Evaluation of Crystalline Silicotitanate and Self-Assembled Monolayers on Mesoporous Support for Cesium and Mercury Removal from DWPF Recycle

by

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Heavy metals, Wastewater

Retention Time: Permanent

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Report Date: September 22, 1999

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**WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER TECHNOLOGY CENTER**

**EVALUATION OF CRYSTALLINE SILICOTITANATE AND SELF-
ASSEMBLED MONOLAYERS ON MESOPOROUS SUPPORT FOR CESIUM
AND MERCURY REMOVAL FROM DWPF RECYCLE (U).**

1. SUMMARY

The affinities for cesium and mercury ions contained in DWPF recycle simulants and Tank-22H waste have been evaluated using Crystalline Silicotitanate (CST) and Self-Assembled Monolayers on Mesoporous Support (SAMMS) ion-exchange materials, respectively. Results of the performance evaluations of CST on the uptake of cesium with simulants and actual DWPF recycle samples (Tank 22H) indicate that, in practice, this inorganic ion-exchange material can be used to remove radioactive cesium from the DWPF recycle. SAMMS material showed little or no affinity for mercury from highly alkaline DWPF waste. However, at near neutral conditions (DWPF simulant solution pH adjusted to 7), SAMMS was found to have a significant affinity for mercury. Conventional Duolite® GT-73 ion exchange material showed an increase in affinity for mercury with increase in DWPF recycle simulant pH. Duolite® GT-73 also had a high batch distribution coefficient for mercury uptake from actual Tank 22H waste.

2. INTRODUCTION

High-Level Waste (HLW) is pretreated and vitrified in the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS). The DWPF process generates a large volume of aqueous waste known as DWPF recycle, which is returned to the HLW tank system for storage and evaporation.

The DWPF recycle stream is an aqueous waste stream, which is returned to the Tank Farms through tank 43H and the 2H-evaporator system. The stream is comprised of numerous streams from within DWPF. Waste from the Slurry Mix Evaporator Condensate Tank (SMECT), Off-Gas Condensate Tank (OGCT), and smaller amounts of dilution waters and DWPF laboratory waste are sent to the Recycle Collection Tank (RCT). Batches of this waste are collected in the RCT and then caustic adjusted (inhibition process for corrosion control) before transfer to tank 43H. Waste collected in the RCT may alternate between SMECT and OGCT, that is, one batch may be primarily SMECT while the next batch is OGCT waste. The SMECT waste stream is the main source of organic compounds in the RCT, although some small quantities of organics are also introduced from the DWPF laboratories.

Cesium-137, strontium-90, mercury and traces of transuranic elements are the primary constituents of concern in the DWPF recycle waste. The proposed path is to use ion-exchange technology to decontaminate the DWPF recycle waste stream and send the decontaminated aqueous stream through the general purpose evaporator to the Effluent Treatment Facility (ETF). This approach would eliminate the current practice of sending the DWPF recycle to the HLW tank farm relieving HLW of storage capacity problems. The continuous operation of DWPF would be ensured and the long-term storage problems for the Tank Farms would be alleviated.

The Efficient Separation Program (ESP) funded this investigation with the following principal goals:

- Qualify Crystalline Silicotitanate (CST) ion-exchange material for the removal of radioactive cesium and, possibly, transuranic elements from the DWPF recycle waste stream,
- Evaluate Sodium Titanate (ST) affinity for the uptake of strontium-90 from the DWPF waste stream and the effect of ST particle size on the cross-flow filtration process (currently not part of objective because of limited funding resources), and
- Evaluate and compare the affinity for mercury in the DWPF recycle waste by other ion-exchange materials like the Self-Assembled Monolayers on Mesoporous Support (SAMMS) material and standard Duolite GT-73 resin.

3. EXPERIMENTAL APPROACH

The purpose of this study was to examine the feasibility of using CST for cesium removal from DWPF recycle, and to compare two ion-exchange materials, Duolite GT-73 and SAMMS, for chemisorption of mercury. Important variables in assessing the viability of these materials under conditions found at DWPF are pH, initial cesium concentration, organic concentration, and sodium concentration. Cesium and mercury uptake behavior under the expected range of conditions was conducted for these materials using various simulants for the DWPF recycle stream.

