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BASIC AND ACIDIC LEACHING OF SLUDGE FROM MELTON VALLEY STORAGE TANK W-25*

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ABSTRACT

Bench-scale leaching tests were conducted with samples of tank waste sludge from the Melton Valley Storage Tank (MVST) Facility at Oak Ridge National Laboratory (ORNL) to evaluate separation technology processes for use in concentrating the radionuclides and reducing the volume of waste for final disposal.

This paper discusses the hot cell apparatus, the characterization of the sludge, the leaching methodology, and the results obtained from a variety of basic and acidic leaching tests of samples of sludge at ambient temperature. Basic leaching tests were also conducted at 75 and 95°C.

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 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.

A surprising result was that 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 ambient temperature and 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.

Removing ^{137}Cs from the W-25 sludge with nitric acid 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 558 h removed 84% of the ^{137}Cs. The use of caustic leaching prior to HNO_3 leaching, and the use of HF with HNO_3 in acidic leaching, increased the rate of ^{137}Cs dissolution.

Gel formation proved to be one of the biggest problems associated with HNO_3 leaching of the W-25 sludge. Gel formation was time dependent, and gels were found in many of the leachates and most of the residues. Gels did not form in the caustic leachates.

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INTRODUCTION

One of the greatest challenges facing the Department of Energy (DOE) is the remediation of some 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 greatly reduce the amount of waste requiring storage as high-level waste (HLW). The HLW is to be vitrified as glass logs and stored in canisters.

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 volume of storage tank wastes for final disposal. This paper discusses the hot cell apparatus, the characterization of the sludge, and the results obtained from a variety of basic and acidic leaching tests of sludge samples.

Prior to this study, 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 described should prove useful in the treatment of the waste.

Etiology of MVST Sludge

ORNL served as the pilot plant for the Hanford production facility during the 1940s. Consequently, the waste contained in the ORNL storage tanks is similar 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 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 so that they could 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 is of TRU sludge.[6]

There are 34 significant underground storage tanks at ORNL. Of these, 21 are inactive tanks (no longer in use) and 13 are 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 (≥5,800-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 tanks at MVST and BVEST are the only "double-containment" tanks at ORNL that meet U.S. Environmental Protection Agency requirements for underground storage tanks. As was pointed out previously, there are eight 190,000-L storage tanks at the MVST Facility at ORNL. These horizontal stainless steel tanks are 3.7 m in diameter by 18.3 m long and are located underground in reinforced concrete vaults with stainless steel liners. The tanks contain alkaline evaporator concentrates from various past and present research and development 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-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 holding 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.[8] in 1990 and by Keller et al. in 1996.[9]

MVST W-25 SLUDGE CHARACTERISTICS

Tank Sampling

Samples of sludge (~250 mL each) were retrieved from different depths of the sludge layer in tank W-25 at the MVST facility in April 1993. The sludge layer in this tank was about 1.7 m deep. Figure 1 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. The bottom-opening sludge sampler (~51 cm long) was attached to the end of a long stainless steel segmented tube. Samples were collected at successively lower layers (three samples per vertical core), and this process was repeated four times. To obtain a denser composite sludge mixture, the samples at the top of the sludge layer were excluded from the last two sampling sequences because they were very fluid in nature. 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 diameter. Some of the particles were flaky. Acid dissolution and analyses of a sample 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 as follows: 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, 65- to 80-g 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 deep yellow in color, and the wet sludge solids were tan to dark brown. The supernatant portion from tank W-25 was also characterized (Collins et al.[10]).

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. An average total solids content of the sludge liquid samples of 0.285 g/g 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 the 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, sulfates, 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 Sears et al.[8] and Keller et al.[9] 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 using 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. 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 %, respectively, of the centrifuged, wet sludge solids. If the inorganic carbon is assumed to be in the form of carbonate and bicarbonate in the sludge, the 2.5 wt % carbon equates to about 12.5 wt % carbonate. A separate analysis found the concentration of carbonate to be 67.6 mg per gram of centrifuged, wet sludge, or 11.5 wt % carbonate, which is in reasonable agreement with the analysis described above.

