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# Removal of Cesium from Acidic Radioactive Tank Waste by Using Ionsiv IE-911

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## ABSTRACT

IONSIV IE-911, or the engineered form of crystalline silicotitanate (CST), manufactured by UOP Molecular Sieves, has been evaluated for the removal of cesium from Idaho National Engineering and Environmental Laboratory (INEEL) acidic radioactive tank waste. A series of batch contacts and column tests were performed by using three separate batches of CST. Batch contacts were performed to evaluate the concentration effects of nitric acid, sodium, and potassium ions on cesium sorption. Additional batch tests were performed to determine if americium, mercury, and plutonium would sorb onto IONSIV IE-911. An equilibrium isotherm was generated by using a concentrated tank waste simulant. Column tests using a 1.5 cm$^3$ column and flow rates of 3, 5, 10, 20, and 30 bed volumes (BV)/hr were performed to elucidate dynamic

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cesium sorption capacities and sorption kinetics. Additional experiments investigated the effect of CST batch and pretreatment on cesium sorption. The thermal stability of IONSIV IE-911 was evaluated by performing thermal gravimetric analysis/differential thermal analysis. Overall, IONSIV IE-911 was shown to be effective for cesium sorption from complex, highly acidic solutions; however, sorbent stability in these solutions may have a deleterious effect on cesium sorption.

*Key Words:* Cesium sorption; Thermal stability; Radioactive tank waste; Ion-exchange material.

## INTRODUCTION

The Idaho Nuclear Technology and Engineering Center (INTEC), which is located on the Idaho National Engineering and Environmental Laboratory (INEEL), previously reprocessed irradiated nuclear fuel to retrieve fissionable uranium. The resulting acidic-liquid radioactive waste was solidified into a high-level waste (HLW); calcine solid and was stored in stainless-steel bins enclosed in concrete vaults. In addition to the HLW calcine, approximately 5 million liters of high-activity acidic-liquid waste are stored at the INTEC. This liquid is the result of decontamination activities, evaporator bottoms, and solvent wash activities, and cannot be calcined directly because of its high sodium content. Technologies for the treatment of the radioactive tank waste and calcine have been developed, and range from separation technologies to direct immobilization of the wastes. The current INTEC tank waste management plan includes concentration of the tank waste by evaporation and consolidation into four tanks, resulting in what is referred to as a composite tank waste. The concentration step increases nitric acid, sodium, and potassium concentrations, which may have deleterious effects on cesium sorption.

IONSIV IE-911 is a commercially available ion-exchange material developed by Texas A&M, Sandia National Laboratory, and UOP Molecular Sieves (Mt. Laurel, NJ), and has been shown to be highly effective for removing cesium from solutions over a broad pH range.[1–3] Models of multicomponent ion-exchange equilibrium and fixed-bed column performance by using IONSIV IE-911 have been developed and validated with experimental data.[4,5] The vast majority of work performed to date has been on alkaline waste solutions such as those found at the Department of Energy facilities at Hanford, Savannah River, and Oak Ridge. Limited work has been performed on acidified sludges from alkaline wastes, but, typically, these waste matrices contained 0.5 M $H^+$ or less. This study evaluated the effectiveness of IONSIV IE-911 for separating cesium from highly acidic (>1 M) tank wastes located at the INEEL.

Batch equilibrium and small-scale ion-exchange column experiments were previously performed at the INEEL with IONSIV IE-911 by using non-radioactive dissolved aluminum and zirconium-based pilot-plant calcines in addition to simulants representing the average composition of tank wastes (unconcentrated).[6,7] Small-scale column tests were performed with actual tank waste and simulated unconcentrated tank waste. Batch equilibrium ion-exchange experiments performed with IONSIV IE-911 indicated a high affinity for cesium in high-ionic strength solutions with nitric acid concentrations up to 1.7 M.

## EXPERIMENTAL

### Feed Compositions

Two composite tank waste simulants were used to perform these experiments. To distinguish between simulants, they were appropriately labeled #1 composite and #2 composite. #1 composite represented the composition of the waste presently in INTEC tank WM-180 and in INTEC tanks WM-181, WM-184, and WM-186 after concentration by evaporation. It does not include wastes from other INTEC tanks, which consist mostly of heals; nor does it include projected newly generated liquid waste (NGLW). #2 Composite is similar to #1 composite; however, phosphate and a small number of minor components were removed to avoid precipitation during simulant makeup. The compositions of the #1 composite and #2 composite tank waste simulants, based on sample analysis following filtration, are shown in Table 1.

The composite tank waste simulants used in this work were developed based upon experience, which has been derived from many development projects. The complexity of the actual waste matrices has been reproduced as closely as possible in the simulants. The primary chemical components of the actual waste, as well as many of the minor constituents are present in the simulants. However, the simulated matrix does not account for all minor components found in the actual waste. Feed preparation (removal of suspended solids) was performed by filtering through a 0.45 μm, laboratory filter before use. Simulants were spiked with National Institute of Standards tracers. Feed solutions were allowed to equilibrate 24 hr before testing.

Additional experiments were conducted with feeds containing only nitric acid, with or without various combinations of sodium nitrate and potassium

*Table 1.* Composition of #1 composite and #2 composite tank waste simulants.

| Component | #1 Composite (M) | #2 Composite (M) |
|---|---|---|
| Ag | 3.75E − 05 | 3.09E − 06 |
| B | 1.91E − 02 | 1.91E − 02 |
| Ba | 7.23E − 05 | 7.04E − 05 |
| Ca | 5.76E − 02 | 6.16E − 02 |
| Ce | — | 5.15E − 03 |
| Cd | 3.32E − 03 | — |
| Cr | 4.78E − 03 | 5.72E − 03 |
| Cs | 2.76E − 05 | 1.29E − 05 |
| Eu | 3.50E − 02 | — |
| Fe | 2.71E − 02 | 2.43E − 02 |
| Hg | 1.60E − 03 | 1.45E − 03 |
| K | 2.45E − 01 | 1.82E − 01 |
| Mn | 7.31E − 03 | 1.42E − 02 |
| Mo | 8.43E − 04 | 6.83E − 04 |
| Na | 2.36E + 00 | 1.61E + 00 |
| Nd | — | 8.63E − 04 |
| Ni | 2.27E − 03 | 2.23E − 03 |
| $NO_3$ | 6.1 | 5.6 |
| Pb | 2.01E − 03 | 1.11E − 03 |
| Se | 3.20E − 05 | — |
| Sr | 2.04E − 05 | 1.86E − 05 |
| Zr | 7.31E − 03 | 9.24E − 03 |
| Al | 7.84E − 01 | 6.90E − 01 |
| $SO_4$ | 6.37E − 02 | 7.91E − 03 |
| $PO_4$ | 2.04E − 02 | — |
| F | 7.12E − 02 | 6.38E − 02 |
| Cl | 4.05E − 02 | 2.92E − 02 |
| $H^+$ | 1.64 | 1.90 |

nitrate. The feed solutions used in these experiments contained 15 mg/L Cs (1.1E − 4 M).