3.1 Ion-Exchange Materials

An engineered granular form of CST ion exchange material from UOP*, known as Ionsive® IE-911, (lot # 999096810002), was used in this study (1). Dr. Feng of Pacific Northwest National Laboratory (PNNL) provided the SAMMS material and the Duolite® GT-73, sodium form, was obtained locally on site. Sodium Titanate slurry was obtained from Allied Signal (Allied Signal Research and Technology, 50 East Algonquin Road, Des Plaines, IL 60017-5016).

3.2 DWPF Simulants

DWPF simulants were selected to represent the expected range of constituents and conditions based on consultation with HLW Engineering. As the project proceeded focus of the work shifted to Tank 22 which is currently the intermediate storage destination for DWPF recycle and other Tank Farm dilute waste streams. In addition, a funding shortfall resulted in a delay in analyzing samples from initial CST runs. The analytical results from these runs are suspect. As a result, additional tests were run using a Tank 22 simulant. Table 1 is a summary of the test cases for this study.

The uptake of cesium-137 surrogate with CST was first evaluated with a simulant from earlier CST testing (3) to provide a baseline for the method used in this experiment. This inorganic simulant composition, shown in Table 2, is representative of typical HLW salt waste composition.

Caustic adjustments in the RCT, as described earlier, put sodium concentrations in the RCT in the range of 0.5 to 5.4 molar. Based principally on these sodium concentrations, three types of basic DWPF test solutions (simulants) were used in this study:

* UOP, 307 Fellowship Road, Suite 207, Mount Laurel, NJ (856-727-9400)

Table 1 Summary of Test Cases.

Sorbent Tested / Contam. Removed	Simulant Evaluated	Solution Composition	Results	Experimental Variable
CST / Cs133	Baseline salt simulant composition	Table 2	Table 8	None. Comparison with earlier results (Ref. 3)
CST / Cs133	High sodium/ organic/inorganic DWPF recycle	Tables 3 & 4	None. Funding delay.	pH
CST / Cs133	Avg. sodium/ organic/inorganic DWPF recycle	Tables 5 & 6	None. Funding delay.	pH
CST / Cs133	TNX SMECT sample	Not available except for Cs	None. Funding delay.	pH
CST / Cs133	Tank 22 simulant (low sodium)	Table 7	Tables 9 & 10 Figures 1 & 2	Initial cesium (Cs-133) concentration
CST / Cs133	Tank 22 simulant (low sodium)	Table 7	Table 11 Figure 3	Sodium concentration
CST / Cs137	Tank 22 simulant (low sodium)	Table 7	Table 12	Radioactive cesium
SAMMS, GT-73 & Sulfur / Mercury	High sodium/ organic/inorganic DWPF recycle	Tables 3 & 4	Table 13	Sorbent tested
SAMMS & GT-73 / Mercury	Tank 22 simulant (low sodium)	Table 6	Table 14 Figures 4 & 5	pH

Table 2. Simulant Inorganic Composition Used for Cesium Uptake with CST.

Precursor/ target ion	Target concentration (M)	Precursor per Liter (g/L)
Na ₂ SO ₄ / SO ₄ ⁼	0.17	24.10
NaNO ₂ / NO ₂ ⁻	0.71	48.70
NaNO ₃ / NO ₃ ⁻	1.20	102.00
KNO ₃ /K ⁺	0.015	1.52
CsNO ₃ / (Cs-133)	2.4E-4	0.047
Na ₂ CO ₃ .H ₂ O/ CO ₃ ⁼	0.2	24.8
NaOH/OH ⁻	2.9	116.0
Al(NO ₃) ₃ .9H ₂ O/ Al ⁺³	0.38	142.5

- A. High inorganic/organic and high sodium (5.4 M Na⁺) simulant (Tables 3 and 4).
- B. Average inorganic/organic and average sodium (1.4 M Na⁺) simulant (See Tables 5 and 6).
- C. Average inorganic/organic and low sodium (0.5 M Na⁺) simulants (Table 7).