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 wt %), ^{235}U (0.57 wt %), ^{234}U (0.01 wt %), and ^{233}U (0.14 wt %). 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, sulfates, hydroxides, and oxides. The component percentages and values 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_4^{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 the anion deficiency.

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. A photograph of the hot cell and some of the apparatus behind the hot cell window is provided in Fig. 2.

As described in the previous section, the sludge was mixed and stored for use in a sealed stainless steel tank. A closed-system Lightning™ mixer, which contained a stainless steel shaft with two high-efficiency, axial-flow, stainless steel impellers, was positioned at a 10° angle to provide more effective mixing. A short, stainless steel, valved tube (1.27-cm ID) for sampling the sludge was located at the bottom of the tank. Before any sludge samples were removed, the sludge in the tank was mixed for ~2 h. The test samples (55 to 85 mL each) were placed in preweighed 250-mL widemouthed centrifuge bottles (made of Nalgene™ polypropylene) with sealing caps.

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 dividing the mass of each sludge sample by the density of the sludge. The density of the sludge was determined by weighing a tared 50-mL volumetric flask that had been filled slowly. 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. The sludge liquid and centrifuged, wet sludge solid fractions were then weighed separately. 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 volummetric 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 (Fig. 3). 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 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 such a way that direct contact of the bottle with the steel vessel was prevented. 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 a rate of ~8 cycles/min.

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

RESULTS AND DISCUSSION

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

Samples of centrifuged, wet sludge solids (35.8 to 44.0 g) from MVST W-25 were leached with various combinations of NaOH, HNO_3, and HF at ambient temperature. Table 3 summarizes and compares the cumulative percentages of radionuclides, plutonium, thorium, and uranium 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 (5 h), 0.16 *M* NaOH (22 h), 0.5 *M* HNO_3 (6 h), 3.0 *M* HNO_3 (70 h), 3.0 *M* HNO_3 (50 h), and 6.0 *M* HNO_3 (432 h); *B* represents the test series in which centrifuged, wet sludge solids were sequentially leached with 3.1 *M* NaOH (144 h), 6.4 *M* NaOH (144 h), and 5.7 *M* HNO_3 (117 h); *C* represents the test in which centrifuged, wet sludge solids were leached with 6.0 *M* HNO_3 (117 h) 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 (117 h); *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 (234 h); and *F* represents the test in which the sludge was leached with 3.2 *M* NaOH (4 h) and 6.3 *M* NaOH (4 h) at 95°C and then leached with 6.0 *M* HNO_3 (185 h) 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 of these tests, 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 prior to leaching with HNO_3, and in tests *D* and *E* the acid leach also contained HF. 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 U removed from the sludge solids in all the tests indicated almost total dissolution of these components. The use of HNO_3 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 HNO_3 worked as well as using HF with HNO_3.

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; 76% 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 HNO_3, and the total time the sludge solids were mixed with HNO_3 leaches was 4.8 times longer (558 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 3 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 HNO_3, by adding HF to the HNO_3 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 HNO_3. 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 4 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 the leach behavior of 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 4. In test *C*, in which only HNO_3 was used as a leachant, the nickel, silicon, and sulfate 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 sulfate were removed by the caustic leaching steps prior to leaching the sludge solids with the HNO_3. In tests *C*, *D*, and *E*, only 26, 34, and 32% of the sulfate 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.

Gel Formation in Acidic Leaches

One phenomenon that was encountered in tests *A*, *B*, *C*, *D*, *E*, and *F* was gel formation during or after acidic leaching of the sludge solids. Gel formation in one of the leachates can be seen in in Fig. 5. 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. 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 examined several months after leaching; the residue also contained lots of gel. No noticeable gel formation was observed in the leachates of tests *C* and *E*. However, gel formation was observed in test *D* about 29 days after leaching; a clear gel film appeared in the bottom of the container.

