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R. T. Jubin, D. D. Lee, E. C. Beahm, J. L. Collins, D. J. Davidson, B. Z. Egan,
A. J. Mattus and J. F. Walker, Jr.
Chemical Technology Division
Oak Ridge National Laboratory†
Oak Ridge, Tennessee 37831-6223

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TANK WASTE TREATMENT R&D ACTIVITIES AT OAK RIDGE NATIONAL LABORATORY

R. T. Jubin, D. D. Lee,
E. C. Beahm, J. L. Collins, D. J. Davidson, B. Z. Egan,
A. J. Mattus, R. D. Spence, and J. F. Walker
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee

Abstract

Oak Ridge National Laboratory (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, but it is typically 10 to 100 times less radioactive. It is estimated that nearly 4.9 million liters of legacy waste is stored on the site of ORNL. Of this volume about one-fifth is transuranic sludges. The remainder of the waste volume is classified as low-level waste. The waste contains approximately 130,000 Ci, composed primarily of ^{137}Cs , ^{90}Sr , and small amounts of other fission products. The wastes were originally acidic in nature but were neutralized using Na_2CO_3 , NaOH , or CaO to allow their storage in tanks constructed of carbon steel or concrete (Gunitite). In addition to the legacy waste, about 57,000 L of concentrated waste is generated annually, which contains about 13,000 Ci, consisting primarily of ^{137}Cs , ^{90}Sr , and small amounts of other fission products (TFA 1996). As part of the U.S. Department of Energy's (DOE's) Environmental Management Tanks Focus Area and Efficient Separations and Processing programs, a number of tasks are under way at ORNL to address the wastes currently stored in tanks across the DOE complex. This paper summarizes the efforts in three of these tasks: (1) the treatment of the tank supernatant to remove Cs, Tc, and Sr; (2) the leaching or washing of the sludges to reduce the volume of waste to be vitrified; and (3) the immobilization of the sludges.

Nature of the Waste at Oak Ridge National Laboratory

To begin this discussion it is important to point out that the tank wastes at Oak Ridge National Laboratory (ORNL) are classified as either low-level or transuranic waste based on the definitions for radioactive waste in the United States. High-level waste (HLW) is defined as "highly radioactive material (containing fission products, traces of uranium and plutonium, and other radioactive elements) that results from the chemical reprocessing of nuclear fuels used in nuclear reactors, and the used nuclear fuel itself, if it is not reprocessed" (TFA, 1996). Transuranic waste (TRU waste) is defined as "waste contaminated with alpha-emitting transuranic elements . . . with half-lives greater than 20 years and concentrations of more than one ten millionth of a curie per gram of waste" (TFA, 1996). Low-level waste (LLW) is defined as "waste containing radioactive elements that is not classified as high-level waste, transuranic, spent nuclear fuel, or a specified type of by-product material. Typically the radionuclides contained in this waste are short-lived or the waste has low levels of radioactivity" (TFA, 1996). Because ORNL is a research facility, not a production facility, the wastes are classified as LLW or TRU. Since waste streams classified as HLW are the result of the processes that generate them, LLW at ORNL may contain as much radioactivity as HLW at other sites.

Oak Ridge has radioactive waste sludges stored in four separate tank farms consisting of 26 tanks. These tank farms are referred to as the Gunit and Associated Tanks (GAAT), Old Hydrofracture Facility (OHF), Melton Valley Storage Tanks (MVST), and Bethel Valley Evaporator Service Tanks (BVEST).

Table I provides an abbreviated compositional analysis of selected tanks from each of the four tank farms at ORNL. Note that the columns listing maximum and minimum concentrations on the right side of this table do not correspond to any given tank but rather to the range observed for each listed component across all tanks: that is, a given tank could contain the minimum amount of one component while at the same time contain the maximum amount of another. Extensive supporting data can be found in Keller et al. (1996, 1997a, 1997b), MACTEC (1996), and Bayne, et al. (1996). Based on this table, it is clear that while there are areas of similarity between the tank farms, significant variations also exist. Of the eight Resource Conservation and Recovery Act (RCRA) metals, mercury and lead are the two most significant and are important in all ORNL tank farms. Chromium is important for all but the MVST. Nickel is close to the threshold for all of the tanks (Spence, 1996). The major matrix components for each tank farm are shown below.

Tank farm	Cation	Anion	Nuclide
GAAT	Na, Al, U, Ca, Fe	Nitrate	⁹⁰ Sr, ¹³⁷ Cs
BVEST	Na, U, Ca, K, Th, Mg, P	Nitrate, inorganic carbon, total organic carbon, Sulfate	⁹⁰ Sr, ⁶⁰ Co, ¹³⁷ Cs, ¹⁵² Eu, ¹⁵⁴ Eu, ¹⁵⁵ Eu, ²⁴⁴ Cm, ⁹⁵ Zr
MVST	Na, Ca, K, U, Mg, Al	inorganic carbon	⁹⁰ Sr, ¹³⁷ Cs, ¹⁵² Eu
OHF	Th, Ca, Al, P, Na, Fe, Si	inorganic carbon, total organic carbon	⁶⁰ Co, ⁹⁰ Sr, ¹³⁷ Cs, ¹⁵² Eu, ²⁴⁴ Cm

(Spence, 1996; Bayne, 1996)

Supernatant Treatment Studies

Batch Studies

The scope of this technology includes the separation of the solid and liquid supernatant portions of ORNL MVST waste in a hot cell and treatment of the supernatant to separate and remove the radionuclides. The supernatant is utilized in testing various sorbents for removing Cs, Sr, and Tc from the highly alkaline saline solution. Small-column tests are made on selected sorbents to verify the batch data and to obtain additional data for process design.

