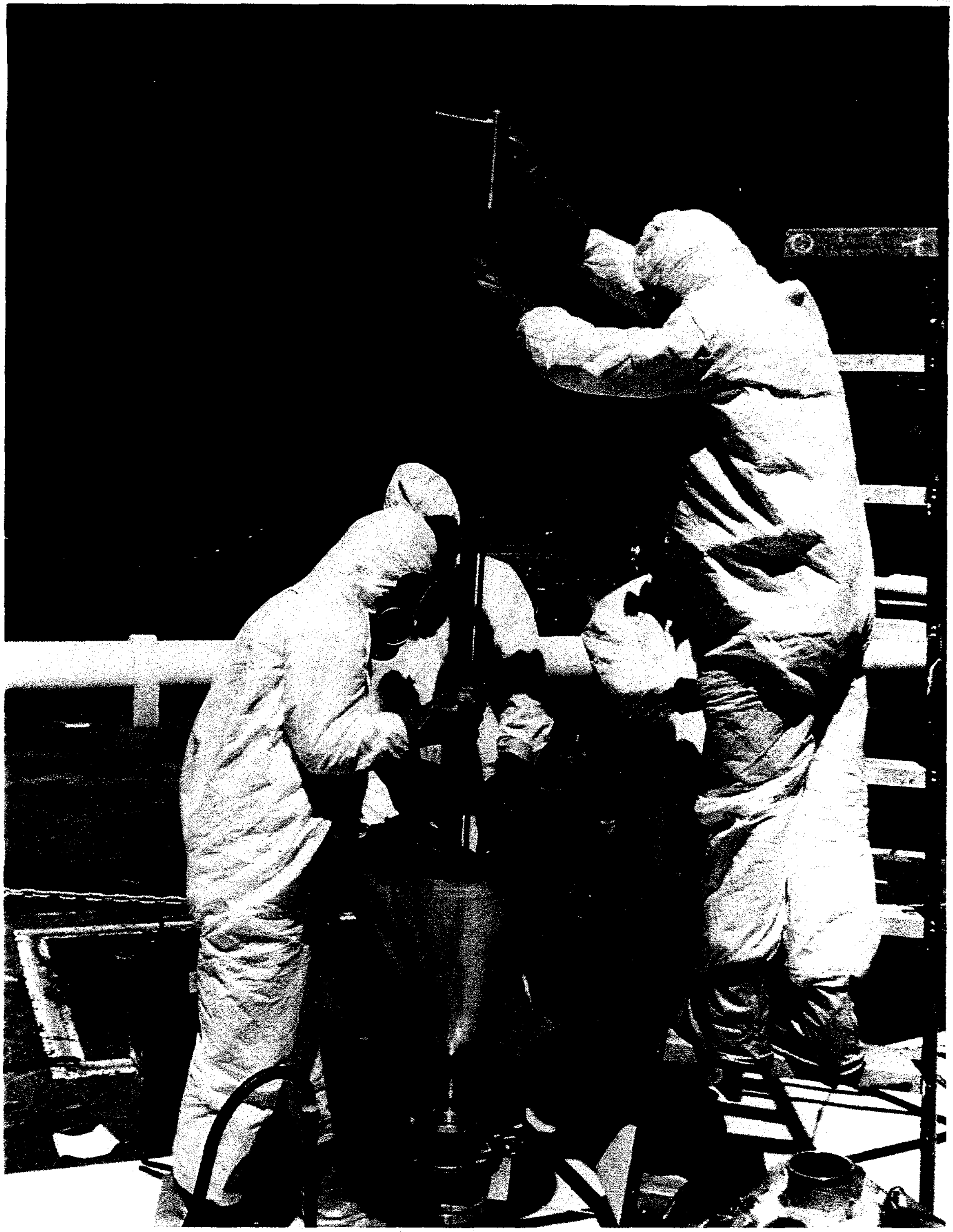

Fig. 4. Operators removing sludge sample from MVST W-25.

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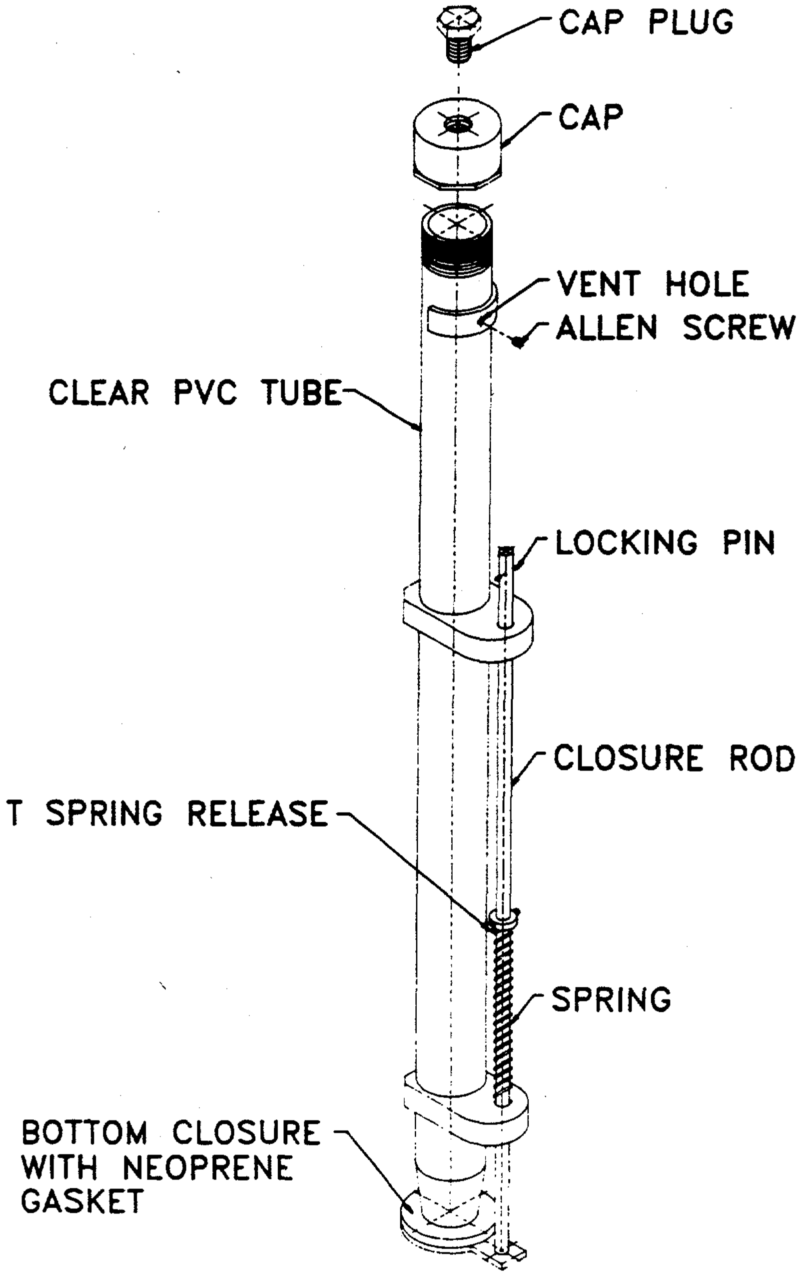

Fig. 5. Bottom-opening sludge sampler.

top of the sludge layer were excluded from the last two sampling sequences because they were very fluid. Samples taken at the bottom of the sludge layer were thick and brown, with hard gritty black particles that were 1 to 3 mm in diam. Some of the particles were flaky. Acid dissolution and analyses of a sample of a number of these particles showed them to be high in Ca, Mn, and U. The weight fractions of the total cation mass of the major constituents were 25% Ca, 22% Mn, 18% U, 7% Na, 3% Ni, 3% Mg, and 3% Th. The manganese and nickel were probably responsible for the black color of the particles. Samples from the top two zones were soft and yellow.

The sludge samples were transferred to a stainless steel tank located in a hot cell in Building 4501. The volume of the composite sludge mixture was ~5 L. After the tank contents had been mixed for 18 h, and while mixing continued, samples of the equilibrated stock sludge were poured into tared, 250-mL polypropylene bottles for characterization. The sludge liquid and sludge solids were separated by centrifugation. The sludge liquid was a deep yellow color, and the wet sludge solids were tan to dark brown. A detailed description of the hot cell apparatus and experimental methodology is provided in Sect. 3. The supernatant portion from tank W-25 was also characterized by Collins et al.[12]

2.2 Sludge Characterization

The densities of the sludge mixture, the centrifuged, wet sludge solids, and the decanted sludge liquid were 1.362, 1.52, and 1.206 g/mL, respectively. Samples of sludge and of centrifuged, wet sludge solids were air dried to constant weights to determine the total solids contents of each; these values were 0.464 and 0.590 g/g, respectively. The average total solids content of the sludge liquid samples was 0.285 g/g. This was determined by drying samples of sludge liquid to constant weight in a drying oven at 95°C. The pH of the sludge liquid was 13. The average volume ratio of the decanted sludge liquid to the centrifuged, wet sludge solids was 1:1. Two samples of centrifuged, wet sludge solids (~6 g each) were also heated at higher temperatures for several hours; one was heated at 185°C and the other at 435°C. In each case the sample was first heated slowly to about 95°C and held at that temperature for about 2 h before slowly ramping to the higher temperature. The results from these tests showed that the total water content (including water of hydration) of the centrifuged, wet sludge was about 48%. The total solids content of the sludge was 0.520 g/g. For each gram of centrifuged, wet sludge, only 0.07 g more water was removed at the high temperatures than was removed by air drying the sludge. The solids that were heated at 435°C were then slowly reheated to 950°C and held at that temperature for 1 h. The final solids content was 0.396 g/g; 60.4% of the initial sample weight was lost. On the basis of 1 g of sludge, 0.124 g was lost in the conversion of nitrates, phosphates, sulphates, and hydroxides to oxides. The halides were probably vaporized as alkali halides. Any remaining alkali elements would probably have formed hydroxides and carbonates during the cool-down period before the sample was put in the desiccator. The sodium and potassium nitrates in the centrifuged, wet sludge solids would have decomposed to oxides at the higher temperatures.

Air-dried samples of centrifuged, wet sludge were analyzed to determine the concentrations of radionuclides, other metals, and anions. Detailed descriptions of the analytical methods that were used are found in the reports by Keller[11] and Sears.[10] Samples of the centrifuged, wet sludge solids were solubilized by three different microwave-assisted acid-digestion methods: (1) HNO_3; (2) HNO_3 and HF; and (3) HNO_3 and HF, followed by adding boric acid to the vessel and heating at 80°C for 30 min. The leachates were analyzed by the following methods: gross alpha and alpha pulse, gross beta, and gamma spectrometry for radionuclides; inductively coupled plasma (ICP), atomic emission spectroscopy (AES), and graphite furnace atomic absorption (GFAA) spectroscopy for metals; cold-vapor atomic absorption spectroscopy for mercury; and ion chromatography for anions. Total carbon (TC) and total organic carbon (TOC) were analyzed with a Dohrmann DC-90 carbon analyzer. The total inorganic carbon was determined by subtracting the value obtained for the TOC from the TC value. Tables 1 and 2 give the results of these analyses along with the concentrations of the constituents in the sludge liquid and calculated values for the centrifuged, wet sludge solids. The average masses of centrifuged, wet sludge solids and of mixed sludge samples that yield 1.0 g of air-dried centrifuged solids were 1.695 and 3.08 g, respectively. In the tables the calculated values for the concentrations of constituents in 1-g samples of centrifuged, wet sludge solids were obtained by dividing the concentrations of the air-dried constituents in the tables by 1.695 (or multiplying by 0.590). The TC, TOC, and inorganic carbon contents were ~5.5, ~3.0 and ~2.5 wt % of the centrifuged, wet sludge solids, respectively. If the inorganic carbon is assumed to be in the form of carbonate and bicarbonate in the sludge, the 2.5% carbon equates to about 12.5% carbonate. A

Table 1. Radiochemical analysis of MVST W-25 sludge solids

Radionuclides	Sludge liquid[a] (μCi/g)	Centrifuged, wet sludge solids[b] (μCi/g)	Air-dried sludge solids[c] (μCi/g)
^{137}Cs	2.9	22.0	37.37
^{60}Co	0.014	2.7	4.55
^{154}Eu	0.003	2.1	3.55
^{90}Sr	44.8	303	513.5
^{241}Am	BDL[d]	0.41	0.7
^{244}Cm	BDL	5.1	8.67
Pu	BDL	0.77	1.3[e]

[a] The liquid was removed by decantation after centrifugation of the sludge. The density of the sludge liquid was 1.206 g/mL.

[b] Calculated values based upon analyses of air-dried solids.

[c] Analyses based upon centrifuged, wet sludge solids that were air dried to a constant weight.

[d] BDL = below detection limit.

[e] About 67% of the activity is from ^{238}Pu and the remainder from $^{239/240}$Pu.

Table 2. Nonradioactive components of MVST W-25 sludge solids

Component	Sludge liquid[a]	Centrifuged, wet sludge solids[b]	Air-dried sludge solids[c]
Other metals, mg/g			
Al	0.38	15.2	25.8
Ba[d]	0.001	0.3	0.5
Ca	0.008	56.7	96.1
Cd[d]	BDL[e]	0.035	0.06
Co	BDL	0.024	0.04
Cr[d]	0.042	0.35	0.6
Cs	0.00016	0.0015	0.0026
Cu	BDL	0.18	0.3
Fe	BDL	5.1	8.6
Hg[d]	BDL	0.12	0.2
K	11.6	8.5	14.4
Mg	BDL	7.9	13.5
Mn	BDL	0.47	0.8
Na	73	64.9	110
Ni	BDL	0.24	0.4
Pb[d]	BDL	1.2	2.0
Si	BDL	9.0	15.3
Sr	0.0003	0.33	0.56
Th	0.0003	33.8	57.4
Tl	BDL	0.24	0.4
U[f]	0.0043	16.2	27.6
Zn	0.0008	0.47	0.8
Anions, mg/g			
Br^-	BDL	0.41	0.7
Cl^-	3.1	2.2	3.7
F^-	0.3	1.1	1.9
CO_3^{2-}	0.26	67.6	115
NO_3^-	195	105	179
PO_4^{3-}	BDL	17.4	29.5
SO_4^{2-}	2.0	4.1	7.0

[a] The liquid was removed by decantation after centrifugation of the sludge. The sludge liquid density was 1.206 g/mL.
[b] Calculated values based upon analyses of air-dried solids.
[c] Analyses based upon centrifuged, wet sludge solids that were air dried to a constant weight.
[d] RCRA metals.
[e] BDL = below detection limit.
[f] Weight percent of uranium isotopes (^{238}U = 99.28, ^{235}U = 0.57, ^{234}U = 0.01, and ^{233}U = 0.14).

specific test described in Sect. 4.6.3 was also conducted to determine the carbonate content of the sludge. That analysis found the concentration of carbonate to be 67.6 mg per gram of centrifuged, wet sludge (Table 2), or 11.5% carbonate, which is in reasonable agreement with the analysis described above.

To calculate the concentration of the constituents in a mixed sludge sample, the concentrations of the air-dried constituents in Tables 1 and 2 would be divided by 3.08. However, in cases in which there are measurable concentrations of the constituents in the decanted sludge liquid, those values were also considered in the calculations. Centrifugation of 1 g of mixed sludge yielded about 0.45 g (0.373 mL) of decanted sludge liquid and 0.55 g (0.362 mL) of centrifuged, wet sludge solids. Cesium-137 and sodium are examples of constituents of significant concentration in the sludge liquid—2.9 μCi/g and 73 mg/g, respectively. The activity of the ^{137}Cs and the mass of sodium in a 1-g sample of mixed sludge were calculated as follows:

$$[(0.55\ \text{g}) \times (22\ \mu\text{Ci/g})] + [(0.45\ \text{g}) \times (2.9\ \mu\text{Ci/g})] = 13.4\ \mu\text{Ci, and}$$

$$[(0.55\ \text{g}) \times (65\ \text{mg/g})] + [(0.45\ \text{g}) \times (73\ \text{mg/g})] = 68.6\ \text{mg}\ .$$

Because of the high solubility of alkali salts, it was expected that these alkali elements would be associated primarily with the sludge liquid. However, large fractions of these elements were found in the sludge solids. On the average, about 41% of the mass of a sample of centrifuged, wet sludge solids is removed by air drying the sample to a constant weight. For the examples above, this means that 0.22 g of the 0.55 g of centrifuged, wet sludge solids was free water. The water equated to about 0.27 g of sludge liquid, which contained about 0.78 μCi of ^{137}Cs and 19.7 mg of sodium. The cesium and sodium remained with the air-dried sludge solids in the residue of the entrained sludge liquid. The amounts of ^{137}Cs and sodium actually bound in the solids were as follows:

$$[(0.55\ \text{g}) \times (22\ \mu\text{Ci/g})] - [(0.27\ \text{g}) \times (2.9\ \mu\text{Ci/g})] = 11.3\ \mu\text{Ci, and}$$

$$[(0.55\ \text{g}) \times (65\ \text{mg/g})] - [(0.27\ \text{g}) \times (73\ \text{mg/g})] = 16.0\ \text{mg}\ .$$

From these calculations and a similar one for K, it was determined that ~7% of the Cs, ~55% of the Na, and ~67% of the K in centrifuged samples were associated with the sludge liquid of the centrifuged, wet sludge solids. Conversely, 93% of the ^{137}Cs, 45% of the sodium, and 33% of the potassium were bound in the solids.

Table 1 shows that the major gamma- and beta-emitting radionuclides in the centrifuged, wet sludge solids were ^{137}Cs (22.0 μCi/g), ^{60}Co (2.7 μCi/g), ^{154}Eu (2.1 μCi/g), and ^{90}Sr (303 μCi/g). The total concentrations of the Cs, Co, and Sr were 0.0015, 0.024, and 0.33 mg/g, respectively. Of these, 17% of the Cs was ^{137}Cs, 0.12% of the Co was ^{60}Co, and 0.63% of the Sr was ^{90}Sr. The concentration of the europium was below the detection limit using chemical analysis techniques. The effective specific radioactivities were 1.47E+04 μCi/mg for ^{137}Cs, 1.12E+02 μCi/mg for ^{60}Co, and 9.15E+02 μCi/mg for ^{90}Sr.

There were also significant concentrations of actinides in the centrifuged, wet sludge solids: 33.8 mg/g for Th, 16.2 mg/g for U, 0.76 μCi/g for Pu, 0.41 μCi/g for ^{241}Am, and 5.1 μCi/g for ^{244}Cm. Of these, only uranium (4.3E−03 mg/mL) and thorium (3.0E−04 mg/mL) were measurable in the sludge liquid. The isotopic distribution for uranium in weight percent was ^{238}U (99.28), ^{235}U (0.57), ^{234}U (0.01), and ^{233}U (0.14). About 67% of the activity of the plutonium was from ^{238}Pu, and the remainder was from $^{239/240}$Pu.

The major metal constituents (Table 2) in the centrifuged, wet sludge solids were Na, Ca, Th, U, Al, Si, K, Mg, and Fe. The major anions (Table 2) were nitrates, carbonates, phosphates, sulphates, hydroxides, and oxides. The component percentages and values (in millimoles) calculated for 1 g of air-dried sludge solids (which equates to 1.695 g of centrifuged, wet sludge solids) were 11.0% Na (4.78 mmol), 9.6% Ca (2.40 mmol), 5.7% Th (0.25 mmol), 2.8% U (0.12 mmol), 2.6% Al (0.96 mmol), 1.5% Si (0.54 mmol), 1.4% K (0.37 mmol), 1.4% Mg (0.56 mmol), 0.9% Fe (0.15), 0.7% other cations (0.15 mmol), 17.9% NO_3^- (2.89 mmol), 11.5% CO_3^{2-} (1.92 mmol), 3.0% PO_4^{3-} (0.31 mmol), 0.7% SO_3^{2-} (0.07 mmol), 0.4% Cl^- (0.1 mmol), and 0.2% F^- (0.1 mmol). The total quantities of cations and anions measured were 10.28 and 5.39 mmol, respectively. Although not determined directly, it is likely that the sludge also contained significant concentrations of hydroxides and oxides, which would account for anion deficiency.

3. EXPERIMENTAL APPARATUS AND PROCEDURES

The leaching experiments were conducted in hot cell A in Building 4501 at ORNL. The contamination level in the hot cell was kept as low as possible to minimize cross-contamination between experiments. The sludge was the major source of activity, and it was shielded to protect sensitive electronic equipment and to allow for hot cell entry for servicing equipment. When possible, the controls for the apparatus were positioned outside the hot cell for ease of operations. To contain spills, most of the equipment used in the hot cell was placed in a large stainless steel tray on a table. Figure 6 is a photograph of the hot cell, and some of the apparatus can be seen through the hot cell window.