Gels were also observed in the leachates in several of the other tests involving acid leaching. In a test to determine the concentration of carbonate, 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 5 gives the free-water 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-water content varied from 61 to 90%. The free-water 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. 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 concentations 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 of >100 mg/L (1.7×10^{-3} *M*) can polymerize, form colloidal particles, and gel.[11,12] In salt solutions, a "salting-out" effect results in 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[11]

$$[Si_nO_{2n-(nx/2)}(OH)_{nx}] + mSi(OH)_4 = [Si_{n+m}O_{2n-(nx/2+2m(2-p)}(OH)_{nx+4(m-p)}] + 2pmH_2O,$$

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.

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 residues at the completion of the leaching tests. The results are provided in Table 6, as well as the percentage of ^{137}Cs removed from the

solids in each test. The weight of the initial air-dried solids was calculated based upon reference samples. 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 HNO_3 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 HNO_3 alone, 63% of the solids was dissolved, but only 22% of the ^{137}Cs was removed. In test *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 ThF_4 by the reaction of HF with the thorium added some mass to the final weight of the air-dried solids.

High-Temperature Caustic Leaching of W-25 Sludge

Table 7 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 with 0.16 *M* NaOH (22 h) 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 (see test B of Table 3). 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 *M* NaOH for 144 h and then with 6.4 *M* NaOH for 144h.

Caustic leaching at 95°C removed 77.7 to 87.1% of the K, 73.0 to 91% of the Na, 9.7 to 26% of the Al, 11.5 to 15.8% of the Cr, 12.8 to 63.8% of the Zn, 1.3 to 10.1% of the Si, 89.9 to 113% of the NO_3^-, 38.9 to 63.4% of the Cl^-, and 23.8 to 31.1% 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; 31% was removed by the 8-h, 95°C test using 3.2 *M* NaOH; and 31% was removed by the 4.0-h, 95°C test using 1.0 *M* NaOH.

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 HNO_3. Leaching the sludge with mild or strong caustic at ambient temperature before leaching it with HNO_3 had no effect on the leachability of the plutonium. However, 93% 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.

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_2^{2-}, OH^-, and O^{2-}. The organic carbon content was about 3.0 ± 1.0%, and 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 greatly reduced 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 HNO_3 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, 3.0, 3.0, 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 HNO_3 are needed to adust 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 consumes about 5 mol of the acid.
8. Pretreatment of the centrifuged, wet sludge solids with strong caustic enhanced the removal of ^{137}Cs with HNO_3 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 temperature. 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 HNO_3 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 HF 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 HNO_3 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 HNO_3 leachant decreased the solubility of thorium, presumably because acid-insoluble ThF_4 was formed. Without the hydrofluoric acid, the HNO_3 leaches removed most of the thorium.
14. Addition of hydrofluoric acid to the HNO_3 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 HNO_3 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.[13]

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 HNO_3 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 HNO_3 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, 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 HNO_3 causes copious evolution of CO_2. One kilogram of centrifuged, wet sludge solids can liberate up to 27.4 L of CO_2.

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TABLE I. 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 $^{233}U = 0.14$).

TABLE 3. COMPARISON OF PERCENTAGES OF RADIONUCLIDES REMOVED BY LEACHING W-25 SLUDGE AT AMBIENT TEMPERATURE

Radionuclide	Cumulative Percentage of Radionuclides 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
^{90}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 (5 h), 0.16 *M* NaOH (22 h), 0.5 *M* HNO_3 (6 h), 3 *M* HNO_3 (70 h), 3 *M* HNO_3 (50 h), and 6 *M* HNO_3 (432 h).

[b]Sludge solids sequentially leached with 3.1 *M* NaOH (144 h), 6.4 *M* NaOH (144 h), and 5.7 *M* HNO_3 (117 h).

[c]Sludge solids leached with 6.0 *M* HNO_3 (117 h).

[d]Sludge solids leached with a 5.8 *M* HNO_3 and 1.0 *M* HF solution (117 h).

[e]Sludge solids leached with a 5.6 *M* HNO_3 and 1.9 *M* HF solution (234 h).