Supernatant samples have been retrieved from MVST W-25, W-27, and W-29 and characterized. These supernatants have many similarities to supernatants in tanks at other U.S. Department of Energy (DOE) sites. While many sorbents have been proposed for waste treatment, most have not been tested on actual waste supernatant solutions. Approximately 1 L of supernatant from MVST W-25 was prepared for batch tests by filtering it through 0.45 μ nylon filters to remove the particulates. The specific gravity and the total solids content of the supernatant were 1.232 g/mL and 0.338 g/mL, respectively. The pH was 12.6. About 94% of the activity in the supernatant is contributed by ^{137}Cs . Other radionuclides include ^{134}Cs , ^{60}Co , and ^{90}Sr . The major cations in the supernatant are sodium (3.9 M) and potassium (0.36 M) and the major anions are nitrate (3.8 M) and chloride (0.1 M). Smaller amounts of Al, Cr, Zn, and Ca are present.

The distribution coefficients and percentage removal of cesium from MVST W-25 supernatant using several ion-exchange materials have been measured. The ion exchangers tested include resorcinol/formaldehyde resin (RF resin from Boulder Scientific); crystalline sodium silicotitanate (CST, from Sandia National Laboratories); Duolite CS-100 (Rohm and Haas); granular and powdered potassium cobalt hexacyanoferrate, and composite microspheres containing sodium and potassium cobalt hexacyanoferrates in hydrous titanium oxide and phosphate (prepared at ORNL). In typical experiments, 10 mL of supernatant was mixed with 50 mg of sorbent for periods ranging from 15 min to 144 h. The cesium distribution coefficients ranged from 34 to 44 mL/g for CS-100; from 138 to 764 mL/g for the RF; from 451 to 958 mL/g for the CST; and from 26,000 to 46,000 mL/g for granular potassium cobalt hexacyanoferrate. In loading tests, the cesium sorption by the different exchangers was about 8 g/kg for RF resin, 15 g/kg for CST, and 18 g/kg for granular potassium cobalt hexacyanoferrate. These results were used in evaluating and selecting sorbents for small-column tests in a hot cell for removing cesium from ORNL MVST supernatant and supported the design and operation of the cesium removal demonstration described below.

Several sorbents, including iron filings, Reillex HPQ, Reillex 402, Amberlite IRA-904, and Amberlite IRA-40 were tested in batch tests for removing technetium from MVST W-29 supernatant. A supernatant-to-exchanger ratio of 200/1 and equilibration times of 2 and 24 h were used. All of the anion exchangers removed the pertechnetate anion reasonably well. The hydroxide forms of the exchangers appeared to be superior to the nitrate forms. Overall, the hydroxide form of Reillex 402 gave the most promising results.

A small-column test used Reillex HPQ anion-exchange resin to measure the removal of pertechnetate from ORNL MVST W-27 supernatant (Figure 1). Because of the relatively low technetium content of the supernatant, ammonium pertechnetate was added to the feed to adjust the technetium concentration to about 3.0 mg/L. The preconditioned resin bed was 6.3 cm in height, providing a packed bed of about 10.4 cm³. Supernatant solution was passed through the column at a rate of about 6 bed volumes (BV) per hour. Selected eluate fractions were analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS) to determine the technetium concentration. A 50% technetium breakthrough occurred after about 45 column volumes. The

technetium was stripped from the column using an eluent solution containing 0.017 M stannous chloride, 0.1 M ethylenediamine, and 0.075 M sodium hydroxide.

Several ion exchangers have been tested to determine the removal of strontium from MVST supernatant. The exchangers tested included Amberlite IRC-718, sodium titanate, CST, RF resin, hydrous titanium oxide/polyacrylonitrile (TiO-PAN), sodium titanate/polyacrylonitrile (NaTiO-PAN), titanium monohydrogen phosphate microspheres, Duolite C-467, and Chelex 100. The inorganic ion exchangers outperformed the organic resins in removing the strontium, with the fine powders of sodium titanate and CST giving the best results. Of the organic resins tested, Duolite C-467 gave the most favorable results overall.

Hot Cell Cs Recovery Studies

Cesium, strontium, and technetium radionuclides are a small fraction by mass of the mainly sodium and potassium salts in storage tank supernatants at Hanford, Oak Ridge, Savannah River, and Idaho that DOE must remediate. Nuclide-removal technologies have been previously proposed and tested in small batch and column tests using simulated and actual supernatants. These technologies are now being tested in larger-scale flowing systems to obtain engineering data using actual tank waste supernatants.

The experimental equipment used in these hot cell tests is shown in the flow diagram in Figure 2. It provides a test bed for investigating new technologies, such as 3M's WEB and AEA Technology's electro dialysis-ion exchange (EIX) electrochemical elution system, and complements the comprehensive supernatant task by using larger engineering-scale, continuous equipment to verify and expand the batch studies. Data obtained with this equipment was used in the selection of the sorbent material for the pilot-scale Cesium Removal Demonstration (CsRD) at Oak Ridge. As the CsRD was operated, parallel tests were conducted using this equipment to identify any potential operational difficulties, to provide an evaluation and comparison of the performance, and to provide loaded sorbent material for evaluation with regard to waste acceptance criteria.

A 60-L supernatant sample was retrieved from the MVST tank W-27 and characterized. It has many similarities with supernatants in tanks at other DOE sites and provides a common basis to test different sorbents to remove cesium from actual radioactive storage tank supernatant. The sorbents are tested using a 1.5- by 15-cm column containing about 10–12 cm³ of sorbent at flow rates of 3–9 column volumes (CV) per hour. Other sorbent-containing apparatus, such as the 3M WEB, can also be easily connected to the system. The breakthrough of cesium from the sorbent is followed by an on-line gamma spectrometer, and the effluent is also fractionated for chemical and radiological analyses. Sorbents that can be eluted and regenerated are cycled in place through loading, elution, and regeneration. Sorbents can also be analyzed by removal from the cell and counting on another gamma spectrometer to determine the total loading and/or the efficiency of elution.