As described in the previous section, the sludge was mixed and stored for use in a sealed stainless steel tank. A photograph of the tank before it was placed in the hot cell is shown in Fig. 7; in Fig. 6, it is shown mounted to the back wall of the hot cell. The top of the tank was a stainless steel, flanged lid that contained two portal openings with valved lines, one for venting the tank and the other for use as an access port. A closed-system Lightning™ mixer (Fig. 8) was also attached to the stainless steel lid. The mixer, which contained a stainless steel shaft with two high-efficiency, axial-flow, stainless steel impellers (overall diameter of 8.6 cm), was positioned at a 10° angle to provide more effective mixing. A stainless steel valved tube (1.27-cm ID) for sampling the sludge was located at the bottom of the tank. The section of tube above the valve was made as short as possible to prevent sludge solids from collecting there and resisting suspension during mixing. The volume of this section of tube was only 2.5 mL. Before sludge samples were removed, the sludge in the tank was mixed for ~2 h. While still mixing the sludge and before taking samples of sludge for testing, ~10 mL of sludge was drained into a separate bottle. The test samples (55 to 85 mL each) were placed in preweighed 250-mL widemouthed centrifuge bottles (made of Nalgene™ polypropylene) with sealing caps. After sampling, the end of the sampling tube was sealed with a small stoppered bottle to catch any drops of the remaining sludge in the line and to prevent any sludge remaining in the tube from drying.

A calibrated Mettler PM4000 top-loading balance (4000-g capacity, 0.01-g readability) with a glass cover was used to weigh the samples. The volumes of sludge samples were determined by

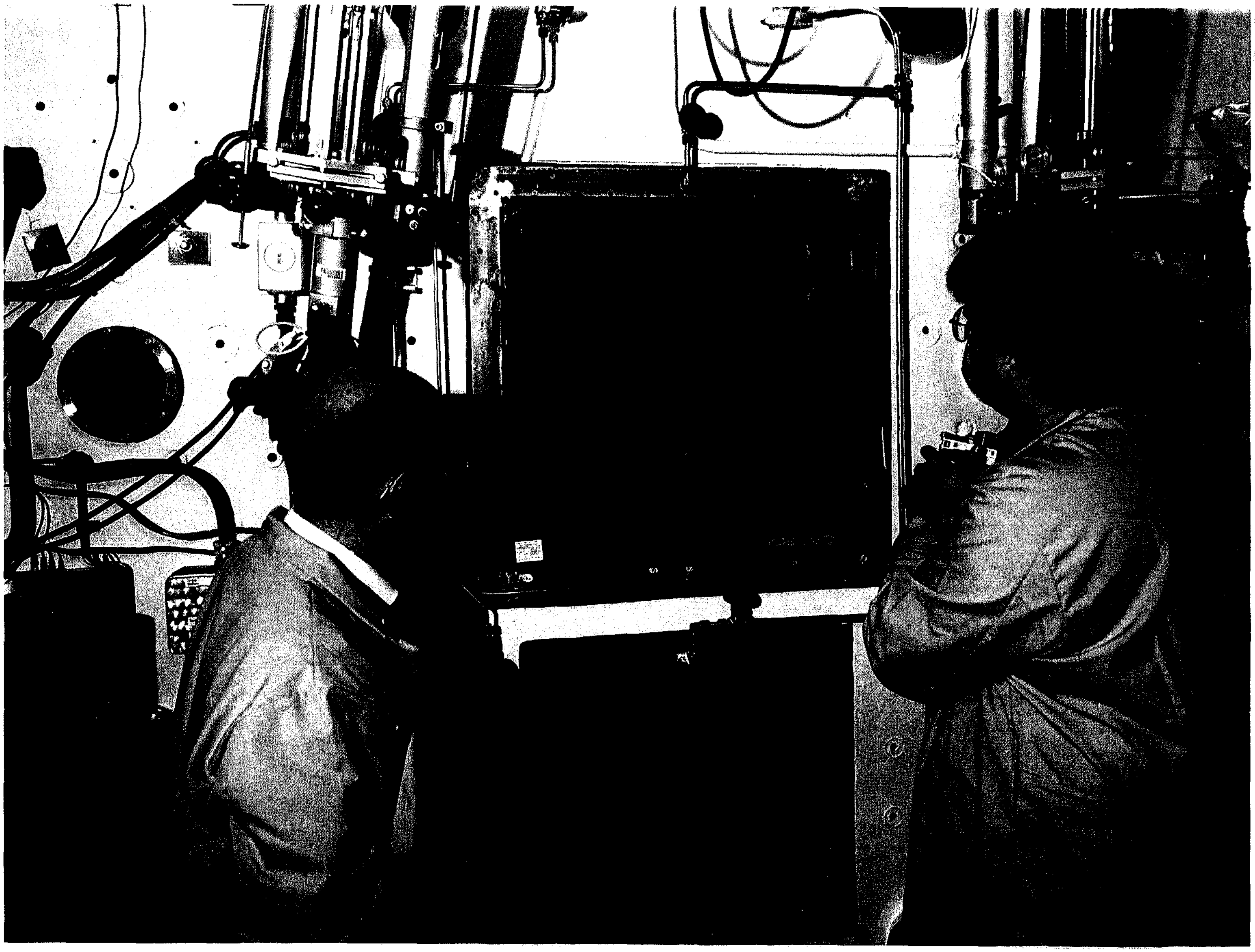

Fig. 6. Sludge leaching apparatus as viewed through the hot cell window.

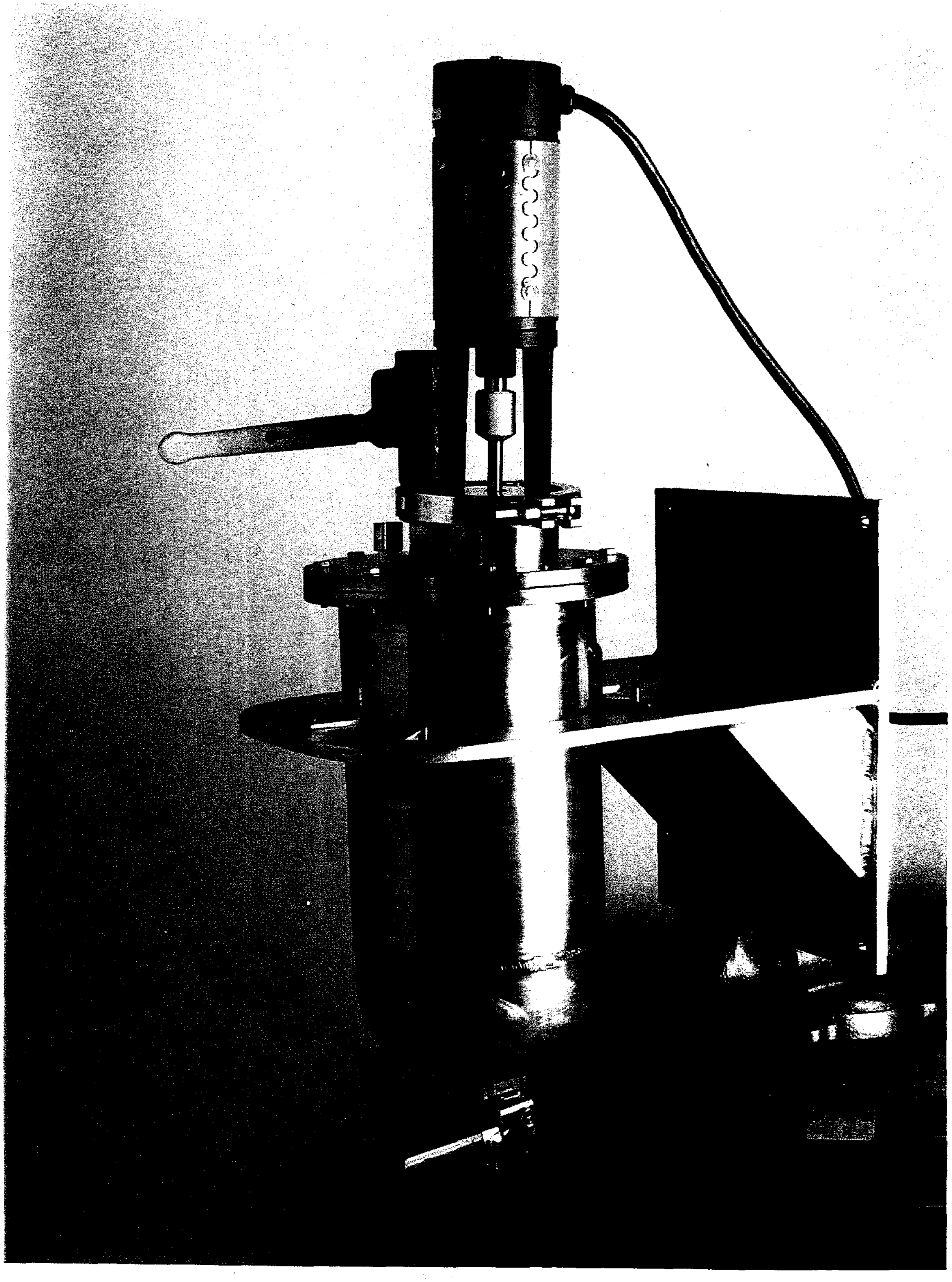

Fig. 7. Stainless steel tank for storing and mixing MVST W-25 sludge.

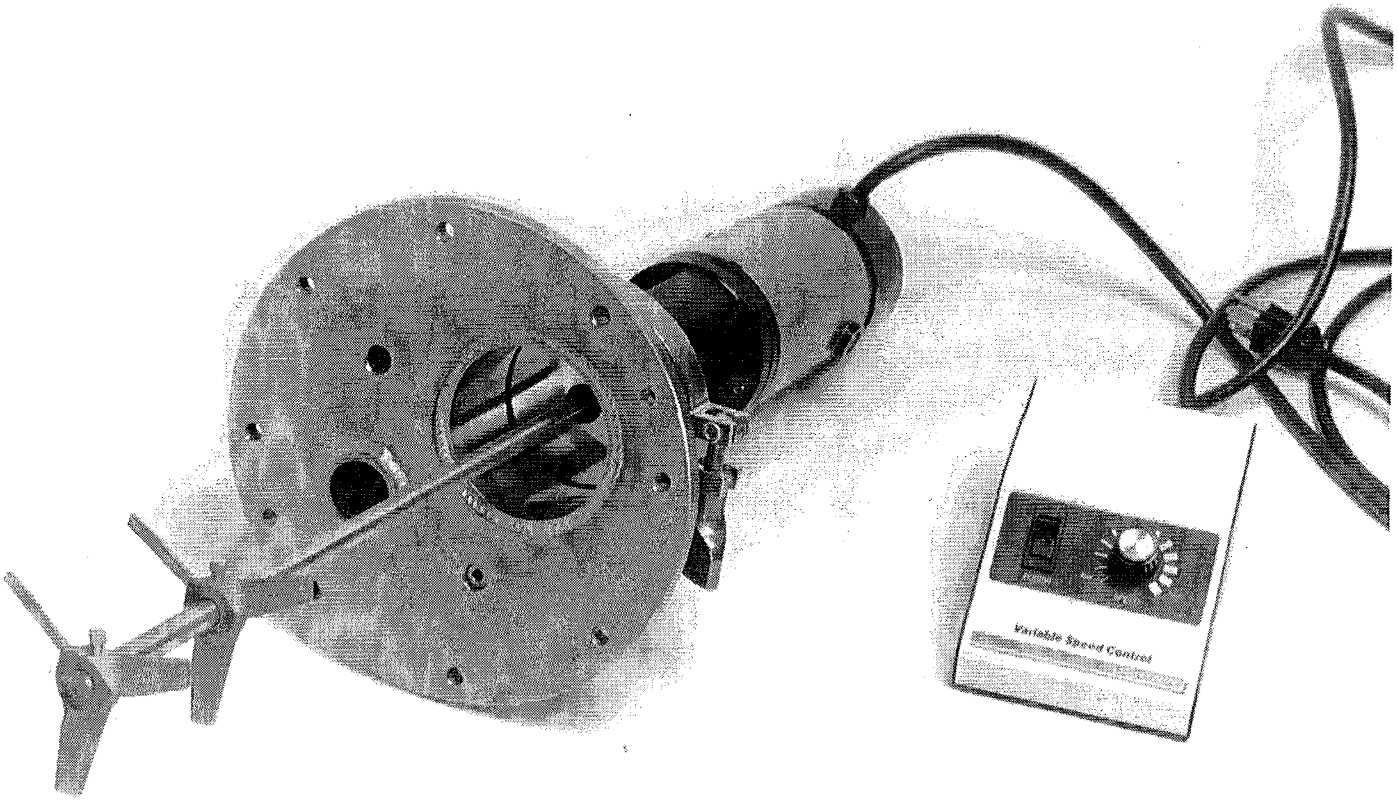

Fig. 8. Closed-system mixer used to mix MVST W-25 sludge in storage tank.

dividing the masses of the sludge samples by the density of the sludge. The density of the sludge was determined by slowly filling a tared 50-mL volumetric flask to the meniscus and weighing. The measured density was 1.362 g/mL.

An International Equipment Company (IEC) Centra-GP8 tabletop centrifuge was used to separate sludge liquid from the sludge solids. The sludge liquid was decanted from the centrifuged, wet sludge solids into another tared 250-mL centrifuge bottle with a specially designed vacuum decantation apparatus. Afterwards, the sludge liquid and centrifuged, wet sludge solid fractions were separately weighed. The photograph in Fig. 6 shows a technician using the vacuum decantation apparatus. An ORION Research digital pH meter and an ORION 8103 ROSS combination electrode were used for pH measurements.

A basic or acidic leachant was then added to the centrifuged, wet sludge solids, and a vortex mixer was used to suspend the solids in the leachant. Because of the high concentration of carbonate in the sludge solids, acid leachants were added to the samples in small incremental steps. This prevented the CO_2 produced from ejecting solids from the centrifuge bottle. A custom-designed rotator that turned the bottles end-over-end was used to mix the test samples for predetermined periods of time. After mixing, the samples were again centrifuged for 30 min at 4500 rpm (4450 × g) and the leachates were transferred to tared 250-mL centrifuge bottles by vacuum decantation. Samples of leachate to be analyzed were filtered with 0.45-μm Teflon syringe filters. The density of the filtered leachate was determined by weighing 50 mL of leachate in a tared volumetric flask. The molarity of the unreacted HNO_3 in the leachate was determined by titrating 2-mL aliquots of the filtered leachate with standard 0.1 *M* NaOH.

Following any primary acidic leaching step, the centrifuged, wet sludge solids were washed twice with 100-mL volumes of 0.1 *M* HNO_3 to remove entrained leachate. A vortex mixer was used to suspend and mix the solids. The mass and density of the composite wash solution were determined, and samples were taken for analysis.

A mixing apparatus was designed and built to leach samples of sludge solids at temperatures up to 95°C (see photographs in Figs. 9 and 10). The design allowed higher-temperature leaching experiments using the 250-mL polypropylene centrifuge bottles. The centrifuge bottle containing the sludge and leachant was placed in a Teflon holder inside a stainless steel vessel, which was

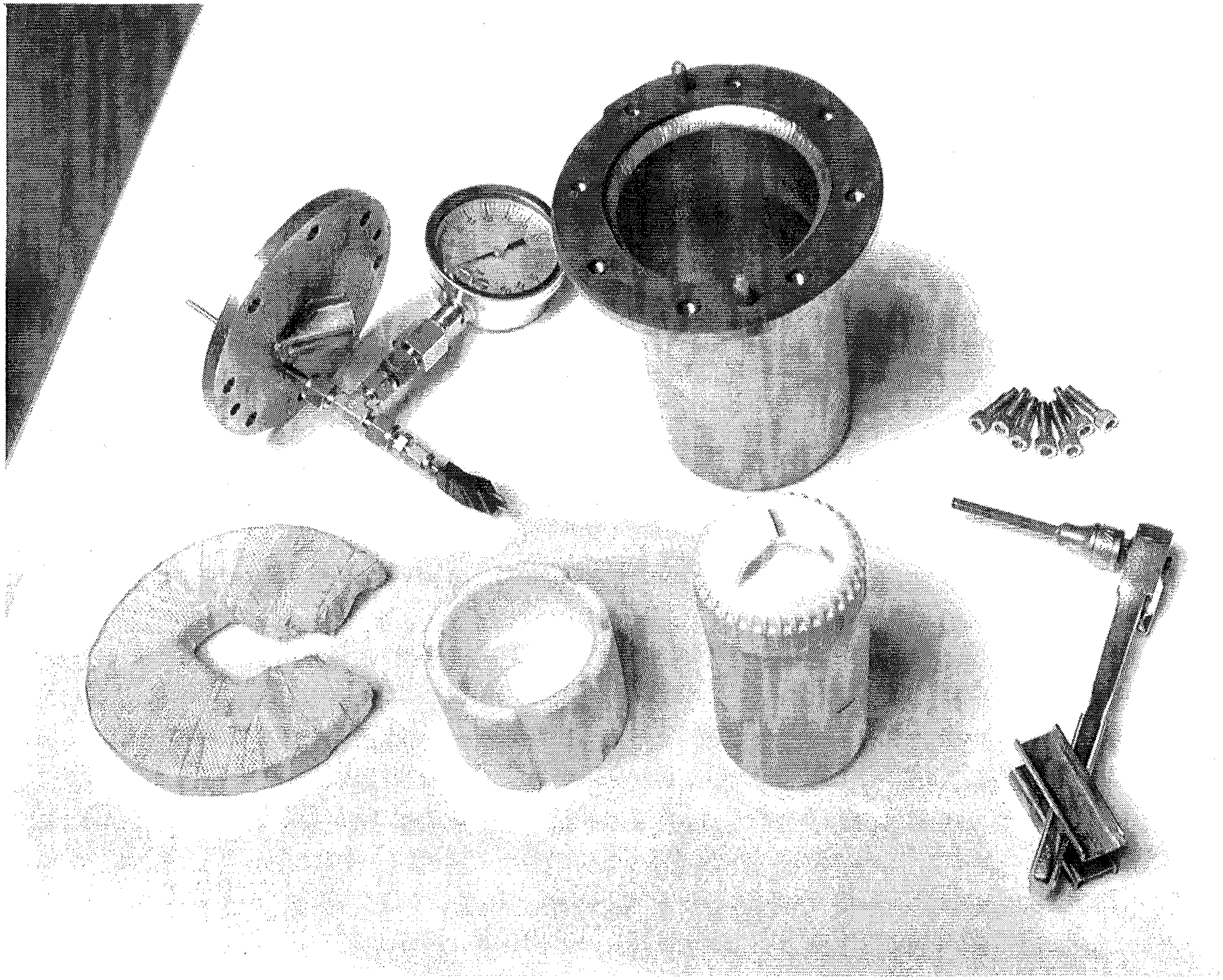

Fig. 9. Components of apparatus used to mix and heat sludge with caustic at elevated temperatures.