## IONSIV IE-911

IONSIV IE-911 was obtained from UOP Molecular Sieves, Mt. Laurel, NJ. Three production lots of IONSIV IE-911 were used: Lot # 899902081000009, Lot # 999096810002, and Lot # 999096810004, respectively. To distinguish between batches, they were labeled A (899902081000009), B (999096810002), and C (999096810004). Preparation of IONSIV IE-911 was first performed by screening through 60 mesh (246 μm) and 150 mesh (104 μm) screens. Samples remaining on the 150-mesh screen were used in all experiments. Although optimum column diameters should be at least 40 times greater than the average particle diameter, a factor of $>30$ was determined to be adequate for this testing (column diameter used in this testing was 9.5 mm).[8]

A pretreatment step for using IONSIV IE-911 in acidic media, as recommended by UOP, was performed by recirculating a solution of 2 M $HNO_3$, which is comparable, or a slightly higher acidity than the waste solution being treated, through the bed in a closed loop, down-flow direction. It should be noted that the pretreatment of IONSIV IE-911 was not performed before batch equilibrium experiments and was performed before only one column experiment.

## Batch Equilibrium Experiments

A series of batch equilibrium experiments was performed with IONSIV IE-911. All three batches of IONSIV IE-911 were used for equilibrium experiments. All batch equilibrium experiments were initiated by dispensing a 10-mL aliquot of feed solution into a 20-mL borosilicate glass test tube containing the weighed sorbent. Solution volume to sorbent mass ratios varied between 25 and 1000. Test tubes were mixed constantly throughout the experiment by using a mechanical rotary mixer (ROTO-TORQUE model 7637) adjusted to approximately 15 rotations per minute. The speed of rotation was selected to maintain good contact between solid and liquid phases, and was expected to minimize ion diffusion resistance from the liquid-to-solid phase (i.e., particle diffusion was expected to be the rate limiting step).[9] Contacts were performed for a 24-hr period, which was followed by centrifugation for 5 min. The system does not reach complete equilibrium in 24 hr, but cesium exchange between the solid and liquid phases has been shown to approach equilibrium in 24 hr.[1,9] Aliquots were filtered through a Gelman 0.45-μm Acrodisc syringe filter to remove suspended solids before analysis.

Tests were performed at ambient temperature (23°C ± 5°C) with the exception of one set of experiments performed at both 25°C and 50°C. Batch experiments performed at elevated temperatures were performed by mixing solutions in a bench-top oven. The bench-top oven (Precision Inc., Model 18EM) was used to house the mixer, while the temperature was adjusted with an external thermostatic controller. Temperature was monitored with a thermometer inserted in the top of the oven. This arrangement provided constant temperature during the contact time.

## Column Experiments

A 1.5-cm$^3$ column was used for all column experiments. The column was fabricated from 304 stainless-steel and incorporated a transparent Plexiglas bed section. The bed section of the column was 21.5-mm high and had an inside diameter of 9.5 mm. The Plexiglas bed section allowed for visual inspection of the bed material during loading and operation. The column was designed for upward or downward flow. However, downward flow was used for all experiments.

An (FMI) valveless metering pump (Model QVG-50) was used to supply feed solution to the column. Flow rates were maintained by controlling the pump with a 10-turn potentiometer Fluid Metering Inc. (FMI) stroke rate controller (Model V100). The pump was calibrated before each test to ensure the appropriate flow rate to achieve the desired residence time in the column. Column effluents from tests were collected at constant intervals via an Eldex universal fraction collector (Model UFC) accompanied by a U-200 collection rack and 18-mm borosilicate glass test tubes.

## Column Preparation

A consistent procedure was used to load each column. The top of the column was removed and the column was filled with deionized water before loading. A glass frit was placed at the bottom of the column before sorbent addition to prevent particle loss. A precisely measured amount of dry IONSIV IE-911 was transferred into the column and allowed to gravity settle. The column was gently tapped while the particles collected into a uniform bed. Quantitative sorbent transfer was verified during each loading by inspecting the weighing dish to ensure all particles were transferred to and remained in the column. Verification of sorbent volume was performed by precisely marking the column at a height of 21.5 mm, which is equivalent to 1.5 cm$^3$. A visual inspection of the column after sorbent addition verified the bed height. After column preparation was completed, several milliliters of deionized water were processed through the column to flush unwanted fines. Removal of fines was not quantified, but the solution leaving the column during the wash step was milky in appearance, indicating the presence of fines. After the wash step, the height of the column was again verified. Parameters of the IONSIV IE-911 column experiments are listed in Table 2.

*Table 2.* Parameters of the IONSIV IE-911 column experiments.

| Test volumes | IONSIV IE-911 Lot # | Feed | Bed volume ($cm^3$) | Flow rate (BV/hr) | Total bed volumes processed |
|---|---|---|---|---|---|
| CST99-1 | B | #1 | 1.5 | 3 | 806 |
| CST99-2 | B | #1 | 1.5 | 5 | 476 |
| CST99-3 | B | #1 | 1.5 | 10 | 491 |
| CST99-4 | C[a] | #1 | 1.5 | 5 | 519 |
| CST99-5 | C | #1 | 1.5 | 20 | 532 |
| CST99-6 | B | #1 | 1.5 | 20 | 523 |
| CST99-7 | C | #1 | 1.5 | 30 | 507 |
| CST99-8 | C | #1 | 1.5 | 5 | 519 |
| CST00-1 | A | #2 | 1.5 | 5 | 1,036 |
| CST00-2 | A | #2 | 1.5 | 10 | 671 |
| CST00-3 | A | #2 | 1.5 | 20 | 671 |

[a] Pretreated before use.

