WSRC-TR-98-00196

Radioactive Waste Decontamination Using Selentec Mag*Sep^{SM} Particles

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DOE Contract No. **DE-AC09-96SR18500**

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WSRC-TR-98-00196, Rev. 0

Keywords: Ion exchange,
Radioactive waste disposal,
Crystalline silicotitanates

Retention: Permanent

RADIOACTIVE WASTE DECONTAMINATION USING SELENTEC MAG*SEP$^{\text{SM}}$ PARTICLES

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Publication Date: June 1, 1998

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

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By D. D. WALKER

SUMMARY

A sorbent containing crystalline silicotitanate (CST) tested for cesium removal from simulated Savannah River Site (SRS) soluble high activity waste showed rapid kinetics (~1 h contact time) and high distribution coefficients (K_d~4000 mL/g of CST). The sorbent was prepared by Selective Environmental Technologies, Inc., (Selentec) as a MAG*SEP^{SM} particle containing CST obtained from the Molecular Sieve Department of UOP, LLC. Results of preliminary tests suggest potential applications of the Selentec MAG*SEP^{SM} particles to radioactive waste decontamination at SRS.

INTRODUCTION

Cesium-137 is the primary gamma-radiation source found in soluble, alkaline, high level waste at SRS and other DOE sites. CST has been widely studied and reported as an extremely effective sorbent for cesium in alkaline media.[1,2] Selentec prepared a particle form of CST that allows magnetic separation from the treated solution. The Selentec particles contain the CST (UOP IONSIV® IE-910 Ion Exchanger and magnetite cores in an acrylic matrix. The CST comprises approximately 25% of the particle weight. The magnetite cores provide a high degree of magnetic susceptibility used in magnetic separation of the particles. Selentec provided MAG*SEP^{SM} particles to the Savannah River Technology Center (SRTC) prepared specifically for removal of cesium from alkaline media.

Magnetic separation of the cesium-loaded particles offers several advantages over ion exchange columns and filtration methods. Magnetic separation requires no pre-filtration of the feed stream as required for ion exchange column processes to prevent large pressure drops and column plugging. This advantage assumes entrained particles need not be removed to achieve the required decontamination. Magnetic separation allows higher process rates compared to ion exchange or filtration processes. Magnetic separation simplifies the solid-liquid separation problem compared to filtration and requires fewer valves and less piping than comparable ion exchange processes.

A successful application of magnetic separation requires the following properties in the cesium-removal particles:

- Rapid adsorption kinetics,
- Large distribution coefficients for cesium,
- Efficient separation of particles from treated solution, and
- High capacity for cesium.

Using the MAG*SEP^{SM} particles provided by Selentec, SRTC demonstrated the rapid adsorption kinetics, high distribution coefficients, and efficient separation of the particles from the solution. The successful trial suggests the need for additional work to determine the capacity of the particles for cesium and the behavior in multiple contact cycles. Additional testing of the magnetic separation method is also recommended.

TEST DESIGN

The MAG*SEP^{SM} particles that Selentec provided to SRTC were designated Batch #PA-103-1. The following information was provided by Selentec and was not further verified. The particles contained 36.8% solids and 63.2% moisture. CST comprised approximately 25% of the solid weight. The MAG*SEP^{SM} particle size ranged from 100 to 500 microns in diameter. The particles were pretreated in 5 M sodium ion solution prior to delivery to SRTC. The pretreated particles were weighed into two 500-mL polyethylene bottles. Bottle A contained 10 g (dry weight equivalent) and Bottle B contained 20 g (dry weight equivalent) of PA-103-1 particles.

Simulated SRS soluble high activity waste was prepared from reagent grade chemicals. Table I lists the composition of the salt solution. The salt solution included Cs-137 (New England Nuclear, carrier free, >99% radionuclide purity) at ~1×10^6 d/m/mL. The spiked salt solution (200 mL) was added to each of the polyethylene bottles containing the MAG*SEP^{SM} particles. The bottles were sealed and then continuously agitated on a platform shaker. After approximately 1, 2, 3, 6, and 24 hours, the bottles were removed from the shaker and placed on a magnet for 1 minute. A sample (3.0 mL) was removed by pipette from the upper portion of the clear salt solution. At 24 hours, an additional sample was removed and filtered through a disposable nitrocellulose filter (0.2 micron nominal pore size). The Cs-137 activity of the samples (3.0 mL) was measured from the gamma emission of the Ba-137m daughter (661.2 keV) using a Canberra Model 45 multichannel analyzer and EG&G Ortec Model GEM-10175 high-purity germanium detector. The ratio of the activity of the sample to the original salt solution was used to calculate the final cesium concentrations from the initial concentration (0.17 mM).