The last simulant type (Type C) was designed to reflect waste from Tank-22 which is currently the intermediate storage destination for DWPF recycle and other Tank Farm dilute waste streams. A range of cesium concentrations were tested (6-60 mg/L Cs-133) with Tank 22 simulant to assess variation of batch distribution coefficient with initial cesium concentration. Experiments were also conducted with cesium-137 spiked Tank 22 simulant (20 µg/L Cs-137) which is more representative of actual Tank 22 cesium concentration. Finally, ranges of sodium concentrations were tested for Tank 22 simulant to assess the impact of ionic strength on cesium uptake.

In the comparative evaluations of SAMMS and Duolite[®] GT-73 resin for mercury uptake from DWPF recycle, simulant Types A and C spiked with mercury solutions were used. Some mercury solutions were prepared directly from mercuric chloride. Russ Eibling of SRTC provided other mercuric test solutions from old TNX process SMECT test runs already containing organic compounds. Cesium-133, as cesium nitrate precursor, was used as the surrogate for radioactive cesium-137.

Table 3. DWPF Simulants: High Inorganic/Sodium Compositions.
(Inorganic components for simulant type A)

Chemical (Inorganic)	RCT Simulant- High	
	g/L	M/L
KOH	2.000	0.356 [K ⁺]
NH ₃	0.600	0.008 [NH ₃]
	g/L	[Na ⁺], M/L
Na ₂ B ₄ O ₇	0.150	1.49E-3
NaCOOH	0.870	0.013
Na ₂ C ₂ O ₄	60.00	0.896
NaCl	0.008	1.368E-4
NaF	0.017	4.048E-4
NaNO ₂	37.00	0.536
NaNO ₃	120.00	1.412
NaOH	100.00	2.500
Na ₂ SO ₄	0.080	0.014
TOTAL [Na⁺]		5.373 M/L
CsNO ₃ (Cs-133 precursor)	0.004 g/L	3.55E-3 M/L Cs
	ppm	
Phosphate	2,200	
Fluoride	880	
Formate	160	
Chloride	900	
Cesium	2.3	
Carbonate	190	

Table 4. DWPF Simulants: High Organic/ Sodium Compositions.

(Organic components for simulant Type A)

Organic Compound	mg/L	Comments
Benzene	10	Not used due to its properties
Aniline	130	
	1	
Sodium Phenoxide 2-	620	
Sodium nitrophenoxide 4-	170	
Nitrobenzene	350	
Sodium dinitrophenoxide 2,4-	1700	
Sodium phenylphenoxide 2-	4	
Sodium phenylphenoxide 2-	11	
Sodium phenylphenoxide 4-	11	
Sodium phenylazophenoxide4-	25	
Glycerine	200	
Acetonitrile	150	
Acetone	75	
Methylene Chloride	73	
Hydrogen peroxide	51	
Surfyol 420	50	
Quinone	10	
Biphenyl	10	
Terphenyl-0	10	
Terphenyl-m	10	
Terphenyl-p	10	
Diphenylamine	10	
Triphenylamine	10	
Nitrodiphenylamine	10	
Phenylformamide	10	
Diphenylformamide	5	
Carbazole	10	
3H-phenoxazin-3-one	5	

Table 5. DWPF Simulants: Average Organic Compositions.

(Organic components for simulant Type B)

Organic Compound	mg/L	Comments
Benzene	1	Not used due to its properties
Aniline	30	
Nitrobenzene	0.2	
Sodium Phenoxide 2-	90	As phenol
Sodium nitrophenoxide 4-	50	
Sodium nitrosophenoxide 4-	90	
Sodium dinitrophenoxide 2,4-	410	
Sodium phenylphenoxide 2-	< 0.6	
Sodium phenylphenoxide 2-	<1	
Sodium phenylphenoxide 4-	<1	
Sodium phenylazophenoxide 4-	6	
Glycerine	3.2	Lab. Chemical in RTC
Acetonitrile	5	Lab. Chemical in RTC
Acetone	2.5	Lab. Chemical in RTC
Methylene Chloride	2.4	
Hydrogen peroxide	0.85	
Surfyol 420	25	
Quinone	1	
Biphenyl	3	
Terphenyl-0	1	
Terphenyl-m	1	
Terphenyl-p	1	
Diphenylamine	3	nitrophenylamine used
Triphenylamine	1	nitrophenylamine used
Nitrodiphenylamine	<1	nitrophenylamine used
Phenylformamide	<5	
Dihenylformamide	1	
Carbazole	<1	
3H-phenoxazin-3-one	1	Not available