The MVST supernatants used are shown in Table 2; some were prepared by adjusting the "as-received" material to meet specific test conditions. These included tests to simulate conditions at other DOE sites. The average ¹³⁷Cs level was about 3–4 × 10⁵ Bq/mL.

Six different sorbents and resins were tested in continuous loading tests using W-27 supernatant at pH 13.3 and 7 × 10⁻⁶ M cesium and/or pH 14.0 and 7.5 × 10⁻⁵ M cesium. Included were (1) two different lots of RF resin made by Boulder Scientific; (2) IBC Advanced Technologies SuperLig[®] 644C, batch 3695-GM1121; (3) Rohm & Haas CS-100 resin; (4) 3M SLIG WWL 644 WEB with SuperLig[®] 644 imbedded; (5) CSTs developed by Sandia National Laboratories/Texas A&M and supplied by UOP as IONSIV[®] IE-911;

and (6) Eichrom, Inc., granular potassium cobalt hexacyanoferrate (KCoFeC), lot JW-40-021. These test results are summarized in Figure 3 and discussed below.

3M SuperLig 644 WWL WEB material was contained in a Gelman 25-mm in-line stainless steel filter holder with filter volumes (FV) of 1.29 mL. The apparatus was loaded at 1 mL/min (49.78 FV/h) in an upflow mode through one cycle of loading, elution, and regeneration. During the loading phase of this test, the effluent was brown in color for the first several FV after the supernatant feed began. Loading was 65 FV to 50% breakthrough. The filter was eluted with 0.5 M HNO₃ and regenerated with caustic solution.

Eichrom KCoFeC granular sorbent (7.272 g) was loaded at 9 CV/h using W-27 supernatant at pH 13.32. Normal column operation with low cesium breakthrough continued for over 250 CV, but then the sorbent began to disintegrate and the cesium level in the effluent rose rapidly and could not be removed using 0.2- μ m filters.

SuperLig[®] 644C was run at 6 CV/h using 3.779 g of dry resin (11.2-mL volume) and W-27 supernatant at pH 13.3. During the loading phase, considerable discoloration of the effluent was noted for the initial few CV of feed through the column. After the breakthrough had reached 50% at about 100 CV, the loaded cesium was eluted with 0.5 M HNO₃ at 3 CV/h. Colored liquid also accompanied the first few CV of acid eluent. The elution curve was very sharp and was 95% complete in 6 CV. The resin has a very low density and could be compressed easily (30% or greater); therefore, calculations were adjusted for the smaller column volume due to compression, giving a revised 50% breakthrough of about 138 CV.

SuperLig[®] 644C was loaded with pH 14.0 W-27 supernatant at 3.5 CV/h. Elution used 0.5 M HNO₃ and regeneration used 2 M NaOH. The first cycle had a total cesium concentration of 1.1×10^{-5} M in the feed, and the following three had 7.5×10^{-5} M cesium. The bed volume changed by up to 50% when switching from feed to deionized water to acid and then caustic and feed. The first loading had 50% breakthrough at about 167 CV. Elution was complete in about 6 CV of 0.5 M HNO₃. In the next three loadings with high-cesium supernatant feed, 50% cesium breakthroughs occurred at 77, 65, and 50 CV, respectively. The second and third loading curves were approximately parallel to the first curve, while the fourth was completely different. Color was seen in the effluent from the bed at the start of each loading and regeneration.

RF resin was prepared and used in three tests with W-27 supernatant at pH 13.3. At 7 CV/h, 50% breakthrough of cesium occurred at 45 CV. At 2.9 CV/h, the 50% breakthrough occurred at 36 CV and the shape of the curve was similar to, but steeper than, that in the 7-CV/h RF run. In the third test, RF resin was loaded, eluted, regenerated, and then rinsed five times at 6.0 CV/h. For the first 3-4 CV of feed or regenerant through the bed, brown-colored liquid exited the bed. The 50% breakthroughs were consistent at about 45 to 50 CV, but some operational problems began to develop during the last two loadings. Elution was completed with 0.5 M HNO₃ at about 3 CV/h, and the resin volume shrank from about 10 cm³ to about 5.5 cm³. Approximately 9-12 CV was required for complete cesium elution.

Additional RF was obtained from the ORNL Radiochemical Engineering Development Center and loaded with pH 14.0 W-27 supernatant feed containing 1×10^{-5} M cesium at 3.5 CV/h to 70% breakthrough. Cesium initially broke through at 7 CV, and the curve was then very steep to 50% at about 18 CV. The elution was with 0.5 M HNO₃.

A third RF obtained from AEA Technology (BSC 187) was used with the pH 13.3 W-27 supernatant at a feed rate of 6 CV/h. The loading was continued through 75 CV, with the breakthrough reaching only

about 1.1–1.2%. The loading curve showed that the initial breakthrough did not occur until 15 CV, and the curve was then very shallow to 1% at about 65 CV. Brown color was also seen in the column effluent.

CST from UOP, IONSIV IE-911 Lot 07398-38B, was first tested at 3 CV/h in downflow using pH 13.3 W-27 supernatant for a total of over 435 CV. No problems that could be attributed to the ion exchanger occurred during the continuous run of more than 6 days (24 h/day). The 1% cesium breakthrough came after 100 CV, 10% breakthrough at about 190 CV, and 50% breakthrough at 350 CV. At 6-CV/h loading, the breakthrough of cesium was very close (340 CV) to that obtained at 3 CV/h. No difficulties with the system were observed during either loading.

CST-38B was next loaded to greater than 55% breakthrough at 6 CV/h with W-27 supernatant at pH 14.0 and a cesium concentration of $7.48 \times 10^{-5} M$. The loading curve was parallel to the previous 6-CV/h curve, as expected, with the 50% breakthrough occurring at 272 CV, the 10% breakthrough at 122 CV, and the 1% breakthrough at 55 CV. Again, no difficulties were observed during operation.

