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**Batch Test Equilibration Studies Examining the Removal  
of Cs, Sr, and Tc from Supernatants from ORNL  
Underground Storage Tanks by Selected Ion Exchangers\***

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# Batch-Test Equilibration Studies Examining the Removal of Cs, Sr, and Tc from Supernatants from ORNL Underground Storage Tanks by Selected Ion Exchangers

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## ABSTRACT

Bench-scale batch equilibration tests have been conducted with supernatants from two underground tanks at the Melton Valley Storage Tank (MVST) Facility at Oak Ridge National Laboratory (ORNL) to determine the effectiveness of selected ion exchangers in removing cesium, strontium, and technetium.<sup>1</sup> Seven sorbents were evaluated for cesium removal, nine for strontium removal, and four for technetium removal. The results indicate that granular potassium cobalt hexacyanoferrate was the most effective of the exchangers evaluated for removing cesium from the supernatants. The powdered forms of sodium titanate (NaTiO) and crystalline silicotitanate (CST) were superior in removing the strontium; however, for the sorbents of suitable particle size for column use, titanium monohydrogen phosphate (TiHP  $\phi$ ), sodium titanate/polyacrylonitrile (NaTiO-PAN), and titanium monohydrogen phosphate/polyacrylonitrile (TiP-PAN) gave the best results and were about equally effective. Reillex™ 402 was the most effective exchanger in removing the technetium; however, it was only slightly more satisfactory than Reillex™ HPQ.

## INTRODUCTION

The goal of this batch-test equilibration study was to evaluate the effectiveness of certain ion exchangers for removing cesium, strontium, and technetium from supernatants taken from underground storage at the MVST Facility located at ORNL.<sup>1</sup> The exchangers tested were selective for removing cesium, strontium, or technetium from alkaline supernatant solutions with high salt concentrations. Since the supernatants of evaporator concentrates stored in tanks at the MVST facility<sup>2,3</sup> have compositions similar to some of those stored in tanks at Hanford,<sup>4</sup> the data generated in this study should prove useful in the overall evaluation of the ion exchangers for applications to Hanford and other U.S. Department of Energy (USDOE) sites. This work was conducted for the Comprehensive Demonstration of Sludge and Supernate Processing Program (CDSSPP).

Liquid low-level wastes (LLLWs) that are generated at the ORNL site are concentrated in an LLW evaporator. The evaporator concentrates are stored in 12 stainless steel, 50,000-gal tanks—8 at the MVST facility and 4 at the evaporator facility. Operators at the MVST site estimated, in March 1995, that the combined volume of waste contained in the 8 tanks at the MVST site was 287,000 gal; the associated supernatant volume was assumed to be about 175,000 gal. The volume of waste in the 4 tanks at the evaporator facility was 138,000 gal.

At the Hanford site, there are 177 underground tanks containing wastes with different compositions. The total volume stored in these tanks is estimated at 60 million gallons with a radioactivity level of >200 MCi. Major contributors to the radioactivity are Cs and Sr, and the major actinides are U, Pu, and Am. The radionuclides <sup>137</sup>Cs and <sup>90</sup>Sr are responsible for contributing 97% of the beta-gamma activity. Cesium-137 is the major contributor to the activity of the supernatants.<sup>4,5</sup> Technetium, a pure beta-emitter as <sup>99</sup>Tc, is present in the waste at much lower concentrations. Its predominant form under the oxic conditions of the alkaline supernatant waste is the pertechnetate anion (TcO<sub>4</sub><sup>-</sup>). Because of its solubility, long half-life, and ability to migrate, technetium would be a major contributor to the long-

term environmental hazard associated with any low-level waste stream. As with the cesium and strontium, technetium partitioning is also under consideration.<sup>6</sup>

A goal of the waste processing effort at Hanford is to remove enough cesium to ensure that the resulting LLW will meet the Nuclear Regulatory Commission (NRC) 10 CFR 61 class A limit for <sup>137</sup>Cs (1 Ci/m<sup>3</sup> or 1 μCi/mL). The separated cesium may be concentrated and vitrified for disposal in the high-level waste repository. The decontaminated effluent would be solidified for near-surface disposal.<sup>5,7</sup>

## MATERIALS

The supernatant stock solutions used in the batch tests were sampled directly from the supernatant layers in MVSTs W-25 and W-29. Before characterization or testing procedures, these solutions were passed through 0.45-μm nylon filters to remove particulates. The specific gravity and the total solids content were 1.232 and 0.388 g/mL for the W-25 supernatant and 1.226 and 0.379 mg/mL for the W-29 supernatant, respectively. The pH levels of the W-25 and W-29 supernatants were 12.6 and 13.2.

The concentrations of total carbon (TC) and inorganic carbon (IC) in the filtered supernatants were determined using a Dohrmann DC-90 Carbon Analyzer. For the W-25 supernatant, the TC and IC were 2110 and 310 mg/L, respectively. The total organic carbon (TOC) was determined by difference (TOC = TC - IC) to be 1800 mg/L. The TC, IC, and TOC values for the W-29 supernatant were 930, 470, and 460 mg/L, respectively.