### Analysis

Cesium-137, americium-241, and mercury-203 activities, for all experiments, were determined by gamma spectrometry by using a high efficiency, germanium detector. Activities of $^{238}$Pu were determined by alpha scintillation. Cadmium, Ca, Cr, Eu, Fe, Pb, Mn, Mo, Zr, Ba were analyzed by using inductively coupled plasma atomic emission spectrophotometry. Sodium and K were analyzed by atomic absorption (flame AA). Total Cs was analyzed separately by atomic emission (flame AE). Total measurement uncertainties varied as a function of analyte concentration but were typically within $\pm 5\%$

## EXPERIMENTAL RESULTS AND DISCUSSION

### Batch Distribution Coefficient ($K_d$)

The batch distribution coefficient ($K_d$) is an equilibrium measure of the overall ability of the solid-phase ion-exchange material to remove an ion from solution under the particular environmental conditions that existed during the contact. The batch distribution coefficient $K_d$ can also be used as an indicator of the selectivity and affinity of an ion in the presence of a complex matrix of interfering ions. Larger $K_d$ values indicate a greater amount of ions are concentrated onto the sorbent material.

Several factors need to be considered to ensure accurate comparison of $K_d$ results. Experimental conditions such as volume/mass ratio, temperature, solution composition, and material pretreatment can affect $K_d$ and must be identical. Distribution coefficient $K_d$ values were calculated according to the following formula:

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{M}$$

where $C_0$, initial concentration of the ion in solution before contacting sorbent; $C_e$, final equilibrium concentration of the ion in solution after contacting sorbent; $V$, volume of solution (mL); $M$, mass of sorbent (g).

## Effects of $H^+$, Na, and K on Cs Distribution Coefficient

Previous studies have evaluated the effects of protons, sodium, and potassium on cesium sorption by using IONSIV IE-911.[2,4] Zheng et al. proposed ion-exchange mechanisms for $H^+$, Cs, K, and Rb, which represented an ion-exchange unit of crystalline silicotitanate (CST) by $Na_3X$, where X represents the framework of the solid phase. Protons, K, and Rb can be exchanged for one or more of the sodium ions on the solid framework. Cesium can only be exchanged for a single sodium ion of the three sites.

Solutions containing 15 mg/L (1.1E − 4 M). cesium and 10 mg/L (1.1E − 4 M) strontium, and varying molar concentrations of nitric acid, sodium nitrate, and potassium nitrate were prepared to evaluate the relative effect that competing ions may have on cesium sorption. Samples of IONSIV IE-911 (Lot B) were used for this test. This test was meant to be qualitative and to only assess the relative effects of the competing ions. No attempt was made to do an exhaustive quantitative assessment. Batch distribution coefficient $K_d$ values and experimental conditions are shown in Table 3.

Cesium-137 $K_d$ values decrease when increasing the $HNO_3$ concentration from 1 to 2 M. Further, it appears that the $HNO_3$ concentration has a larger effect on $^{137}Cs$ sorption compared with the addition of $NaNO_3$. However, when adding molar concentrations of $KNO_3$, $^{137}Cs$ $K_d$ values decrease even further. It appears that $^{137}Cs$ sorption is largely affected by an increasing concentration of $KNO_3$ and $HNO_3$ and to a lesser extent, $NaNO_3$.

## Sorption of Plutonium, Americium, and Mercury

The sorption of transuranic (TRU) elements, such as plutonium or americium, by IONSIV IE-911 could render the spent sorbent to be classified as

***Table 3.*** Batch equilibrium experimental conditions and results.

| Spike | Feed | Mass (g) | Volume (mL) | Approx. vol/mass | $K_d$ |
|---|---|---|---|---|---|
| $^{137}$Cs | 1 M $HNO_3$ | 0.103 | 10 | 100 | 16,890 |
| $^{137}$Cs | 2 M $HNO_3$ | 0.104 | 10 | 100 | 6,576 |
| $^{137}$Cs | 1 M $HNO_3$, 1 M $NaNO_3$ | 0.105 | 10 | 100 | 8,512 |
| $^{137}$Cs | 1 M $HNO_3$, 2 M $NaNO_3$ | 0.100 | 10 | 100 | 4,309 |
| $^{137}$Cs | 1 M $HNO_3$, 0.25 M $KNO_3$ | 0.107 | 10 | 100 | 2,358 |
| $^{137}$Cs | 1 M $HNO_3$, 0.5 M $KNO_3$ | 0.105 | 10 | 100 | 1,334 |
| $^{137}$Cs | 2 M $HNO_3$, 0.25 M $KNO_3$ | 0.100 | 10 | 100 | 1,314 |
| $^{137}$Cs | 2 M $HNO_3$, 1 M $KNO_3$ | 0.106 | 10 | 100 | 410 |
| $^{137}$Cs | 1 M $HNO_3$ | 0.019 | 10 | 1,000 | 5,055 |
| $^{137}$Cs | 2 M $HNO_3$ | 0.015 | 10 | 1,000 | 3,913 |
| $^{137}$Cs | 1 M $HNO_3$, 1 M $NaNO_3$ | 0.010 | 10 | 1,000 | 4,125 |
| $^{137}$Cs | 1 M $HNO_3$, 2 M $NaNO_3$ | 0.017 | 10 | 1,000 | 2,550 |
| $^{137}$Cs | 1 M $HNO_3$, 0.25 M $KNO_3$ | 0.010 | 10 | 1,000 | 1,530 |
| $^{137}$Cs | 2 M $HNO_3$, 0.25 M $KNO_3$ | 0.015 | 10 | 1,000 | 844 |
| $^{137}$Cs | 2 M $HNO_3$, 1 M $KNO_3$ | 0.013 | 10 | 1,000 | 171 |

a TRU waste, which could affect the eventual storage and disposal options. Likewise, the sorption of heavy metals, such as mercury, could also complicate spent sorbent handling and disposal, either by requiring additional treatment steps to render the sorbent nonhazardous or by imposing additional regulations on handling and disposal.