For the CsRD qualification of CST with W-29 supernatant, the CST was adjusted to pH 12.6 and then fluidized to remove fines using a simulant containing 4.5 M NaNO₃ and 0.1 M NaOH. The loading was continued at 6 CV/h for 560 CV with a minor upset after 50 CV but was completed uneventfully during the next 500 CV. Data for the different cesium analyses gave 50% breakthroughs of 504–546 CV. The analyses showed that the CST loaded Ba, Ca, Cs, Sr, U, and Zn, but not Hg, Cd, Tc, Cr, Ru, Rb, Ni, Na, K, and Al. The higher breakthrough was due to lower total cesium, lower nitrate, and lower pH in the W-29 supernatant. The apparent breakthroughs for the U, Sr, and Pb were 433, 1164, and 3327 CV, respectively. Sorbent from the loaded column was subjected to a modified Toxic Characteristic Leaching Procedure (TCLP) process and showed no unacceptable values.

Comparison of the column data for all sorbents tested with the W-27 feed with the data obtained using simulant and actual supernatants at other sites showed good agreement and predictability from batch equilibrium to column testing — except for the RF resin, which varied greatly from batch to batch. For comparisons to be valid, however, it is critical that one take into account not only cesium concentrations but also the pH, the other anions and cations in the supernatant, and the ratios of other cations to the cesium concentration.

These comparative evaluations using actual tank supernatant provided critical data for the selection of the sorbent for the CsRD, as well as data applicable to other DOE sites. This data included not only the cesium-removal capacity of the materials tested but also the operational characteristics during continuous-loading experiments. The organic sorbents RF, SuperLig[®], and 3M SLIG 644 WWL WEB materials all produced colored products upon the first introduction of feed or during regeneration after elution. These sorbents also exhibited volume changes during various stages of the preparation, loading, elution, and regeneration. The high pH of the feed supernatant to the Eichrom KCoFeC resulted in its chemical breakdown and loss in the column effluent. No operational problems were noted for the CSTs.

Cesium Removal Demonstration (CsRD)

The CsRD project was designed to treat approximately 100,000 L of high-salt supernatant stored in the MVST at ORNL. This engineering-scale process employs a modular, mobile ion-exchange system utilizing modular shielding and existing facilities at the tank site for off-gas treatment, secondary containment, and utilities. Figure 4 provides an isometric view of the modular unit.

The CST ion-exchange material was selected based on its effectiveness in batch and small-scale column tests previously described using both simulants and actual waste supernatants from the MVST. The operational phase of the CsRD using the CST sorbent has been completed. A total of four runs were made. The first was a single-column, minimal-loading run designed to test the system and procedures prior to the full-loading runs. This run was completed in September 1996. A total of ~23 Ci of ^{137}Cs was loaded onto 38 L of sorbent. The sorbent from this run was shipped to the Savannah River Site for use in a vitrification demonstration. The vitrified material will be used to verify compatibility with waste acceptance criteria and eventual disposal at the Nevada Test Site. The second run also consisted of a single 38-L column of sorbent operated at 3 BV/h. Approximately 18,000 L of MVST supernatant was processed prior to 50% breakthrough of ^{137}Cs and ~154 Ci of ^{137}Cs was loaded. The third run consisted of two 38-L columns of sorbent operated in series at a flow rate of 6 BV/h. Approximately 39,000 L of supernatant was processed, with the first and second columns reaching ~80% and ~47% breakthrough of ^{137}Cs , respectively. The first column loaded a total of ~222 Ci of ^{137}Cs , and the second column loaded ~112 Ci of ^{137}Cs . The fourth run was a three-column run, with each column containing 38 L of sorbent. The system was initially started with two columns in series. Column 1 reached 55% breakthrough of ^{137}Cs after processing ~28,000 L and loading ~253 Ci of ^{137}Cs . Column 1 was then removed from service, column 2 was moved into the first column position, and a column (column 3) with new sorbent was placed in the second column position. Preliminary analyses indicate that column 2 loaded ~266 Ci of ^{137}Cs and column 3 loaded ~112 Ci of ^{137}Cs for a total of ~631 Ci ^{137}Cs removed during run 4.

During the entire operational period, ~116,000 L of supernatant was processed and ~1,142 Ci of ^{137}Cs was removed from that supernatant and loaded onto 70 gal of sorbent. This operation successfully completed DOE milestones to complete processing of up to 95,000 L (25,000 gal) of MVST supernatant and to remove at least 520 Ci of radioactive cesium. The sorbent from the last three runs will be stored in a dry state at the ORNL solid waste storage area until it can be shipped off-site for permanent disposal. Laboratory analysis (TCLP) of CST, loaded in ORNL hot cells under the same conditions used for each CsRD run, has shown that the loaded sorbent is nonhazardous and that no further stabilization is necessary.

In comparing the breakthrough curves from the full-scale CsRD and the bench tests, it was found that the data on cesium breakthrough agreed very well. Fifty percent breakthrough for the full-scale system occurred at approximately 500 CV processed. As noted previously, the hot cell tests using W-29 waste also resulted in a 50% cesium breakthrough at ~500 CV.

Sludge Treatment Studies

Sludge Washing/Leaching

Any treatment of waste sludge will likely begin with washing, followed by basic and/or acidic leaching. Basic and acidic leaching tests were conducted with samples of sludge taken from storage tank W-25 at the MVST facility at ORNL. The tests evaluated separation technologies for use in sludge processing to concentrate the radionuclides and reduce the volumes of storage tank waste for final disposal. The studies reported here include (1) characterization of the sludge, (2) caustic leaching of sludge samples at ambient temperature and at 95°C, and (3) acid leaching of sludge samples at ambient temperature.

