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Large-Scale Treatment of High-Salt, High-pH Wastewater
For ^{137}Cs and ^{90}Sr Removal, Using Crystalline Silicotitanate Resin

P. A. Taylor*
J. F. Walker
D. D. Lee
Oak Ridge National Laboratory**
P.O. Box 2008
Oak Ridge, Tennessee 37831-6044
Phone: 423-574-6792

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
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*To whom correspondence should be addressed.

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Large-Scale Treatment of High-Salt, High-pH Wastewater For ^{137}Cs and ^{90}Sr Removal, Using Crystalline Silicotitanate Resin

P. A. Taylor

Oak Ridge National Laboratory¹
Bldg 3017, P.O. Box 2008
Oak Ridge, TN 37831-6044

J. F. Walker

Oak Ridge National Laboratory
Bldg 2528, P.O. Box 2008
Oak Ridge, TN 37831-6330

D. D. Lee

Oak Ridge National Laboratory
Bldg 4501, P.O. Box 2008
Oak Ridge, TN 37831-6221

ABSTRACT

A full-scale demonstration of cesium removal technology has been conducted at Oak Ridge National Laboratory (ORNL). This demonstration utilized a modular, mobile ion-exchange system and existing facilities for the off-gas system, secondary containment, and utilities. The ion-exchange material, crystalline silicotitanate (CST), was selected on the basis of its effectiveness in laboratory tests. The CST, which was developed through a Cooperative Research and Development Agreement between DOE and private industry, is highly selective for removing Cesium (Cs) from solutions containing high concentrations of other contaminants, such as sodium and potassium. Approximately 116,000 L of supernate was processed during the demonstration with ~ 1142 Ci of ^{137}Cs removed from the supernate and loaded onto 266 L (70 gal) of the CST sorbent. The supernate processed had a high salt content, about 4 M NaNO_3 , and a pH of 12 to 13. The CST also loaded Ba, Pb, Sr, U and Zn. Analysis of the spent sorbent has shown that it is not hazardous under the Resource Conservation and Recovery Act (RCRA). The cesium breakthrough curves for the lab- and full-scale columns agreed very well, suggesting that lab-scale tests can be used to predict the performance of larger systems. The cesium breakthrough curves for runs at different flowrates show that film diffusion is significant in controlling the mass transfer process. Operational factors that increase the effect of film diffusion include the small size and high porosity of the CST sorbent, and the relatively low liquid velocity through the sorbent.

I. INTRODUCTION

Oak Ridge National Laboratory (ORNL) has about 950,000 L of liquid low-level radioactive waste (LLLW), and 435,000 L of sludge, stored in eight 190,000 L stainless steel underground storage tanks. The waste has been accumulating in the Melton Valley Storage Tanks (MVST) since 1984. The LLLW has a high salt content, 4 to 8 M NaNO_3 , and a pH of 7 to 13. The LLLW was generated from various processes, including research reactors, radioisotope production and laboratory research, and has been concentrated by evaporation to save space in the MVST's. The generation rate for new LLLW concentrate has averaged about 20,000 gal/yr for the past several years. Similar LLLW solutions are being stored at other U.S. Department of Energy (DOE) facilities, including the Hanford and Savannah River Sites.

The DOE's Offices of Science and Technology, and Waste Management co-funded the cesium removal demonstration (CsRD) at ORNL, the first large-scale demonstration of the new state-of-the-art sorbents for radionuclides, that are being developed jointly by DOE and private industry. The primary objectives for the CsRD are to (1) process up to 100,000 L (25,000 gal) of radioactive supernate; (2) demonstrate the use of modular, mobile equipment in existing facilities; (3) evaluate decontamination for hands-on maintenance and possible transfer to

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other sites; (4) compare bench- and full-scale data; (5) provide loaded sorbent for vitrification studies; (6) concentrate the cesium on small-volume, solid waste forms and package these to meet the Waste Acceptance Criteria (WAC) for the Nevada Tests Site (NTS); and (7) provide a full-scale operational system for use in baseline activities at ORNL after the demonstration has been completed.

II. MATERIALS AND METHODS

A. Sorbent

The sorbent used for the Cesium Removal Demonstration (CsRD) is a crystalline silicotitanate (CST) granular ion-exchanger (IONSIV IE-911) produced by UOP Molecular Sieves, Inc. (Mt. Laurel, NJ). The CST material was developed, in a powder form, at Texas A&M University and Sandia National Laboratory^{1,2}, and was commercialized in an engineered form by UOP. Because of its crystalline lattice spacing, the CST material is highly selective for cesium, even in the presence of high concentrations of sodium and potassium. The CST sorbent has been found to be effective in removing cesium from waste streams ranging from highly acidic to highly alkaline, and also removes strontium ions from neutral to alkaline solutions.