Table 6. DWPF Simulants: Average Inorganic Compositions
(Inorganic components for simulant Type B)

Inorganic Compound	RCT Simulant- Average		Comments
	g/L	M/L	
KOH	0.090	1.60E-3	competing ion for Cs
NH ₃	0.300	0.004 [NH ₃]	As ammonium nitrate
	g/L	[Na ⁺], M/L	
Na ₂ B ₄ O ₇	0.037	3.68E-4	As sodium chloride
NaCOOH	0.210	0.003	
Na ₂ C ₂ O ₄	1.300	0.019	
NaCl	0.002	3.42E-5	
NaF	0.004	9.52E-5	
NaNO ₂	6.000	0.087	
NaNO ₃	2.600	0.306	
NaOH	40.000	1.000	
Na ₂ SO ₄	0.020	0.003	
TOTAL [Na⁺]		1.418 M/L	
CsNO ₃ (Cs-133 precursor)	0.001 g/L	8.875E-4 M/L Cs	
	ppm		
Phosphate	37		Lab. Chemical in RTC
Fluoride	15		Lab. Chemical in RTC
Formate	2.7		Lab. Chemical in RTC
Chloride	15		Lab. Chemical in RTC
Cesium	0.038		Lab. Chemical in RTC
Carbonate	3.1		Lab. Chemical in RTC

Table 7. Organic and Inorganic Components for Tank 22 H Simulant Solution.

(Organic and inorganic components for simulant Type C)

<u>Inorganic components</u>	<u>Concentration, Moles/L</u>
KOH	1.783E-2
NH ₃ as NH ₄ NO ₃	4.706E-4
NaCl	2.222E-4
NaF	3.175E-5
NaNO ₂	2.900E-5
NaNO ₃	1.020E-2
NaOH	0.333
Na ₂ SO ₄	4.700E-5
CsNO ₃	0.00024 (32 ppm Cs-133)
<u>Organic component</u>	<u>Concentration, mg/L</u>
Sodium oxalate	433.3
Sodium formate	70
Aniline	30.0
Nitrobenzene	0.2
Sodium phenoxide 2-	90 (as phenol)
Sodium nitrophenoxide 4-	50.0
Sodium nitrosophenoxide 4-	90.0
Sodium dinitrophenoxide 2,4-	410.0
Sodium penylphenoxide 2-	0.6
Sodium penylphenoxide 4-	1.0
Sodium phenylazophenoxide 4-	6.0
Glycerine	3.2
Acetonitrile	5.0
Acetone	2.5
methylene chloride	2.4
Hydrogen peroxide	0.8
Surfyol 420	25.0
Quinone	1.0
Biphenyl	3.0
Terphenyl-o	1.0
Terphenyl-m	1.0
Terphenyl-p	1.0
Diphenylamine	3.0
Triphenylamine	1.0 as diphenylamine
Nitrodiphenylamine	1.0 as nitrophenylamine
Phenylformamide	5.0
Diphenylformamide	1.0
Carbazole	1.0

3.3 Method

The uptake of cesium with CST, or mercury onto Duolite GT-73 or SAMMS, was studied by a batch technique. The batch distribution coefficient (K_d , mL/g) is an equilibrium measure of the overall ability of a solid phase ion exchange material to remove ions of interest from solution. It represents the theoretical volume of solution that can be processed per given mass of the ion exchanger under equilibrium conditions (2).