Samples of centrifuged wet sludge that had been air dried were analyzed to determine the concentrations of radionuclides, actinides, nonradioactive cations, and anions. The major gamma- and beta-emitting radionuclides were ^{137}Cs (37.8 $\mu\text{Ci/g}$), ^{60}Co (4.6 $\mu\text{Ci/g}$), ^{154}Eu (3.8 $\mu\text{Ci/g}$), and ^{90}Sr (514 $\mu\text{Ci/g}$). The concentrations of the alpha-emitting actinides were 0.7 $\mu\text{Ci/g}$ for ^{241}Am , 8.9 $\mu\text{Ci/g}$ for ^{244}Cm , and 1.32 $\mu\text{Ci/g}$ for plutonium. The major nonradioactive cations (≥ 2 mg/g) were Na (110 mg/g), Ca (96.1 mg/g), Th (57.4 mg/g), U (27.6 mg/g), Al (25.8 mg/g), Si (15.3 mg/g), K (14.4 mg/g), Mg (13.5 mg/g), Fe (8.6 mg/g), and Pb (2 mg/g). The concentrations of the anions were 179 mg/g for NO_3^- , 115 mg/g for CO_3^{2-} , 29.5 mg/g for PO_4^{3-} , 7 mg/g for SO_4^{2-} , 3.7 mg/g for Cl^- , and 2 mg/g for F^- . Concentrations of oxides and hydroxides in the sludge were not determined. The organic carbon content of the dried solids was 30 ± 10 mg/g.

Caustic leaching of centrifuged sludge solids with 0.16, 3.1, and 6.4 M NaOH at ambient temperature removed significant amounts of several components. A leachant/sludge solids ratio of $\sim 2.3/1$ was used. In one test, sludge solids were mixed twice with 0.16 M NaOH for a total of 27 h. The significant percentages of metals removed ($>1.3\%$) were as follows: K (80.5%), Cr (10.3%), Al (6.6%), Cs (5.7%), and Zn (1.4%). About 25.8% of the SO_4^{2-} was removed. In another test, a sample of sludge solids was mixed first for 144 h with 3.1 M NaOH and then for 144 h with 6.4 M NaOH. The composite percentages of metals removed were as follows: K (79.6%), Zn (31.7%), Si (16.4%), Pb (9.9%), Cr (7.2%), Al (6.0%), and Cs (7.1%). The greater fractions of the zinc and silicon were removed in the 6.4 M NaOH leaching step. In this test series, most of the SO_4^{2-} was removed, with the largest fraction being removed by the 3.1 M NaOH. Less than 1.2% of the PO_4^{3-} was removed in these tests.

Samples of MVST sludge were also leached for 4 h at 95°C with 1.0, 3.2, and 6.3 M NaOH. The 1 M NaOH removed about 12% of the cesium, while the 3.2 M NaOH leach removed about 15%. When the residue from the 3.2 M NaOH leach was leached with 6.3 M NaOH, an additional 27% of the cesium was removed, for a total cesium removal of 42%. Other elemental analyses of the leachates indicated that sequential leaching of the sludge with 3.2 M and 6.3 M NaOH at 95°C removed about 83% of the K, 64% of the Zn, 26% of the Cu, 19% of the Al, 16% of the Cr, 12% of the Pb, 10% of the Si, and 1% of the U. About 100% of the NO_3^- , 64% of the Cl^- , 30% of the SO_4^{2-} , and 2% of the PO_4^{3-} were removed. In general, the amounts of materials removed increased significantly at the higher temperature.

A number of acidic leaching tests were conducted at various HNO_3 and HF concentrations. Table 3 summarizes and compares the cumulative percentages of radionuclides that were removed by five different test series. All of the leaching tests were conducted at room temperature. In each test, the sludge solids were mixed for 117 h with 6.0 M HNO_3 ; however, in test B the sludge solids were leached with strong caustic solutions prior to leaching with the HNO_3 , and in tests D and E, the acid leach also contained HF. The acid concentrations of the resulting 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 of the tests

indicated almost total dissolution of each of these radionuclides. The use of HNO_3 alone (test C) removed the smallest amount of ^{137}Cs (22%). The use of strong caustic in test B and the use of HF in tests D and E improved the removal of ^{137}Cs to 55, 89, and 82%, respectively. The dissolution of plutonium was unaffected by the caustic pretreatment step. The removal of the plutonium in tests A, B, and C ranged from 56 to 60%. The use of HF with the HNO_3 improved the leachability of the plutonium; in tests D and E, 76 and 97% of the plutonium were removed, respectively. The addition of HF had a negative effect on the removal of thorium; only 9% was removed in test D and 7% in test E. In contrast, 89 and 80% of the thorium were removed in tests B and C, respectively. A heavy white precipitate that formed in each of the HF tests was probably ThF_4 .

In test A, a total of 84% of the ^{137}Cs was removed from the sludge solids. This percentage is much larger than the percentages obtained for tests B and C and is similar to the amount removed in tests D and E, in which HF was used. The main differences were that the sludge solids in test A were given mild caustic washes prior to leaching them with HNO_3 and the total time the sludge solids were mixed with HNO_3 leaches was 4.8 times longer (557 h). In summary, the data in Table 3 indicate that ^{137}Cs removal from the sludge solids is enhanced by (1) leaching with caustic prior to leaching with HNO_3 , (2) adding hydrofluoric acid to the HNO_3 leaches, or (3) leaching for longer periods of time.

A phenomenon that was encountered in these tests was gel formation during or after acidic leaching of the sludge solids. Gel was initially observed in the leachate of the first 3 M HNO_3 leach in test A after the solution had stood for several days. It is postulated that the gel is some form of amorphous silica precipitated from silicic acid. No gels were observed in the acid leachates for tests B, C, D, and E.

Quantitative dissolution of the solids in each test was determined by comparing the calculated air-dried mass of the initial sludge solids with the post-test mass of the air-dried solids. The results are given in Table 4. The percentages of dissolved solids varied from 62.6 to 81.5%. For test A, the cesium dissolution paralleled the solid dissolution. In test C, in which the solids were leached with HNO_3 alone, 62.3% of the solids was dissolved, but only 22% of the ^{137}Cs was removed. In tests D and E, in which HF was used with the HNO_3 , 75 and 73% of the solids were dissolved and 89 and 82% of the ^{137}Cs were removed, respectively. In tests D and E, 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. Consequently, the weights were not as definitive.