The results of the radiological and chemical analyses for the two supernatants are provided in Table 1. The concentrations of <sup>137</sup>Cs were similar,  $2.5 \times 10^8$  Bq/L for the W-25 supernatant and  $2.2 \times 10^8$  Bq/L for the W-29 supernatant. The composite mass concentrations of the cesium isotopes (<sup>137</sup>Cs, <sup>134</sup>Cs, <sup>135</sup>Cs, and <sup>133</sup>Cs) for the supernatants were 0.19 and 0.57 mg/L. About 41% of the total mass of cesium in the W-25 supernatant was <sup>137</sup>Cs; it was only 12% for the W-29 supernatant. The W-25 value (0.19 mg/L) was consistent with the calculated concentration of total cesium based on fission yield calculations using the ORIGEN computer program.<sup>1,8</sup> The activity levels for strontium (<sup>90</sup>Sr) and technetium (<sup>99</sup>Tc) were  $1.0 \times 10^6$  and  $2.1 \times 10^4$  Bq/L and  $2.4 \times 10^6$  and  $2.0 \times 10^4$  Bq/L, respectively, for the W-25 and W-29 supernatants. Following the same order, the total concentrations for each of these elements were 0.4 and 0.032 mg/L and 1.0 and 0.031 mg/L. Knowledge of the total concentration of element to be removed in ion-exchanger studies is important because all of the isotopes of the element are sorbed equally well by ion-exchange material.

The major cations in the supernatants were Na<sup>+</sup> and K<sup>+</sup>, and the major anions were NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>. The Na and K concentrations were 3.87 and 0.36 M for the W-25 supernatant and 4.43 and 0.29 M for the W-29 supernatant; the respective Na/K mol ratios were 10.8 and 15.3. Considering the NO<sub>3</sub><sup>-</sup> concentrations of these supernatants, 3.8 M for W-25 and 4.5 M for W-29, it is apparent that the major constituents of their total solids contents were primarily alkali nitrates.

## ION EXCHANGERS EVALUATED TO REMOVE RADIONUCLIDES FROM SUPERNATANTS

### Exchangers Tested for Cesium

The following ion exchangers were used to evaluate the removal of cesium from the W-25 and W-29 supernatants: resorcinol/formaldehyde resin (SRR) [35 to 28 mesh (Tyler)] that was developed at the Savannah River Site and prepared by the Boulder Scientific Company;<sup>1,3,5,9,10</sup> Duolite™ CS-100 resin that has been manufactured commercially by Rohm and Haas, Inc.;<sup>3,5</sup> crystalline silicotitanate (CST) (a fine powder, lot DG-114) that was invented and developed through a collaborative effort between Sandia National Laboratories (SNL) and Texas A&M University;<sup>5,11-13</sup> granular potassium cobalt hexacyanoferrate [KCoCF(gr)] that was prepared at ORNL using a modification of the patented procedure developed by W. P. Prout et al;<sup>1,14</sup> hydrous titanium oxide/potassium cobalt hexacyanoferrate(II) microspheres (HTiO/KCoCF φ, 32 to 60 mesh) that were prepared at ORNL by the internal gelation process [hydrous titanium oxide microspheres were homogeneously embedded with very fine K<sub>2</sub>CoFe(CN)<sub>6</sub> powder (~20 wt %) in the process];<sup>1,15</sup> titanium monohydrogen phosphate/sodium cobalt hexacyanoferrate(II) microspheres (TiHP/NaCoCF φ, ~20 wt % NaCoCF, 32 to 60 mesh) that

were prepared at ORNL by the internal gelation method;<sup>1,15</sup> and SuperLig™ 644 resin that was developed by IBC Advanced Technologies.<sup>16</sup>

When SuperLig™ 644 was added to the supernatant, a large fraction of it floated. To resolve this problem, samples of sorbent were first mixed with 0.1 M NaOH for 36 h before testing them with the supernatant. A few batch tests were also conducted with samples of SuperLig™ 644 that had been preconditioned with water, along with some that had not been preconditioned.

All the sorbents used in the cesium batch tests, except CST, were of suitable particle size for column operations. Efforts are currently underway to develop CST into an engineered matrix for use in columns.<sup>17</sup>

### Exchangers Tested for Strontium

The ion exchangers examined for strontium removal were as follows: SRR (Na<sup>+</sup> form); CST; sodium titanate (ST) that was obtained from Boulder Scientific Company; hydrous titanium oxide/polyacrylonitrile (TiO-PAN) and sodium titanate/polyacrylonitrile (NaTiO-PAN) that were developed by F. Sebesta et al. at the Czech Technical University of the Czech Republic;<sup>13</sup> titanium monohydrogen phosphate microspheres (TiHP  $\phi$ , 32 to 60 mesh) that were prepared at ORNL by the internal gelation method;<sup>1,15</sup> Amberlite™ IRC-718; Duolite™ C467; and Chelex™ 100.

### Exchangers Tested for Technetium

Four ion exchangers (anion resins only) were examined for technetium removal were: Reillex™ HPQ,<sup>6</sup> Reillex™ 402, Amberlite™ IRA-904, and Amberlite™ IRA-400. The hydroxide and nitrate forms of these exchangers were tested.

### TEST PROCEDURES

Four separate supernatant stock solutions were used in this study: two for cesium, one for strontium, and one for technetium. Stock solutions of filtered W-25 and W-29 supernatants were used for the cesium batch-equilibration tests. Only filtered supernatants from tank W-29 were used for the strontium and technetium tests. These were prepared by first mixing each supernatant twice for 24 h with fresh resorcinol/formaldehyde ion-exchange resin (sodium form) and then twice for 2 h with granular potassium cobalt hexacyanoferrate to remove most of the cesium and strontium activity so as to improve analyses.