B. Equipment

The demonstration system is composed of three compact, skid-mounted modules, one for handling the feed solution, one for the ion-exchange treatment, and the third for handling the ion-exchange sorbent. The first skid contains a 1900-L feed tank and two Moyno progressive-cavity feed pumps, each controllable from 0 to 25 L/min. The pumps can be used individually or in parallel. The second skid contains a filter, with a 25-micron stainless steel cartridge, and two ion-exchange columns. The ion-exchange columns are each 30 cm I.D. with a capacity of 55 L. The columns operate in a downflow mode, and each column has two 100-mesh Johnson screens at the bottom for effluent discharge. The ion-exchange columns can be used individually, in parallel or in series. The third skid contains equipment for sorbent handling, dewatering, and drying. Each skid has secondary containment and modular radiation shielding³. The system was designed by TTI Engineering (Walpole, MA) and built at Walter N. Yoder & Sons (Cumberland, MD). The skids were placed in a building, adjacent to the underground MVST tanks, which was previously used for solidifying supernate in concrete. The building has a transfer line that is connected to the MVST's through a pump module, with valving to pump out of, or drain back to, either tank W-29 or W-30. The building also has a filtered off-gas system and utilities, such as water and compressed air.

C. Operation

Most of the CsRD equipment is operated remotely, with a computer running data acquisition and control software from Intellution, Inc. (Norwood, MA). Sorbent is added to the columns by manually adding the material to the new-resin tank, and then using air and water to sluice the sorbent into one of the ion-exchange columns. Supernate from MVST W-29 is added batchwise to the CsRD feed tank. The supernate is then pumped through the filter and through either or both ion-exchange columns (see Figure 1), and then back to MVST W-30. Supernate processing continues until the desired loading is obtained on the sorbent. Spent sorbent is sluiced to the dewatering drum using air and water (see Figure 2). The dewatering drum contains a series of spiral-wound filter cartridges that are connected to a dewatering pump and blower. The dewatering pump, an air-driven double diaphragm pump, removes the bulk of the water, and then the blower pulls air through the sorbent to finish the drying process. The fillhead is removed from the dewatering drum using a remotely-operated crane, and then the drum lid is remotely attached and the drum is moved to a shielded storage vault using the crane and a shielded transfer carrier. An automated sampling system can take liquid samples from four different sampling points, before and after the filter and after each ion-exchange column. The samples are pumped into 100-mL, safety-coated glass bottles with Teflon-lined silicon septums. The samples are manually removed from the sampler, packaged in lead pigs, and delivered to the analytical lab.

Figure 1. Process Flow Diagram For The Cesium Removal Demonstration System

Figure 2. Resin Sluicing Diagram For The Cesium Removal Demonstration System

D. Process Development

Small-scale tests using surrogate solutions and actual waste solutions were performed to measure the capabilities of the CST sorbent for treating the MVST W-29 supernate (see Table 1), and to provide scale-up comparisons with the CsRD equipment. The primary objectives of the laboratory-scale tests were (1) to allow direct comparisons of the breakthrough curves for the lab- and full-scale systems using the same feed and similar operating conditions and (2) to provide samples of loaded sorbent for analysis to document that the loaded CST sorbent from the CsRD was not hazardous as defined by the Toxicity Characteristic Leaching Procedure (TCLP) for Resource Conservation and Recovery Act (RCRA) metals. Five lab-scale tests (~10 mL CST sorbent per column) were conducted. These tests demonstrated that the CST sorbent was very effective in removing cesium from the W-29 supernate, with 50% breakthrough occurring at about 500 bed volumes⁴.

A pilot-scale facility was built and operated to determine the handling and hydraulic properties of the CST sorbent using nonradioactive surrogate solutions. These tests demonstrated that the sorbent could be easily sluiced to and from the ion-exchange columns using air and water, and that the sorbent was easily dewatered and dried. The tests showed that there would be a minimal pressure drop (1-2 psi) across the ion-exchange columns at the flowrates of 19 and 38 L/min (3 to 6 bed volumes/hour) planned for the CsRD. The pilot-scale facility was also used to prepare the CST sorbent for use in the CsRD runs. As received, the sorbent is slightly acidic and contains fines. The pH of the sorbent was stabilized at 12.5 using a dilute sodium hydroxide solution, and the fines were removed by backwashing with water. The prepared sorbent was sluiced from the system into a storage drum and dewatered. The CsRD equipment was tested extensively using a surrogate solution to verify the operation of all of the equipment and to train the technicians that operated the system.