For this study a known quantity of the resin (approximately 0.1 grams) was placed in contact with 25 ml of the simulant in a 50-ml polyethylene bottle. All samples were prepared in either duplicate or triplicate. The polyethylene bottles were placed in an orbital shaker and the mixture agitated for 24 hours at 26 ± 2 °C. After this contact time, the used resin was separated from the solution by filtering through a 0.2-micron nylon filter. The decanted portion, without resin, was submitted for metal concentration analysis. The K_d values were calculated using Equation (1),

$$K_d = ((C_i - C_f)/C_f) * (v/m * F) \quad (1)$$

Where, C_i is the initial concentration of the metal ion of interest, C_f is the final metal concentration after contact, v is the volume of simulant used, m is the sorbent exchanger mass and F is the F-factor (ratio by weight of dry sorbent to wet sorbent). In the above equation, it is assumed that the mass of dry ion exchange sorbent is approximately equal to that of wet ion exchange sorbent used ($F \approx 1.0$). Note that the amount of metal on the resin following sorption is calculated by difference in the solution ($C_i - C_f$).

For radioactive samples, or simulants spiked with radionuclides, K_d values were determined using equation (2),

$$K_d = ((A_i - A_f)/A_f) * v/m. \quad (2)$$

Where A_i and A_f are the activities of the radionuclide in solution at the beginning and at the end of sorption, respectively, v is the volume in ml of the solution used for equilibration and m is the weight of the adsorbent in grams.

4. RESULTS AND DISCUSSION

4.1 Cesium Uptake with CST in an Inorganic DWPF Simulant

In the initial characterization of cesium uptake with CST a 5.6 M Na^+ simulant (upper limit simulant) without organic additives was used. The simulant inorganic ion composition and concentrations are shown in Table 2 above. In this initial batch study, three simulant samples with an average Cs-133 concentration of 3.86 ± 0.21 mg/L were used. The average K_d obtained was 1509 ± 95 ml/g. This K_d value for cesium uptake agrees with earlier results obtained by McCabe (3). The K_d values obtained and total

potassium ion concentration in each sample is summarized in Table 8. Note that potassium concentration is listed because it can act as a competing ion for cesium uptake with CST.

Table 8. K_d values for cesium uptake with CST (5.6 M Na^+).

Run #	[Cs-133] mg/L	[K^+] mg/L	Cs-133 K_d
1	3.66	464.095	1601.78
2	3.84	463.085	1514.97
3	4.08	517.120	1411.15
Average	3.86 ± 0.21		1509 ± 95

4.2 Cesium Uptake with CST in Organic and Inorganic DWPF Simulants

DWPF simulants were prepared with both inorganic and organic components based on Types A and B simulants (i.e., high and average sodium/organic/inorganic DWPF recycle simulants). The pH of these simulant solutions was 13.3. Since the effectiveness of cesium uptake by CST was also to be evaluated at other pH conditions (13, 7 and 2), solutions of the original high and average simulants were adjusted with nitric acid (1.0 M) to the desired pH levels. In all, six sample types of simulant solutions were prepared for K_d measurement; High RCT (DWPF Type A simulant) at pH's of 13, 7 and 2, and Average RCT (DWPF Type B simulant) at pH's of 13, 7 and 2. Corresponding blanks without CST were also prepared. Cesium-133 concentration in each sample was approximately 32 mg/l. These particular sets of samples were prepared in triplicate. K_d measurements were made using the procedure described in the method section above.

For comparison, SMECT sample from TNX operations, which already contained mercury and DWPF organic compounds, was also used in determining batch K_d values for CST. With this TNX SMECT sample, an equivalent amount of cesium nitrate (0.0118 g) was introduced into a 250-ml sample to bring its cesium concentration to 32 mg/L. The pH of three 25-ml representative samples from this batch of modified SMECT samples was adjusted with sodium hydroxide, respectively, to pH values of 2, 7, and 13. Each of the 25-ml samples, with different pH values (2, 7 and 13), was treated with 0.10 g CST as described previously.

Residual cesium analysis of all the above samples, which were contacted with CST, were delayed for about 4 months due to funding problems. After this delay a selected number of the samples were analyzed, yielding an average K_d value of 2400 ± 50 ml/g. This value is significantly different from an average batch K_d value of 1500 ± 95 ml/g obtained for the baseline simulant without organic components (Table 2). Here one expects a decrease in K_d values with organic components in the simulant. The increase in K_d value was attributed to the plating out of cesium with organic films onto the sides of the sample vials or containers during the four months delay.