Sludge Immobilization

It is currently envisioned that the bulk of the waste stored in the ORNL tanks (as well as the tank waste stored throughout the DOE complex) will be processed or treated for disposal by private-sector companies. As part of that effort, the tank sludges in the four ORNL tank farms will be consolidated into one tank farm between 1998 and 2002 for ultimate retrieval and immobilization. The retrieval and immobilization is currently planned to begin in 2002.

The initial effort has focused on the TRU in the MVST, and tests using the average sludge composition from these tanks are in progress. To support the use of surrogates, a comparative test program evaluating waste-form performance was also initiated in which both an actual sludge and a surrogate sludge (which represents the actual waste chemically) will be immobilized. Sludge from MVST W-25 has been analyzed, and a surrogate waste to represent it chemically has been prepared. The work is being performed in a hot cell where equipment is available for making a silica-based glass (e.g., soda-lime-silica or borosilicate) and a cement-based grout from both the surrogate and the actual radioactive sludge. Teams at the Savannah River Technology Center and ORNL will develop tailored formulations for glass and grout waste

forms, respectively, which will then be used to produce test specimens of both glass and grout using both the surrogate and actual W-25 sludge. These specimens will undergo a battery of tests to compare the performance of the actual and surrogate waste forms. Testing will include the TCLP for both glass and grout, as well as the Product Consistency Test for glass-forming elements and selected radionuclides and the ANSI/ANS-16.1 leach test for the cement-based grouts. Grout testing will include unconfined compressive strength as well as an investigation of potential bleed-water problems during the curing stage. Data from the comparison of test results will be available for use as a benchmark of potential performance to gauge private-sector proposals. The data will also be used to evaluate the viability of using a chemical surrogate to represent the actual tank sludge.

Hot cell grouting tests with surrogate waste and with actual W-25 sludge have been completed and all of the equipment and procedures designed for use in the cell with the thick grout pastes performed well. No problems were encountered in mixing, pouring, and handling the modified grouting equipment using the cell manipulators. When samples were mixed with the cement-based formula, a thick paste was formed that could be handled and packed for the performance testing.

The bleed-water test results with surrogate sludge showed that there was a small amount of bleed water that was absorbed in a few hours after slurry preparation. When using the actual waste, no bleed water formed on the surface of the grout paste. Penetration-resistance tests showed that the actual waste produced a grout that set much faster and finally resulted in a penetration resistance greater than 5.5×10^7 N/m² (8000 psi). This observation seems to be consistent with the fact that the actual waste produced a grout that was thicker and yielded no bleed water. The visual appearance and handling characteristics of both the surrogate and actual waste sludge were similar. Testing of the glass formulations using both the W-25 simulant and actual sludge are scheduled, and this work will be extended to include hot tests of the other tank farm sludges.

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Table 2. Analyses of the MVST W-27 and W-29 supernatants

	MVST W-27, pH 13.3	MVST W-27, pH 14.02	MVST W-29, pH 12.68
Radiochemicals	(Bq/mL)	(Bq/mL)	(Bq/mL)
⁶⁰ Co	680	330	500
¹³⁷ Cs	320,000	340,000	460,000
¹³⁴ Cs	1,400	920	7,600
⁹⁰ Sr	65,000	31,000	4,100
⁹⁹ Tc	270		342
Gross alpha	0.9	0.4	30
Gross beta	525,000	430,000	550,000
Cations	(mg/L)	(mg/L)	(mg/L)
Al	0.847	<0.146	4.17
As	0.0089	<0.0250	<0.25
Ba	8.04	5.61	0.865
Ca	89.1	3.1	1.42
Cd	0.22	<0.11	0.24
Cr	2.96	3.49	3.44
Cs	0.935	9.95	0.58
Cu	<0.0319	0.15	0.07
Hg	0.09	0.117	0.258
K	10,300	12,000	14,700
Na	113,000	127,000	95,400
Ni	1.22	0.73	1.04
Pb	0.0092	<10	2.89
Rb	1.1	2.06	1.28
Si		29.3	44.1
Sr		26.3	1.65
U	<1.0	0.485	13.3
Zn	0.473	<0.148	1.35
Anions	(mg/L)	(mg/L)	(mg/L)
Br	288	<50.0	
Cl	3,180	2.96	3,050
NO ₂		2,720	20,400
NO ₃	322,000	298,000	250,000
SO ₄	1,540	1,380	15,506
	(M)	(M)	(M)
Total anion concentration	5.3897	6.0063	4.4754
Total cation concentration	5.1983	5.8320	4.5256
Difference	0.1914	0.1743	-0.0503
Other^a			
TIC, mg/L		300	980
TOC, mg/L		390	500
Density, mg/L	1.27	1.30	1.233
TDS, mg/L		79,000	81,000
TS, mg/L		580,000	390,000
TSS, mg/L		500,000	310,000
Na/Cs ratio	701,451	12,764	164,483
K/Cs ratio	37,446	1,206	25,345

^aTIC = Total inorganic carbon; TOC = total organic carbon; TDS = total dissolved solids; TS = total solids; TSS = total suspended solids.