[f]Sludge solids sequentially leached with 3.2 *M* NaOH (4 h), 6.3 *M* NaOH (4 h) at 95°C and then with 6.0 *M* HNO_3 (185 h) at ambient temperature.

TABLE 4. CUMULATIVE PERCENTAGES OF METALS AND ANIONS REMOVED BY LEACHING OF W-25 SLUDGE AT AMBIENT TEMPERATURE

Component	Cumulative percentages removed				
	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_4^{2-}	119	26	34	32	86

[a]Sludge solids sequentially leached with 3.1 *M* NaOH (144 h), 6.4 *M* NaOH (144 h), and 5.7 *M* HNO_3 (117 h).
[b]Sludge solids leached with 6.0 *M* HNO_3 (117 h).
[c]Sludge solids leached with a 5.8 *M* HNO_3 and 1.0 *M* HF solution (117 h).
[d]Sludge solids leached with a 5.6 *M* HNO_3 and 1.9 *M* HF solution (234 h).
[e]Sludge solids sequentially leached at 95°C with 3.2 *M* NaOH (4 h), 6.3 *M* NaOH (4 h), and then with 6.0 *M* HNO_3 (185 h) at ambient temperature.

TABLE 5. MOISTURE CONTENT OF CENTRIFUGED, WET SLUDGE 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 (5 h), 0.16 *M* NaOH (22 h) and 0.5 *M* HNO_3 (6 h), 3 *M* HNO_3 (70 h), 3 *M* HNO_3 (50 h) and 6 *M* HNO_3 (432 h).

[c]Sludge solids sequentially leached with 3.1 *M* NaOH (144 h), 6.4 *M* NaOH (144 h), and 5.7 *M* HNO_3 (117 h).

[d]Sludge solids leached with 6.0 *M* HNO_3 (117 h).

[e]Sludge solids leached with a 5.8 *M* HNO_3 and 1.0 *M* HF solution (117 h).

[f]Sludge solids leached with a 5.6 *M* HNO_3 and 1.9 *M* HF solution (234 h).

[g]Sludge solids sequentially leached at 95°C with 3.2 *M* NaOH (4 h), 6.3 *M* NaOH (4 h), and then with 6.0 *M* HNO_3 (185 h) at ambient temperature.

TABLE 6. CESIUM REMOVAL AS A FUNCTION OF DISSOLUTION OF SLUDGE SOLIDS[a]

Leach treatment	Air-dried solids		Dissolved solids (%)	^{137}Cs removed (%)
	Before leaching (g)	After leaching (g)		
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 (5 h), 0.16 *M* NaOH (22 h), 0.5 *M* HNO_3 (6 h), 3 *M* HNO_3 (70 h), 3 *M* HNO_3 (50 h), and 6 *M* HNO_3 (432 h).

[c]Sludge solids sequentially leached with 3.1 *M* NaOH (144 h), 6.4 *M* NaOH (144 h), and 5.7 *M* HNO_3 (117 h).

[d]Sludge solids leached with 6.0 *M* HNO_3 (117 h).

[e]Sludge solids leached with a 5.8 *M* HNO_3 and 1.0 *M* HF solution (117 h).

[f]Sludge solids leached with a 5.6 *M* HNO_3 and 1.9 *M* HF solution (234 h).

[g]Sludge solids sequentially leached at 95°C with 3.2 *M* NaOH (4 h), 6.3 *M* NaOH (4 h), and then with 6.0 *M* HNO_3 (185 h) at ambient temperature.

TABLE 7. SUMMARY OF CAUSTIC LEACHING OF W-25 SLUDGE

Component	Percentage removed					
	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	<1	0.1
^{90}Sr	0.03	0.05	0.08	0.27	0.02	
Metals						
Al	26.0	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	<0.01
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		11.1		<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	<0.01
U	0.08	0.2	<0.3	1.0	0.26	0.3
Zn	12.8	39.3	43.4	63.8	27.2	1.4
Anions						
Cl^-	57.2	50.0	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	31.1	29.1	26.0

[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.

LIST OF FIGURES

Fig. 1. Operators removing sludge sample from MVST W-25.