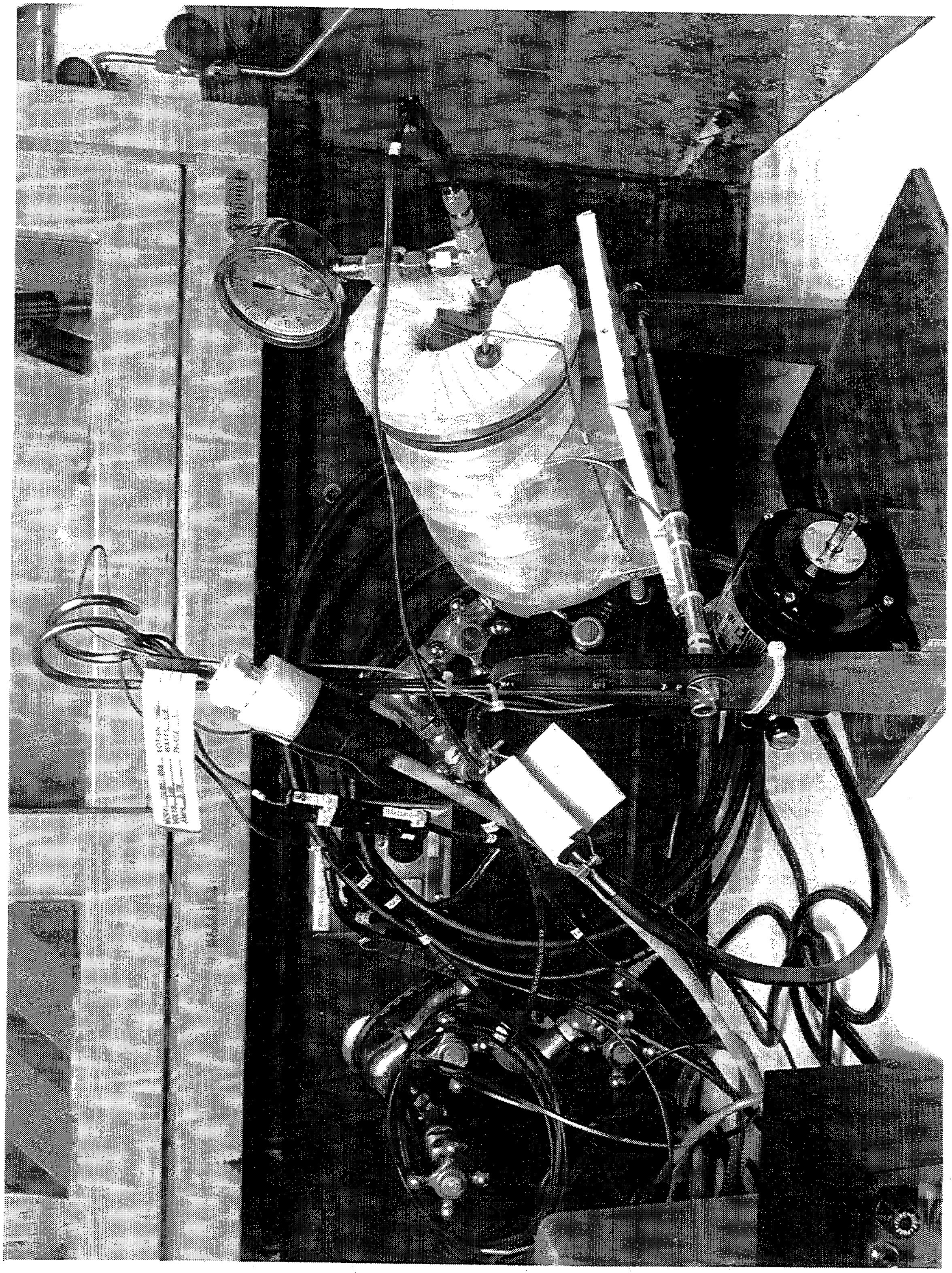

Fig. 10. Assembled high-temperature leaching apparatus.

sealed by compressing a Viton gasket between the lip of the vessel and a stainless steel lid. The Teflon holder positioned the bottle inside the vessel in a way that prevented direct contact of the bottle with the steel vessel. The temperature inside the vessel was measured with a calibrated J-type thermocouple, which also served as the control measurement. The 1/8-in.-diam Iron/Constantan thermocouple was positioned in the middle of the gap between the inner surface of the vessel and the outside surface of the centrifuge bottle. During a test, about half of the volume of the free space in the vessel was filled with deionized water to improve heat transfer and temperature control. To prevent leakage, slow heat-up and cool-down rates were utilized to balance the vapor pressure inside the centrifuge bottle with the vapor pressure of the water inside the vessel.

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) with a temperature indicator. The furnace assembly was attached to a rocking mixer that rocked the assembly from −45° to +45° from the horizontal plane at ~8 cycles per minute. A typical leachate temperature profile for a 95°C test is shown in Fig. 11.

In the high-temperature caustic leaching tests described in Sect. 5, the centrifuge bottles containing the sludge and leachate were removed from the vessel after the temperature of the heating vessel reached room temperature. Afterwards, the samples were handled and treated in the same manner as those that were leached at ambient temperature as described above.

4. LEACHING OF MVST W-25 SLUDGE AT AMBIENT TEMPERATURE

4.1 Sequential Leaching of W-25 Sludge with Dilute Sodium Hydroxide and Nitric Acid

A series of sequential washing and leaching tests was conducted to determine the removal of radionuclides by dilute caustic washing and acid leaching of the solids. The results are given in Table 3. A 44.0-g sample of the centrifuged, wet sludge solids (~26 g of air-dried solids)—containing 970 μCi of ^{137}Cs, 92 μCi of ^{154}Eu, and 118 μCi of ^{60}Co—was washed twice with

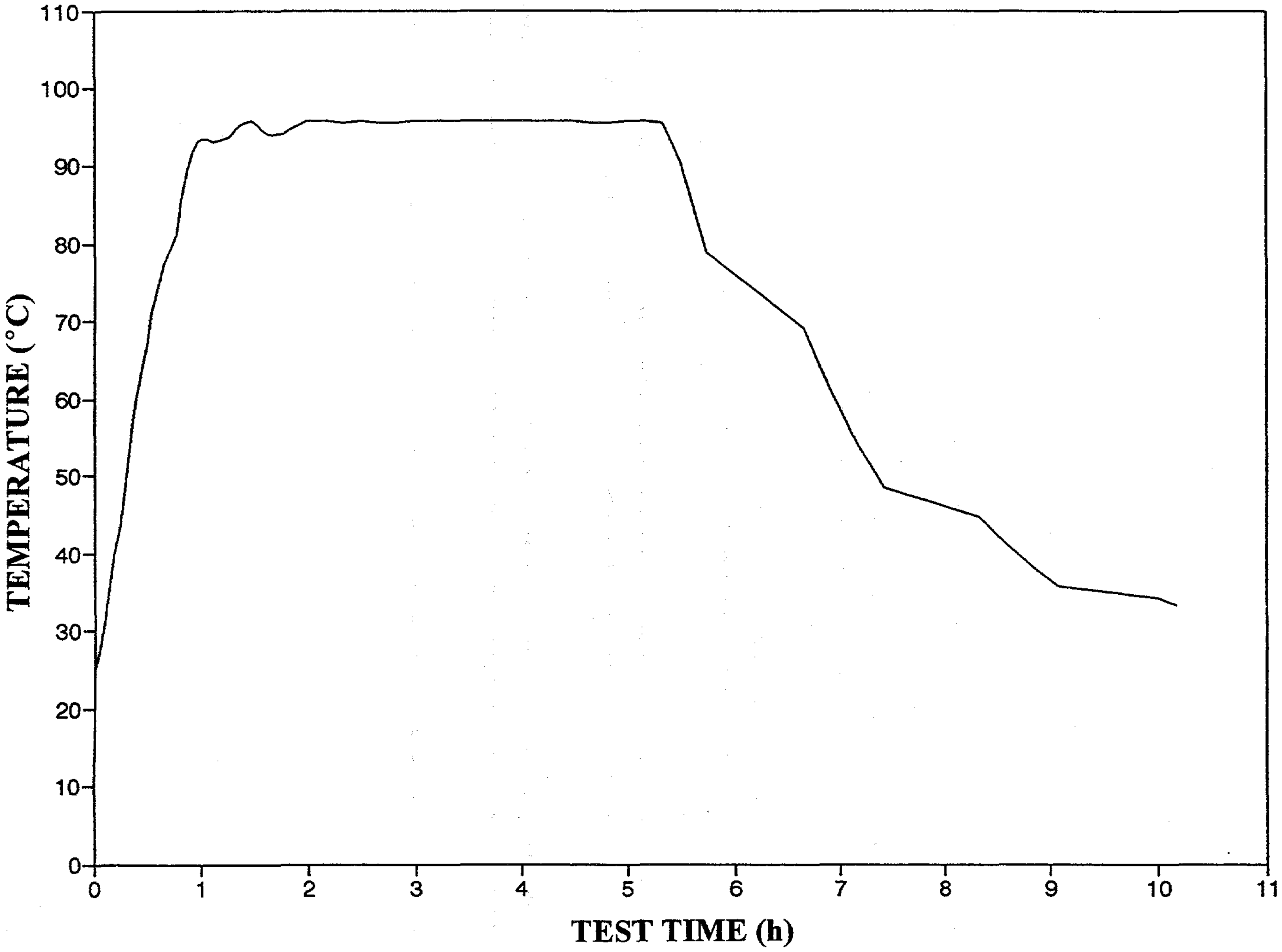

Fig. 11. Example of a heating profile for a 95°C caustic leaching test.

Table 3. Sequential leaching of W-25 sludge[a]

Leaching steps	Solids[b] (g)	Mixing time (h)	Radionuclide content of remaining solids (μCi)		
			^{137}Cs	^{60}Co	^{154}Eu
Initial sample	80.0		1060	119	92.3
⇓					
Centrifuge[c]	44.0		970	118	92.2
⇓					
0.16 *M* NaOH leach	42.0	5	926	118	92.2
⇓					
0.16 *M* NaOH leach	41.9	22	916	118	92.2
⇓					
0.5 *M* HNO_3 leach[d]	39.6	6	904	118	92.2
⇓					
3 *M* HNO_3 leach[e]	28.1	70	746	24.3	16.4
⇓					
3 *M* HNO_3 leach[f]	18.5	50	507	6.5	2.2
⇓					
6 *M* HNO_3 leach[g]	20.4	432	213	2.5	0.6
⇓					
6 *M* HNO_3 rinses	19.1	20	157	1.8	0.3

[a] Procedure: 100-mL quantities of indicated leachants were added to sludge solids and mixed at room temperature.
[b] Weight of centrifuged, wet sludge solids after leaching.
[c] The W-25 MVST sludge sample was centrifuged to separate the sludge solids from the sludge liquid.
[d] The pH of the leachate was 7.6.
[e] The final acid concentration of the leachate was 1.3.
[f] The final acid concentration of the leachate was 2.7.
[g] The final acid concentration of the leachate was 5.7.

100 mL of 0.16 *M* sodium hydroxide. The mixing times were 5 and 23 h, respectively, on a rotator in the hot cell. Together, the dilute caustic washes removed only 54.4 μCi of the ^{137}Cs from the wet sludge solids, with about 81% of this quantity being removed in the first wash. Only trace amounts of the ^{154}Eu and ^{60}Co were removed. The small quantity of europium and cobalt removed from the pH 13.2 washes was expected because these elements would likely be present as precipitated forms. On the other hand, the limited amount of cesium removal was unexpected because most cesium compounds are soluble in aqueous solutions. The percentage of the ^{137}Cs removed by the two caustic washes was only 5.6%. Most of the cesium that was removed was probably present in the interstitial sludge liquid that was not physically removed by centrifugation. The cesium that remained after the caustic washes was presumably bound in the solids. The mass of the wet, centrifuged sludge solids decreased from 44.0 to 42.0 g and then to 41.8 g after these two washes. A portion of the weight loss resulted from the replacement of the interstitial liquid containing high salt content with 0.16 *M* NaOH leachant. Analyses of the decants from the two caustic rinses showed that 6.6% of the Al, 0.1% of the Ca, 10.3% of the Cr, 80.5% of the K, 0.02% of the Mg, 65.2% of the Na, 0.3% of the U, 1.4% of the Zn, 50.6% of the Cl^-, 17.3% of the F^-, 87.9% of the NO_3^-, 0.3% of the PO_4^{3-}, and 25.8% of the SO_4^{3-} were removed from the sludge.

The washed, centrifuged sludge solids were then leached by mixing for 5.6 h with 100 mL of 0.5 *M* HNO_3. The pH of the resulting solution was 7.6. This dilute acid leach removed about 12 μCi of ^{137}Cs or 1.2%. When included with the cesium removed by the caustic washes, a total of 6.8% was removed. Only trace amounts of cobalt and europium were removed. The mass of the decanted, wet sludge solids was 39.6 g. Analyses of the decant revealed that 8% of the K, 9.5% of the Na, 21.2% of the Mg, 0.3% of the Ca, and 0.2% of the Th were removed. Cumulatively, including the fraction removed by the caustic rinses, 88.5% of the potassium and 72.7% of the sodium were removed. These data show that, for the alkaline earths (Ca, Mg, Sr), Mg was the first to be solubilized.

In the next two leaching steps, the wet sludge solids were successively leached with 3.0 *M* HNO_3 (100 mL each) for mixing periods of 70 and 50 h, respectively. The nitric acid concentration of the solution after the first leach was 1.3 M; after the second leach, it was 2.7 *M*. Of the 39.6 g of wet sludge solids, about 28.1 g remained after the first leach, and about 18.5 g remained after the second leach. The first leach removed 158 μCi of ^{137}Cs, and the second leach removed 239 μCi of ^{137}Cs, leaving 507 μCi in the remaining wet sludge solids. A total of 463 μCi (or about 47.8%) of the ^{137}Cs had been removed from the solids at this point. The cumulative amount of cesium removed after the first 3.0 *M* HNO_3 leach was 23.1%. Over 80% of the ^{60}Co and ^{154}Eu was removed from the solids by the first 3.0 *M* HNO_3 leach, and less than 10% remained after the second leach. It was noted that a gelatinous precipitate appeared in the leachate from the first 3.0 *M* HNO_3 leach after the solution had stood for several days. This gelatinous material was postulated to be some form of amorphous silica precipitated from silicic acid.

The remaining sludge solids from these leaches were mixed with 100 mL of 6.0 *M* HNO_3 for 18 days. After mixing, the nitric acid concentration of the leachate was 5.7 *M*. This leaching step removed an additional 294 μCi of ^{137}Cs, along with 1.6 μCi of ^{154}Eu and 4.0 μCi of ^{60}Co. The amount of ^{137}Cs remaining in the sludge solids at this stage of the leaching process was 213 μCi. The mass of the centrifuged, wet sludge solids was 20.4 g, which was actually 1.9 g more than was obtained from the previous leaching step. The solids were less rigid than those observed in the previous leaching steps and contained more liquid that could not be removed by centrifugation and decantation.

To determine how much ^{137}Cs, ^{154}Eu, and ^{60}Co were present in the interstitial liquid associated with the remaining wet sludge solids after centrifugation, the wet sludge solids were washed with two 50-mL volumes of 6.0 *M* HNO_3. Each time, the sample was mixed for 10 min on a vortex mixer before centrifuging. The composite washes removed an additional 56 μCi of ^{137}Cs, 0.3 μCi of ^{154}Eu, and 0.7 μCi of ^{60}Co. The remaining solids contained 157 μCi of ^{137}Cs, 0.3 μCi of ^{154}Eu, and 2 μCi of ^{60}Co. The weight of the centrifuged, wet sludge solids was 19.1 g. A portion of the wet solids was air dried to a constant weight, yielding a solid content of 0.2503 g/g. Based upon this value, the calculated final mass of air-dried solids was 4.8 g.

The longer mixing time in the 6.0 *M* HNO_3 leaching step probably resulted in the formation of silicic acid, which formed a silica gel that stayed with the solids during centrifugation, causing the solids to retain more of the leachate. Based upon the dry mass of sludge solids at the beginning (26 g) and at the end (4.8 g) of the sequential basic and acidic leaching test series, about 81.5% of the initial solids was dissolved.

Table 4 gives the leaching results for the other radionuclides that were removed from the sludge solids by the sequential leaching steps. The leaching behavior of ^{90}Sr, ^{244}Cm, ^{241}Am, and U was like that of ^{60}Co and ^{154}Eu, as seen in Table 3. Very little or no amount of these elements was removed from the solids by the two 0.16 *M* NaOH and the 0.5 *M* HNO_3 leaches. The pH values of the leachates were ≥7.6. The elements U, Th, Pu, Am, Cm, Eu, Sr, and Co are precipitated as hydrous oxides in the pH range 2 to 7 and would be expected to have low solubilities in these solutions. The largest amounts of these elements were removed from the solids by the initial 3.0 *M* HNO_3 leach, which was the first of the sequential leaches to yield an acidic leachate (1.3 *M* free HNO_3). The plutonium behaved differently. Like the other elements, plutonium was not removed from the solids by the first three leaches; unlike the other elements, however, it was much more resistant to leaching in the subsequent acid leaching steps. Only about 16% of the plutonium was removed by the first 3.0 *M* HNO_3 leach. The second 3.0 *M* HNO_3 leach removed an additional 27.7% of the plutonium. Cumulatively for all the leaches, about 60% of the plutonium was removed.

Table 5 compares the cumulative amounts of ^{137}Cs, ^{60}Co, ^{154}Eu, ^{241}Am, ^{90}Sr, ^{244}Cm, plutonium, and uranium that were obtained in the sequential leaching steps based on sludge data given in Table 1 for 26 g of air-dried, centrifuged, wet sludge solids. These data show that ≥89% of the ^{60}Co, ^{154}Eu, ^{241}Am, ^{90}Sr, ^{244}Cm, and uranium and 84% of the ^{137}Cs were removed from the sludge solids.

Results of the sequential leaching steps are shown in Fig. 12. The leachability of cesium from the centrifuged wet solids appears to be directly related to the dissolution of the solids. Europium and cobalt were readily dissolved. A gel appeared in the first 3.0 *M* HNO_3 leachate several days after decantation. Gel formation also occurred during the mixing step with 6 *M* HNO_3, making the interpretation of the dissolution results more difficult.

4.2 Sequential Leaching of W-25 Sludge with Sodium Hydroxide and Nitric Acid

A sample of centrifuged, wet sludge solids was leached twice with NaOH. The sample (36.72 g) was first mixed with 88.64 g (80.8 mL) of 3.1 *M* NaOH for 144 h. After centrifugation, the remaining solids were mixed with 94.34 g (77.1 mL) of 6.4 *M* NaOH for 144 h. After the leachate was removed, the solids were washed twice with 0.16 *M* NaOH. The total volume of the decanted wash solution was 98.5 g (97.4 mL). Each of the leaching and wash steps was conducted

Table 4. Removal of strontium and actinides by sequential leaching of W-25 sludge

	Leaching steps[a]	Quantities removed				
		^{90}Sr (μCi)	^{241}Am (μCi)	^{244}Cm (μCi)	Pu (μCi)	U (mg)
1	0.16 *M* NaOH	14	BDL[b]	BDL	BDL	BDL
2	0.16 *M* NaOH	6	BDL	BDL	BDL	BDL
3	0.5 *M* HNO_3	197	BDL	1	BDL	BDL
4	3.0 *M* HNO_3	10,100	12.8	179	5.6	606
5	3.0 *M* HNO_3	1,880	3.2	35	9.7	45.6
6	6.0 *M* HNO_3	305	BDL	4	3.9	12.7
7	6.0 *M* HNO_3	48	BDL	1	1.8	1.8
	Total removed	12,550	16.0	220	21.0	666.1

[a] For information about leaching steps, see Table 3.

[b] BDL = below detection limit.

Table 5. Cumulative removal of radionuclides by the sequential caustic and acidic leaching of W-25 sludge[a]

	Initial amount		Cumulative amount removed by leaching		
Radionuclide	μCi	mg	μCi	mg	%
^{137}Cs[b]	970	6.70E-02	813	5.60E-02	84
^{60}Co[b]	119	1.03E+00	117	1.02E+00	98
^{154}Eu[c]	92.2	6.00E-04	92	6.00E-04	100
^{90}Sr[c]	13,300	1.45E+02	12,600	1.37E+02	95
^{241}Am[c]	18	5.70E-03	16	5.00E-03	89
^{244}Cm[c]	225	2.80E-03	220	2.70E-03	98
Pu	35		21		60
U		7.16E+02		6.66E+02	93

[a] The weight of the centrifuged, wet sludge solids was 44.0 g. See Table 3 for leach description.
[b] The mass was calculated using the effective specific activities (Sect. 2), giving the total mass of the element.
[c] The mass was calculated only for the radionuclide, using the specific activity of the radionuclide.