In preparation of the supernatant stock solution that was used in the strontium batch tests, enough strontium nitrate, which was traced with the gamma emitter <sup>85</sup>Sr, was added to provide a strontium concentration of 2.0 mg/L ( $2.3 \times 10^{-5}$  M). The supernatant was equilibrated by mixing it on a Labquake™ shaker for several days; then it was filtered through 0.45- $\mu$ m and 0.2- $\mu$ m nylon filters to remove undissolved strontium particulates and analyzed by gamma counting. The concentration of the soluble strontium in the supernatant was 1.5 mg/L ( $1.7 \times 10^{-5}$  M). Subsequent checks showed that no additional precipitation occurred in the strontium concentration during the period of time the batch tests were conducted.

Technetium-99, as ammonium pertechnetate, was added to the other treated W-29 supernatant stock solution to provide a <sup>99</sup>Tc concentration of 4.0 mg/L ( $4 \times 10^{-5}$  M); this concentration also included the <sup>99</sup>Tc that was already in the supernatant 0.031 mg/L ( $3.2 \times 10^{-7}$  M). The adjusted concentration was chosen because it was the average concentration of <sup>99</sup>Tc for the supernatants in 17 Hanford underground storage tanks that were recently characterized by N. G. Colton et al. at Pacific Northwest Laboratory.<sup>4</sup> The range of <sup>99</sup>Tc concentrations for those tanks was  $6.0 \times 10^{-7}$  to  $6.0 \times 10^{-4}$  M.

The sorption measurements were made using batch equilibration tests. The supernatants and the exchangers were contacted in 15-mL, screw-cap, polypropylene centrifuge tubes by mixing with a Labquake™ shaker. The action of the mixer is a back-and-forth motion that was set to rock from -45° to +45° from the horizontal plane at ~20 cycles per minute. The exchangers and the supernatants were weighed, in consecutive steps, into tared tubes. The volumes of supernatant (normally about 10 mL) were calculated from the specific gravity of the supernatant. At the end of the equilibration periods, the

tubes were reweighed to determine if any leakage had occurred. The tubes were then centrifuged for 30 min at 3000 rpm with an International Equipment Company Centra 7 tabletop centrifuge. Following this step, ~2-mL volumes of the clarified supernatants were transferred to clean centrifuge tubes by pipet and again centrifuged for 30 min. With a syringe filtering system, the clarified supernatants were filtered successively through 0.45- $\mu$ m and 0.2- $\mu$ m nylon filters to remove any of the remaining fine particulates. Samples (0.5 mL) of the filtered supernate were pipetted into counting tubes for radiochemical analysis.

The gamma activities of  $^{137}\text{Cs}$  and  $^{85}\text{Sr}$  were determined using an LKB Wallac 1282 Compugamma Universal Gamma Counter. Beta counting for  $^{99}\text{Tc}$  was performed using a Packard Bell Model Tri-Carb 2200 CA Liquid Scintillation Analyzer instrument. The counting solution (cocktail) was prepared by thoroughly mixing a 0.5-mL sample with 10 mL of Ecolite(+)<sup>TM</sup> liquid scintillation liquid (ICN Biomedicals, Inc.).

Postequilibration pH measurements were made on each sample using an ORION Research Digital pH Meter and an ORION 8103 ROSS combination electrode. The electrode was calibrated with pH 7 and pH 10 buffer solutions.

Duplicate batch tests were conducted with each exchanger. Control tests were also run; 10-mL samples of the supernatants were added to 15-mL propylene centrifuge tubes and mixed for 2, 24, and 72 h. No detectable change in the cesium, strontium, or technetium activities of the supernatants was noted in the control tests.

Cesium and strontium sorption data for equilibration times of 0.25, 2, 24, 72 or 144 h were determined for each exchanger tested. Only 2-h and 24-h tests were conducted for technetium. In each test, a mass of exchanger equivalent to ~0.050 g of air-dried exchanger and a supernatant volume of 10 mL were employed, giving a supernatant/air-dried exchanger ratio of 200/1. In tests with the HTiO/NaCoCF  $\phi$  or TiHP/KCoCF  $\phi$ , the mass of microspheres was increased to ~0.175 g, so as to contain ~0.050 g of NaCoCF or KCoCF. The matrix materials, HTiO and TiHP, do not sorb cesium from alkaline saline solutions; however, but they do sorb strontium.

## CALCULATIONS

Results of batch tests are reported as percentage removal (% R) and distribution ratio (D). These values are calculated in the following manner:

$$\% R = 100[(C_o - C)/C_o],$$

$$D = [(C_o - C)/C][V/m] \text{ (units are mL/g).}$$

The pretest and posttest count rates of  $^{137}\text{Cs}$ ,  $^{85}\text{Sr}$ , or  $^{99}\text{Tc}$  are denoted by  $C_o$  and  $C$ , respectively. The D is an expression of the ratio of concentration of a radionuclide sorbed on the ion exchanger to the concentration remaining in the test solution after a specified mixing time, where  $V$  is the volume of supernatant and  $m$  is the mass of exchanger.

## TEST RESULTS

### Distribution Measurements for Cesium Removal

Table 2 gives the results of batch tests performed to measure the rate of cesium adsorption with ion exchangers SRR, CST, Duolite<sup>TM</sup> CS-100, KCoCF(gr), HTiO/KCoCF  $\phi$ , and TiHP/NaCoCF  $\phi$ . In each test, as described in the TEST PROCEDURES section, a mass of exchanger equivalent to ~0.050 g of air-dried material was mixed with 10 mL of MVST W-25 supernatant (see Table 1) for 0.25, 2, 24, 72, or 144 h. Duplicate samples were run with each exchanger.