Batch tests were performed at 25°C and 50°C by using IONSIV IE-911 (Lot B) and the #1 composite tank waste simulant. Tests were performed to measure the sorption distribution coefficients of Cs, Am, and Hg from simulated composite tank waste. Additional batch tests using IONSIV IE-911 (Lot C) and the #1 composite tank waste simulant were performed at ambient temperature to measure the sorption distribution coefficient of Pu. Batch distribution coefficient $K_d$ values and experimental conditions are shown in Tables 4 and 5.

Results indicate a decrease in $^{137}$Cs $K_d$ of approximately 40% when increasing the temperature from 25°C to 50°C. Similar results observed by Taylor and Mattus also showed decreased cesium $K_d$ values with increasing temperature for alkaline solutions. Batch equilibrium experiments performed by Taylor and Mattus varied temperatures from 30°C to 120°C with a significant decrease in $K_d$ at 120°C.[10]

Distribution coefficient values of zero suggest $^{241}$Am and $^{203}$Hg sorption did not occur. In addition, no difference in $K_d$ for Am and Hg can be

*Table 4.* Batch equilibrium experimental conditions and results.

| Spike | Feed | Mass (g) | Volume (mL) | Approx. vol/mass | Temperature (°C) | $K_d$ |
|---|---|---|---|---|---|---|
| $^{137}$Cs | #1 | 0.407 | 10 | 25 | 25 | 189 |
| $^{137}$Cs | #1 | 0.101 | 10 | 100 | 25 | 152 |
| $^{137}$Cs | #1 | 0.401 | 10 | 25 | 50 | 109 |
| $^{137}$Cs | #1 | 0.102 | 10 | 100 | 50 | 96 |
| $^{241}$Am | #1 | 0.407 | 10 | 25 | 25 | 0.00 |
| $^{241}$Am | #1 | 0.101 | 10 | 100 | 25 | 0.00 |
| $^{241}$Am | #1 | 0.401 | 10 | 25 | 50 | 0.00 |
| $^{241}$Am | #1 | 0.102 | 10 | 100 | 50 | 0.00 |
| $^{203}$Hg | #1 | 0.407 | 10 | 25 | 25 | 0.00 |
| $^{203}$Hg | #1 | 0.101 | 10 | 100 | 25 | 0.00 |
| $^{203}$Hg | #1 | 0.401 | 10 | 25 | 50 | 0.00 |
| $^{203}$Hg | #1 | 0.102 | 10 | 100 | 50 | 0.00 |

distinguished between contacts performed at 25–50°C. Plutonium-238 $K_d$ values of 0 and 5.0 indicate Pu is not sorbed onto IONSIV IE-911.

## Equilibrium Isotherm

Experimental results for batch isotherm experiments are shown in Table 6. Tests were performed with IONSIV IE-911 (Lot A) and the #2 composite tank waste simulant spiked with stable cesium to total cesium concentrations of 450 and 2000 mg/L. The equilibrium isotherm curve was generated by plotting the equilibrium solid-phase concentration in mg Cs/g IONSIV IE-911 as a function of liquid-phase concentration of Cs in mg Cs/L. An isotherm plot using Lot A and the #2 composite tank waste simulant (with additional cesium added) is shown in Fig. 1. The Langmuir fit indicates that the maximum

*Table 5.* Batch equilibrium experimental conditions and results.

| Spike | Feed | Mass (g) | Volume (mL) | Approx. vol/mass | $K_d$ |
|---|---|---|---|---|---|
| $^{137}$Cs | #1 | 0.402 | 10 | 25 | 151 |
| $^{137}$Cs | #1 | 0.101 | 10 | 100 | 153 |
| $^{238}$Pu | #1 | 0.402 | 10 | 25 | 0.00 |
| $^{238}$Pu | #1 | 0.102 | 10 | 100 | 5.0 |

*Table 6.* Batch isotherm experimental conditions and results.

| Mass (g) | Volume (mL) | $K_d$ | Approx. vol/mass | Liquid phase (mg Cs/L) | Solid phase (mg Cs/g) |
|---|---|---|---|---|---|
| 0.200 | 10 | 68.38 | 50 | 844.8 | 57.76 |
| 0.250 | 10 | 80.22 | 40 | 665.4 | 53.38 |
| 0.500 | 10 | 147.3 | 20 | 239.0 | 35.22 |
| 0.503 | 10 | 176.1 | 20 | 203.9 | 35.92 |
| 0.100 | 10 | 192.9 | 100 | 153.6 | 29.64 |
| 0.202 | 10 | 277.2 | 50 | 68.76 | 19.06 |
| 1.000 | 10 | 213.3 | 10 | 89.50 | 19.10 |
| 0.303 | 10 | 336.5 | 33.3 | 40.55 | 13.65 |
| 2.500 | 10 | 265.5 | 4 | 29.70 | 7.88 |
| 0.503 | 10 | 407.0 | 20 | 21.07 | 8.58 |
| 4.003 | 10 | 298.5 | 2.5 | 16.60 | 4.96 |
| 0.750 | 10 | 438.9 | 13.3 | 13.26 | 5.82 |
| 1.000 | 10 | 464.3 | 10 | 9.49 | 4.41 |
| 2.006 | 10 | 500.6 | 5 | 4.45 | 2.23 |
| 3.006 | 10 | 604.3 | 3.33 | 2.47 | 1.49 |
| 5.001 | 10 | 672.2 | 2 | 1.33 | 0.90 |

solid phase cesium concentration, for this waste matrix, is approximately 70.4 mg Cs/g of IONSIV IE-911.