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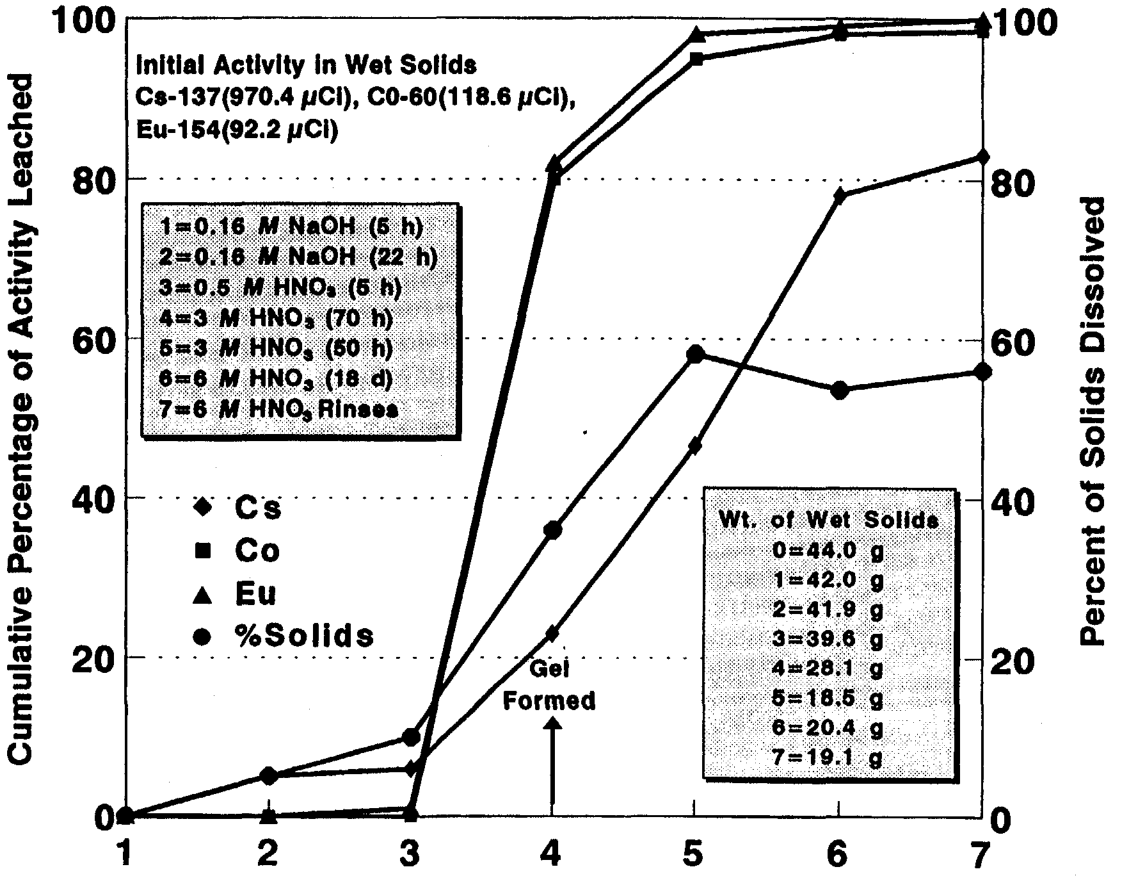

Fig. 12. Leaching results of solids from MVST W-25 sludge.

at room temperature. The leaching results are shown in Table 6. Cs-137 was the major radionuclide removed by the caustic leaching and washing steps; a total of 58.1 μCi (7.2%) was removed, primarily by the 3.1 *M* NaOH leach. This fraction of cesium removal is equal to that associated with the entrained sludge liquid in the centrifuged, wet sludge solids. The stronger caustic leaches removed only 1.5% more cesium than was removed from the sludge sample that was leached twice with 0.16 *M* NaOH (Sect. 4.1).

Small amounts of the ^{60}Co and ^{154}Eu were removed (0.7 and 0.3%, respectively). Any quantity of ^{90}Sr, ^{244}Cm, ^{241}Am, and plutonium that might have been leached was below the detection limits. Nonradioactive metals that were removed from the solids in significant amounts (>4%) included Al, Cr, Cu, K, Pb, Si, and Zn. Only 1.2% of the uranium and 0.1% of the thorium were removed. The K, Si, and Al were more affected by the 6.4 *M* NaOH leach, with 246, 44, and 27 mg being solubilized, respectively. The anion results indicated that the caustic leaches dissolved most of the sulfate, 56% of the chloride, and 22% of the nitrate. Very little of the phosphate dissolved. The low percentage of nitrate removal in caustic, despite the fact that most nitrate compounds are water soluble, indicates that the nitrate is present in a stable solid.

Following the caustic leaches and rinses, the centrifuged, wet sludge solids were mixed with 111.52 g (99.9 mL) of 5.7 *M* HNO_3 for 117 h at room temperature. After centrifugation, the leachate was removed by decantation; 123.1 g (101.3 mL) was obtained. The unreacted HNO_3 concentration was 3.4 *M*, based upon titration of aliquots of the leachate with standardized 0.1 *M* NaOH. The centrifuged, wet sludge solids were then washed twice with 0.1 *M* HNO_3 using the vortex mixer (~10 min each) to remove entrained leachate. The total volume of the decanted washes was 107.1 g (102.3 mL). The cumulative percentages of ^{60}Co, ^{154}Eu, ^{90}Sr, ^{241}Am, and ^{244}Cm removed by the sequential caustic and acidic leaching indicate that these radionuclides were completely removed from the sludge solids. Only about 55% of the ^{137}Cs and 56% of the plutonium were removed. These results are given in Table 7. The fractions of the other metals and anions that were dissolved and removed from the sludge solids by the 6 *M* HNO_3 and 0.1 *M* HNO_3 rinses are given in Table 8. With the exception of silicon, large percentages of the other major metals (>73%) were removed from the solids; only 21.2% of the silicon was removed. All of the sulphate, 70% of the chloride,

Table 6. Sequential caustic leaching of W-25 sludge at ambient temperature[a]

Component	Sludge solids[b]	3.1 *M* NaOH leachate[c]	6.4 *M* NaOH leachate[d]	0.16 *M* NaOH rinses[e]	Total removed	
Radionuclides	(μCi)	(μCi)	(μCi)	(μCi)	(μCi)	(%)
^{137}Cs	810	36.8	15.7	5.6	58.1	7.2
^{60}Co	99	0.4	0.2	0.1	0.7	0.7
^{154}Eu	77	0.1	0.03	0.07	0.2	0.3
Metals	(mg)	(mg)	(mg)	(mg)	(mg)	(%)
Al	559	4.3	22.9	6.1	33.3	6.0
Ba	10	0.002	0.03	0.1	0.13	1.2
Ca	2080	0.2	0.6	21.1	22.0	1.1
Cr	13	0.4	0.4	0.1	0.94	7.2
Cu	7	0.04	0.2	1.5	1.69	4.1
Fe	186	0.02	0.5	1.7	2.26	1.2
K	312	192	53.9	2.4	246.8	79.6
Mg	292	0.1	0.1	2.3	2.51	0.9
Ni	9	0.01	0.02	0.1	0.1	1.1
Pb	43	1.1	2.5	0.7	4.27	9.9
Si	331	5.7	38.4	10.2	54.3	16.4
Th	1240	0.02	0.04	1.0	1.06	0.1
U	598	0.9	1.3	5.1	7.36	1.2
Zn	17	0.02	3.7	1.7	5.39	31.7
Anions	(mg)	(mg)	(mg)	(mg)	(mg)	(%)
Cl$^-$	80	22.7	22	5.5	50.3	62.9
NO$_3^-$	3810	840	14.7	282.5	1136.4	29.8
PO$_4^{3-}$	639	0.7	6.8		7.5	1.2
SO$_4^{2-}$	152	149.3	9.1	1.0	159.5	104.6

[a] A 36.72-g sample of centrifuged, wet sludge solids was used in leaching tests.

[b] Total amounts of radionuclides, metals, and anions in sludge sample at start of leaching.

[c] Solids were mixed with 88.64 g (80.8 mL) of 3.1 *M* NaOH for 144 h. These results are based upon 83.35 g (74.3 mL) of recovered leachate.

[d] Solids were mixed with 94.34 g (77.1 mL) of 6.4 *M* NaOH for 144 h. These results are based upon 88.70 g (73.5 mL) of recovered leachate.

[e] The solids were rinsed twice with 0.16 *M* NaOH. The results are based upon 98.5 g (97.4 mL) of recovered rinses.

Table 7. Radionuclide removal by sequential caustic and acidic leaching of W-25 sludge[a]

Radionuclide	Sludge solids[b] (μCi)	Caustic leachates[c] (μCi)	5.7 M HNO_3 leachate[d] (μCi)	0.1 M HNO_3 rinses[e] (μCi)	Total removed	
					μCi	%
^{137}Cs	810	58	289	100	447	55
^{60}Co	99	0.7	75	28	104	104
^{154}Eu	77	0.2	62	16	78	101
^{90}Sr	11,100	BDL[f]	9,860	1,220	11,080	100
^{241}Am	15.2	BDL	14	3	17	112
^{244}Cm	187.4	BDL	145	36	181	97
Pu	28.6	BDL	14.9	1.2	16	56

[a] A 36.72-g sample of centrifuged, wet sludge solids was used at the start of the leaching steps.

[b] Total amounts of radionuclides in sludge sample at start of leaching.

[c] See footnotes in Table 6.

[d] The solids were mixed with 111.52 g (99.9 mL) of 5.7 M HNO_3 for 117 h at room temperature. These results are based upon 123.1 g (101.3 mL) of recovered leachate. The final acid concentration of the leachate was 3.4.

[e] The solids were rinsed twice with 0.1 M HNO_3. The results are based upon 107.1 g (102.3 mL) of recovered solution.

[f] BDL = below detection limit.

Table 8. Removal of nonradioactive components from W-25 sludge by sequential caustic and acidic leaching[a]

Component	Sludge solids[b] (mg)	Caustic leachates[c] (mg)	5.7 M HNO_3 leachate[d] (mg)	Total removed	
				mg	%
Metals					
Al	559	33	516	549	98
Ba	11	0.1	10.9	11	100
Ca	2080	22	2121	2143	103
Cr	13	0.6	8.9	9.5	73
Cu	7	1.7	6.6	8.3	119
Fe	186	2.3	163	138.3	75
K	312	247	26	273	88
Mg	292	2.5	247	249.5	85
Mn	19	BDL[e]	17	17	90
Ni	9	0.1	8.6	8.7	97
Si	331	54	16.3	70.3	21
Th	1240	1.1	1099	1100.1	89
U	598	7.4	616	623.4	104
Zn	17	5.4	11.8	17.2	101
Anions					
Cl^-	80	50.3	5.3	55.6	70
NO_3^-	3810	1136			
PO_4^{3-}	639	BDL	502	502	79
SO_3^{2-}	152	159	22	181	119

[a] A 36.72-g sample of centrifuged, wet sludge solids was used at the start of the leaching steps.

[b] Total amount of metals and anions in sludge sample at the start of leaching.

[c] See footnotes to Table 6.

[d] The solids were mixed with 111.52 g (99.9 mL) of 5.7 M HNO_3 for 117 h at room temperature. Following the acid leaching step, the solids were rinsed twice with 0.1 M HNO_3 [total vol. was 103.6 mL (104.8 g)]. The values given are the composite values for the acid leach and the rinses. See footnotes in Table 7.

[e] BDL = below detection limit.

and 79% of the phosphate were removed. It is also assumed that all of the carbonate was removed by conversion to carbon dioxide gas.

Based upon the results of a reference sample of centrifuged, wet sludge solids that was air dried to a constant weight, it was calculated that the air-dried weight of the initial centrifuged, wet sludge solids (36.72 g) was 21.66 g, representing 59% of the wet weight. After the last leaching step, the weight of the centrifuged, wet sludge solids was 33.9 g. The decrease from the initial weight was only 7.7%. These solids—which were air dried at room temperature to a constant weight—weighed 5.86 g, which is only 27% of the initial air-dried weight. The posttest centrifuged, wet sludge solids contained 83% water, compared with 41% for the initial solids. The difference is believed to be the result of a silica gel formation from silicic acid, which retained more water in the solids. No additional gel formation was observed in the caustic and acidic leachates and washes over a period of several months.

4.3 Leaching of W-25 Sludge with 6 *M* HNO_3

The goal of this experiment was to leach a sample of the centrifuged, wet sludge solids with strong acid, without first washing the solids with caustic. A well-mixed 69.40-g sample of W-25 sludge was centrifuged, and the sludge liquid was separated from the solids by decantation. The weight of the centrifuged, wet sludge solids was 39.48 g. (The calculated air-dried weight was 23.29 g.) The solids were mixed at room temperature for 117 h with 92.61 g (78.0 mL) of 6.0 *M* HNO_3 on the rotator. Centrifugation and decantation yielded 88.17 g (69.6 mL) of leachate and 43.92 g of wet solids. The concentration of the unreacted HNO_3 was determined to be 3.4 *M* by titrating samples of the leachate with 0.1 *M* NaOH. The centrifuged solids were then rinsed with two 50-mL volumes of 0.1 *M* HNO_3 to remove any dissolved radionuclides in the remaining interstitial liquid. The rinsing was accomplished by mixing the sample on a vortex mixer—each time for ~10 min followed by centrifuging. The cumulative rinses, which were removed by decantation, weighed 103.74 g (96.6 mL). The centrifuged sludge residue weighed 40.77 g. The residue was air dried at room temperature to a constant weight of 8.7 g, which was 37% of the initial weight of the air-dried solids prior to leaching.

The leaching results for the radionuclides are given in Table 9. Interestingly, only 22% of the ^{137}Cs was removed by the leach and wash steps, while large percentages (90 to 110%) of the ^{60}Co, ^{154}Eu, ^{90}Sr, ^{241}Am, and ^{244} Cm were removed from the solids. About 56% of the plutonium was removed.

The leachabilities of the other metals and anions are summarized in Table 10. Large percentages (>71%) of the Na, Ca, Th, U, Al, K, Mg, and Fe were dissolved and removed by the 6.0 *M* HNO_3 leaching and the two washing steps. Along with silicon, these elements represent the bulk of the mass of the metals. Only 3% of the silicon was removed. For the anions, most of the Cl^- and F^- were removed, along with about 77% of the PO_4^{3-}. It is also likely that all of the CO_3^{2-} and most of the OH^- was neutralized. Only 26% of the SO_4^{2-} was removed.

4.4 Leaching of W-25 Sludge with a Solution Containing 5.8 *M* HNO_3 and 1.0 *M* HF

This experiment repeated the leaching test described in Sect. 4.3, with hydrofluoric acid added to the nitric acid. A well-mixed sludge sample (66.09 g) was centrifuged, and the sludge liquid was removed by decantation. The weight of the centrifuged, wet sludge solids was 35.75 g. The calculated mass of the air-dried sludge was 21.09 g. The solids were mixed with the rotator at room temperature for 117 h with 119.49 g (100.9 mL) of a solution containing 5.8 *M* HNO_3 and 1.0 *M* HF. Centrifugation and decantation yielded 129.56 g (104.9 mL) of leachate and 25.68 g of wet solids. (The final acid concentration of the leachate was 3.1 M; this was determined by titrating aliquots of leachate with 0.1 *M* NaOH.) The centrifuged solids were then washed with two 50-mL volumes of 0.1 *M* HNO_3 to remove any dissolved radionuclides in the remaining interstitial liquid. The washing was accomplished by mixing the sample on a vortex mixer, each time for ~10 min followed by centrifuging. The total wash solution weighed 99.40 g (98.2 mL). The centrifuged, wet sludge solids weighed 23.53 g. The solids weighed 5.24 g after they were air dried at room temperature to a constant weight; about 75% of the initial amount of air-dried solids was dissolved.

Table 11 gives the leaching results for the radionuclides. These data show that the use of HF in the 5.8 *M* HNO_3 leachant resulted in the removal of considerably more ^{137}Cs and plutonium from the solids than in the previous test (Sect. 4.3), in which only 6.0 *M* HNO_3 was used. About 89% of the ^{137}Cs and 78% of the plutonium were removed, compared with 22% of the ^{137}Cs and 56% of

Table 9. Removal of radionuclides from W-25 sludge using 6.0 M HNO_3[a]

Radionuclide	Sludge solids[b] (μCi)	6.0 M HNO_3 leachate[c] (μCi)	0.1 M HNO_3 rinses[d] (μCi)	Total removed μCi	Total removed %
^{137}Cs	871	126.6	68.8	145.4	22.4
^{60}Co	106	68.1	41.6	109.7	103.5
^{154}Eu	83	55.6	25.3	80.9	97.5
^{90}Sr	11,960	7,780	1,880	11,660	97.5
^{241}Am	16.5	12.6	5.7	18.3	110
^{244}Cm	202	131.5	52	183.5	90.8
Pu	30.7	15.4	2	17.6	56.6

[a] A 39.48-g sample of centrifuged, wet sludge solids was used at the start of the leaching steps.

[b] Total amounts of radionuclides in the sludge sample at the start of leaching.

[c] The solids were mixed with 92.61 g (78.0 mL) of 6.0 M HNO_3 for 117 h at room temperature. These results are based upon 88.17 g (69.6 mL) of recovered leachate. The final acid concentration of the leachate was 3.4.

[d] The solids were rinsed twice with 0.1 M HNO_3. The results are based upon 103.74 g (96.6 mL) of recovered solution.

Table 10. Removal of nonradioactive components from W-25 sludge using 6.0 *M* HNO_3[a]

Component	Sludge solids[b] (mg)	6.0 *M* HNO_3 leachate[c] (mg)	0.1 *M* HNO_3 rinses[d] (mg)	Total removed mg	Total removed %
Metals					
Al	601	385	180	561	93
Ba	11	8.6	2.5	11	100
Ca	2236	1677	557	2234	100
Cd	1.3	1.0	0.3	1.3	100
Co	0.9	0.6	0.2	0.8	89
Cr	14	7.6	1.6	9.2	66
Cu	7	5.1	2.4	7.5	107
Fe	200	116	50.9	166.9	84
K	335	197	59.5	256.5	77
Mg	314	192	55.5	247.5	79
Mn	18.6	13.7	3.8	17.5	94
Na	2562	1397	430	1827	71
Ni	93	5.2	1.4	6.6	7
Pb	46.6	24.4	11.3	35.7	77
Si	331.4	3.3	6.1	9.4	3
Th	133	929	146	1075	80
U	643	504	126	630	98
Zn	18.6	12.1	4.5	16.6	89
Anions					
Cl^-	86	53.7	57.0	110.7	129
F^-	44	20	20.2	40.2	91
PO_4^{3-}	687	428	98	528	77
SO_4^{2-}	163	32.3	10.6	42.9	26

[a] A 39.48-g sample of centrifuged, wet sludge solids was used at the start of the leaching steps.

[b] Total amounts of metals and anions in sludge sample at the start of leaching.

[c] The solids were mixed with 92.61 g (78.0 mL) of 6.0 *M* HNO_3 for 117 h at room temperature. These results are based upon 88.17 g (69.6 mL) of recovered leachate. The nitric acid concentration of the leachate was 3.4.

[d] The solids were rinsed twice with 0.1 *M* HNO_3. The results are based upon 103.74 g (96.6 mL) of recovered solution.

Table 11. Removal of radioactive components from W-25 sludge leached with 5.8 M HNO_3 and 1.0 M HF[a]

Radionuclide	Sludge solids[b] (μCi)	5.8 M HNO_3 1 M HF leachate[c] (μCi)	0.1 M HNO_3 rinses[d] (μCi)	Total removed	
				μCi	%
^{137}Cs	788	502	197	699	89
^{60}Co	96	83.2	19	102.2	106
^{154}Eu	75	66.1	9.5	75.6	101
^{90}Sr	10,830	11,000	929	11,929	110
^{241}Am	14.8	13.4	3.1	16.5	111
^{244}Cm	183	164	23.5	187.5	101
Pu	27.9	18.1	3.2	21.3	76

[a] A 35.75-g sample of centrifuged, wet sludge solids was used at the start of the leaching steps.

[b] Total amounts of radionuclides in sludge sample at start of leaching.

[c] The solids were mixed with 119.49 g (100.9 mL) of solution containing 5.8 M HNO_3 and 1.0 M HF for 117 h at room temperature. These results are based upon 129.56 g (104.9 mL) of recovered leachate. The final acid concentration of the leachate was 3.1 M.

[d] The solids were rinsed twice with 0.1 M HNO_3. The results are based upon 99.40 g (98.2 mL) of recovered solution.

the plutonium in the other test. The percentages of ^{60}Co, ^{154}Eu, ^{90}Sr, ^{241}Am, and ^{244}Cm removed (101 to 110%) indicated complete removal of these constituents, which was also the case in the previous test.

The results for the nonradioactive metals and anions are summarized in Table 12. With the exception of thorium, >78% of the total metal content was removed from the solids by the leachant and washes. However, only 9% of the thorium was removed, compared with 80% in the previous test. This was not unexpected, because thorium forms an acid-insoluble fluoride (ThF_4) with HF. This result was also consistent with the formation of a heavy white precipitate that formed when the leachant was added and mixed with the solids. The HF also had a dramatic effect on the leachability of silicon and nickel. In this test, 85 and 92% of the silicon and nickel, respectively, were removed, compared with 3 and 7% in the previous tests. Gelation was observed in the leachate about 29 days after leaching. There was a clear gel film in the bottom of the container.

The anions results in Table 12 show that most of the Cl^- and ~71% of the PO_4^{3-} were removed. It can also be assumed that all of the CO_3^{2-} and most of the OH^- were removed. Only 34% of the SO_4^{2-} was removed, which was similar to the 26% removed in the previous test.

Calcium, rare earth elements, titanium, and zirconium are known for forming insoluble fluorides under slightly acidic conditions. Hydrous metal oxides of Sm, Nd, Gd, Eu, and Ce can adsorb more than 1 mol of F^- per mole of metal in the pH range 1 to 6. However, under the strongly acidic conditions of this experiment, the leach data clearly showed that the fluoride ions were not stabilized by calcium and europium. Both elements were completely removed from the sludge solids by the leachant.