Table 3. Comparison of percentages of fission products and actinides removed by different leach tests

Radionuclide	Cumulative percentage of radionuclide removed ^a				
	A	B	C	D	E
¹³⁷ Cs	84	55	22	89	82
⁶⁰ Co	98	104	103	106	93
¹⁵⁴ Eu	100	101	97	101	87
⁹⁰ Sr	95	100	97	110	80
²⁴¹ Am	89	112	110	111	NM ^b
²⁴⁴ Cm	98	97	90	101	102
Pu	60	56	56	76	97
Th	NM ^b	89	80	9	7
U	93	104	98	124	102

^aA = sludge solids sequentially leached with 0.16 M NaOH and 0.5, 3, and 6 M HNO₃; B = sludge solids sequentially leached with 3.1 M NaOH, 6.4 M NaOH, and 5.7 M HNO₃; C = sludge solids leached with 6.0 M HNO₃; D = sludge solids leached with a 5.8 M HNO₃ and 1.0 M HF solution; E = sludge solids leached with a 5.6 M HNO₃ and 1.9 M HF solution.

^bNM = not measured.

Table 4. Cesium removal as a function of dissolution of sludge solids

Leach treatment ^a	Air-dried solids ^b		Dissolved solids (%)	¹³⁷ Cs removal (%)
	Before leaching (g)	After leaching (g)		
A	25.96	4.80	81.5	84
B	21.67	5.86	73.0	55
C	23.29	8.70	62.6	22
D	21.09	5.24	75.0	89
E	25.89	6.86	73.0	82

^aSee Table 3 for test descriptions.

^bBased upon centrifuged wet-sludge solids being air dried at room temperature for 9 days.