## Column Experiments

Breakthrough curves were generated from each test by plotting the number of bed volumes (BV) of feed processed against the percent breakthrough $(C/C_0) \times 100$. These parameters are defined as follows:

$$\%\ \text{Breakthrough} = \frac{C}{C_0}\frac{[\text{Effluent tracer activity (Bq/mL)}]}{[\text{Feed tracer activity (Bq/mL)}]} \times 100$$

$$\text{BV} = \frac{\text{Total volume feed processed (mL)}}{\text{Bed size (mL)}}$$

## Small-Scale Column Experiments

Shown in Fig. 2 are $^{137}$Cs, $^{241}$Am, and $^{203}$Hg breakthrough curves for CST99-1. The percent breakthrough is plotted as a function of the BVs of solution passed through the column. Fifty percent $^{137}$Cs breakthrough

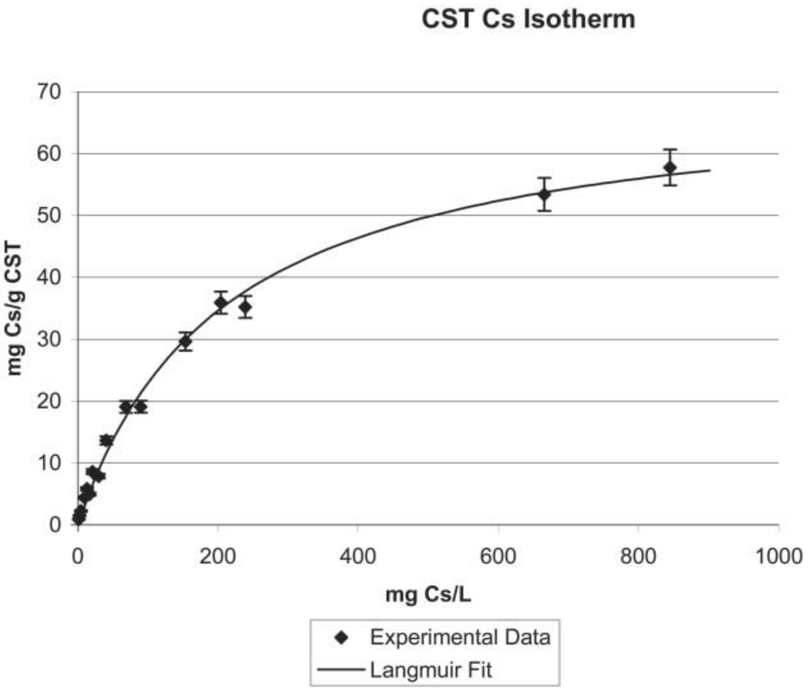

*Figure 1.* Cesium equilibrium isotherm plot by using IONSIV IE-911 (Lot A) and the #2 composite tank waste simulant.

occurred at approximately 163 BV. Americium-241 and $^{203}$Hg were not sorbed on the IONSIV IE-911, as evidenced by ~100% breakthrough for the duration of the test. Hg-203 results in Fig. 2 were not corrected for decay time; therefore, in the last half of the test, breakthrough drops below 100%. This is due solely to decay of Hg-203 ($T^{1/2} = 46\,\mathrm{d}$), and the time elapsed during the column test and sample counting.

Figure 3 displays the Na, K, Cd, Ca, Cr, Eu, Fe, Pb, Mn, Mo, Ni, Zr, Ba, and total Cs breakthrough curves for the same column test (CST99-1). The percent breakthrough is plotted as a function of the BVs of solution passed through the column. Fifty percent breakthrough of total cesium was observed at approximately 160 BVs, which is in agreement with the $^{137}$Cs data above. Sodium, K, Cd, Ca, Cr, Eu, Fe, Pb, Mn, Mo, Ni, Zr, and Ba are not sorbed on the IONSIV IE-911, as evidenced by the ~100% breakthrough for the duration of the test. Relatively high concentrations of Zr observed in initial samples are believed to be the result of dissolution of the IONSIV IE-911 matrix-binder material [$Zr(OH)_4$].[11]

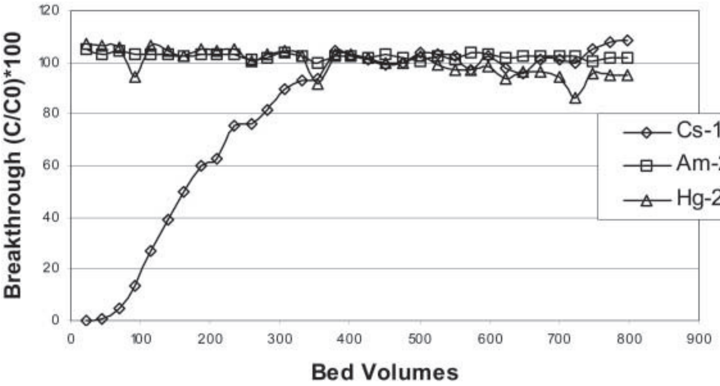

*Figure 2.* Cs-137, Am-241, and Hg-203 breakthrough curves (CST99-1) performed at 3 BV/hr by using Lot B and Feed #1.

## Cs-137 Breakthrough as a Function of Flow Rate

Cesium-137 breakthrough curves for CST99-1, CST99-2, CST99-3, and CST99-6 by using the #1 composite tank waste simulant and IONSIV IE-911 (Lot B) are shown in Fig. 4. Flow rates for CST99-1, CST99-2,

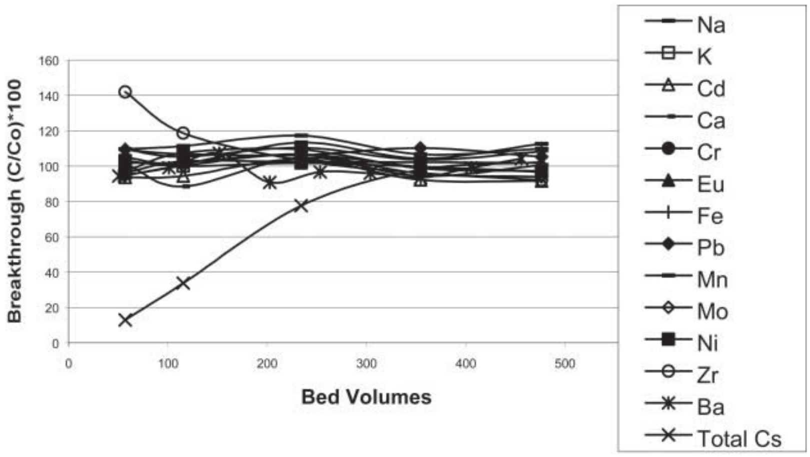

*Figure 3.* Na, K, Cd, Ca, Cr, Eu, Fe, Pb, Mn, Mo, Ni, Zr, Ba, and total Cs breakthrough curves at 3 BV/hr for the #1 composite tank waste simulant and IONSIV IE-911 (Lot B).