4.3 SRS Tank 22 Measurements

Tank 22 is currently the intermediate storage destination for DWPF recycle and other Tank Farm dilute waste solutions. The chemical makeup of Tank 22 waste stream was reviewed with the plant customer to tailor some of the K_d experiments towards cesium removal from Tank 22. The simulant composition for Tank 22 was determined to be similar to the existing DWPF average simulant make up with only 0.5 molar sodium ion concentration and an average organic content (Type C simulant). A summary of the organic and inorganic concentrations is presented in Table 7.

This phase of the CST work was also designed to address, among other things, questions dealing with the variation of K_d with cesium concentration and the ionic strength of the recycle waste stream.

4.4 Variation of Batch Distribution Coefficient With Cesium Concentration

The effect of initial cesium concentration on batch K_d measurements for CST were evaluated using Tank 22 simulant and cesium concentrations ranging from 5.87 to 61.30 mg/L. The Tank 22 simulant was based on composition shown in Table 7 and had solution pH of 13. Batch K_d measurements were made using the procedure summarized in the method section. Under this ionic strength condition, increase in K_d with increase in cesium concentration leveled off after about 35 mg/l of cesium. Results are summarized in Table 9 and Figure 1.

Table 9. K_d Variation with Initial Cesium Concentration.

[Cs-133] mg/L	K_d (ml/g)
5.87	31112
10.98	32467
16.90	34958
26.04	38967
30.01	38583
40.27	43923
52.64	42577
61.30	40789

Figure 1. Variation of K_d With Initial Cesium Concentration.

Based on equation (1) above, the batch distribution coefficient is expected to be linear with respect to the decontamination factor, C_i/C_f , [within the linear response region of Figure 1 above (i.e., below 30 mg/L)]. A summary of the basic equations gives:

$$K_d = ((C_i - C_f)/C_f) * (v/m).$$

If $\beta = v/m$, then

$$K_d = \beta (C_i/C_f - 1) = \beta C_i/C_f - \beta \quad (3)$$

To validate equation (3) several of the K_d measurements in the cesium concentration region of interest were plotted with the corresponding decontamination factor. Using a test solution volume of 25 ml and CST weight of 0.1g equation (3) becomes:

$$K_d = 250 C_i/C_f - 250. \quad (4)$$

Experimentally, per equation (4), a plot of K_d versus C_i/C_f (decontamination factor) should give a straight line with a slope equal to 250 and intercept of -250.

The experimental results confirming equation (3) with Tank 22 simulant are summarized in Table 10 and Figure 2. The slope and intercept from the experimental data, 250 and 250.81 respectively, are in excellent agreement with the theoretical values of equation 4.

Table 10. K_d variation with decontamination factor.

C_i , mg/L	C_f , mg/L	K_d , ml/g	$[C_i]/[C_f]$
5.871	0.047	31112	125.45
10.980	0.084	32467	130.87
16.900	0.120	34958	140.83
26.040	0.166	38967	156.87

Figure 2. Linear Response of K_d with Cesium Decontamination Factor.**4.5 Variation of Batch Distribution Coefficient With Ionic Strength.**

The effect of ionic strength on batch K_d measurements for CST were evaluated using Tank 22 simulant at ionic strengths of 0.5, 1.4 and 5.4 molar sodium. Each solution contained an average of 0.26 ± 0.15 moles of cesium per liter. The K_d values obtained are summarized in Table 11 and Figure 3. The data clearly shows that K_d increases with a decrease in the ionic strength of the test solution.

Table 11. K_d Variation with Ionic Strength.

$[Cs]_i$ (moles)	$[Na^+]_i$, moles	K_d (ml/g)	$([Na^+]/[Cs])_i$ mole/mole
0.24925	0.5	37400	2.0060
0.26060	1.4	8000	5.3722
0.28045	5.4	1300	19.2547

Figure 3. Variation of K_d with Ionic Strength.