4.5 Leaching of W-25 Sludge with a Solution Containing 5.6 *M* HNO_3 and 1.9 *M* HF

A 77.4-g sample of sludge was centrifuged and the sludge liquid removed by decantation. The centrifuged, wet sludge solids weighed 43.88 g, which equates to about 25.9 g of air-dried solids. The wet solids were mixed with 122.1 g (102.6 mL) of a solution containing 5.6 *M* HNO_3 and 1.9 *M* HF for 234 h at room temperature. After the mixture was centrifuged, 140.4 g (113.5 mL) of leachate was removed by decantation. The wet residue weighed 25.7 g. The specific gravity of the leachant increased from 1.19 to 1.237 g/mL for the leachate. The solids were subsequently washed

Table 12. Removal of nonradioactive components from W-25 sludge using 5.8 *M* HNO_3 and 1.0 *M* HF[a]

Component	Sludge solids[b] (mg)	5.8 *M* HNO_3 + 1.0 *M* HF leachate[c] (mg)	0.1 *M* HNO_3 rinses[d] (mg)	Total Removed	
				mg	%
Metals					
Al	544	591	106	697	128
Ba	11	10.9	1.8	12.7	115
Ca	2025	2098	275	2373	117
Cd	1.1	1.3	0.2	1.5	136
Co	0.8	0.7	0.1	0.8	100
Cr	12.7	9.8	1.7	11.5	91
Cu	6.3	5.4	0.6	6.0	95
Fe	181	172	38	211	116
K	304	246	39	285	94
Mg	285	250	31	281	99
Mn	17	17	2.3	19.3	114
Na	2320	1385	423	1808	78
Ni	8.4	6.7	1.0	7.7	92
Pb	42	30	6.4	36.4	87
Si	323	72.8	202	274.8	85
Th	1211	104	4.5	108.5	9
U	582	642	81	723	124
Zn	16.8	15.6	2.2	17.8	106
Anions					
Cl^-	78	77.6	54	131.6	169
PO_4^{3-}	622	409	33	442	71
SO_3^{2-}	148	41	8.9	49.9	34

[a] A 35.75-g sample of centrifuged, wet sludge solids was used at the start of the leaching steps.

[b] Total amounts of metals and anions in the sludge sample at the start of leaching.

[c] The solids were mixed with 119.49 g (100.9 mL) of a solution containing 5.8 *M* HNO_3 and 1.0 *M* HF for 117 h at room temperature. The results are based upon 129.56 g (104.9 mL) of recovered leachate. The final acid concentration of the leachate was 3.1.

[d] Subsequently, the solids were rinsed twice with 0.1 *M* HNO_3. The results are based upon 99.4 g (98.2 mL) of recovered solution.

with two 50-mL volumes of 0.1 *M* nitric acid. The cumulative weight of the washes was 110.4 g (106.4 mL). The centrifuged, wet sludge residue weighed 17.62 g. Samples of the leachate and washes were filtered and analyzed. The solid residue was air dried to a constant weight of 6.86 g. About 73% of the solids were dissolved in this test, similar to the test in which 1.0 *M* HF was used.

The results in Table 13 show that about 82% of the ^{137}Cs, 93% of the ^{60}Co, 87% of the ^{154}Eu, 80% of the ^{90}Sr, 102% of the ^{244}Cm, and 97% of the Pu were removed from the solids by the leaching and washing steps. Increasing the concentration of the HF from 1.0 to 1.9 *M* increased the percentage of plutonium removed from the solids from 78 to 97%.

The leaching results for the other metals and anions are given in Table 14. These data show that, with the exception of Th, Zn, Si, and Na, ≥70% of the quantity of other metals was removed from the solids; of these metals, ≥90% of Al, Ba, Ca, Cd, Co, Fe, K, Mn, and U was removed. Only 7% of the Th, 18% of the PO_4^{3-}, and 32% of the SO_4^{2-} were removed. In the previous test in which 1.0 *M* HF was used, similar results were obtained for the thorium and sulphate; 9 and 34% were removed, respectively. Also, as was the case in the previous test, a heavy white precipitate presumed to be ThF_4, formed when the leachant was added to the solids. No similar precipitate was observed in any of the acid leaching tests in which HF was not used.

4.6 Other Acid Leaching Tests

4.6.1 Gelation in acidic leachates

Two samples of W-25 sludge were leached with 3.0 *M* HNO_3 to provide leachates to examine gel formation as a function of time. As in the other tests, sludge was centrifuged and the sludge liquid was removed by decantation. One sample of the centrifuged, wet sludge solids (SL-19) weighed 31.04 g, and the other (SL-20) weighed 16.54 g. The different weights were used to examine the effect of leachant-to-solid ratio on gel formation. Each sample was leached at ambient temperature for 21 h with about 100 mL of 3.0 *M* HNO_3. Afterwards, the samples were centrifuged and the leachates removed by decantation. The volumes of SL-19 and SL-20 leachates were 106.4 mL (123.57 g) and 101.6 mL (115.27 g), respectively. Samples of the leachates that were taken for analysis and for gel formation observation were filtered through 0.45-μm Teflon syringe

Table 13. Removal of radionuclides from W-25 sludge leached with 5.6 *M* HNO_3 and 1.9 *M* HF[a]

Radionuclide	Sludge solids[b] (μCi)	5.6 *M* HNO_3 + 1.9 *M* HF leachate[c] (μCi)	0.1 *M* HNO_3 rinses[d] (μCi)	Total removed μCi	Total removed %
^{137}Cs	980	646	162	808	82
^{60}Co	119	99	11	110	93
^{154}Eu	98	78	7	85	87
^{90}Sr	13,295	9,816	825	10,639	80
^{244}Cm	244	206	42	248	102
Pu	34	25	8	33	97

[a] A 43.88-g sample of centrifuged, wet sludge solids was used at the start of the leaching steps.

[b] Total amounts of radionuclides in the sludge sample at the start of leaching.

[c] The solids were mixed with 122.1 g (102.6 mL) of a solution containing 5.6 *M* HNO_3 and 1.9 *M* HF for 234 h at room temperature. The results are based upon 140.4 g (113.5 mL) of recovered leachant.

[d] Subsequently, the solids were rinsed twice with 0.1 *M* HNO_3. The results are based upon 110.4 g (106.4 mL) of recovered solution.

Table 14. Removal of nonradioactive components from W-25 sludge leached with 5.6 *M* HNO_3 and 1.9 *M* HF[a]

Component	Sludge solids[b] (mg)	5.6 *M* HNO_3 + 1.9 *M* HF leachate[c] (mg)	0.1 *M* HNO_3 rinses[d] (mg)	Total removed	
				mg	%
Metals					
Al	668	681	90.1	771.1	115
Ba	13	11.7	1.4	12.1	94
Ca	2485	2338	270	2608	105
Cd	1.6	1.4	0.1	1.5	94
Co	1	0.8	0.1	0.9	90
Cr	15.5	10.5	1.3	10.8	70
Cu	7.8	5.6	0.5	6.1	79
Fe	223	185	29.4	214.4	96
K	373	296	47.2	343.2	92
Mg	350	277	0.7	277.7	80
Mn	20.7	18	2	20	97
Na	2848	1146	489	1635	57
Ni	10.4	6.7	0.8	7.5	72
Pb	51.8	38.2	4.6	42.8	84
Si	396	84.4	101.5	185.9	47
Th	1486	96	3.0	99	7
U	715	646	85	731	102
Zn	20.7	6.7	1.8	8.5	41
Anions					
Cl^-	96	91	7	98	102
PO_4^{3-}	765	83	51	134	18
SO_3^{2-}	181	46	11	57	32

[a] A 43.88-g sample of centrifuged, wet sludge solids was used at the start of the leaching steps.

[b] Total amounts of metals and anions in sludge sample at the start of leaching.

[c] The solids were mixed with 122.1 g (102.6 mL) of a solution containing 5.6 *M* HNO_3 and 1.9 *M* HF for 234 h at room temperature. The results are based upon 140.4 g (113.5 mL) of recovered leachate.

[d] Subsequently, the solids were rinsed twice with 0.1 *M* HNO_3. The results are based upon 110.4 g (106.4 mL) of recovered solution.

filters. Equal volumes of the leachates were measured into small test tubes to observe any gel formation.

Gel formation was observed starting 2 days after leaching sample SL-19. Initially, the gel consisted of small specks on the walls of the sample tube. Thirteen days after leaching, a gel collar was observed at the liquid-air interface. This Vaseline-like collar grew thicker for 2–3 days and then stabilized.

A gel coating appeared on the wall of the tube containing SL-20 leachate about 3 days after leaching. This was followed by specks of gel forming on the walls of the tube that were observed at 4 days and later. Fifteen days after leaching, a very light collar of gel appeared at the liquid-air interface. This collar was slightly thicker 18 days after leaching.

A clear layer was observed at the top of both of the leachates 3 weeks after leaching. This may have been due to settling or depletion of colloids at the top of the sample due to the formation of the gel collars. In the SL-19 leachate sample, a suspended gel was observed 28 days after leaching. An opaque layer of settled colloids formed on the bottom of the SL-20 leachate tube after 22 days.

Since the sludge solids were not rinsed after leaching, the total fractions of the metals dissolved by the leaches were not determined. However, the fractions removed in the leachate are of interest. The SL-19 test analytical results were as follows: Al (78%), Ca (103%), Cr (58%), Cu (53), Fe (64%), K (78%), Mg (80%), Mn (78%), Ni (60%), Si (86%), Th (77%), and U (100%). The following are the results for SL-20: Al (85%), Ca (108%), Cr (63%), Cu (68%), Fe (73%), K (81%), Mg (81%), Mn (83%), Ni (64%), Si (91%), Th (97%), and U (106%). The leachates were not analyzed for anion and radionuclide concentrations.

The concentrations of silicon in the SL-19 and SL-20 leachates were initially 2250 and 1330 mg/mL, respectively. In solutions at pH <7, silica concentrations >100 mg/L (1.7×10^{-3} *M*) can polymerize, form colloidal particles, and gel.[13,14] In salt solutions, a "salting-out" effect results in lower silica solubilities. Consequently, silica gel formation in leachates is likely.

4.6.2 Effect of pH in differential dissolution of sludge

This test was designed to study the solubility behavior of the sludge constituents by gradually increasing the acidity of the leach solutions. A 41.68-g sample of centrifuged, wet sludge solids

(24.58 g of air-dried solids) was processed in the following manner: washed twice with 100-mL volumes of 0.16 *M* NaOH (pH 13), leached with 90.85 mL of 1.6 *M* HNO_3 for 68 h (pH 6.6), leached with 45 mL of 0.5 *M* HNO_3 for ~448 h (pH 4.6–6), rinsed twice with 50-mL volumes of 3.5×10^{-5} *M* HNO_3 (pH 4.4), leached with 120.5 mL of 1.0 *M* HNO_3 for 119 h (pH 0.45), and rinsed twice with 50-mL volumes of 1.0 *M* HNO_3. The results are given in Table 15.

In the first step the sample was washed twice with 100-mL volumes of 0.16 *M* NaOH to remove the interstitial liquid at a pH of about 13. After the samples were mixed for ~20 min, they were centrifuged and the wash solutions were removed by decantation. A total of 198 mL (199.1 g) was recovered. Gamma analysis showed that 54 μCi, or 5.9%, of the ^{137}Cs was removed. This value is similar to the 5.6% removal achieved in the test described in Sect. 4.1, in which the solids were also washed twice with 50- mL volumes of 0.16 *M* NaOH. Trace amounts of ^{60}Co (0.34 μCi) and ^{154}Eu (0.04 μCi) were also removed. Analyses showed that 83.3% of K, 36% of the Na, 6.8% of the Al, 0.07% of the U, 1.7% of the Zn, 91% of the nitrate, 52% of the chloride, 27% of the sulfate, and 0.3% of the phosphate were removed. In determining the initial quantity of sodium removed from the sludge solids, the 736 mg of sodium that was added to the sludge as NaOH was subtracted from the sodium found in the decant solution.

In the second step the centrifuged residue (39.98 g) was leached with 90.85 mL of 1.6 *M* HNO_3 for 68 h, resulting in a final leachate pH of 6.6. Centrifugation yielded 34.12 g of solids and 100.13 g (92.97 mL) of leachate. This leach removed only 3.9% of the ^{137}Cs and 0.5% of the ^{154}Eu; however, 50.3% of the ^{60}Co and 57.8% of the ^{90}Sr were removed. In addition to the Sr, similar leaching results were obtained for the other alkaline earth elements: Ba (40.7%), Ca (68.3%), and Mg (71.1%). These elements most likely were present in the sludge as carbonates and hydroxides. The dissolution behavior of ^{60}Co suggests that it was probably present in the sludge as a hydroxide. Cobalt begins to precipitate above pH 6.8.[15] The fractions of other constituents removed were as follows: Cr (0.1%), Fe (0.03%), K (11.7%), Mn (3.0%), Na (16.9%), Ni (29.6%), Pb (1.0%), Si (0.4%), Th (0.4%), U (27.3%), Zn (9.3%), Cl (6.9%), and sulfate (3.5%). In solutions free of carbonate, the approximate pH above which precipitation occurs for hydrous metal oxides are as follows: Cu^{2+}, Ni^{2+}, and Zn^{2+} (pH 6 to 7); Fe^{2+} (5.5); aluminum (pH 4.1); Th^{4+} (pH 3.6); U^{6+} (pH 3.2 to 4.2); Pu^{4+}, Am^{3+}, and Cm^{3+} (pH ~3); and Fe^{3+} (pH 2 to 3).[15] Since the pH of the leachate was 6.6, it was expected that the Fe, Cu, Zn, Pu, Am, and Cm might not dissolve. The solubility of uranium can be explained by its speciation behavior in a carbonate-bicarbonate system. Depending on the pH, uranium forms different soluble complexes. According to Langmuir,[16] at a pH of 6.6, the primary species would be $UO_2(CO_3)_2^{2-}$. Also, if soluble phosphate is available, the soluble uranyl phosphate complex $UO_2(HPO_4)_2^{2-}$ can form. Uranyl (UO_2^{2-}) fluoride complexes and uranyl ions dominate below pH 5. From about pH 4 to 7.5, $UO_2(HPO_4)_2^{2-}$ is the principal species, while at higher pHs, UO_2CO_3, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ predominate.[16] A gel formed in the leachate about 6 months after leaching.

In the third step, the residue was leached with about 45 mL of 0.5 *M* HNO_3 for ~18 days. About 46.5 g (44.5 mL) of supernatant was obtained after centrifugation. The pH of the leachate was 4.6 to 6. The sludge residue weighed 29.11 g. The residue was then rinsed two times with 50-mL volumes of 3.5×10^{-5} *M* (pH = 4.4) HNO_3. The weight of the centrifuged residue decreased to 27.47 g. The decanted wash solution weighed 104.01 g (103.6 mL). Table 15 gives the cumulative percentages of the radionuclides and cations removed by the leach and rinses. Together, the leach and rinses removed the following percentages of elements: Al (37.2%), Ba (43.1%), Ca 43.6 (%), Cr (32.7%), Cu (37.8%), Fe (32.8%), K (4.7%), Mg (40.8%), Mn (47.7%), Na (7.1%), Ni (23.5%), Pb (47.5%), Si (5.0%), Th (41.6%), U (46.8%), and Zn (40.6%). Only 2.5% of the ^{137}Cs, 1.0% of the ^{154}Eu, 0.6% of the ^{241}Am, 0.3% of the ^{254}Cm, and 0.006% of the plutonium were removed. On the other hand, 14.5% of the ^{60}Co and 17.1% of the ^{90}Sr were removed

In the next step, 120.53 mL of 1.0 *M* HNO_3 was added to the residue and it was then leached for about 119 h. The mixture was again centrifuged, and the leachate was removed by decantation. About 112.15 mL (117.65 g) of leachate and 29.05 g of solids were obtained. The pH of the leachate was 0.45; this value was acidic enough, as can be seen in Table 15, to solubilize the ^{154}Eu (69.0%), ^{241}Am (56.4%), and ^{254}Cm (78.4%), but only 3.3% of the plutonium.

The cumulative percentages of the radionuclides and metals removed are given in Table 15. Only 20% of the ^{137}Cs was removed by these leaches, which compared closely with the 23% that was removed after the first 3.0 *M* HNO_3 leach of the test sequence described in Sect. 4.1 (Table 3). In that test the solids were also rinsed twice with 0.16 *M* NaOH and then with 0.5 *M* HNO_3. One slight difference in the two tests was the amount of acid used. A total of 13.5 mmol of HNO_3 per gram

Table 15. Washing of W-25 sludge with 0.16 *M* NaOH and sequential leaching with HNO_3[a]

		Percentage removed				
Component	Sludge solids[b]	0.16 *M* NaOH washes	1.6 *M* HNO_3 leach[c]	0.5 *M* HNO_3 leach[d]	1.0 *M* HNO_3 leach[e]	Total
Radionuclides	(μCi)					
^{137}Cs	919	5.9	3.9	2.5	8.0	20
^{60}Co	112	0.3	50.3	14.5	21.7	87
^{154}Eu	87	0.05	0.5	1.0	69.0	71
^{90}Sr	12,600	BDL[f]	57.8	17.1	21.9	97
^{241}Am	17.2	BDL	BDL	0.6	56.4	57
^{254}Cm	213	BDL	BDL	0.3	78.4	79
Pu	32	BDL	BDL	0.01	3.3	3
Metals	(mg)					
Al	634	6.8	BDL	37.2	62.3	106
Ba	12.3	BDL	40.7	43.1	BDL	103
Ca	2362	0.1	68.3	43.6	1.0	113
Cr	14.7	10.9	0.1	32.7	57.8	102
Cu	7.4	BDL	BDL	37.8	38.3	76
Fe	211	BDL	0.03	32.8	44.2	77
K	354	83.3	11.7	4.7	3.0	103
Mg	332	BDL	71.1	40.8	2.0	114
Mn	19.7	BDL	3.0	47.7	35.5	86
Na	2700	36	16.9	7.1	0.3	60
Ni	9.8	BDL	29.6	23.5	27.6	81
Pb	49.2	BDL	1.0	47.5	53.5	102
Si	376	BDL	0.4	5.0	67.6	73
Th	1410	0.06	0.4	41.6	13.7	56
U	678	0.07	27.3	46.8	39.4	114
Zn	19.7	1.7	9.3	40.6	45.2	97

[a] A 41.68-g sample of centrifuged, wet sludge was used at the start of the leaching.

[b] Total amounts of radionuclides and metals in the sludge sample at the start of the leaching test.

[c] Leachate pH was 6.6 after 68-h mixing time.

[d] Leachate pH was 4.6 to 6 after 432-h mixing time.

[e] Leachate pH was 0.45 after 119-h mixing time.

[f] BDL = below detection limit.

of air-dried sludge was added in the previous test, compared with a total of 12.2 mmol of HNO_3 per gram of air-dried sludge in this test. About 87% of the ^{60}Co, 71% of the ^{154}Eu, 97% of the ^{90}Sr, 57% of the ^{241}Am, 79% of the ^{254}Cm, and 3% of the plutonium were removed. For the nonradioactive metals and anions, the following fractions were removed: Al (106%), Ba (103%), Ca (113%), Cr (102%), Cu (76%), Fe (77%), K (103%), Mg (114%), Mn (86%), Na (60%), Ni (81%), Pb (102%), Si (73%), Th (61%), U (114%), and Zn (97%).

4.6.3 Acidic leaching of W-25 sludge to determine the carbonate concentration

A 38.81-g sample of centrifuged, wet sludge solids (22.90 g of air-dried sludge solids) was slowly acidified with 101.81 g of 3.0 *M* HNO_3 to determine the carbonate concentration. A specially designed sealing cap was fabricated for the 250-mL widemouthed polypropylene centrifuge bottle. The cap had three stainless steel tubes with valves: one to supply nitric acid from a separatory funnel to the bottle, one to supply argon gas to sweep the carbon dioxide gas out of the bottle, and one to vent the carbon dioxide gas to a preweighed trap containing granular (8 to 20 mesh) Ascarite to quantitatively absorb carbon dioxide. The active component is sodium hydroxide, which reacts with the carbon dioxide to form sodium carbonate. Drierite ($CaSO_4$) traps were placed at each end of the Ascarite trap to prevent any moisture from getting into the trap. The trap (Fig. 13) was a flanged, thin-walled, 19-cm-long by 3.8-cm-diam stainless steel tube that was sealed at the bottom end. The lid was a stainless steel disk with a Viton gasket. There were valved, stainless steel tubes at each end for the gas inlet and exit. The trap contained a stainless steel wire-mesh tube (80 mesh) with both ends covered with the wire mesh. This tube was centrally positioned with wire spacers and occupied about three-fourths of the length of the trap at the top. The smaller diameter of the tube allowed a 1/2-in. annular gap for adding the Ascarite. The bottom of the trap and the annular gap were filled with the Ascarite. Quartz wool was used at both ends of the trap to prevent any loss of Ascarite during handling or testing. The gas inlet tube at the top of the trap was directed into the wire-mesh tube. The trap was designed so that most of the carbon dioxide from the sludge would react with the Ascarite in the annular gap. The wire-mesh tube prevented plugging. Before conducting the test, the trap was sealed and weighed to determine the mass of the Ascarite.