Eric K. Sliger (Selentec) provided data from a preliminary, non-radioactive test performed in Selentec's Atlanta laboratory. The results agree with the radioactive testing and are included for comparison. The Selentec test used a simulant recipe similar to the salt solution listed in Table I, but containing 0.0036 M Cs^+ (480 mg/L). Cesium concentrations were measured colorimetrically. Moisture content of the particles was 25%. Salt solution (100 mL) was treated with 5 g (dry weight equivalent) of PA-103-1 particles. Samples were agitated with an arm shaker.

RESULTS

Table II lists the cesium concentration in the salt solution samples from the three tests. Figure 1 shows the change in concentration as a function of time. The plot shows that the cesium concentration dropped rapidly during the first hour of shaking and the rate of

TABLE I. Composition of Simulated Waste Solution

Component	Concentration (molar)
Na^+	5.0
K^+	0.020
Cs^+	0.00017 (23 mg/L)
OH^-	1.36
NO_3^-	1.9
NO_2^-	0.61
AlO_2^-	0.32
CO_3^{2-}	0.17
SO_4^{2-}	0.15
Cl^-	0.023
F^-	0.015
$C_2O_4^{2-}$	0.015
PO_4^{3-}	0.009
SiO_3^{2-}	0.003
MoO_4^-	0.0004

TABLE II. Cesium Concentrations in Treated Simulated Waste Solution

		Experiment	
	SRTC	SRTC	Selentec
	50 g/L*	100 g/L*	50 g/L*
	Bottle A	Bottle B	Nonradioactive
Elapsed Time (h)		Cesium Concentration (mM)	
0	0.17	0.17	3.6
1			0.49
1.25	0.0070		
1.27		0.0029	
2			0.195
2.28	0.0052	0.0025	
3			0.122
3.55	0.0048	0.0024	
5.70	0.0052	0.0022	
6			0.097
24			0.024
24.63	0.00366	0.00176	
24.7 0.2 micron filter	0.00367	0.00174	
K_d (mL/g)**	3.6×10^3	3.8×10^3	11.9×10^3

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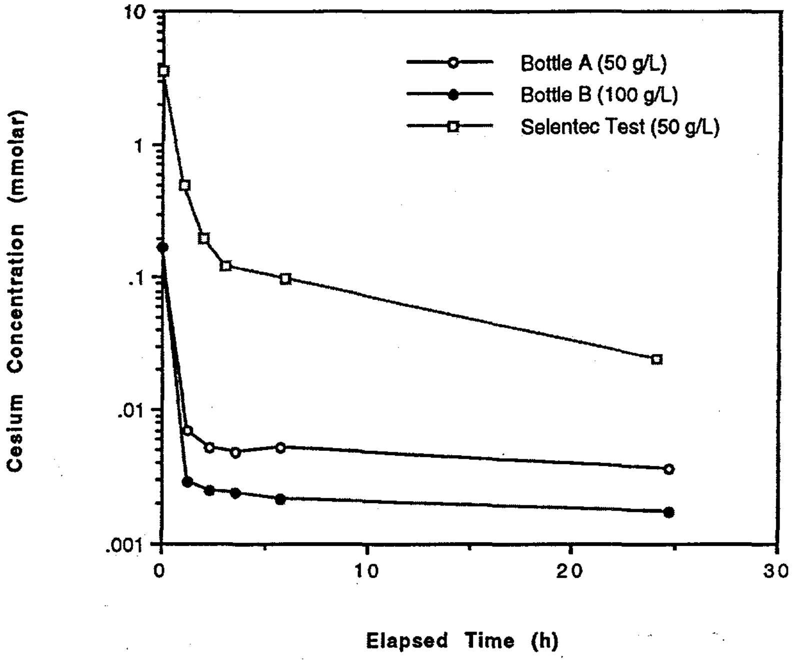
* Based on grams of dry Selentec MAG*SEP^{SM} particles.