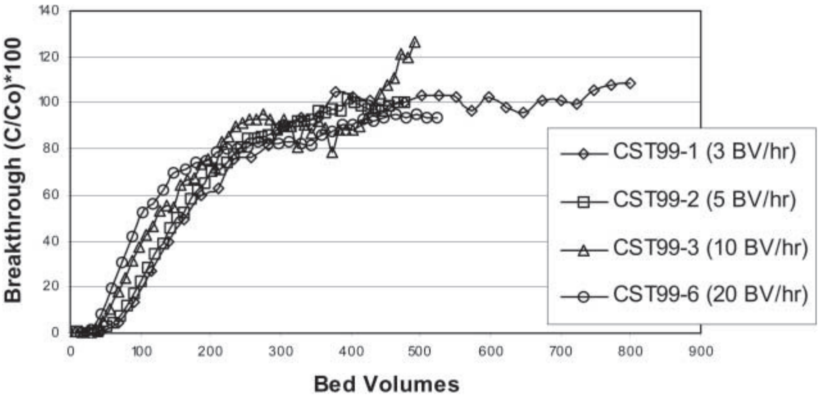

*Figure 4.* Cs-137 breakthrough curves at 3, 5, 10, and 20 BV/hr for the #1 composite tank waste simulant and IONSIV IE-911 (Lot B).

CST99-3, and CST99-6 were 3, 5, 10, and 20 BV/hr, respectively. As expected, a decrease in cesium loading can be observed with increasing flow rate. Similar results were obtained for column experiments by using the #1 composite tank waste simulant and IONSIV IE-911 (Lot C). Cesium-137 breakthrough curves for CST99-5, CST99-7, and CST99-8 performed at flow rates of 5, 20, and 30 BV/hr are shown in Fig. 5.

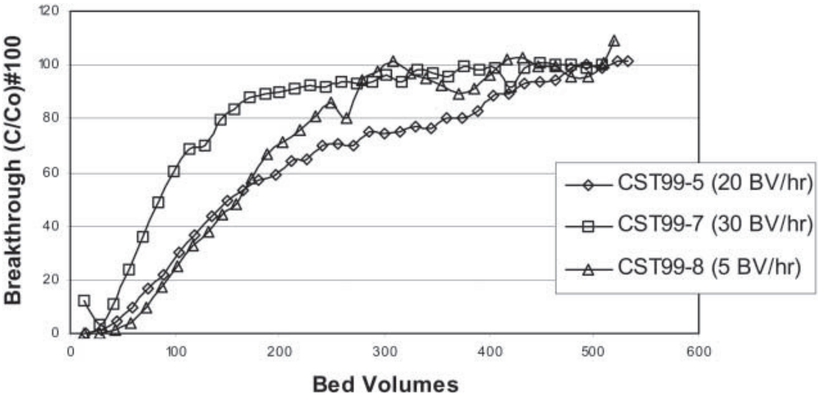

*Figure 5.* Cs-137 breakthrough curves at 5, 20, and 30 BV/hr for the #1 composite tank waste simulant and IONSIV IE-911 (Lot C).

## Cs-137 Breakthrough as a Function of IONSIV IE-911 Batch

Figure 6 displays $^{137}$Cs breakthrough curves for CST99-2, CST99-8, CST99-5, and CST99-6 as a function of differing batches of IONSIV IE-911. All tests used the #1 composite tank waste simulant. Column tests CST99-2 and CST99-8 were performed at flow rates of 5 BV/hr by using IONSIV IE-911 Lots B and C. CST99-5 and CST99-6 were performed at flow rates of 20 BV/hr by using Lots B and C sorbents. Little difference in $^{137}$Cs loading was observed for tests performed with IONSIV IE-911 (Lot B) and IONSIV IE-911 (Lot C) at flow rates of 5 BV/hr. However, $^{137}$Cs breakthrough for test CST99-6 by using Lot B at 20 BV/hr, occurred sooner than for test CST99-5, which was performed with Lot C at 20 BV/hr. All tests were run with sorbent particle sizes between 104 and 246 μm and similar loading procedures were used. The data for CST99-6 as shown in both Figs. 5 and 6 indicate higher cesium loading than would be expected. There is no apparent explanation for this based on experimental conditions (i.e., different temperature, particle size, void fraction, etc.)

## Cesium-137 Breakthrough as a Function of Feed Composition

Cesium-137 breakthrough curves for CST00-1, CST00-2, CST00-3, CST99-2, CST99-3, and CST99-6 as a function of feed composition are shown in Fig. 7. A higher cesium loading by using the #2 composite tank

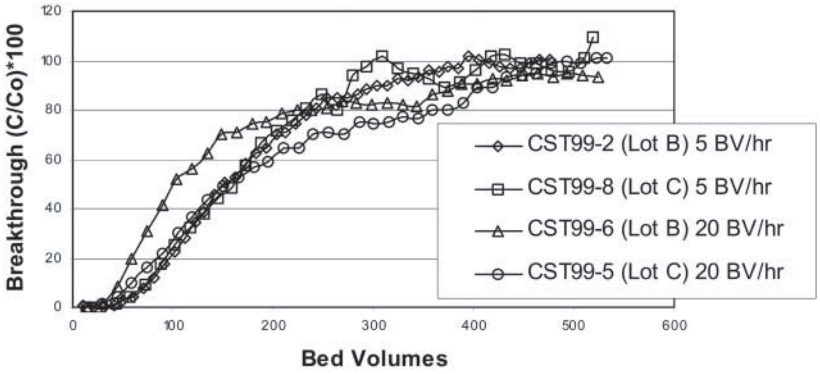

***Figure 6.*** Cs-137 breakthrough curves as a function of dissimilar lots of IONSIV IE-911 (Lot B and C) performed at 5 and 20 BV/hr by using the #1 composite tank waste simulant.