III. RESULTS

A. CsRD Run 1

A total of four CsRD runs were conducted. The first CsRD run was a limited-loading run with the goal of loading ~25 Ci of ¹³⁷Cs prior to shutting down, to provide information for later runs, when loadings would be much higher (i.e., >200 Ci of ¹³⁷Cs per column). The information to be provided included verification of operational procedures, system functionality, spent sorbent sluicing and drying, sampler operation, and measurement of radiation levels during sluicing and transfer of the loaded sorbent to assist in determining the expected radiation levels at higher loadings. About 23 Ci of ¹³⁷Cs was loaded onto 38 L (10 gal) of sorbent. The sorbent from this run was shipped to the Savannah River Site for use in a demonstration to show that the sorbent can be vitrified into a glass form for disposal.

B. CsRD Run 2

The second run consisted of a single 38-L column of sorbent operated at 19 L/min (3 bed volumes/hr). Approximately 18.028 L of MVST supernate was processed prior to 50% breakthrough of ¹³⁷Cs. Figure 3 shows a comparison of ¹³⁷Cs breakthrough between the CsRD and a lab-scale test for the same conditions. Breakthrough curves for ¹³⁷Cs, ¹³⁴Cs and ⁹⁰Sr during run #2 are presented in Figure 4. The sorbent loaded 154 Ci of ¹³⁷Cs, 2.1 Ci of ¹³⁴Cs and 0.77 Ci of ⁹⁰Sr. The CST sorbent removed essentially all of the ⁹⁰Sr from the supernate. The analysis for ⁹⁰Sr depends on a chemical separation from the other radionuclides, primarily ¹³⁷Cs, and false positives can occur if the separation is not complete, as can be seen in Figure 4. Breakthrough curves for barium (Ba), lead (Pb), rubidium (Rb), uranium (U) and zinc (Zn) are presented in Figure 5. The CST did not load any of the other contaminants in the supernate.

Figure 3. Cs-137 Breakthrough Curves For CsRD Run 2 and Lab-Scale Test

Figure 4. Radionuclide Breakthrough Curves For CsRD Run 2.

Figure 5. Metals Breakthrough Curves For CsRD Run 2.

Table 1. Average Analytical Results for Supernate Used in Lab-Scale Tests and CsRD Runs

Contaminant	Concentration		Contaminant	Concentration	
	Supernate #1	Supernate #2		Supernate #1	Supernate #2
¹³⁷ Cs (Bq/mL)	408,000	490,000	Mg (mg/L)	0.21	0.25
¹³⁴ Cs (Bq/mL)	5410	13,000	Na (mg/L)	94,000	-
⁶⁰ Co (Bq/mL)	384	320	NO ₃ (mg/L)	270,000	-
⁹⁰ Sr (Bq/mL)	1478	823	Pb (mg/L)	1.51	0.35
Ba (mg/L)	0.70	0.32	Rb (mg/L)	3.39	2.19
Ca (mg/L)	3.33	69.2	Sr (mg/L)	1.20	0.43
Cr (mg/L)	3.54	4.03	U (mg/L)	10.3	20.2
Cs (mg/L)	1.39	0.68	Zn (mg/L)	0.85	0.98
Hg (mg/L)	0.08	0.17	pH	12.7	-
K (mg/L)	16,400	20,100			

C. CsRD Run 3

For the third run, two 38-L columns of sorbent were operated in series at a flow rate of 38 L/min, which is 6 BV/h for each individual column and 3 BV/h for both in series. Approximately 39,100 L of supernate was processed with the lead and lag columns reaching 76% and 47% breakthrough of ¹³⁷Cs, respectively. The lead column loaded a total of 222 Ci of ¹³⁷Cs and the lag column loaded 112 Ci of ¹³⁷Cs. Breakthrough curves for both columns acting in series are shown in Figure 6. The results compare well with the second CsRD run, which was also conducted at 3 BV/h for one column. The ¹³⁷Cs loadings for both columns during the third run totaled 334 Ci, an average of 4.4 Ci/L, which compares favorably with the second run average of 4.1 Ci/L. Figure 7 shows that the fractional breakthrough for the first column in the third CsRD run was almost 80%. Breakthrough curves for the other contaminants were similar to those for the second CsRD run.