The region of interest for cesium-133 removal from DWPF recycle (less than 1 mg/L cesium or 7.519 E-6 moles of cesium-133/Liter) cannot be fully characterized with cesium-133 simulant. This problem is due, in part to the question of minimum detection limit for cold cesium (Cs-133) using standard ICP-MS analytical techniques. To get around this problem Tank 22 simulant (0.5 M Na^+) was spiked with cesium-137 and the K_d determined by quantifying cesium-137 using gamma counting and equation (2) above.

4.6 Experiments With Cesium-137 Spiked Tank-22 Simulant

Four samples (25-mL solutions of Tank 22 simulant each) were spiked with 0.5 mL Cs-137 tracer (concentration of 20.8 ppb Cs-137 or 9.2E05 d/min-mL). Cesium-137 concentration in grams was based on 87g Cs-137/1.23E12 d/min-ml. The average amount of cesium-137 in each sample was 6.584E-07 g or 4.95E-09 moles. A volume of 2.5 ml from each sample was used for gamma counting (10,000-sec count) after overnight contact with approximately 0.1 g of CST.

The results are summarized in Table 12, which shows an average K_d value of 74,500 ml/g. The final cesium concentration, after uptake with CST, may not differ greatly from background readings for cesium-137 in the area where the analysis was carried out. Consequently, the fourth sample was re-counted for a longer period of time (50,000-sec. count) resulting in a K_d of 327,425 ml/g versus 77,752 ml/g for a 10,000-second count.

Table 12. Data Summary for Tank-22 Simulants Spiked with Cesium-137.

Run #	Initial Cs-137 activity, Gamma count; d/min-ml	Final Cs-137 activity d/min-ml	K _d (ml/g)
1	1.71E04	60	61,207
2	1.66E04	47	82,288
3	1.68E04	53	76,694
4	1.70E04	50	77,752
Average	1.69 E04 ± 0.02 E04	52.5 ± 3.8	74,500 ± 3900

Actual Tank 22 waste was recently secured and evaluated for cesium-137 removal with CST (3). The average K_d value reported was $14,850 \pm 2,380$ ml/g. The K_d values in reference 3 are significantly lower than that reported here. This is probably because of the effect of low sodium and cesium-137 concentration in the Cs-137 spiked simulant.

4.7 Mercury Removal From DWPF Simulant

The uptake of mercury from DWPF simulant using the Self-Assembled Monolayers on Mesoporous Support (SAMMS) material from PNNL (4) was evaluated with the Type A DWPF simulant ($[Na^+]$ of 5.4 M and pH of 13) containing mercury. The SAMMS material was expected to outperform standard GT-73 ion exchange material for mercury removal from DWPF waste stream.

The contact results of this SAMMS and GT-73 ion exchange material with DWPF simulant containing both mercury and organic compound (Table 13 below) shows that the SAMMS material, in its current configuration, has no affinity for DWPF waste stream mercury ($K_d = 0.0$). Even ordinary sulfur powder showed a better affinity for mercury than SAMMS at a solution pH of 13. The K_d value for mercury removal from DWPF simulant using GT-73 averaged about 8,900 ml/g. The SAMMS material does, however, show K_d values less than 600 ml/g when there are no organic compounds in the simulant waste stream.

The mercury removal evaluations with SAMMS and Duolite GT-73 resins were repeated with Tank 22 simulant. This time, the pH of the simulant solution was adjusted to 2, 7 and 13 before the batch K_d work with the resins. Concentrated nitric acid and 0.10 M solution of sodium hydroxide were used for pH adjustments. The new K_d values are summarized in Table 14 and plotted in Figures 4 and 5.

Table 13. K_d Values for SAMMS and Duolite GT-73 Resin for Mercury Removal from Type A DWPF Simulant.

Sample ID	C_i [Hg] ppm	C_f [Hg] ppm	K_d s (ml/g)	Average k_d
Initial [Hg]	38.739			
GT-73 run 1	38.739	1.0875	8646	8918
GT-73 run 2	38.739	1.0250	9189	
SAMMS run 1	38.739	39.9	0.0	0.0
SAMMS run 2	38.739	39.0	0.0	
SAMMS run 3	117.08	34.67	594.2	594.2
Sulfur run 1	38.739	5.625	1470	1544
Sulfur run 2	38.739	5.1750	1619	

Table 14. K_d Values for SAMMS and Duolite GT-73 Resin for Mercury Removal from Tank-22 Simulant.