Fig. 2. Sludge leaching apparatus as viewed through the hot cell window.

Fir. 3. Apparatus used to mix and heat sludge with caustic at elevated temperatures.

Fig. 4. Percentages of Cs, Pu, Th, U, and Cm removed from MVST W-25 sludge as a function of leaching method.

Fig. 5. Example of gel formation in acidic leachate.

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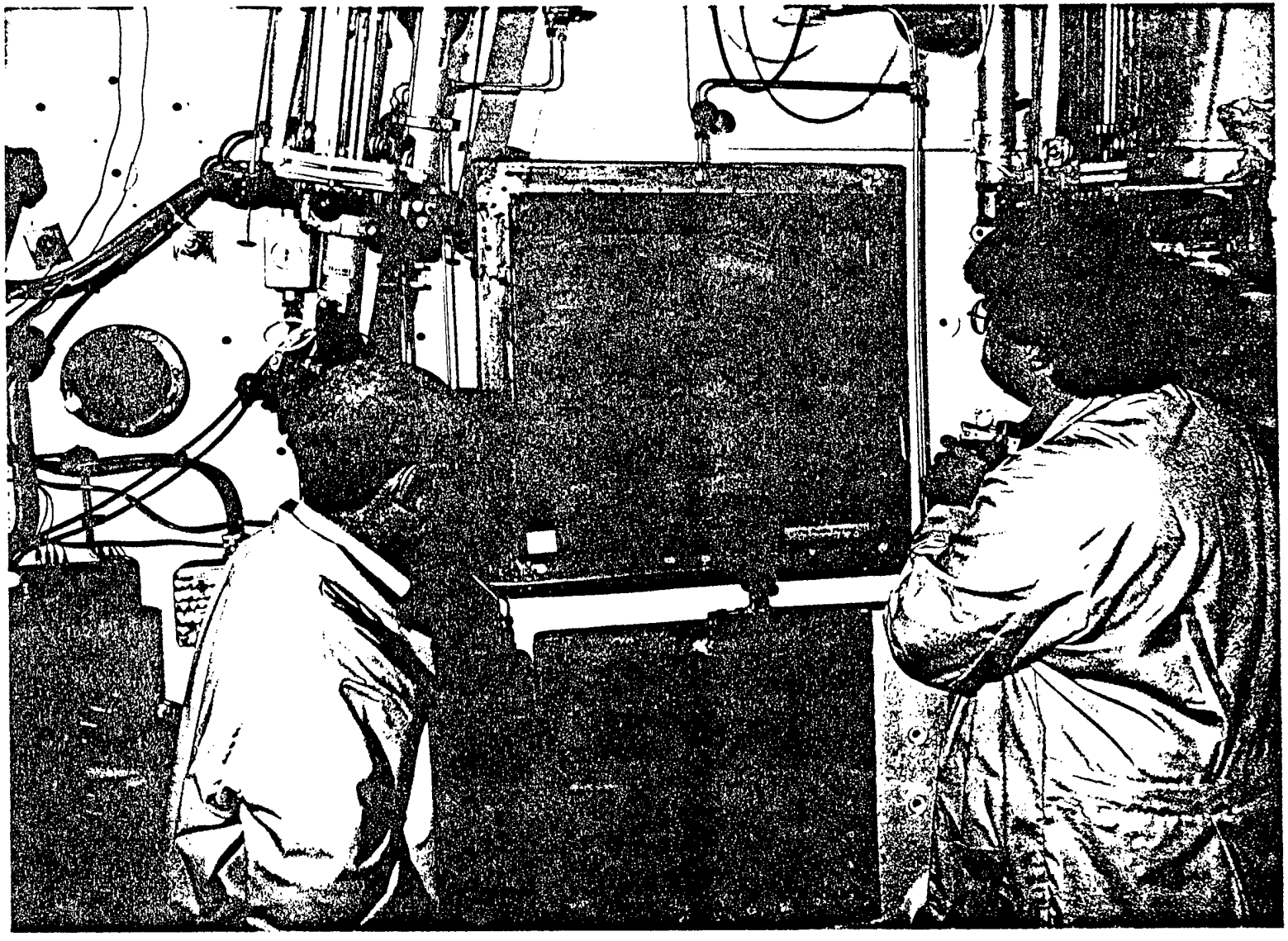