D. CsRD Run 4

The fourth run used a total of three columns, at a flowrate of 38 L/min, with each column containing 38 L of sorbent. Supernate from another MVST tank was mixed into tank W-29 before this run, to provide enough volume to load three batches of sorbent. The system was initially started with two columns in series. The lead column (column 1) reached 55% breakthrough of ¹³⁷Cs after processing 28,346 L and loading 252 Ci of ¹³⁷Cs. Column 1 was then removed from service, and the sorbent was sluiced into a dewatering drum. The lag column (column 2) was moved into the lead column position, and new sorbent was loaded into the empty column (called column 3), which was placed in the lag position. After processing an additional 28,390 L of supernate, column 2 had loaded a total of 267 Ci of ¹³⁷Cs, with a breakthrough of 71%, and column 3 loaded 112 Ci of ¹³⁷Cs, with a breakthrough of 51% (see Figure 8). A total of 631 Ci of ¹³⁷Cs was loaded onto 114 L of CST resin, an average of 5.5 Ci/L. The supernate used for this run contained a higher concentration of ¹³⁷Cs, but a lower total Cs concentration, so the loading of ¹³⁷Cs was higher than for the previous runs.

Figure 6. Breakthrough Curves For CsRD Run 3 and Comparable Lab-Scale Test.

Figure 7. Cesium-137 Breakthrough Curves for Each Column In CsRD Run 3.

Figure 8. Cesium-137 Breakthrough Curves For CsRD Run 4.

During the entire CsRD operation, ~115,757 L (30,583 gal) of supernate was processed and ~1142 Ci of ^{137}Cs was removed from that supernate and loaded onto 266 L (70 gal) of sorbent. The drums of sorbent from runs 2-4 are being stored at ORNL until they can be shipped to the Nevada Test Site (NTS) for permanent disposal. Solid samples of the loaded sorbents from the bench runs were taken and subjected to TCLP analysis for RCRA metals, which showed that the spent sorbent was not RCRA hazardous.

E. Calculations

Doulah and Jafar⁵ have developed a method to calculate the ion-exchange transport parameters, such as distribution coefficient and mass transfer zone height, from the shape of the breakthrough curve. The breakthrough curves for run #2 and for the first column in runs 3 & 4 were used to calculate the parameters. The results are shown in Table 2. A method for predicting distribution coefficients specifically for the CST sorbent, based on the composition of the feed solution, has been developed by Zheng² et.al. The results from this method are also listed in Table 2.

Runs 2 & 3 used the same feed solution at two different flowrates. Since the mass transfer coefficient increases almost linearly as the flowrate (and the fluid velocity) increases, film diffusion is significant in controlling the mass transfer process. The feed solution for run 4 contained a much lower total cesium concentration, which lowered the saturation capacity of the sorbent. The columns used in the CsRD were relatively short and squat, having an aspect ratio of 1:1.5, diameter to bed height, which gives a low number of theoretical plates. This results in relatively early breakthrough of Cs, since the height of a theoretical plate (mass transfer zone) is only slightly shorter than the bed height of the CST sorbent in the columns. The two different methods for calculating the distribution coefficient give similar results. The Zheng method predicts a lower distribution coefficient for run 4, based on the lower cesium and higher potassium concentration in the feed solution, than for runs 2 & 3. The breakthrough curve analysis shows that run 4 actually had a higher distribution coefficient.

Table 2. Run Conditions and Ion-Exchange Transport Parameters for CsRD Runs.

Run Conditions	Run #2	Run #3	Run #4
CST Bed Height (cm)	45	45	45
Flowrate (bed volumes hr)	3.0	6.0	6.0
Superficial Velocity (cm/min)	2.58	5.17	5.17
Initial Cs concentration (meq/L)	0.0135	0.0135	0.0051
Calculated Parameters			
Distribution Coefficient (L/kg)	831	856	1035
Height of a Theoretical Plate (cm) (Mass Transfer Zone, 5% to 95%)	37.0	41.0	38.8
Number of Theoretical Plates	1.22	1.10	1.16
Liquid Phase Mass Transfer Coef. (1/hr)	0.0040	0.0074	0.0064
Cs Saturation Capacity (meq/g)	0.011	0.012	0.0053
Zheng ² et.al. Distribution Coefficient (L/kg)	885	885	861

Operational factors in the CsRD process that increase the effect of film diffusion on the process include the small size and high porosity of the CST sorbent, and the relatively low liquid velocity through the sorbent. It should be possible to improve the performance of the CST sorbent by using taller columns and correspondingly higher liquid velocities.

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