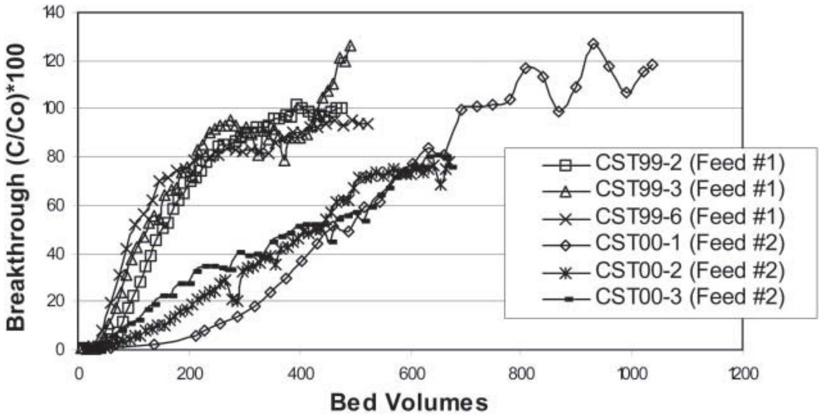

***Figure 7.*** Cs-137 breakthrough curves as a function of feed composition.

waste simulant is indicated by a larger amount of BVs processed before 50% breakthrough. Moreover, 50% breakthrough is much earlier for tests performed with the #1 composite tank waste simulant than with tests performed with the #2 composite simulant. As stated earlier, Cs loading is greatly affected by the presence of competing ions such as K and Na. The #1 composite tank waste simulant contains total Cs concentrations more than two times higher than the #2 composite tank waste simulant, as well as higher Na and K concentrations. The decrease in cesium loading for CST99-2, CST99-3, and CST99-6 is most likely due to: (1) the difference in total Cs concentrations found in waste simulants and (2) higher K and Na concentrations in composite #1. Cesium concentrations in column effluents from tests CST-99-3, CST-00-1 exceed Cs feed concentrations. The variation in these data are greater than the expected experimental error. There are a number of possible explanations for this, however, additional testing may be required to fully understand. One possible explanation is that Cs may be desorbing off the column (chromatographic effect) or is being displaced by another cation (such as $H^+$, Na, or K). Competition for ion-exchange sites can be either direct (exchange directly for a site that can exchange with Cs), or indirect (exchange with an adjacent site to a Cs exchange site).[2,4] At the high acid concentrations of the waste matrix, protons are expected to directly compete with cesium for cesium exchange sites. Because the binder material (Zr) appears to be dissolving, in situ generation of fines during the test may be occurring, which eventually are carried out of the column. However, these explanations fail to account for similar tests where this phenomena was not observed. Another possible explanation may be that the temperature in the laboratory increased at the end of those specific tests; however, this explanation cannot be confirmed. Temperature data at the end of these tests were not recorded.

## Cesium-137 Breakthrough as a Function of Sorbent Pretreatment

Figure 8 displays the $^{137}$Cs breakthrough curves for CST99-4 and CST99-8 by using the #1 composite tank waste simulant at 5 BV/hr. Both CST99-4 and CST99-8 used IONSIV IE-911 (Lot C), however, CST99-4 underwent a pretreatment step before testing. Pretreatment of IONSIV IE-911 was performed as recommended by UOP, by recirculating a solution of 2 M $HNO_3$ through the bed in a closed loop, down-flow direction. In Fig. 8, the percent breakthrough is plotted against the BVs of solution passed through the column. Fifty percent $^{137}$Cs breakthrough for CST99-4 and CST99-8 was observed at approximately 100 and 160 BVs, respectively.

As observed in Fig. 3 and subsequent testing, the [$Zr(OH)_4$] binder in IONSIV IE-911 appears to dissolve in nitric acid and the acidic waste matrix used in these tests. This could have a number of deleterious effects on the sorption of cesium, namely, changes in the physical configuration of the sorbent, resulting in a reduced number of exchange sites, or the generation of fines, which may carry some cesium with them. Pretreatment of IONSIV IE-911 with acid solutions, therefore, is not recommended.

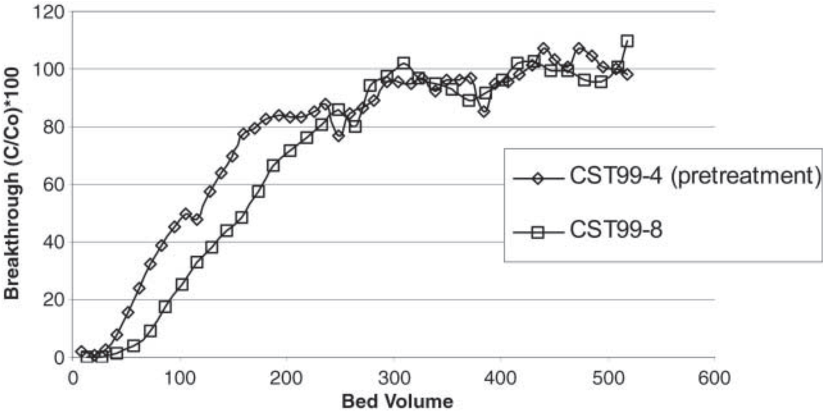

*Figure 8.* Cs-137 breakthrough curves as a function pretreatment and no pretreatment at 5 BV/hr by using the #1 composite tank waste simulant and IONSIV IE-911 (Lot C).

## Column Capacities

Data plots of throughput volume (L) against column effluent Cs concentration (mg/L) were generated by using experimental column breakthrough data presented previously. A second-order kinetic equation was fit to each of these data sets to obtain a relationship for Cs effluent concentration as a function of throughput volume.[12] This equation for Cs concentration was then substituted into the following relationship to calculate column capacity (CC):

$$\mathrm{CC} = \frac{\int_0^v (C_0 - C)dv}{M}$$

where $v$, volume at a specified breakthrough (L); $C_0$, initial Cs concentration (mg/L); $C$, Cs concentration in the column effluent (mg/L); $M$, mass of sorbent (g, dry weight)

Column capacity estimates were obtained by evaluating the integral numerically with upper-limit volume values corresponding to approximately 50% and 100% Cs breakthrough. Column capacities at 50% and 100% breakthrough for the small-scale column experiments are shown in Table 7.