The highest cesium removal was obtained with KCoCF(gr). The range of D values was 26,000 to 46,200 mL/g; the percentage removal (% R) range was 99.3 to 99.6. Duolite<sup>TM</sup> CS-100 was the least effective in removing cesium; the highest D and % R values were 44 mL/g and 22 %, respectively. SRR and CST were similar in sorbing cesium from the supernatant, with the D values ranging from 138

to 764 mL/g for the SRR and 451 to 958 mL/g for the CST. After 144 h of mixing, the SRR and CST removed 78.7 and 83.8% of the cesium, respectively. In the shorter, 0.25-h tests, CST removed 71.5%, and the SRR removed 41% of the cesium. This is not surprising because the CST is a fine powder and has more surface area that is readily available for cesium adsorption. After 2-h mixing time, the % R values for CST and SRR were about equal.

A mass of microspheres that contained 0.050 g of embedded KCoCF or NaCoCF was used in each test with microspheres. Separate tests with TiHP  $\phi$  and HTiO  $\phi$  were also conducted. Without the embedded hexacyanoferrates, these materials removed <5% of the cesium from the MVST W-25 supernatant after mixing times of 2 and 72 h. The microspheres that contained KCoCF or NaCoCF removed >70% of the cesium in 2 h. For the longer mixing times, the percentages of cesium removed were similar to those obtained using KCoCF(gr). The D values obtained for the microspheres containing hexacyanoferrate were lower because larger total masses were used in the calculations. If only the mass (0.050 g) of the embedded KCoCF or NaCoCF were used in the calculation of the D values, the D values would be similar to those obtained for the KCoCF(gr). In the 2-h tests, only 72% of the cesium was removed by the HTiO/KCoCF  $\phi$ , as compared with 96.6% for the TiHP/NaCoCF  $\phi$ . However, for the longer mixing times, the percentage removal by the HTiO/KCoCF  $\phi$  increased. Diffusion of cesium ions into the matrix of the microspheres seems to be enhanced by increased hydration. The HTiO microspheres exhibited more swelling in aqueous solution than the TiHP microspheres, but the swelling of the HTiO occurred more slowly. Under these test conditions, the KCoCF(gr) was the most effective exchanger and its kinetics were the most rapid.

Similar tests for cesium removal were also conducted with MVST W-29 supernatant (see Table 1) using the ion exchangers SRR, CST, KCoCF(gr), HTiO/KCoCF  $\phi$ , and SuperLig™ 644. (The SuperLig™ 644 was not evaluated with the W-25 supernatant.) Duplicate tests were conducted for mixing times of 0.25, 2, 24, 72, and 144 h. The results, given in Table 3, were similar to those obtained for the MVST W-25 supernatant. The relative removals of cesium were: KCoCF(gr) > CST > HTiO/KCoCF  $\phi$  > SuperLig™ 644 > SRR. The data for SuperLig™ 644 in Table 3 are for samples that had first been mixed with 0.1 M NaOH for 36 h before being mixed with the supernatant. Although the results are not given in Table 3, sets of 2-h and 24-h batch tests were also conducted with samples of SuperLig™ 644 that had received no pretreatment and samples that had been preconditioned with water for 36 h. The D and % R values obtained for the water-treated SuperLig™ 644 were 682 mL/g and 77.3 for the 2-h tests, and 787 mL/g and 80.7 for the 24-h tests. The values for SuperLig™ 644 that was mixed for 36 h with 0.1 M NaOH (Table 3) were somewhat lower, 385 mL/g and 67.3% for the 2-h tests and 549 mL/g and 73.8 for the 24-h tests. The values were even lower for the samples that received no pretreatment, 202 mL/g and 60.2% for the 2-h tests and 377 mL/g and 68.5% for the 24-h tests. In the tests where the SuperLig™ 644 was added directly to the supernatant, a large portion of it floated, resulting in less surface exposure to the supernatant. The effectiveness of the SuperLig™ 644 was improved by preconditioning.

Table 4 gives isotherm data for removing cesium from MVST W-25 supernatant with SRR, CST, and KCoCF(gr) for mixing periods of  $\geq 24$  h. The supernatant/exchanger (S/E) ratio was varied from 2000/1 to 100/1 (mL/g). This was accomplished by using a constant volume of supernatant (10 mL) and varying the mass of ion exchanger from 0.005 to 0.100 g. The S/E used for the SRR and CST tests covered the range of 1000/1 to 100/1; an S/E range of 2000/1 to 200/1 was examined for KCoCF(gr) because it showed higher cesium sorption. These data are plotted in Fig. 1. Results are also included from two additional 24-h batch tests in which CST and granular KCoCF were mixed at an S/E ratio of 5000/1 (about 2 mg of sorbent was mixed with 10 mL of supernatant). In those tests, 92 and 27% of the cesium were removed by the granular KCoCF and CST, respectively. The corresponding D values were 51,800 and 1850 mL/g.

The maximum cesium sorbed under these conditions was 5.8 meq/kg for KCoCF(gr), 0.9 meq/kg for SRR, and 1.9 meq/kg for CST. Ion-exchange column tests are needed to determine the cesium loading capacities for these sorbents with the MVST W-25 supernatant.