** Based on grams of dry CST and cesium concentration after 24 hours. No volume correction made for the removal of earlier samples.

FIGURE 1. Cesium Concentrations in Simulated Waste Solutions



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removal slowed significantly after two hours. The knee in the curve likely reflects an approach to equilibrium between cesium on the resin and cesium in solution. The steep portion of each curve probably represents the approach to equilibrium between the solution cesium and cesium on CST embedded at the surface of the MAG*SEP^{SM} particles. The region following the knee represents the approach to equilibrium with cesium on CST internal to the MAG*SEP^{SM} particles.

After 24 hours, portions of the treated salt solutions were filtered through 0.2 micron filters. The cesium activities in the filtered samples did not significantly differ from activities in samples obtained by magnetic separation. This result appears to demonstrate the MAG*SEP^{SM} particle integrity and that extended shaking does not produce non-magnetic fines. No turbidity of the salt solution was noted, as was typical of previous CST column testing.[1] However, CST fines (2.4 g/mL) are more dense than the salt solution (1.2 g/mL) and may have settled due to gravity.

The cesium distribution coefficient (K_d) for each of the three tests has been calculated from the following equation (see Appendix A).

$$K_d\ (\text{mL/g}) = \frac{(C_0 - C_1)}{C_1}\ \frac{V}{M}$$

Where C_0 = the initial cesium concentration in the feed solution
C_1 = the final cesium concentration after treatment,
V = the solution volume in mL, and
M = mass of dry CST in grams.

Table II lists the calculated distribution coefficients for the three experiments. The distribution coefficients exceed those listed in the product information provided by UOP (Appendix A). The graph in the product information bulletin indicates a cesium K_d at pH 14 of approximately 1000 compared to the K_d of 3800 to 11900 in the Selentec MAG*SEP^{SM} particles and simulated SRS soluble waste.

DISCUSSION

The following significant conclusions derive from this test of Selentec MAG*SEP^{SM} particles loaded with CST.

- Selentec MAG*SEP^{SM} particles containing CST significantly reduce cesium concentrations in simulated SRS soluble waste (containing 1.36 molar OH^-).
- Cesium distribution coefficients were not adversely affected by inclusion of CST in Selentec's MAG*SEP^{SM} particles.
- Rapid cesium extraction kinetics occurred with the MAG*SEP^{SM} particles. Cesium removal reached 86-98% within the first hour of contact.
- Magnetic separation of the particles appears effective, simple, and rapid. Non-magnetic fines were not detected in this test.

Based on these results, several SRS applications of the MAG*SEP^{SM} particles appear promising. These applications include the following waste treatment problems.

- DWPF recycle stream
    - multiple contacts probably required
    - potentially simpler than ion exchange
    - avoids sending DWPF recycle to tank farm
    - removal of other components besides cesium also required
- R Basin water decontamination
    - potential single step treatment
    - simpler than ion exchange
    - removal of Sr-90 also required
- RBOF treatment
    - avoid sending effluent to tank farm
- SRTC waste streams
    - avoid shipping waste to tank farm
- SRS high activity waste
    - requires multiple contacts
    - magnetic separation simpler than ion exchange or filtration

Additional testing of the MAG*SEP^{SM} particles is required to evaluate their usefulness in these applications.

FURTHER TESTS

Complete evaluation of the Selentec MAG*SEP^{SM} particles requires measurements of the cesium capacity. Successful application of this product requires multiple contacts to achieve high decontamination factors and to reduce the mass of particles required per unit volume of treated waste. Economic implementation requires that the total sorption capacity of the particles prove very much greater than shown in the single contact tests. Repeated treatments must produce very high decontamination factors. This work suggest the need for the following two tests.

Test#1: Treat a volume of SRS simulated waste with MAG*SEP^{SM} particles, isolate the particles, and then treat a second volume of SRS simulated waste with the used particles. Repeat the treatments with fresh batches of simulated waste until the particle performance becomes unacceptable.

Test#2: Treat a volume of SRS simulated waste with MAG*SEP^{SM} particles, remove the particles, and then treat the solution a second time with fresh particles. Repeat the treatments until 99.998% of the cesium is removed (decontamination factor of 50,000) or the resin becomes ineffective. Because of the high decontamination factor required, this test may require use of actual waste samples.