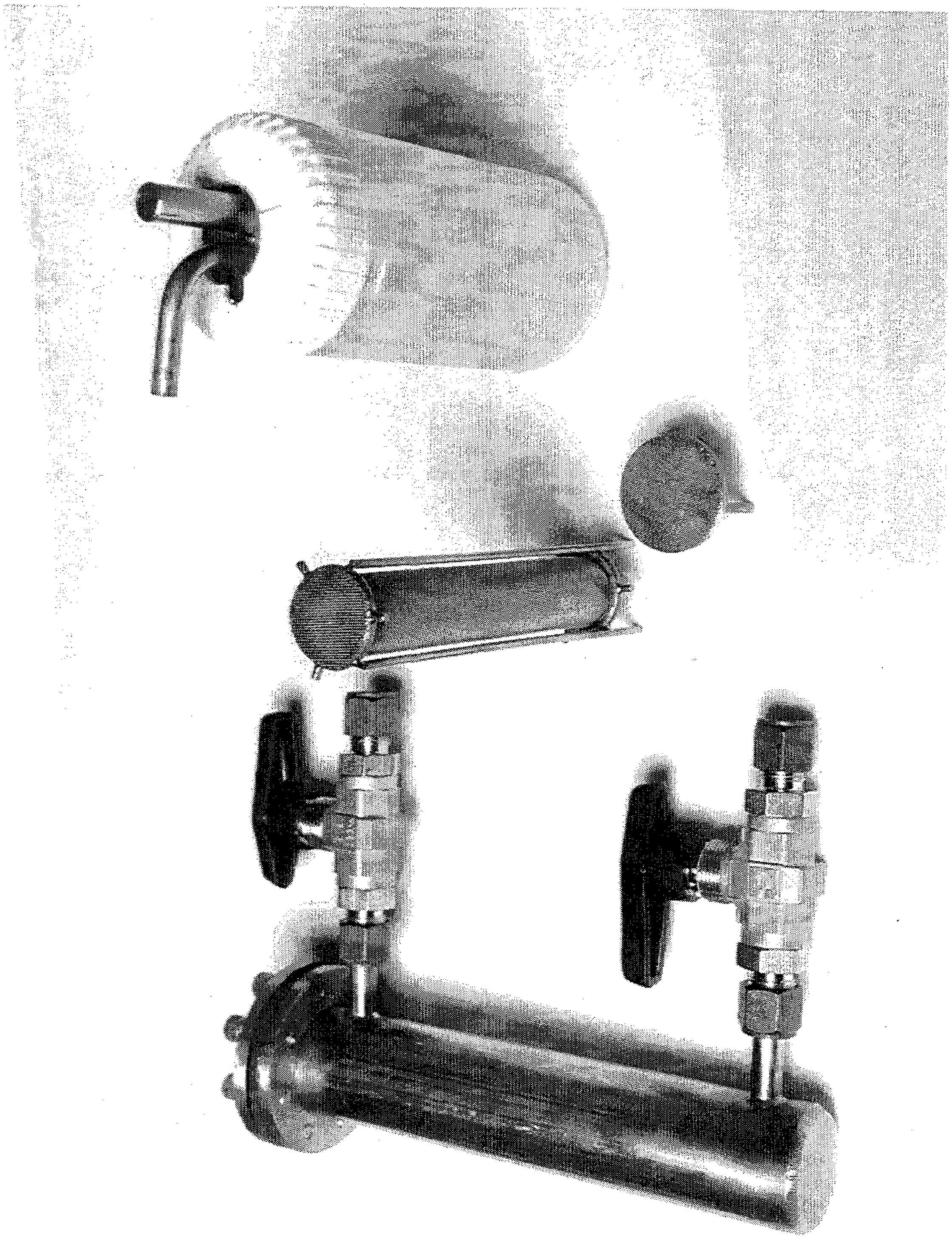

Fig. 13. Ascarite trap for trapping CO_2.

The test was conducted by slowly adding 10- to 20-mL volumes of the 3.0 *M* HNO_3 to the sludge in successive steps. This was done to prevent the bubbling CO_2 from ejecting solids from the centrifuge bottle. After each addition of acid, the valves to the sealing cap were closed and the bottle was shaken gently with the vortex mixer. The vent valve to the Ascarite trap was opened frequently to prevent overpressurization of the bottle. After the bubbling had slowed with each addition, argon gas was passed through the system at a rate of 450 cc/min for several minutes to ensure transport of the carbon dioxide to the Ascarite trap. A total of 101.81 g (93.1 mL) of the acid was transferred to the sludge bottle over a period of about 1.5 h. To make sure all of the carbonate was decomposed, the sludge was shaken at 10-min intervals for an additional hour. Each time the system was purged with the argon flow for a few minutes. Afterwards, valves on the Ascarite trap were closed. After the trap was cooled to room temperature, it was reweighed. The difference in the weight was 1.929 g, which equates to 2.630 g of carbonate in the 22.9 g of air-dried sludge.

Afterwards the original tared sealing cap was put back on the bottle of sludge and the sludge was mixed on the rotator for about 13 h. The total time of contact with the acid was about 15.5 h. The sample was then centrifuged, and the leachate was removed by decantation. About 100.27 g (85.63 mL) of leachate was obtained. The pH of the leachate was 2.2. The sludge residue was then given two 10-min rinses with 50-mL volumes of 0.1 *M* HNO_3. The cumulative volume of the rinses was 101.08 mL (104.62 g). (A total of 13.3% of the ^{137}Cs, 88.4% of the ^{60}Co, and 91.4% of the ^{154}Eu were removed from the sludge.) The weight of the centrifuged, wet sludge residue after rinsing was 28.95 g. Gel formation occurred about 24 days after leaching. The gel thickened a few days after the initial observation and then stabilized.

5. HIGH-TEMPERATURE CAUSTIC LEACHING OF MVST W-25 SLUDGE

5.1 Leaching of W-25 Sludge for 4.2 h at 95°C with 1.0 *M* NaOH

A sample of centrifuged, wet sludge solids (46.39 g) was mixed with 108.51 g (104.54 mL) of 1.00 *M* NaOH for 4.2 h at 95°C. The calculated air-dried weight of the sludge solids was 27.39 g. Centrifugation and decantation yielded 112.01 g (105.2 mL) of leachate and 42.89 g of wet sludge solids. The solids were then rinsed three times at room temperature with 50-mL volumes of 0.16 *M*

NaOH. The final weight of the centrifuged wet residue was 39.07 g, which equates to a 15.8% decrease in weight. The residue was then air dried to a constant weight of 19.79 g. Based upon the change in air-dried weights, there was a 28% decrease in mass.

The analytical results are given in Table 16. Cesium-137 was the primary radionuclide leached from the sludge solids; about 11.9% was removed. This fraction was slightly more than the 7.2% removed from a sample of sludge that was leached at ambient temperature with 3.1 *M* and 6.4 *M* NaOH for 288 h (Sect. 4.2). Small amounts of ^{60}Co (0.3%) and ^{90}Sr (0.3%) were also removed.

The decrease in the mass of the sludge solids can be primarily attributed to the removal of K (79.9%), Na (73%), Al (26%), nitrate (106%), and chloride (57.2%). Based upon the analytical results for the leachate and the rinses, the sum of the mass of the metals and anions removed was 7.7 g, or 28% of the initial air-dried mass of 27.39 g. This compares with the 31% obtained from the pretest and posttest measurements of air-dried weight.

5.2 Sequential Leaching of W-25 Sludge at 95°C with 3.2 and 6.3 *M* NaOH Followed with 6.0 *M* HNO_3 at Ambient Temperature

A 37.5-g sample of centrifuged, wet sludge solids (calculated air-dried weight of 22.13 g) was sequentially leached at 95°C, first with 3.2 *M* NaOH and then with 6.3 *M* NaOH. After each leach, the sample was centrifuged and the leachate was removed by decantation. Following each leach, the solids were rinsed with 50-mL volumes of 0.16 *M* NaOH, twice after the first leach and three times after the last leach. In the first leach, 101.93 g (91.01 mL) of 3.2 *M* NaOH was mixed with the sludge solids at 95°C for 4 h. Centrifugation yielded 106.08 g (91.01 mL) of leachate and 98.96 g (96.74 mL) of composite rinse solution. In the second leach, 97.61 g (78.80 mL) of 6.3 *M* NaOH was mixed at 95°C for 4 h. The amount of decanted leachates and rinses obtained after centrifugation were 117.27 g (97.08 mL) and 152.19 g (146.76 mL), respectively. The weight of the centrifuged wet residue was 31.94 g. A comparison of the weights of centrifuged, wet sludge solids measured before and after the first caustic leach and rinses showed a 15% decrease in weight. There was no additional decrease as a result of the 6.3 *M* NaOH leach and rinses. The fraction of the solids removed by these two leaches was about the same as that removed in the 1.0 *M* NaOH leaching test (Sect. 5.1), which was also conducted at 95°C for 4 h. On the other hand, there was only a 5% loss

Table 16. Leaching of W-25 sludge for 4.2 h at 95°C with 1.0 *M* NaOH[a]

Component	Sludge solids[b]	1.0 *M* NaOH leachate[c]	Percentage removed
Radionuclides	(μCi)	(μCi)	(%)
^{137}Cs	1036	123.3	11.9
^{60}Co	126	0.29	0.2
^{154}Eu	104	BDL[d]	BDL
^{90}Sr	14,054	4.6	0.03
Metals	(mg)	(mg)	(%)
Al	706	183.5	26.0
Ba	10.9	0.02	0.18
Ca	2628	0.84	0.03
Cr	16.4	2.2	13.4
Cu	8.2	0.08	1.0
Fe	235	0.03	0.01
K	394	315	79.9
Mg	370	<0.7	<0.2
Na	3010	2198	73
Pb	54.7	<0.4	<0.7
Si	419	5.4	1.3
Sr	153	0.01	0.007
Th	1571	0.05	0.004
U	755	0.6	0.08
Zn	21.9	2.8	12.8
Anions	(mg)	(mg)	(%)
Cl^-	101	57.8	57.2
F^-	52	20.1	38.7
NO_3^-	4899	5173	106
PO_4^{3-}	807	<5.6	<0.7
SO_4^{2-}	192	56.0	29.2

[a] A 46.39-g sample of centrifuged, wet sludge solids was used in the leaching tests.
[b] Total amounts of radionuclides, metals, and anions in the sample at the start of the leaching.
[c] Solids were mixed with 104.7 mL of 1.0 *M* NaOH for 4.2 h at 95°C.
[d] BDL = below detection limit.

in weight obtained by washing the sludge solids with 0.1 *M* NaOH (Sect. 4.1) at ambient temperature.

The percentages of radionuclides, metals, and anions removed from the sample of centrifuged, wet sludge solids for each leach (including the rinses) and the cumulative percentages removed are given in Table 17. For the 3.2 *M* NaOH leach, 14.5% of the ^{137}Cs, 0.5% of the ^{60}Co, and 0.9% of the ^{154}Eu were removed. The primary metals and anions removed were K (77.7%), Al (10.5%), Zn (39.3%), Cr (11.5%), Pb (11.8%), Si (8.4%), NO_3^- (107%), and Cl^- (50%). For the 6.3 *M* NaOH leach and rinses, an additional 27.3% of the ^{137}Cs, 1.1% of the ^{60}Co, and 1.2% of the ^{154}Eu were removed. An additional removal of aluminum (8%) and zinc (24.5%) was noted. Also, copper was more affected by the stronger caustic; 23% was removed. Little additional SO_4^{2-} (2.4%) was removed. Cumulatively, 41.8% of the ^{137}Cs, 1.5% of the ^{60}Co, and 2.1% of the ^{154}Eu were removed. The percentages of the metals and anions removed were as follows: K (82.9%), Al (18.5%), Zn (63.8%), Cr (15.8%), Pb (11.8%), Si (10.1%), NO_3^- (113%), and CL^- (63.6%). Only 30.1% of the SO_4^{2-} and 2% of the PO_4^{3-} were removed.

After the caustic leaching and rinsing steps, the centrifuged, sludge residue was mixed for ~185 h with 114.31 g (92.7 mL) of 6.0 *M* HNO_3. Following centrifugation and removal of the leachate by decantation, the residue was rinsed four times with 50-mL volumes of 0.1 *M* HNO_3. The masses of the leachate and rinses were 102.9 g (86.7 mL) and 204.6 g (195 mL), respectively.

The centrifuged, wet sludge residue, which was very gelatinous, was air dried to a constant weight of 4.13 g, which was about 19.4% of the weight of the initial air-dried sample. About 81% of the solid mass was dissolved and removed, which was about the same percentage (82%) removed in the test in which a sample of sludge solids was sequentially leached at ambient temperature with 0.16 *M* NaOH, 0.5 *M* HNO_3, 3.0 *M* HNO_3, and 6.0 *M* HNO_3 (Sect. 4.1). The quantity of ^{137}Cs removed in that test (84%) was almost identical to that removed in this test (81%). For comparison, only 55% of the ^{137}Cs was removed in the test in which the solids were sequentially leached at ambient temperature with 3.1 *M* NaOH (144 h), 6.4 *M* NaOH (144 h), and 5.7 *M* HNO_3 (117 h) (Sect. 4.2). In that test only 7% of the ^{137}Cs was removed by the caustic leaches. Also, in that test a smaller fraction (75%) of the solids was dissolved.

Table 17. Sequential caustic leaching of W-25 sludge at 95°C[a]

Component	Sludge solids[b]	Percentage removed 3.2 *M* NaOH leach step[c] 95°C (4 h)	 6.3 *M* NaOH leach step[c] 95°C (4 h)	 Cumulative
Radionuclides	(μCi)			
^{137}Cs	827	14.5	27.3	41.8
^{60}Co	101	0.5	1.1	1.6
^{154}Eu	79	0.9	1.2	2.1
^{90}Sr	11360	0.05	0.22	0.27
Metals	(mg)			
Al	571	10.5	8.0	18.5
Ba	8.9	0.18	0.32	0.5
Ca	2125	0.04	0.04	0.1
Cr	13.3	11.5	4.3	15.8
Cu	6.6	3.0	23	26
Fe	190	0.01	0.01	0.02
K	319	77.7	5.2	82.9
Mg	298	0.01	BDL[d]	0.01
Na	2434	80.9	10.1	91.0
Pb	44.3	11.8	BDL	11.8
Si	339	8.4	1.5	10.1
Sr	124	0.02	0.06	0.08
Th	1270	0.004	0.12	0.12
U	611	0.2	0.8	1.0
Zn	17.7	39.3	24.5	63.8
Anions	(mg)			
Cl^-	82	50	13.9	63.6
F^-	42	8.8	BDL	8.8
NO_3^-	3961	107	6.4	113.3
PO_4^{3-}	653	0.6	1.4	2.0
SO_4^{2-}	155	27.7	2.4	30.1

[a] A 37.5-g sample of centrifuged, wet sludge solids was used in the leaching tests.
[b] Total amounts of radionuclides, metals, and anions in the sludge sample at the start of the leaching.
[c] These values also include the amounts removed by two 0.16 *M* NaOH rinses.
[d] BDL = below detection limit.

The fractions of radionuclides, other metals, and anions removed from the solids by the sequential caustic and acidic leaches are summarized in Tables 18 and 19. These data show that almost all of the ^{60}Co, ^{154}Eu, ^{90}Sr, ^{241}Am, and plutonium were removed and—with the exception of silicon and phosphate—most of the metals and anions were also removed. About 93% of the plutonium was solubilized in this test, compared with 56% that was solubilized in the test described in Sect. 4.2, in which the sludge sample was treated in similar manner with caustic at ambient temperature. Apparently, in the test at 95°C, the fraction of insoluble plutonium in the sludge was metathesized to the hydroxide or some other acid-soluble form by heating the sludge with strong caustic.

Heavy gels were observed in the leachate and cumulative rinses when they were examined several months after leaching. The exact time the gelation began after leaching was not determined.

5.3 Leaching of W-25 Sludge for 8 h at 95°C with 3.2 *M* NaOH

A 30.4-g sample of centrifuged, wet sludge solids was mixed with 117.78 g (105.16 mL) of 3.16 *M* NaOH for 8 h at 95°C. The calculated air-dried weight of the sludge solids was 17.94 g. Centrifugation and decantation yielded 121.2 g (93.95 mL) of leachate. The residue was then rinsed three times at room temperature with 50-mL volumes of 0.16 *M* NaOH. The final weight of the residue was 25.54 g. The total amount of the rinses was 158.57 g (156.38 mL). The residue was air dried to a constant weight of 12.29 g, representing a 31.5% decrease in mass.

The analytical results, which are provided in Table 20, show that 21.7% of ^{137}Cs, 0.4% of the ^{60}Co, and 0.08% of the ^{90}Sr were removed. Much of the decrease in the mass of the sludge solids can be attributed to the removal of Na (84.1%), K (87.1%), Al (9.7%), nitrate (89.9%), chloride (38.9%), and sulphate (23.8%). Also, about 14.4% of the chromium and 43.4% of the zinc were removed.

5.4 Leaching of W-25 Sludge for 8 h at 75°C with 3.2 *M* NaOH

A sample of centrifuged, wet sludge solids (30.69 g) was mixed for 8 h with 108.8 g (97.84 mL) of 3.16 *M* NaOH at 95°C. The calculated air-dried weight of the sludge solids was 18.11 g. Centrifugation and decantation yielded 112.05 g (99.25 mL) of leachate. The solids were

Table 18. Radionuclide removal by sequential leaching of W-25 sludge with caustic at 95°C followed by 6.0 *M* HNO_3 at ambient temperature[a]

Radionuclide	Sludge solids[b] (μCi)	Caustic leachates[c] (μCi)	6.0 *M* HNO_3 leachate[d] (μCi)	Total removed	
				μCi	%
^{137}Cs	827	346	327	673	81
^{60}Co	101	0.5	103	104	102
^{154}Eu	79	1.7	75	77	97
^{90}Sr	11,360	BDL[e]	10,080	11,080	98
^{241}Am	16	BDL	17	17	106
Pu	29	BDL	27	27	93

[a] A 37.5-g sample of centrifuged, wet sludge solids was used at the start of the leaching steps.

[b] Total amounts of radionuclides in the sludge sample at the start of leaching.

[c] See footnotes in Table 17.

[d] The residue was mixed with 114.3 g (92.7 mL) of 6.0 *M* HNO_3 for 185 h at room temperature. Following the acid leaching step, the solids were rinsed four times with 50-mL volumes of 0.1 *M* HNO_3.

[e] BDL = below detection limit.

Table 19. Removal of nonradioactive components by sequential leaching of W-25 sludge with caustic at 95°C followed by 6.0 *M* HNO_3 at ambient temperature[a]

Component	Sludge solids[b] (mg)	Caustic leachates[c] (mg)	6.0 *M* HNO_3 leachate[d] (mg)	Total removed mg	Total removed %
Metals					
Al	571	105.6	585	691	121
Ba	11	0.04	13.7	13.7	125
Ca	2127	17	2620	2637	124
Cr	13.3	2.1	9.5	11.6	87
Cu	6.6	1.7	6.2	7.9	120
Fe	190	3.8	217	241	116
K	319	265	63	328	103
Mg	298	3	321	324	109
Mn	19	BDL[e]	21.4	21.4	113
Ni	8.9	BDL	7.7	7.7	87
Si	339	34.2	6.3	40.5	12
Th	1270	1.1	1402	1403	110
U	611	6.1	744	750	123
Zn	17.7	11.3	9.2	20.5	116
Anions					
Cl^-	82	63.6	18.2	64.8	79
F^-	42	3.7	43.8	47.5	113
NO_3^-	3961	1136			
PO_4^{3-}	653	13	50.4	63.5	8
SO_3^{2-}	155	46.7	86.2	133	86

[a] A 37.5-g sample of centrifuged, wet sludge solids was used at the start of the leaching steps.

[b] Total amounts of metals and anions in the sludge sample at the start of leaching.

[c] See footnotes to Table 17.

[d] The solids were mixed with 114.3 g (92.7 mL) of 6.0 *M* HNO_3 for 185 h at room temperature. Following the acid leaching step, the solids were rinsed four times with 50-mL volumes of 0.1 *M* HNO_3.

[e] BDL = below detection limit.