### Distribution Measurements for Strontium Removal

Before the strontium batch-equilibration tests were conducted, the solubility of strontium in the tank W-29 supernatant was determined. For this determination, the strontium concentration of a 200-mL sample of treated tank W-29 supernatant (see TEST PROCEDURE section) was adjusted to 70 mg/L with strontium nitrate which was traced with  $^{85}\text{Sr}$ . After being mixed for a 48-h period, a 0.5-mL sample was filtered through 0.45- $\mu\text{m}$  and 0.2- $\mu\text{m}$  nylon filters, and counted. After counting, the sample was added back to the original test sample. This process was then repeated several times over a 45-d period. The activity of each sample was calculated taking into account the half-life of  $^{85}\text{Sr}$  (64.8 d). After 2, 16, 17, 25, 30, 36, 40, and 45 d, the concentration of strontium decreased for those times in the following order: 57, 10, 5.6, 3.8, 3.7, 3.1, 2.5, and 2.3 mg/L. These data indicate that the maximum strontium concentration for the W-29 supernate was  $\sim 2$  mg/L. Interestingly, the initial concentration of strontium in the W-29 supernatant was 1 mg/L.

Batch-equilibration tests were conducted with nine different ion-exchanger materials to measure their effectiveness in removing strontium from the pretreated W-29 supernatant. The results are given in Table 5. The inorganic ion exchangers outperformed the organic resins in removing the strontium with the fine powders of NaTiO and CST giving the best results. The largest D (31,500 mL/g) and % R (99.4%) were obtained with NaTiO in the 0.15-h test. For the sorbents of particle size suitable for column use, TiHP  $\phi$ , NaTiO-PAN, and TiP-PAN gave the best results and were about equally effective. The most effective organic resin tested was Duolite<sup>TM</sup> C-467. For the organic exchange resins tested (Duolite<sup>TM</sup> C-467, Chelex<sup>TM</sup> 100, Amberlite<sup>TM</sup> IRC-718, and SRR), Duolite<sup>TM</sup> C-467 gave the most favorable results overall. The largest D and % R for it were 1,290 mL/g and 86.9, respectively.

### Distribution Measurements for Technetium Removal

Batch tests were conducted with four different anion-exchange resins — Reillex<sup>TM</sup> HPQ, Reillex<sup>TM</sup> 402, Amberlite<sup>TM</sup> IRA-904, and Amberlite<sup>TM</sup> IRA-400 — to measure their effectiveness in removing pertechnetate anions from the adjusted W-29 supernatant. In each test, the mass exchanger, which was equivalent to 0.050 g of air-dried exchanger, was mixed with 10 mL of supernatant for 2-h and 24-h. The nitrate form of Amberlite<sup>TM</sup> IRA-400, as well as the hydroxide and nitrate forms of three other exchangers, were tested.

Table 6 shows that all of the anion exchangers removed the pertechnetate anion reasonably well; however, results for the hydroxide forms of the exchangers were superior to those for the nitrate forms. Considering both mixing periods, the hydroxide form of Reillex<sup>TM</sup> 402 worked best. The distribution coefficients (Ds) were 430 mL/g for the 2-h tests and 786 mL/g for the 24 h tests; 69 and 80% of the technetium were removed in those time periods.

### CONCLUSIONS

All of the experiments described in this report were batch extraction studies. Future columnar studies are implicit to the use of these materials in actual process applications. All materials except the CST exchanger are already available in particle sizes suitable for column studies. Efforts are currently under way to develop CST into an engineered matrix for use in columns.

The data indicate that granular KCoCF was the most effective of the exchangers evaluated for removing cesium from the W-25 and W-29 supernatants. KCoCF efficiently extracted cesium when prepared as a stable granular particle or when occluded in titanium monohydrogen phosphate or hydrous titanium oxide microspheres. However, it was noted that the microspheres containing potassium cobalt hexacyanoferrate powder showed a somewhat slower uptake of cesium than the granular KCoCF, requiring 2 to 24 h as opposed to  $\sim 0.25$  h for near-maximum removal.

Of the nine sorbents tested for removing strontium from the W-29 supernatant, the fine powders of NaTiO and CST were superior in removing the strontium; however, for the sorbents of particle size suitable for column use, TiHP  $\phi$ , NaTiO-PAN, and TiP-PAN gave the best results and were about equally effective. The most effective organic resin tested was Duolite<sup>TM</sup> C-467.

The nitrate form of Reillex™ 402 was the most effective of the anion resins in removing the technetium; however, it worked only slightly better than the Reillex™ HPQ.

In summary, the Hanford storage tanks and the tanks at other U.S. Department of Energy sites contain supernatants with a wide range of alkalinities and salt contents and, therefore, may require a variety of treatment options. Supernatants with the highest alkalinities and salt contents might be amenable to cesium partition with SRR and/or CST. Supernatants in the appropriate pH range (0 to 12.5) could be treated directly with granular KCoCF or a composite form such as HTiO/KCoCF. Supernatants from several tanks might be blended, if chemically compatible, to improve the effectiveness of exchangers for removing cesium by reducing the pH or the salt concentration.