Column capacities for tests by using the #2 composite tank waste simulant (CST00-1, 2, 3) are higher than capacities for column tests performed with the #1 composite tank waste simulant, despite cesium concentrations greater than two times higher in the #1 composite tank waste simulant. This is apparently due to significantly higher K and Na concentrations in the #1 composite tank

***Table 7.*** Column capacities for small-scale column experiments.

| Test | Column capacity at 50% breakthrough (mg Cs/g sorbent) | Column capacity at 100% breakthrough (mg Cs/g sorbent) |
|---|---|---|
| CST99-1 | 0.505 | 0.678 |
| CST99-2 | 0.463 | 0.652 |
| CST99-3 | 0.352 | 0.495 |
| CST99-4 | 0.307 | 0.473 |
| CST99-5 | 0.435 | 0.724 |
| CST99-6 | 0.199 | 0.438 |
| CST99-7 | 0.255 | 0.394 |
| CST99-8 | 0.472 | 0.603 |
| CST00-1 | 0.740 | 0.853 |
| CST00-2 | 0.598 | 0.767 |
| CST00-3 | 0.532 | 0.750 |

waste simulant. Sorbent pretreatment with $HNO_3$ and increasing flow rates generally reduced column capacities.

## Thermal Gravimetric/Differential Thermal Analysis

Studies to determine the thermal stability of IONSIV IE-911 were performed by thermal gravimetric analysis/differential thermal analysis. Results are shown in Fig. 9. A sample of IONSIV IE-911 (Lot A) was heated at approximately 1°C/min and the mass of the sample, as well as temperature effects from the sample recorded.

A gradual decrease in weight can be observed with increasing temperature. Approximately 82% of the sample was present at 500°C, indicating that little of the sample was lost up to 500°C. Most of the mass loss can be attributed to water of hydration. Results agree with Nyman et al. [11]. A small endotherm was observed at 68°C, followed by two small endotherms at 150°C and 246°C. The first endotherm was most likely due to loss of water from the sample. A small exotherm of approximately 0.1 W/g was observed at approximately

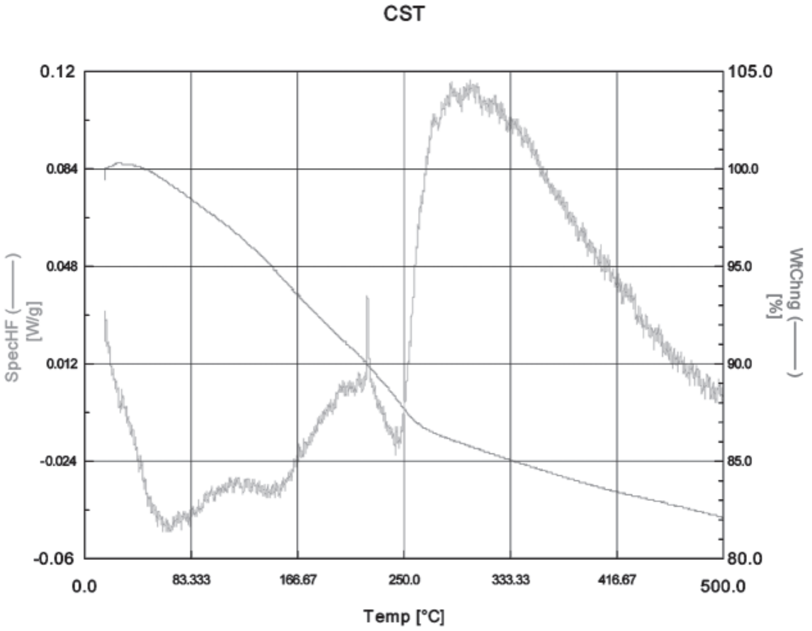

*Figure 9.* TGA/DTA plot for IONSIV IE-911. *(View this art in color at www.dekker.com)*

300°C. Due to the relatively small column diameters required to treat the INEEL wastes (approximately 30 cm), the temperature of IONSIV IE-911 would not be expected to reach temperatures exceeding 300°C, even if loaded with Cs-137; therefore, the thermal stability of IONSIV IE-911 appears to be adequate for processing acidic radioactive wastes.

## CONCLUSIONS

A series of batch equilibrium and small-scale column tests have been completed by using IONSIV IE-911. Batch equilibrium data indicate that IONSIV IE-911 has a high affinity for cesium. However, competing cations and increased temperatures decrease that affinity. Batch tests at 50°C decreased $^{137}$Cs $K_d$ about 60% when compared with tests performed at 25°C. Competing cations affect the sorption in the order $\mathrm{K} \approx \mathrm{H}^+ > \mathrm{Na}$, with K reducing cesium sorption by the greatest extent. Batch equilibrium data also indicate that americium, plutonium, and mercury are not adsorbed.

Small-scale column tests were performed to demonstrate the effects of flow rate, pretreatment, and IONSIV IE-911 production (Lot) number on cesium breakthrough. Column tests preformed at 3, 5, 10, 20, and 30 BV/hr typically displayed expected breakthrough curves with a decrease in cesium loading with increasing flow rate. Column capacities were calculated at 50% and 100% breakthrough for all dynamic small-scale column experiments.

Comparative column tests were performed by using pretreated and as-received IONSIV IE-911. Results indicate that $^{137}$Cs breakthrough occurred sooner for the pretreated IONSIV IE-911 than for the nontreated sorbent, possibly due to displacement by another cation, physical changes due to dissolution of the binder, or potential temperature increases in the laboratory near the end of column testing. In addition, comparative column tests performed with different lots of IONSIV IE-911 displayed variation in cesium sorption at 20 BV/hr.

Overall, the performance of IONSIV IE-911 indicates it should be an effective sorbent for the separation of cesium from acidic liquids; however, additional testing to quantify binder ($Zr(OH)_4$) stability in acid, and the effects that binder dissolution has on cesium sorption and sorbent mechanical properties should be performed.

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