Table 20. Leaching of W-25 sludge for 8 h at 95°C with 3.2 *M* NaOH[a]

Component	Sludge solids[b]	3.2 *M* NaOH leachate[c]	Percentage removed
Radionuclides	(μCi)	(μCi)	(%)
^{137}Cs	670	145.4	21.7
^{60}Co	81.6	0.33	0.4
^{154}Eu	63.7	BDL[d]	BDL
^{90}Sr	9210	7.7	0.08
Metals	(mg)	(mg)	(%)
Al	463	44.7	9.7
Ba	9.1	BDL	BDL
Ca	1724	1.4	0.08
Cr	10.8	1.5	14.4
Cu	5.4	0.3	5.0
Fe	154	BDL	BDL
K	2220	225	87.1
Mg	242	BDL	BDL
Mn	14.3	BDL	BDL
Na	1973	1660	84.1
Ni	7.2	BDL	BDL
Pb	35.9	BDL	BDL
Si	274	19.3	7.1
Th	1030	0.02	0.04
U	495	BDL	BDL
Zn	14.5	6.2	43.4
Anions	(mg)	(mg)	(%)
Cl^-	66.4	26.0	38.9
F^-	34.1	11.5	34.4
NO_3^-	3211	2870	89.9
PO_4^{3-}	529	BDL	BDL
SO_4^{2-}	126	29.5	23.8

[a] A 30.40-g sample of centrifuged, wet sludge solids was used in leaching tests.
[b] Total amounts of radionuclides, metals, and anions in the sample at the start of leaching.
[c] Solids were mixed with 3.16 *M* NaOH for 8 h at 95°C and rinsed three times with 0.16 *M* NaOH (see Sect. 5.3).
[d] BDL = below detection limit.

then rinsed three times at room temperature with 0.16 *M* NaOH. The total amount of rinses was 132.33 g (130.24 mL). The final weight of the centrifuged wet residue was 24.93 g. The residue was air dried to a constant weight of 12.49 g. The mass of the air-dried solids decreased by 31%.

Table 21 gives the leaching results for the test. The most interesting result was that only 6.9% of the ^{137}Cs was leached from the solids. This is the same percentage that was removed in the long-term caustic leaching test in which a sample of sludge solids was leached at ambient temperature with 3.1 and 6.4 *M* NaOH (Table 6 and Sect. 4.2). About 0.5% of the ^{60}Co was removed. Much of the decrease in the mass of the sludge solids can be attributed to the removal of Na (15.1%), K (89.7%), Al (7.5%), nitrate (98.7%), and chloride (54.6%). Also, about 12.3% of the chromium and 27.2% of the zinc were removed.

6. DISCUSSION

6.1 Caustic and Acid Leaching of MVST W-25 Sludge at Ambient Temperature

Samples of centrifuged, wet sludge solids from MVST W-25 were leached with various combinations of sodium hydroxide, nitric acid, and hydrofluoric acid at ambient temperature. Table 22 summarizes and compares the cumulative percentages of radionuclides, uranium, and thorium that were removed by six different test series. In the table, *A* represents the test series in which centrifuged, wet sludge solids were sequentially leached with 0.16 *M* NaOH and 0.5 *M* HNO_3, 3.0 *M* HNO_3, and 6.0 *M* HNO_3; *B* represents the test series in which centrifuged, wet sludge solids were sequentially leached with 3.1 *M* NaOH, 6.4 *M* NaOH, and 5.7 *M* HNO_3; *C* represents the test in which centrifuged, wet sludge solids were leached with 6.0 *M* HNO_3 alone; *D* represents the test in which centrifuged, wet sludge solids were leached with a solution containing 5.8 *M* HNO_3 and 1.0 *M* HF; *E* represents the test in which centrifuged, wet sludge solids were mixed with a solution of 5.6 *M* HNO_3 and 1.9 *M* HF; and *F* represents the test in which the sludge was leached with 3.2 *M* NaOH and 6.3 *M* NaOH at 95°C and then leached with 6.0 *M* HNO_3 at ambient temperature. All of the other leaching tests were conducted at ambient temperature. Tests *B*, *C*, *D*, *E*, and *F* were conducted under similar conditions. In each test the sludge solids were mixed with 6.0 *M* HNO_3; however, in tests *B* and *F* the sludge solids were leached with strong caustic leaches prior to leaching

Table 21. Leaching of W-25 sludge solids for 8 h at 75°C with 3.2 *M* NaOH[a]

Component	Sludge solids[b]	3.2 *M* NaOH leachate[c]	Percentage removed
Radionuclides	(μCi)	(μCi)	(%)
^{137}Cs	677	46.8	6.9
^{60}Co	82.4	0.39	0.5
^{154}Eu	64.3	BDL[d]	BDL
^{90}Sr	9300	2.0	0.02
Metals	(mg)	(mg)	(%)
Al	467	34.9	7.5
Ba	9.1	BDL	BDL
Ca	1740	0.7	0.04
Cr	10.9	1.34	12.3
Cu	5.4	0.14	2.5
Fe	156	BDL	BDL
K	261	234	89.7
Mg	244	BDL	BDL
Mn	14.5	BDL	BDL
Na	1992	301	15.1
Ni	7.2	BDL	BDL
Pb	36.2	BDL	BDL
Si	277	9.6	3.5
Th	1039	0.02	0.04
U	500	1.3	0.26
Zn	14.5	3.9	27.2
Anions	(mg)	(mg)	(%)
Cl^-	67.0	36.6	54.6
F^-	34.4	3.3	9.6
NO_3^-	3241	3200	98.7
PO_4^{3-}	534	4.6	0.9
SO_4^{2-}	127	37	29.1

[a] A 30.69-g sample of centrifuged, wet sludge solids was used in leaching tests.
[b] Total amounts of radionuclides, metals, and anions in the sample at the start of leaching.
[c] Solids were mixed with 3.16 *M* NaOH for 8 h at 75°C and rinsed three times with 0.16 *M* NaOH (see Sect. 5.4).
[d] BDL = below detection limit.

Table 22. Comparison of percentages of radionuclides removed by leaching W-25 sludge at ambient temperature

Radionuclide	Cumulative percentage of radionuclide removed					
	A[a]	*B*[b]	*C*[c]	*D*[d]	*E*[e]	*F*[f]
^{137}Cs	84	55	22	89	82	81
^{60}Co	98	104	103	106	93	102
^{154}Eu	100	101	97	101	87	97
^{v90}Sr	95	100	97	110	80	98
^{241}Am	89	112	110	111		106
^{244}Cm	98	97	90	101	102	
Pu	60	56	56	76	97	93
Th		89	80	9	7	110
U	93	104	98	124	102	123

[a] Sludge solids sequentially leached with 0.16 *M* NaOH and 0.5, 3, and 6 *M* HNO_3. See Sect. 4.1 and Table 5.

[b] Sludge solids sequentially leached with 3.1 *M* NaOH, 6.4 *M* NaOH, and 5.7 *M* HNO_3. See Sect. 4.2 and Table 7.

[c] Sludge solids leached with 6.0 *M* HNO_3. See Sect. 4.3 and Table 9.

[d] Sludge solids leached with a 5.8 *M* HNO_3 and 1.0 *M* HF solution. See Sect. 4.4 and Table 11.

[e] Sludge solids leached with a 5.6 *M* HNO_3 and 1.9 *M* HF solution. See Sect. 4.5 and Table 13.

[f] Sludge solids sequentially leached at 95°C with 3.2 *M* NaOH, 6.3 *M* NaOH, and then with 6.0 *M* HNO_3 at ambient temperature. See Sect. 5.2 and Tables 17 and 18.

with the nitric acid, and in tests *D* and *E* the acid leach also contained HF. The acid mixing times were 117 h for tests *B*, *C*, and *D*; 234 h for test *E;* and 185 h for test *F*. The acid concentrations of the leachates were 3.4 *M* for both *B* and *C*, and 3.1 *M* for *D*. The cumulative percentages of ^{60}Co, ^{154}Eu, ^{90}Sr, ^{241}Am, ^{244}Cm, and uranium removed from the sludge solids in all of the tests indicated almost total dissolution of each of these components. The use of nitric acid alone (test *C*) removed the smallest amount of ^{137}Cs (22%). The use of strong caustic in tests *B* and *F* and the use of HF in tests *D* and *E* improved the removal of ^{137}Cs to 55, 81, 89, and 82%, respectively. Heating the sludge solids in caustic at 95°C in test *F* prior to leaching with nitric acid worked as well as using HF with nitric acid.

The dissolution of plutonium was unaffected by caustic pretreatment at ambient temperature; about 44% of the plutonium remained in the solids. On the other hand, caustic pretreatment at 95°C in test *F* increased the plutonium removal; only 7% of the plutonium remained in the solids. In tests *D* and *E*, the addition of HF also enhanced the removal of the plutonium. Almost all of the plutonium (~97%) was removed in test *E*, in which the HF concentration of the leachant was 1.9 *M*. The use of 1.0 *M* HF in test *D* was less effective in removing the plutonium; 78% was removed.

In test *A*, a total of 84% of the ^{137}Cs was removed from the sludge solids; this value is similar to the percentages removed in tests *D*, *E*, and *F*. The fraction of ^{137}Cs removed in test *A* was much larger than the percentages obtained for tests *B* (55%) and *C* (22%). The main differences were that the sludge solids in test *A* were given mild caustic washes prior to leaching with nitric acid and the total time the sludge solids were mixed with nitric acid leaches was 4.8 times longer (557 h). In fact, the cumulative percentage of cesium removed after the two 3.0 *M* HNO_3 leaches was about 48%. This means that the mild caustic washing steps were about as effective in enhancing the removal of the cesium from the solids as were the stronger caustic leaches at ambient temperature. In summary, the data in Table 22 indicate that ^{137}Cs removal from the sludge solids is enhanced by either leaching with caustic at ambient temperature or 95°C prior to leaching with nitric acid, by adding hydrofluoric acid to the nitric acid leaches, or by leaching for longer periods of time.

In tests *A* and *B*, the centrifuged, wet sludge solids were first given two sequential caustic leaches before leaching with nitric acid. The concentrations of the NaOH leaches in test *B* were 3.1 *M* and 6.4 *M*, which were much stronger than the 0.16 *M* NaOH washes used in test *A*. However, little additional ^{137}Cs was removed by the more concentrated NaOH; 7.1% of the ^{137}Cs was removed by the caustic in test *B* and 5.6% in test *A*. This percentage was identical to that found in the entrained sludge liquid of the centrifuged, wet sludge solids. On the other hand, leaching sludge solids at 95°C (test *F)* appeared to release the cesium from the solid structure.

Figure 14 summarizes the percentages of Cs, Pu, Th, U, and Cm removed from MVST W-25 sludge as a function of the leaching methods *A*, *B*, *C*, *D*, *E*, and *F*. The leach behavior of the U and Cm by all these methods is very similar to leach behavior for Co, Eu, Sr, and Am. As can be seen in the bar graph, Cs, Pu, and Th show the greatest variation in leaching behavior by the methods employed.

The cumulative percentages of the other metals and the anions that were removed by the leaching steps in tests *B*, *C*, *D*, *E*, and *F* are compared in Table 23. In test *C*, in which only nitric acid was used as a leachant, the nickel, silicon, and sulphate were the least solubilized. Large percentages of the other metals and anions were removed. The use of strong caustic in test *B* and the use of HF in tests *D* and *E* enhanced the removal of nickel and silicon, especially nickel. In tests *B* and *F*, large fractions of the sulphate were removed by the caustic leaching steps prior to leaching the sludge solids with the nitric acid. In tests *C*, *D*, and *E*, only 26, 34, and 32% of the sulphate were removed, respectively. The higher concentration of HF in the leachant in test *E* seemed to decrease the percentages of zinc, nickel and phosphate that were solubilized. The percentage of phosphate removed in test *F* was also low.

6.2 Gel Formation in Acidic Leaches

One phenomenon that was encountered in tests *A*, *B*, *C*, *D*, *E*, and *F* (Sect. 6.1) was gel formation during or after acidic leaching of the sludge solids. Gel was first observed in the leachate of the first 3 *M* HNO_3 leach in test *A* after the solution had stood for about 34 days. The sludge solids were leached for 70 h in this step. Gel formation in one of the leachates can be seen in Fig. 15. Gels were not observed in any of the other leachates in the test *A* series. Gels that formed during leaching remained with the solids after centrifugation. The mixing times were 117 h for tests *B*, *C*, and *D*; 234 h for test *E*; and 185 h for test *F*. Thick gels were observed in the test *F* leachate and cumulative rinses when they were examined several months after leaching; the residue also

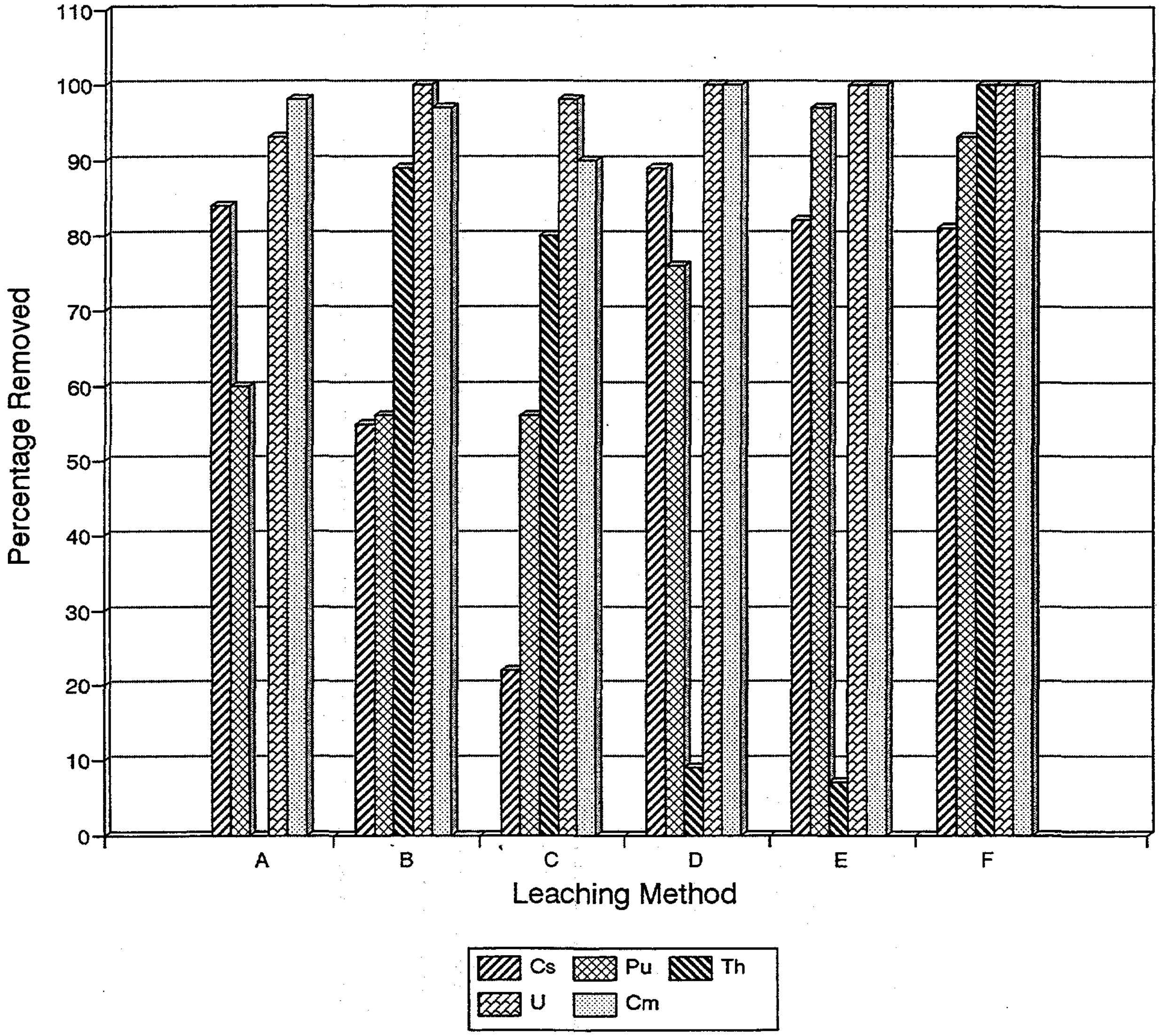

Fig. 14. Percentages of Cs, Pu, Th, U, and Cm removed from MVST sludge as a function of leaching method. *A*—sludge sequentially leached with 0.16 *M* NaOH and 0.5, 3, and 6 *M* HNO_3; *B*—sludge sequentially leached with 3.1 *M* NaOH, 6.4 *M* NaOH, and 5.7 *M* HNO_3; *C*—sludge leached with 6.0 *M* HNO_3; *D*—sludge leached with a 5.8 *M* HNO_3 and 1.0 *M* HF solution; *E*—sludge leached with a 5.6 *M* HNO_3 and 1.9 *M* HF solution; and *F*—sludge sequentially leached at 95°C with 3.2 *M* NaOH and 6.3 *M* NaOH and then with 6.0 *M* HNO_3 at ambient temperature.

Table 23 . Cumulative percentages of metals and anions removed by leaching of W-25 sludge at ambient temperature

	Cumulative percentages removed				
Component	*B*[a]	*C*[b]	*D*[c]	*E*[d]	*F*[e]
Metals					
Al	98	93	128	115	121
Ba	100	100	115	94	125
Ca	103	99	117	105	124
Co	89	89	100	90	
Cr	73	66	91	70	87
Cu	119	107	95	79	120
Fe	75	84	116	96	116
K	88	77	94	92	103
Mg	85	79	99	80	109
Mn	90	94	114	97	113
Na		71	78	57	
Ni	97	7	92	72	87
Pb	54	77	87	84	
Si	21	3	85	47	12
Zn	101	89	106	41	116
Anions					
Cl^-	70	129	169	102	79
F^-	93	91			113
CO_3^{2-}	100	100	100	100	100
PO_4^{3-}	79	77	71	18	8
SO_3^{2-}	119	26	34	32	

[a] Sludge solids sequentially leached with 3.1 *M* NaOH, 6.4 *M* NaOH, and 5.7 *M* HNO_3.

[b] Sludge solids leached with 6.0 *M* HNO_3.

[c] Sludge solids leached with a 5.8 *M* HNO_3 and 1.0 *M* HF solution.

[d] Sludge solids leached with a 5.6 *M* HNO_3 and 1.9 *M* HF solution.

[e] Sludge solids sequentially leached at 95°C with 3.2 *M* NaOH, 6.3 *M* NaOH, and then with 6.0 *M* HNO_3 at ambient temperature.

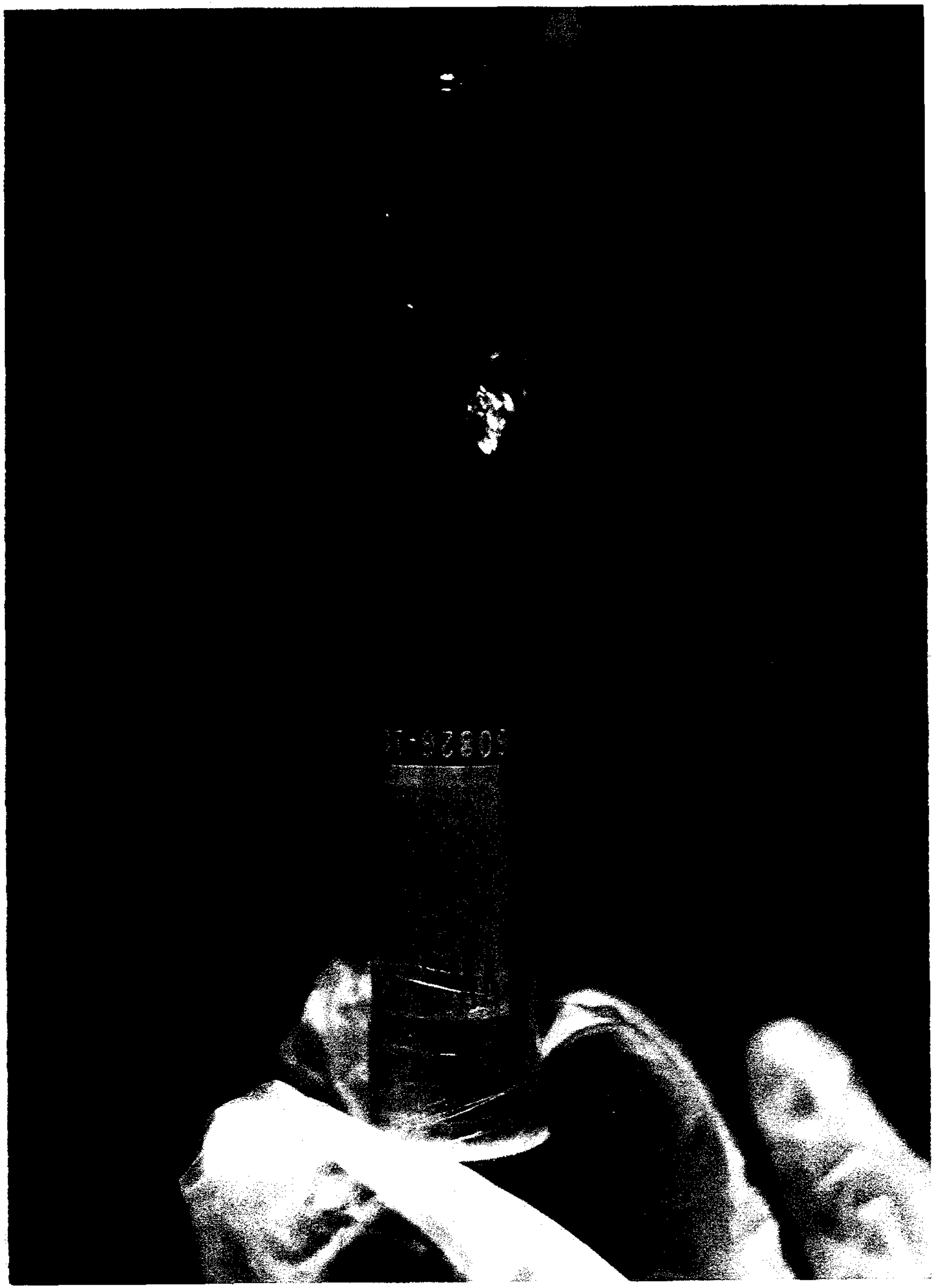

Fig. 15. Example of gel formation in acidic leachate.

contained significant amounts of gel. No noticeable gel formation was observed in the leachates of tests *C* and *E*. Gel formation was observed in test *D* about 29 days after leaching; there was a clear gel film in the bottom of the container.