Both of the suggested tests are required to fully evaluate process flowsheets using the MAG*SEP^{SM} particles. Additional testing related to magnetic separation is also recommended since the encouraging results from the current test could have been due to gravity settling of CST fines.

ACKNOWLEDGMENTS

The author acknowledges the help of Eric K. Sliger, consulting engineer with Selective Environmental Technologies, Inc., in the design of the experiment and for providing the MAG*SEP^{SM} particles, and of Betty H. Croy, who conducted the experiment.

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1. R. Braun, *et al*, "Crystalline Silicotitanates - Novel Commercial Cesium Ion Exchangers," Spectrum '96, August 18-23, 1996.

2. D. D. Lee, J. F. Walker, Jr., and P. A. Taylor, "Cesium-Removal Flow Studies Using Ion Exchange," Environmental Progress, Winter 97.

Product Information for UOP IONSIV® IE-910 Ion Exchanger

UOP **IONSIV®**

PRODUCT INFORMATION

MOLSIV® ADSORBENTS
a product of UOP

IONSIV® IE-910 ION EXCHANGER SERIES

Description

UOP IONSIV® IE-910 Ion Exchanger Series Products are crystalline silicotitanates supplied in the sodium (Na^+) form.

Chemical Formula

Na_2O, SiO_2, TiO_2 + Trade Secret Oxides

Shipping Information

IONSIV® IE-910 Ion Exchanger Series Products are available in powder and 30 x 60 mesh form.

Regeneration

Due to the extremely high Cs selectivity, Cs cannot be reasonably eluted from IONSIV® IE-910 Ion Exchangers. Sr can be eluted by the use of a suitable salt solution.

Typical Application Areas

UOP IONSIV® IE-910 & IE-911 Ion Exchanger Products are effective for the following applications:

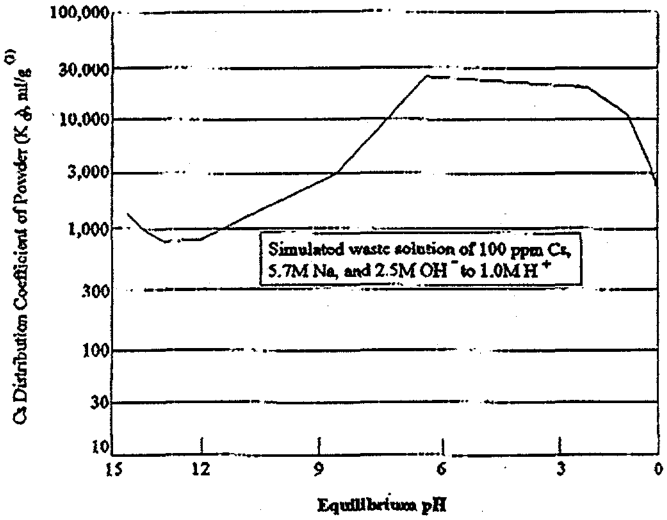
- Removal of Cs & Sr from highly alkaline radwastes and processing solutions.
- Removal of Cs from acidic radioactive waste solutions.
- Removal of Cs & Sr from groundwater that is radioactively contaminated.
- Removal of Cs, Sr & radionuclides from fuel storage & cooling ponds.

Typical Properties

	IE-910	IE-911
Particle Size	Powder (< 1 μm)	Mesh (30x60)
Pore Openings	approx. 4 Å	approx. 4 Å
Bulk Density		
As shipped		60 lbs/cu.ft. 960 kg/cu.m.
Piece Density		2.44 g/ml
Typical Cs K_d (1)		

Additional Information

Bulletins discussing additional application of UOP Molecular Sieves are available.



Crystalline Silicotitanates Exhibit
High Cs Distribution Coefficients
(Data Courtesy Sandia National Laboratories)

(1) $$K_d = \frac{(C_0 - C_1)}{C_1} x \frac{V}{M x F}$$

where: C_0 is the initial counts of the ion of interest in the feed solution before contact. C_1 is the counts after contact; V is the solution volume in ml, M is the CST mass in grams, F is the mass of dry exchanger divided by the mass of wet exchanger.

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