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## REFERENCES

1. Collins, J.L., Egan, B.Z., Anderson, K.K., Chase, C.W., Mrochek, J.E., Bell, J.T and Jernigan, G.E.; *Evaluation of Selected Ion Exchangers for the Removal of Cesium from MVST W-25 Supernate*, ORNL/TM-12938; Oak Ridge National Laboratory, May 1995.
2. Sears, M.B., Botts, J.L., Ceo, R.N., Ferrada, J.J., Griest, W.H., Keller, J.M. and Schenley, R.J.; *Sampling and Analysis of Radioactive Liquid Wastes and Sludges in the Melton Valley and Evaporator Storage Tanks at ORNL*, ORNL/TM-11652; Oak Ridge National Laboratory, September 1990.
3. Campbell, D.O., Lee, D.D. and Dillow, T.A.; *Development Studies for Treatment of ORNL Low-Level Liquid Waste*, ORNL/TM-11798; Oak Ridge National Laboratory, November 1991.
4. Colton, N.G., Orth, R.G. and Aitken, E.A.; *Tank Waste Processing Analysis: Database Development, Tank-by Tank Processing Requirements, and Examples of Pretreatment Sequences and Schedules as Applied to Hanford Double-Shell Tank Supernatant Waste—FY 1993*; PNL-10134, Pacific Northwest Laboratory, September 1994.
5. Bray, L.A., Carlson, C.D., Carson, K.J., DesChane, J.R., Elovich, R.J. and Kurath, D.E.; *Initial Evaluation of Two Organic Resins and Their Ion Exchange Column Performance for the Recovery of Cesium from Hanford Alkaline Wastes*, TWRSPP-93-055; Pacific Northwest Laboratory, August 1993.
6. Schroeder, N.C., Radzinski, S., Ashley, K.R., Ball, J., Stanmore, F. and Whitener, G.; *Technetium Partitioning for the Hanford Tank Waste Remediation System: Sorption of Technetium from DSS and DSSF-7 Waste Simulants Using Reillex™ HPQ Resin*, LA-UR-95-40; Los Alamos National Laboratory, Jan. 6, 1995.
7. 10 CFR 61.1988, U.S. Nuclear Regulatory Commission, "Licensing Requirement for Land Disposal of Radioactive Waste," U.S. Code of Federal Regulations.
8. Croff, A.G.; *ORIGEN2—A Revised and Updated Version of the Oak Ridge Isotope Generation and Depletion Code*, ORNL-5621; Oak Ridge National Laboratory, March 1986.

9. Bray, L.A., Elovich, R.J. and Carson, K.J.; *Cesium Recovery Using Savannah River Laboratory Resorcinol-Formaldehyde Ion Exchange Resin*, PNL-7273; Pacific Northwest Laboratory, March 1990.
10. Bibler, J.P., Wallace, R.M., and Bray, L.A.; "Testing a New Cesium-Specific Ion Exchange Resin for Decontamination of Alkaline High-Activity Waste," in *Waste Management '90*, Vol. 2; R. G. Post, Ed.; 1990; pp. 747-751.
11. Brown, N.E., Stephens, H.P., Dosch, R.G., Bussard, L.D. and Anthony, R.G.; "Crystalline Silicotitanate Ion Exchangers for Removal of Cs from Liquid Defense Radwastes," paper presented at the Efficient Separations and Processing Integrated Program, Underground Storage Tank—Integrated Demonstration; Salt Lake City Meeting, Feb. 3, 1993.
12. Anthony, R.G., Philip, C.V. and Dosch, R.G., "Selective Adsorption and Ion Exchange of Metal Cations and Anions with Silico-Titanates and Layered Titanates," *Waste Manage.* **13**, 503-12 (1993).
13. Marsh, S.F., Svitra, Z.V. and Bowen, S.M., *Distribution of 14 Elements of 60 Selected Adsorbers from Two Simulant Solutions (Acid-Dissolved Sludge and Alkaline Supernate) for Hanford HLE Tank 102-SY*, LA-12654, October 1993.
14. Prout, W.E., Russell, E.R. and Groh, H.J., "Removal of Cesium from Aqueous Solutions by Ion Exchange," U.S. Patent 3,296,123, Jan. 3, 1967.
15. Collins, J.L., Davidson, D.J., Chase, C.W., Egan, B.Z., Ensor, D.D., Bright, R.M. and Glasgow, D.C.; *Development and Testing of Ion Exchangers for Treatment of Liquid Wastes at Oak Ridge National Laboratory*, ORNL/TM-12315; Oak Ridge National Laboratory, March 1993.
16. Brown, G.N., Bray, L.A. and Elovich, R.J.; *Evaluation and Comparison of SuperLig™ 644, Resorcinol-Formaldehyde and CS-100 Ion Exchange Materials for the Removal of Cesium from Simulated Alkaline Supernate*, PNL-10486; Pacific Northwest Laboratory, March 1995.
17. Brown, N.E., Sandia National Laboratory, personal communication, 1994.

Table 1. Analytical data for MVST supernatants.

	Tank	
	W-25	W-29
Radionuclides, Bq/L		
$^{134}\text{Cs}$	7.4E+06	3.4E+06
$^{137}\text{Cs}$	2.5E+08	2.2E+08
$^{60}\text{Co}$	6.3E+06	4.0E+05
$^{154}\text{Eu}$	1.1E+05	BDL <sup>a</sup>
$^{90}\text{Sr}$	1.0E+06	2.4E+06
$^{99}\text{Tc}$	2.1E+04	2.0E+04
Other metals, mg/L		
Al	453	0.43
Ba	1.2	0.36
* Ca	9.5	3.5
Cs	0.19	0.57
Cr	51	2.2
Cu	0.7	0.2
K	14,000	11,400
Na	89,000	102,000
Pb	12.8	7.1
Sr	0.4	1.0
Tc	0.032	0.031
Th	0.3	<0.1
U	4.3	1.3
Zn	9.5	61
Anions, mg/L		
$\text{Br}^-$	345	<50
$\text{Cl}^-$	3,740	3,000
$\text{F}^-$	371	<5
$\text{NO}_3^-$	236,000	280,000
$\text{PO}_4^{3-}$	BDL	<50
$\text{SO}_4^{2-}$	2,370	670

<sup>a</sup>BDL = below detection limit.