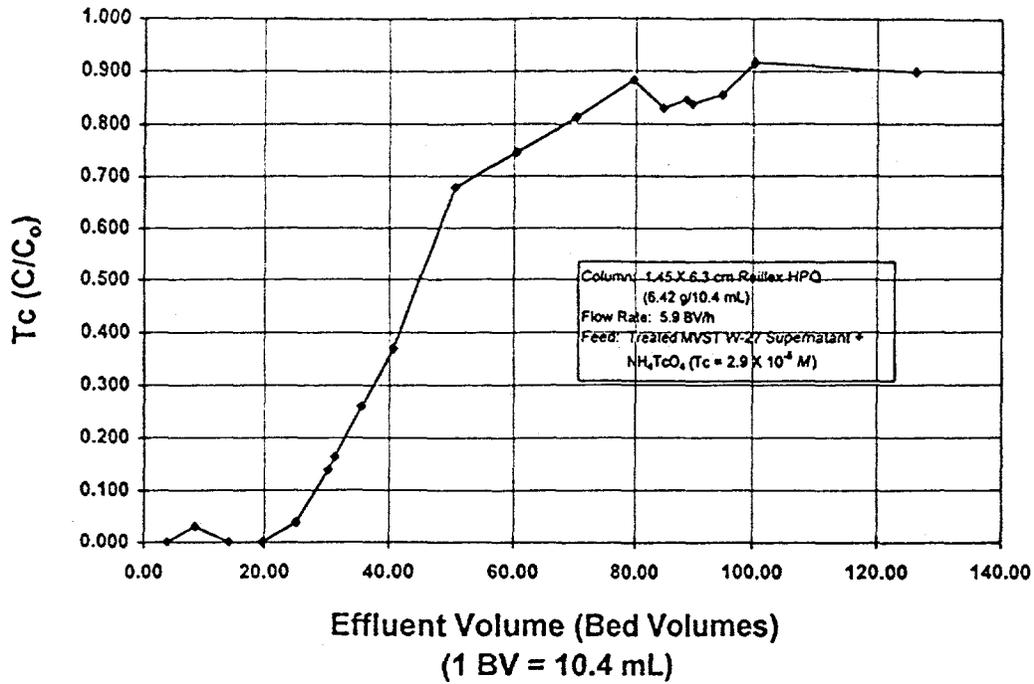


Fig. 1. Pertechnetate removal from MVST W-27 supernatant

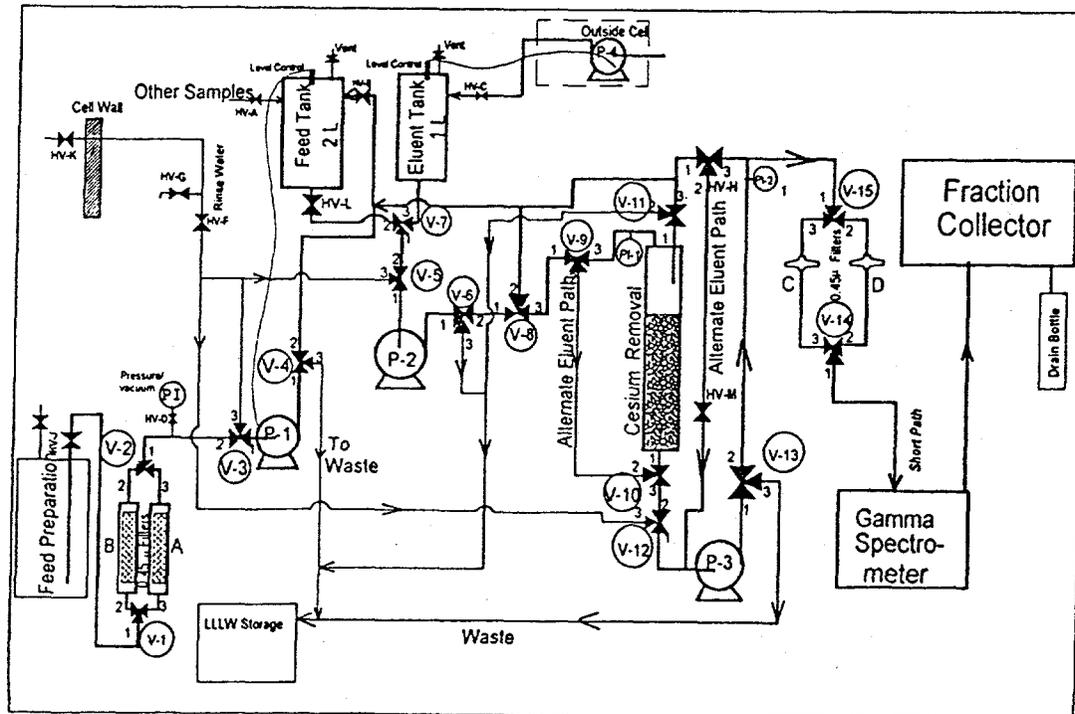


Fig. 2. Equipment diagram for cell system

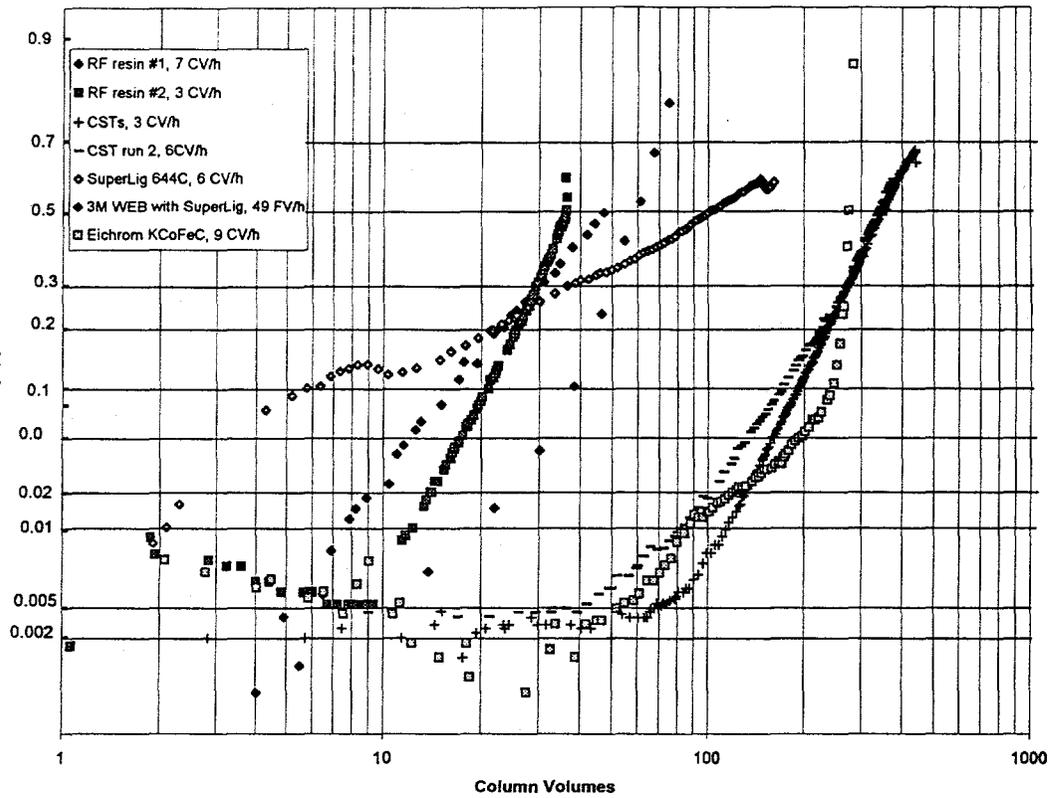


Fig. 3. Comparison of sorbents using MVST W-27 adjusted to pH 13.3

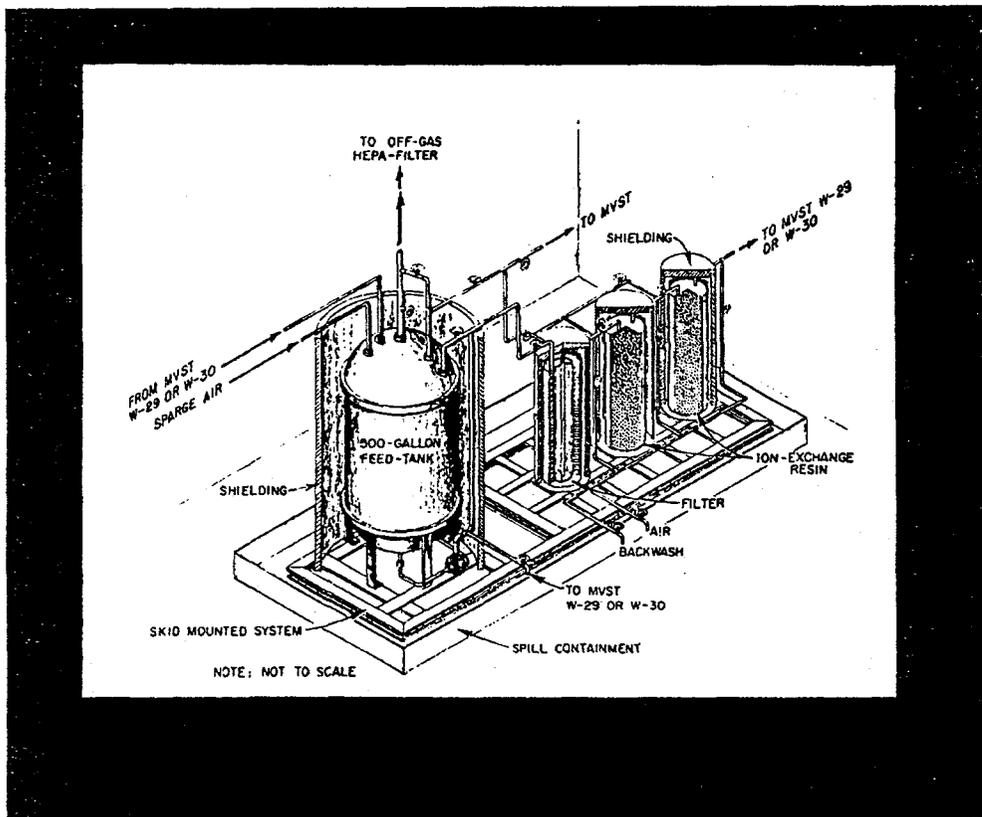


Fig. 4. Conceptual drawing of Cesium Removal Demonstration system

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