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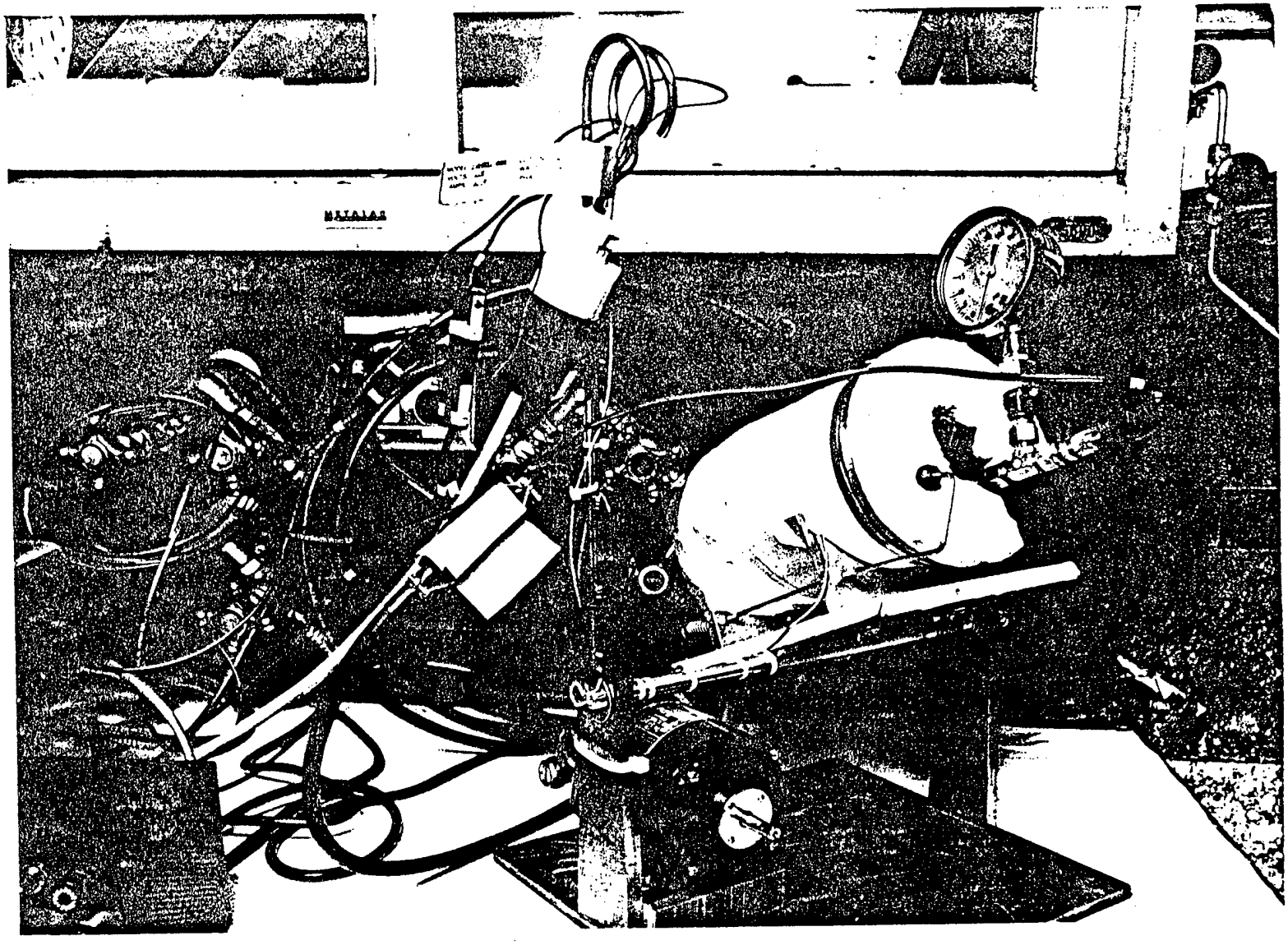