Table 2. Batch adsorption data showing the effect of mixing time on the removal of cesium from MVST W-25 supernatant.<sup>a</sup>

Exchanger <sup>b</sup>	Mixing time (h)									
	(0.25)		(2)		(24)		(72)		(144)	
	D (mL/g)	% R	D (mL/g)	% R	D (mL/g)	% R	D (mL/g)	% R	D (mL/g)	% R
CS-100	34	15.3	35	20.0	34	15.0	42	20.0	44	22.0
SRR	138	41.0	763	79.3	736	79.5	764	79.2	641	78.7
CST	451	71.5	662	77.4	672	77.5	672	77.7	958	83.8
KCoCF(gr)	36,900	99.5	46,200	99.6	36,900	99.5	36,300	99.5	26,000	99.3
TiHP/NaCoCF $\phi$	3,855	99.1	3,148	98.9	3,150	98.8	3,960	99.1	3,970	99.1
HTiO/KCoCF $\phi$	65	66.5	110	72.3	5,550	99.3	5,500	99.3	5,530	99.3

<sup>a</sup>With the exception of the microspheres ( $\phi$ ), each batch test was conducted by mixing a mass of exchanger equivalent to 0.05 g of air-dried exchanger with ~10 mL of supernatant for the times indicated. A mass of  $\phi$  was used in each test that contained 0.05 g of NaCoCF or KCoCF.

<sup>b</sup>The ion exchangers are discussed in the section entitled "Exchangers Tested for Cesium."

Table 3. Batch adsorption data showing the effect of the mixing time on the removal of cesium from MVST W-29 supernatant.<sup>a</sup>

Exchanger <sup>b</sup>	Mixing time									
	(0.25 h)		(2 h)		(24 h)		(72 h)		(144 h)	
	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R
SRR	404	65.7	535	73.0	528	73.0	514	76.0	528	72.6
CST	616	76.0	847	82.0	1,188	85.0	1,078	86.5	1,247	86.2
Superlig™ 644	125	39.4	385	67.3	549	73.8	1,098	84.6	1,300	88.0
KCoCF(gr)	16,500	98.8	17,100	99.0	32,700	99.4	58,500	99.7	33,180	99.4
HTiO/KCoCF $\phi$	996	96.5	761	95.4	2,560	98.6	4,360	99.2	4,590	99.3

<sup>a</sup>Each batch test was conducted by mixing a mass of exchanger equivalent to 0.050 g of air-dried adsorber with 10mL of MVST W-29 supernatant for the times indicated.

<sup>b</sup>The ion exchangers are discussed in the section entitled "Exchangers Tested for Cesium."

Table 4. Isotherm data for removing cesium from MVST W-25 supernatant with sorbents.<sup>a</sup>

Exchanger <sup>b</sup>	S/E <sup>c</sup>	Cs loading (meq/kg)	[Cs] (meq/L)	D (mL/g)	% R
SRR	1000	9.1E-01	5.2E-04	1,500	63.4
	400	4.4E-01	3.4E-04	1,070	76.5
	200	2.3E-01	3.0E-04	760	79.2
	100	1.2E-01	1.9E-04	620	87.0
CST	5000	1.9E+00	1.0E-03	1,850	27.0
	1000	7.9E-01	6.4E-04	1,020	54.9
	400	3.9E-01	4.5E-04	640	67.6
	200	2.2E-01	3.2E-04	670	78.7
	100	1.3E-01	1.3E-04	840	91.2
KCoCF(gr)	5000	5.9E+00	1.1E-04	51,800	92.0
	2000	2.8E+00	3.6E-05	68,400	98.6
	1000	1.4E+00	2.1E-05	59,700	98.5
	400	5.7E-01	8.6E-05	58,400	99.3
	200	2.8E-01	7.1E-06	36,900	99.5

<sup>a</sup>Conditions of batch equilibration tests: 10 mL supernate; masses of exchangers equivalent to 0.100, 0.050, 0.025, 0.010, 0.005, or 0.002 g air-dried exchanger;  $\geq 24$ -h mixing time at room temperature; initial pH of supernate = 12.6. The Na, K, and Cs concentrations in the supernate were 3.97, 0.36, and  $1.4 \times 10^{-6}$  M, respectively.

<sup>b</sup>The ion exchangers are discussed in the section entitled "Exchangers Tested for Cesium."

<sup>c</sup>S/E = ratio of supernate (mL) to mass of sorbent (g).

Table 5. Batch adsorption data showing the effect of mixing time on the removal of strontium from MVST W-29 supernatant.<sup>a</sup>

Exchanger <sup>b</sup>	Mixing time (h)							
	(0.25)		(2)		(24)		(144)	
	D (mL/g)	% R	D (mL/g)	% R	D (mL/g)	% R	D (mL/g)	% R
CST	518	72.6	24,000	99.2	24,900	92.2	903	82.3
NaTiO	31,500	99.3	30,500	99.4	24,200	99.2		
TiHP $\phi$	1,130	84.8	4,500	95.8	5,630	96.6	5,190	96.3
TiP-PAN	505	74.6	2,770	93.7	2,900	94.4	3,030	94.2
NaTiO-PAN	394	66.7	2,830	93.6	3,069	94.0	4,360	95.8
Duolite™ C-467	323	62.6	992	83.1	1,120	84.4	1,290	86.9
Chelex™ 100	245	54.5	611	76.4	673	74.0	1,500	88.3
Amberlite™ IRC-718	161	44.2	589	75.4	857	80.4	1,240	85.9
SRR	97	32.7	210	52.7	321	62.2	320	62.8

<sup>a</sup>Descriptions of the W-29 supernatant stock solution preparation and the batch-test procedure are given in the section entitled "TEST PROCEDURES."