Duolite GT-73 Resin		SAMMS Resin	
pH	K_d (ml/g)	pH	K_d (ml/g)
2	119	2	0
7	1213	7	233,522
13	9179	13	0

The SAMMS material showed a significant affinity for the uptake of mercury at neutral pH of 7. The batch distribution coefficient for mercury removal at this neutral pH was 233500 ml/g. The SAMMS did not remove mercury from simulants with lower or higher pH values (Figure 4). The GT-73 performed as expected. Its affinity for mercury increased with increase in pH (Figure 5).

4.8 Mercury Removal From Tank 22 Sample With GT-73 Resin

McCabe (3) documents the collection and characterization of actual Tank 22 sample used in this part of the mercury removal study. The mercury removal K_d data obtained by McCabe was based on filtered Tank 22 samples. The average K_d reported with GT-73 resin (Na^+ form) was $39,885 \pm 3000$ ml/g. The initial mercury concentration in Tank 22 sample was 10.95 mg/L and the ending mercury concentration was 0.070 ± 0.006 mg/L. 20-ml sample volumes were used with 0.075 g of GT-73 in K_d determinations.

Figure 4. Estimated K_d Variation Profile with pH for Mercury Removal with SAMMS.

Figure 5 Variation of K_d with pH for Mercury Removal with Duolite GT-73.

5. CONCLUSIONS

The results of this evaluation of the performance of CST in the uptake of cesium with simulants and actual DWPF recycle samples (Tank 22) indicate that, in practice, this inorganic ion-exchange material can be used to remove radioactive cesium from the DWPF recycle. Even in high ionic strength environments the CST material has affinity for cesium. Characterization of the effect of organic components on the efficiency of cesium or mercury removal from DWPF simulants using, respectively, CST and SAMMS or Duolite® GT-73 was aborted due to interruption in the analysis of samples due to a funding shortfall. Based on the data obtained the following conclusions are made:

- Batch distribution coefficient (K_d) for cesium removal with alkaline DWPF simulant solution increases with decreasing ionic strength.
- The batch distribution coefficient for alkaline DWPF simulant showed a linear variation with initial cesium-133 concentration up to approximately 35 mg/L.
- The K_d value for cesium uptake from DWPF high ionic sodium salt solution (5.4 M $[Na^+]$) is 1500 ml/g. For low sodium salt solution, (0.5 M $[Na^+]$), the K_d value obtained is 37,000 ml/g.
- Radioactive cesium spiked simulant (0.5 M $[Na^+]$), with cesium-137 activity of 1.69E04 d/min-ml, showed a CST cesium-137 uptake K_d value of 74,500 ml/g.
- Self-Assembled Monolayers on Mesoporous Support from PNNL had no affinity for DWPF simulant mercury. However, with the pH of the simulant adjusted to a value of 7 (neutral pH condition), SAMMS material showed its highest affinity for DWPF mercury (k_d of 233,000 ml/g).
- The K_d for the uptake of mercury from DWPF simulant with conventional Duolite® GT-73 resin was found to increase with increasing pH of the simulant solution.
- GT-73 ion-exchange affinity for mercury from actual Tank 22H sample was quite good. The average determined K_d value was 39,700 ml/g.

Additional work that needs to be carried out before implementing this program includes the following:

- Column performance evaluations with CST in DWPF simulant and actual waste solutions.
- Determination of batch K_d values at different DWPF simulant pH conditions.
- Evaluation of the affinity of CST for other transuranic elements, and
- Evaluation of strontium-90 uptake with Sodium Titanate (ST) and crossflow filtration characterizations with ST.
- Evaluation of the effect of organic loading on the efficiency of CST in removing cesium, and GT-73 and SAMMS in removing mercury.

6. QUALITY ASSURANCE

All experimental work reported in this document was obtained in accordance with the requirements and controls established in the Savannah River Technology Center Conduct of Research and Development manual (WSRC-IM-97-00024). Experimental methods and data are recorded in laboratory notebook, WSRC-NB-96-655.

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