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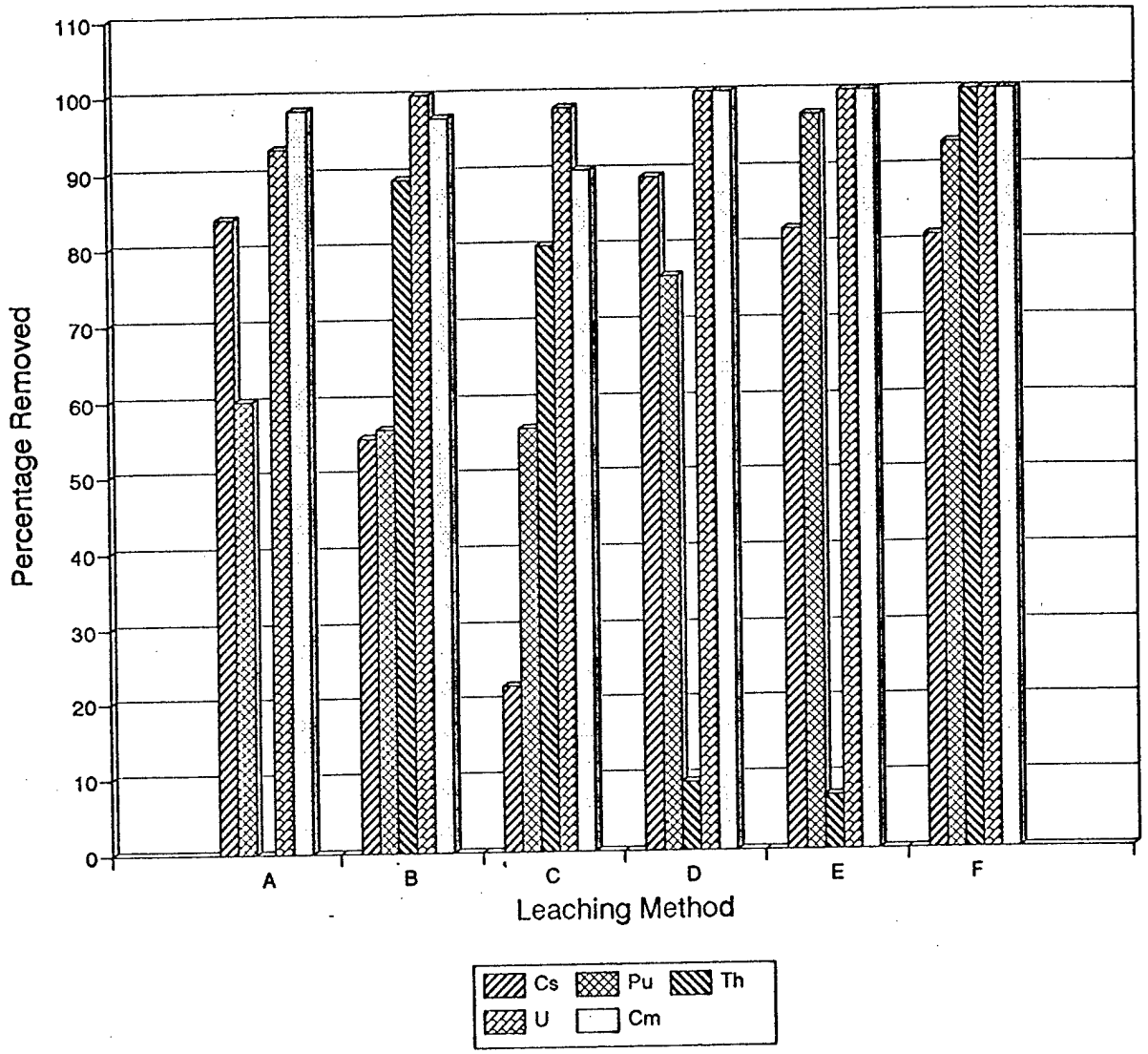