<sup>b</sup>The ion exchangers are discussed in the section entitled "Exchangers Tested for Strontium."

Table 6. Batch adsorption data showing the effect of mixing time on the removal of technetium from MVST W-29 supernatant.<sup>a</sup>

Exchanger <sup>b</sup>	Mixing time (h)			
	(2)		(24)	
	D (mL/g)	% R	D (mL/g)	% R
Reillex <sup>TM</sup> HPQ <sup>c</sup>	282	60	624	76
Reillex <sup>TM</sup> HPQ <sup>d</sup>	149	44	511	72
Reillex <sup>TM</sup> 402 <sup>c</sup>	430	69	786	80
Reillex <sup>TM</sup> 402 <sup>d</sup>	349	64	356	66
Amberlite <sup>TM</sup> IRA-904 <sup>c</sup>	186	48	628	76
Amberlite <sup>TM</sup> IRA-904 <sup>d</sup>	286	59	535	74
Amberlite <sup>TM</sup> IRA-400 <sup>c</sup>	88	31	412	68

<sup>a</sup>Descriptions of the W-29 supernatant stock solution preparation and the batch-test procedure are given in the section entitled "TEST PROCEDURES."

<sup>b</sup>The ion exchangers are discussed in the section entitled "Exchangers Tested for Technetium."

<sup>c</sup>Hydroxide form of exchanger.

<sup>d</sup>Nitrate form of exchanger.



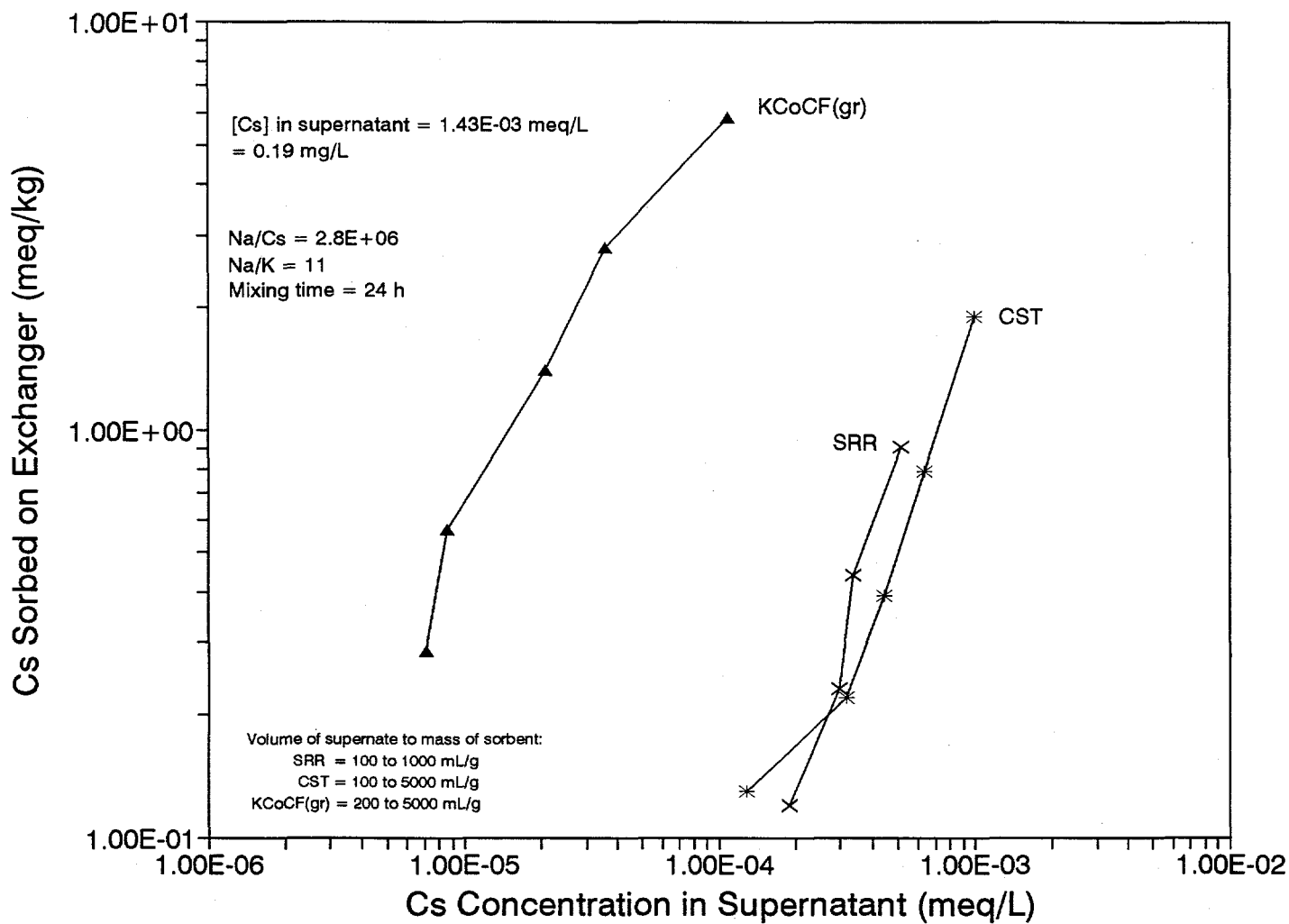


Fig. 1. Cesium sorption isotherms using MVST W-25 supernatant.