Gels were also observed in the leachates in several of the other tests involving acid leaching. In the test to determine the concentration of carbonate (Sect. 4.6.1), a sample of centrifuged, wet sludge solids was leached for about 15.5 h with 3.0 M HNO_3. A clear gel film was observed forming on the bottom of the leachate container about 24 days after leaching. The gel thickened a few days after the initial observation and then stabilized.

Gel formation during leaching made it impossible to determine the fraction of the solids dissolved simply by weighing the centrifuged, wet solids before and after leaching. The gel in the residue retained a considerable amount of leachate upon centrifugation. Table 24 gives the free-liquid content of centrifuged, wet sludge residue in tests *A*, *B*, *C*, *D*, *E*, and *F* after leaching and washing with the acid solutions. This value was determined by weighing the centrifuged, wet sludge residues; air drying them to a constant weight; and reweighing them. The free-liquid content varied from 61 to 90%. The free-liquid content of a reference sample of the original centrifuged, wet sludge solids was 41%. The leached solids, therefore, contained about twice the amount of free liquid as the original sludge solids. These data support the observation of gel formation during the acid leaching steps.

Two samples of W-25 centrifuged, wet sludge solids were leached with ~3 M HNO_3 for 21 h at ambient temperature to examine the gel formation phenomenon. The details and results of these experiments are given in Sect. 4.6.1. One of the samples weighed about twice as much as the other. The different weights were used to examine the effect of leachant-to-solid ratio on gel formation. Gels began forming in each of these leachates within 2 to 3 days after leaching. The volume of gel grew for a period of 2 to 3 weeks and then stabilized. As expected, more gel was formed in the leachate from the larger sludge sample. The concentrations of silicon in the leachates were fairly high, 2250 and 1330 mg/mL, with the concentration of silicon in the leachate from the larger sample being higher.

In near-neutral and acidic solutions, silica concentrations >100 mg/L (1.7×10^{-3} M) can polymerize, form colloidal particles, and gel.[13, 14] In salt solutions, a "salting-out" effect results in

Table 24. Moisture content of centrifuged, wet residues after leaching W-25 sludge[a]

Leach Treatment	Final (wet) (g)	Final (air-dried) (g)	Free water content (%)
A[b]	19.10	4.80	75
B[c]	33.90	5.86	83
C[d]	40.77	8.70	79
D[e]	23.51	5.24	78
E[f]	17.64	6.86	61
F[g]	43.31	4.13	90

[a] Centrifuged, wet sludge solids were air dried at room temperature for 9 days.

[b] Sludge solids sequentially leached with 0.16 *M* NaOH and 0.5, 3, and 6 *M* HNO_3.

[c] Sludge solids sequentially leached with 3.1 *M* NaOH, 6.4 *M* NaOH, and 5.7 *M* HNO_3.

[d] Sludge solids leached with 6.0 *M* HNO_3.

[e] Sludge solids leached with a 5.8 *M* HNO_3 and 1.0 *M* HF solution.

[f] Sludge solids leached with a 5.6 *M* HNO_3 and 1.9 *M* HF solution.

[g] Sludge solids sequentially leached at 95°C with 3.2 *M* NaOH and 6.3 *M* NaOH, and then with 6.0 *M* HNO_3 at ambient temperature.

lower silica solubilities. When the silica solubility is exceeded, precipitation can occur and result in gelation. At the higher silica concentrations, silicic acid polymerizes to form gels, according to the general equation,[13]

$$[\mathrm{Si}_n\mathrm{O}_{2n-(nx/2)}(\mathrm{OH})_{nx}] + m\mathrm{Si(OH)}_4 = [\mathrm{Si}_{n+m}\mathrm{O}_{2n-(nx/2+2m(2-p)}(\mathrm{OH})_{nx+4(m-p)}] + 2pm\mathrm{H_2O}\ ,$$

where n = the number of silicon atoms in a polysilicic acid molecule or particle or polymeric network, x = the number of OH groups per silicon atom in the polymer (not exceeding 4), m = the number of monomeric silicic acid molecules added to the polymer, and p = the fraction of the hydroxyl groups per monomeric silicic acid molecule that is converted to water during the polymerization reaction.

6.3 Cesium Removal as a Function of Acid Dissolution of Sludge Solids

To determine quantitatively the bulk dissolution of the sludge solids, the air-dried weights of the initial sludge solids were compared with the air-dried weights of the sludge solids at the completion of the leaching tests. Table 25 gives the results. The percentage of ^{137}Cs removed from the solids in each test is also shown. The weight of the initial air-dried solids was calculated based upon reference samples. These values represent 59% of the weight of the wet centrifuged, wet sludge solids. The percentages of dissolved solids varied from 63 to 82%. For tests *A* and *F*, the cesium dissolution paralleled the solid dissolution. The caustic leaching step in tests *B* and *F* prior to leaching the sludge solids with nitric acid enhanced the dissolution of the solids and the removal of the cesium. In tests *B* and *F*, 73 and 81% of the solids were dissolved and 55 and 81% of the cesium were removed, respectively. The centrifuged residue in test *F* contained more free water and gel. The fraction of solids dissolved (81%) in test *F* equaled the fraction of ^{137}Cs removed. In test *C*, where the solids were leached with nitric acid alone, 63% of the solids were dissolved, but only 22% of the ^{137}Cs was removed. In tests *D* and *E*, in which HF was used with the nitric acid, 75 and 73% of the solids were dissolved and 89 and 82% of the ^{137}Cs were removed, respectively. In tests *D* and *E*, it is postulated that the formation of $\mathrm{ThF_4}$ by the reaction of HF with the thorium added some mass to the final weight of the air-dried solids.

Table 25. Cesium removal as a function of dissolution of sludge solids[a]

Leach treatment	Air-dried solids Before leaching (g)	Air-dried solids After leaching (g)	Dissolved solids (%)	^{137}Cs removal (%)
A[b]	25.96	4.80	82	84
B[c]	21.67	5.86	73	55
C[d]	23.29	8.70	63	22
D[e]	21.09	5.24	75	89
E[f]	25.89	6.86	73	82
F[g]	22.13	4.13	81	81

[a] Centrifuged, wet sludge solids were air dried at room temperature for ≥9 days.

[b] Sludge solids sequentially leached with 0.16 *M* NaOH and 0.5, 3, and 6 *M* HNO_3.

[c] Sludge solids sequentially leached with 3.1 *M* NaOH, 6.4 *M* NaOH, and 5.7 *M* HNO_3.

[d] Sludge solids leached with 6.0 *M* HNO_3.

[e] Sludge solids leached with a 5.8 *M* HNO_3 and 1.0 *M* HF solution.

[f] Sludge solids leached with a 5.6 *M* HNO_3 and 1.9 *M* HF solution.

[g] Sludge solids sequentially leached at 95°C with 3.2 *M* NaOH, 6.3 *M* NaOH, and then with 6.0 *M* HNO_3 at ambient temperature.

6.4 High-Temperature Caustic Leaching of W-25 Sludge

Table 26 summarizes the percentages of radionuclides, metals, and anions removed from MVST W-25 sludge by leaching with caustic at high temperatures. The results obtained by leaching a sample of W-25 sludge (Sect. 4.1) with 0.16 *M* NaOH are shown for comparison. One of the most interesting differences in the leaching results was that of ^{137}Cs. Cesium solubility was dependent upon leaching temperature and caustic concentration. In the two tests at 95°C (8 h) using 3.2 and 6.3 *M* NaOH, the percentage of ^{137}Cs removed (41.8%) by the 6.3 *M* NaOH was almost twice that removed (21.7%) by the 3.2 *M* NaOH. For the two tests at 95°C with 3.2 *M* NaOH, increasing the leaching time from 4 to 8 h resulted in an increase in the percentage of ^{137}Cs removed from 14.5 to 21.7%. On the other hand, increasing the molarity of the caustic from 1.0 to 3.2 at 95°C only slightly increased the percentage of ^{137}Cs removed, from 11.9 to 14.5%. Caustic leaching at 75°C removed only slightly more ^{137}Cs than was removed by caustic leaching at ambient temperature. This percentage (6.9%) was about the same as that removed by leaching with 0.16 *M* NaOH, or with stronger caustic (3.1 and 6.4 *M* NaOH) at ambient temperature. About 5.6% of the ^{137}Cs was removed with the 0.16 *M* NaOH, and a cumulative 7.2% was removed by sequentially leaching with 3.1 and 6.4 *M* NaOH (Table 6 and Sect. 4.2).

Caustic leaching at 95°C removed 78 to 90% of the K, 73 to 91% of the Na, 10 to 26% of the Al, 12 to 16% of the Cr, 12 to 64% of the Zn, 1.3 to 10% of the Si, 90 to 113% of the NO_3^-, 40 to 63% of the Cl^-, and 24 to 30% of the SO_4^{2-}. Only very small fractions of the Ca, Mg, Sr, Th, U, and PO_4^{3-} were removed. Only 15.1% of the Na was removed with the 3.2 *M* NaOH leachant at 75°C, compared with 65% at ambient temperature.

The leached centrifuged, wet sludge residues for three of the caustic leach tests were air dried to determine the weight loss. Caustic concentration, temperature, and leaching time had no significant effect on the mass of sludge dissolved. Based upon the decrease in air-dried weight, 31% was removed by the 8-h, 75°C test using 3.2 *M* NaOH (Sect. 5.4); 31% was removed by the 8-h, 95°C test using 3.2 *M* NaOH (Sect. 5.3); and 31% was removed by the 4.2-h, 95°C test using 1.0 *M* NaOH.

Table 26. Summary of caustic leaching of W-25 sludge

	Percentage removed					
Component	1.0 *M* NaOH[a]	3.2 *M* NaOH[a]	3.2 *M* NaOH[b]	6.3 *M* NaOH[b]	3.2 *M* NaOH[c]	0.16 *M* NaOH[d]
Radionuclides						
^{137}Cs	11.9	14.5	21.7	41.8	6.9	5.6
^{60}Co	0.2	0.5	0.4	1.6	0.5	0.2
^{154}Eu	<1	0.9	<1	2.1		0.1
^{90}Sr	0.03	0.05	0.08	0.27		
Metals						
Al	26	10.5	9.7	18.8	7.5	6.6
Ca	0.03	0.04	0.08	0.1	0.04	0.1
Cr	13.4	11.5	14.4	15.8	12.3	10.3
Cu	1.0	3.0	5.0	26.0	2.5	0.4
Fe	0.01	0.01	<0.01	0.02	<0.01	<0.001
K	79.9	77.7	87.1	82.9	89.7	80.5
Mg	<0.2	0.01	<0.01	0.01	<0.02	0.02
Na	73.0	80.9	84.1	91.0	15.1	65.2
Pb	<0.7	11.8		11.8		<0.3
Si	1.3	10.1	7.1	10.1	3.5	
Sr	0.01	0.02	0.2	0.1	0.2	
Th	0.004	0.004	<0.04	0.12	<0.01	<0.001
U	0.08	0.2	<0.3	1.0	0.26	0.3
Zn	12	39.3	43.4	63.8	27.2	1.4
Anions						
Cl$^-$	57.2	50	38.9	63.4	54.6	50.6
F$^-$	38.7	8.8	34.4	8.8	9.6	17.3
NO$_3^-$	106	107	89.9	113	98.7	87.9
PO$_4^{3-}$	<0.7	0.6	<1	2.0	0.9	0.3
SO$_4^{2-}$	29.2	27.7	23.8	30.1	29.1	26

[a] Leached at 95°C for 4 h.
[b] Leached at 95°C for 8 h.
[c] Leached at 75°C for 8 h.
[d] Leached at 25°C for 27 h.

In summary, the structural and chemical composition of the sludge seemed to be altered when leached with 1.0 to 6.3 *M* NaOH at 95°C. These changes allowed larger amounts of ^{137}Cs and sodium to be removed compared with those for caustic leaching at 75°C and at ambient temperature. Furthermore, in all of the tests in which the sludge solids were leached first with caustic, ^{137}Cs was more readily removed by subsequent leaching with nitric acid. Leaching the sludge with mild or strong caustic at ambient temperature before leaching it with nitric acid had no effect on the leachability of the plutonium. However, 91% of the plutonium was solubilized with 6.0 *M* HNO_3 (185 h) from sludge residue from a sample that was first heated at 95°C and then leached with 3.2 *M* NaOH (4 h) and 6.3 *M* NaOH (4 h). No gel formations were observed in any of the caustic leachates.

7. SUMMARY

1. The major alpha-, gamma-, and beta-emitting radionuclides in the MVST-25 sludge were ^{137}Cs, ^{60}Co, ^{154}Eu, ^{241}Am, ^{244}Cm, ^{90}Sr, Pu, U, and Th. The other major metals (in addition to the U and Th) and the anions were Na, Ca, Al, K, Mg, NO_3^-, CO_3^{2-}, OH^-, and O^{2-}. The organic carbon content was about 3.0 ± 1.0%. The pH was 13.
2. About 93% of the ^{137}Cs in the centrifuged, wet sludge solids was bound in the solids and could not be solubilized by basic leaching at temperatures from ambient to 75°C. Most of the ^{137}Cs that was solubilized by the caustic rinses or leaches at ambient temperature appeared to be a constituent of the interstitial sludge liquid that remained after centrifugation.
3. The solubility of ^{137}Cs was enhanced by caustic leaching of the sludge at 95°C. Increasing the mixing time and the concentration of the caustic also enhanced the ^{137}Cs solubility. In one of the tests, about 42% of the ^{137}Cs was removed by leaching at 95°C with 6.3 *M* NaOH.
4. The solubility of sodium in the sludge was enhanced by caustic leaching at 95°C. The solubility of sodium was much less when the sludge was leached at 75°C.
5. With the exception of zinc, there was little difference in the solubility of the other sludge constituents when the sludge was leached with caustic at either 75°C or at ambient temperature.

6. Removing ^{137}Cs from the W-25 sludge with nitric acid at ambient temperature was a slow process. About 13% of the ^{137}Cs was removed in 16 h with 3.0 *M* HNO_3. Only 22% of the ^{137}Cs was removed in 117 h using 6.0 *M* HNO_3. Successive leaching of sludge solids with 0.5 *M*, 3.0 *M*, 3.0 *M*, and 6.0 *M* HNO_3 for a total mixing time of 578 h removed 84% of the ^{137}Cs.
7. The acid leaching tests showed that 1.2, 3.4, and 7.9 mol of nitric acid are needed to adjust the pH values of 1 kg of centrifuged, wet sludge solids to 7.6, 6.6, and 2.2, respectively. Mixing 1 kg of centrifuged, wet sludge solids with 6.0 *M* HNO_3 for 117 h comsumes about 5 mol of the acid.
8. Pretreatment of the centrifuged, wet sludge solids with strong caustic enhanced the removal of ^{137}Cs with nitric acid leachant. Sludge that was first leached with 3.1 *M* NaOH (144 h) and 6.4 *M* NaOH (144 h) followed by 6.0 *M* HNO_3 (117 h) at ambient temperature removed 55% of the ^{137}Cs. When the sludge was not first leached with caustic, only 22% of the cesium was removed for the same mixing time and temperatiire. Heating the sludge at 95°C and leaching with 3.2 *M* NaOH (4 h) and 6.3 *M* NaOH (4 h) followed by 6.0 *M* HNO_3 (185 h) removed a total of 81% of the ^{137}Cs. About half of this amount was removed by the caustic leaches.
9. Fairly large percentages of ^{60}Co (50.3%), ^{90}Sr (57.8%), Ca (68.3%), Mg (71.1%), Ni 29.6%, and U (27.3) were solubilized when a sample of centrifuged, wet sludge was leached with nitric acid to a pH of 6.6. In similar tests in which the final pH was 7.6, no ^{60}Co, ^{90}Sr, or uranium was solubilized.
10. Addition of hydrofluoric acid to the 6.0 M HNO_3 leachant enhanced the removal of the ^{137}Cs from the centrifuged, wet sludge solids.
11. Only 56 to 60% of the plutonium was removed from the centrifuged sludge solids by leaching with 6.0 *M* HNO_3.
12. Leaching the sludge with mild or strong caustic at ambient temperature before leaching it with nitric acid had no effect on the leachability of the plutonium. However, 91% of the plutonium was solubilized with 6.0 *M* HNO_3 (185 h) from sludge residue from a sample of sludge that was first heated at 95°C and leached with 3.2 *M* NaOH (4 h) and 6.3 *M* NaOH (4 h). The

insoluble fraction of the plutonium in the sludge probably was metathesized to the hydroxide or some other acid-soluble form by heating the sludge with strong caustic.

13. The use of hydrofluoric acid with the nitric acid leachant decreased the solubility of thorium, presumably because acid-insoluble ThF_4 was formed. Without the hydrofluoric acid, the nitric acid leaches removed most of the thorium.
14. Addition of hydrofluoric acid to the nitric acid leachant enhanced the removal of the plutonium from the sludge. Leaching with 5.6 *M* HNO_3 and 1.9 *M* HF effectively removed all (~97%) of the plutonium. The concentration of plutonium in the sludge was low (~1 to 4 μg/g of centrifuged, wet sludge solids). When the sludge was mixed with nitric acid with high concentrations of fluoride ions, the plutonium probably formed soluble PuF_2^{2+} and PuF_3^{+} complexes. This behavior is very concentration dependent. If the concentration of plutonium in the sludge had been high like that of thorium (33.8 mg/gram of centrifuged, wet sludge solids), most of the plutonium in the sludge probably would have precipitated as PuF_3 and PuF_4.[17]
15. Both the HNO_3 alone and the HNO_3 containing HF removed most of the Sr, Co, Eu, Cm, Am, and U.
16. Based upon the initial and the final air-dried weights of samples of centrifuged, wet sludge solids that were leached in nitric acid at ambient temperature, between 63 and 82% of the solids dissolved. The average was about 73%. An average of about 31% of the air-dried sludge was removed by the high-temperature caustic leaches. The concentration of the caustic leachant did not seem to have much of an effect on the total sludge dissolution.
17. Gel formation proved to be one of the biggest problems associated with nitric acid leaching of the W-25 sludge. The gel formation was time dependent, and gels were found in many of the leachates and most of the residues. Delayed gelation occurred in most of the filtered acidic leachates and some of the acidic rinses. In one of the tests in which the sludge was leached for about 19 h with 3.0 *M* HNO_3 (Sect. 4.6.1), a thin gel coating was observed on the wall of the container 3 days after leaching. However, it took about 2 to 3 weeks for the gel to form at the liquid-air interface, thicken, and stabilize. In most of the tests, longer times were required for

the gels to form, thicken, and stabilize. The gels are postulated to be some form of amorphous silica precipitated from silicic acid.

18. Because of the high carbonate content of the sludge (11.5% of the air-dried sludge weight), the addition of nitric acid causes copious evolution of carbon dioxide. One kilogram of centrifuged, wet sludge solids can liberate up to 27.4 L of carbon dioxide.

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