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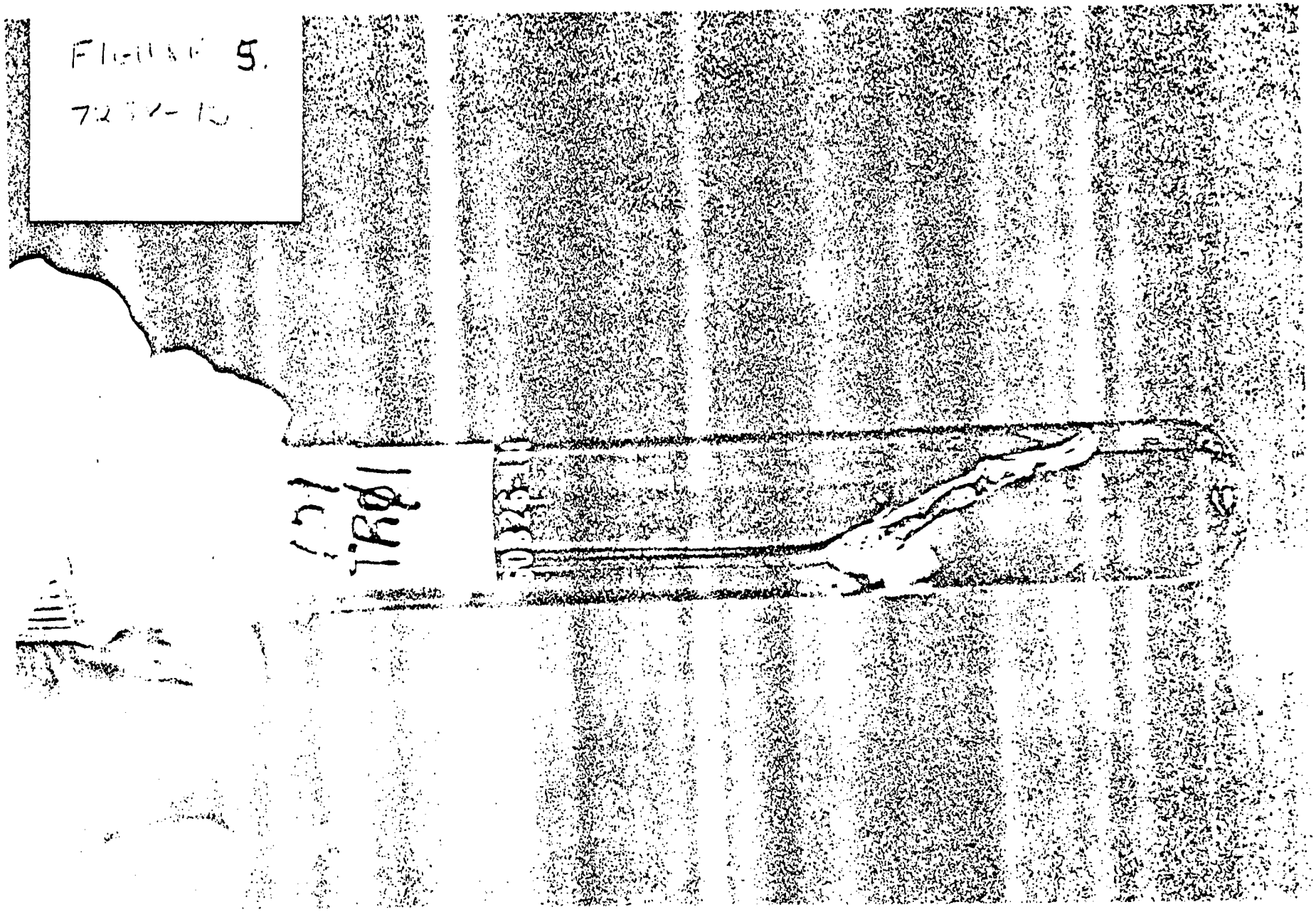

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