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EVALUATION AND TESTING OF INORGANIC ION EXCHANGE SORBENTS FOR THE REMOVAL OF CESIUM-137 FROM ACTUAL IDAHO NUCLEAR TECHNOLOGY AND ENGINEERING CENTER ACIDIC TANK WASTE

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EVALUATION AND TESTING OF INORGANIC ION EXCHANGE SORBENTS FOR THE REMOVAL OF CESIUM-137 FROM ACTUAL IDAHO NUCLEAR TECHNOLOGY AND ENGINEERING CENTER ACIDIC TANK WASTE

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ABSTRACT

Three inorganic ion exchange sorbents were evaluated for ^{137}Cs removal from the Idaho Nuclear Technology and Engineering Center (INTEC), acidic tank waste. A commercially available, Russian manufactured, potassium copper hexacyanoferrate (FS-2), crystalline silicotitanate (IONSIV IE-911), manufactured by UOP, and ammonium molybdophosphate-polyacrilonitrile composite sorbent (AMP-PAN), produced at the Czech Technical University, Prague, were tested. Approximately 800 mLs of actual radioactive tank waste were used to evaluate the FS-2 and IONSIV IE-911 sorbents. Feed flowrates of 6-7 mLs/hr through a 1 cm^3 column were used for both tests. Initial ^{137}Cs breakthrough with IONSIV IE-911 was observed at approximately 100 mLs and 50 % breakthrough was observed at 660 mLs. A ^{137}Cs breakthrough of 20 % was ob-

served after 775 mLs of waste was processed through the column containing FS-2. Tests were also performed with both of these sorbents using simulated tank waste. Results for the IONSIV IE-911 compare well for both tests; however, there are some slight discrepancies with the FS-2 results. These discrepancies are believed to be the result of mercury sorption arising from different mercury speciation between the actual and simulated waste feeds. Over 80 wt% of the cesium loaded onto the FS-2 sorbent was eluted with 8 M HNO_3, while no attempt was made to elute cesium from the IONSIV IE-911 sorbent. The AMP-PAN test used a 1.5 cm^3 column, 1600 mLs of actual radioactive waste, and a flowrate of 40 mLs/hr (26 bed volumes/hr). Initial ^{137}Cs breakthrough was observed after processing 600 mLs, and 0.15 % breakthrough was observed after processing 1550 mLs of waste. Over 83 % of the cesium was eluted using 44 mLs of 5 M NH_4NO_3. Two loading and elution cycles were performed with simulated waste and AMP-PAN. Approximately 4800 mLs (3200 BV) of simulant were processed before 50 % breakthrough was observed. Over 70 % of the cesium was eluted in 85 mL (57 BV). Only 4050 mLs (2700 BV) of simulant were processed before 50 % breakthrough was observed in the second loading cycle and 50 % of the cesium was eluted in 117 mL (78 BV). The results indicate that AMP-PAN has the highest capacity for cesium and sorption appears to not be affected by the presence of mercury in the waste, giving it clear advantages over IONSIV IE-911 and the FS-2 sorbent. The AMP may also be easily dissolved from the PAN binder using sodium hydroxide.

INTRODUCTION

The Idaho Nuclear Technology and Engineering Center (INTEC), located at the Idaho National Engineering and Environmental Laboratory (INEEL), currently has on inventory over 5 million liters of highly radioactive liquid waste. This waste, referred to as sodium-bearing waste (SBW), was generated from past uranium recovery activities and current decontamination and waste treatment processes. SBW is stored in underground 1,100,000 liter stainless steel tanks. The waste is acidic and has high concentrations of sodium and potassium, but the specific composition of the waste varies from tank to tank.

The INTEC historically treated SBW by blending it with fuel reprocessing raffinates and calcining the blend in a fluidized bed operated at 500 ^oC. SBW cannot be calcined by itself because the high sodium and potassium content causes bed agglomerations. All fuel reprocessing raffinates, except for a small heel in one of the tanks, were depleted by calcination in 1994. Non-radioactive aluminum ni-

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trate must now be blended with the SBW in order for it to be calcined. This may not be a viable option for removing the SBW from the storage tanks by deadlines imposed by recent settlement agreements because of the reduced net-throughput realized by the addition of aluminum nitrate. Radionuclide separation technologies are also being evaluated, as an alternative to calcination, for treating the waste and removing it from the tanks.

The goal of the separation processes is to remove the fission products and actinides from the waste so that the bulk of the waste will meet NRC Class A low-level waste as defined by of 10 CFR 61.55. The TRUEX process has been shown to effectively remove the transuranic (TRU) content of the waste to well below the 10 nCi/g limit [1-2], and several technologies have been shown to remove the fission products to below 10 CFR 61.55 limits (1 Ci/m^3 for ^{137}Cs and 0.04 Ci/m^3 for ^{90}Sr) [3-6]. The chlorinated cobalt dicarbollide process has been shown to remove ^{137}Cs (and ^{90}Sr in the presence of PEG) to below the 10 CFR specifications [4-5] and the UNEX process, based on cobalt dicarbollide technology, has been shown to effectively remove TRU, Cs and Sr in a single process [6]. The SREX process has also been shown to remove ^{90}Sr to below 10 CFR limits [3]. Each of these process have been verified with actual SBW using centrifugal contactors.

The purpose of the work reported here, was to evaluate inorganic ion exchange sorbents for removing cesium from the acidic SBW. This paper summarizes results of work performed with three inorganic ion exchange sorbents: a Russian manufactured potassium copper hexacyanoferrate known as FS-2, a Czech manufactured ammonium molybdophosphate-polyacrilonitrile composite (AMP-PAN), and a UOP manufactured form of crystalline silicotitanate (CST) marketed as IONSIV IE-911. The scope of this work included batch contacts and small-scale column tests performed with actual and simulated SBW.

Metal ferrocyanides have been studied extensively as cesium ion exchange materials [7]. However, the lack of an engineered form of these materials has precluded their use in column operation. CST was developed at Sandia National Laboratory for cesium and strontium removal from Hanford's alkaline waste [8], but this material has also shown promise for sorbing cesium from acidic solutions [9-11]. AMP is also a well known inorganic cesium sorbent [12]; however, like the metal ferrocyanides, it was not suitable for column operation. äebesta, et. al., recently developed an engineered form of AMP using PAN [13], and extensive studies by the Czech scientists has shown this material to be very promising [14, 15].

EXPERIMENTAL

Feed Composition

Three SBW feed solutions were used for this work. Actual waste from tank WM-183 was used for all actual waste tests, a simulant representing the average composition of all tank waste was used and is designated Average Simulant, while

Table 1. WM-183 Actual Waste, WM-183 Simulant, and Average SBW Feed Compositions

Component	WM-183	WM-183 Simulant	Average Simulant
Acid (M)	1.77	1.70	1.31
Al (M)	0.64	0.62	0.59
B (M)	0.013	0.013	0.015
Ca (M)	0.040	0.029	0.033
Cl (M)	0.011	0.011	0.034
Cr (M)	0.014	0.017	0.006
Cs (M)	7.11E-5	9.8E-5	7.14E-5
Fe (M)	0.056	0.045	0.024
Hg (M)	0.0023	0.0013	0.0018
K (M)	0.094	0.086	0.13
Na (M)	0.68	0.69	1.04
NO_3 (M)	5.24	4.80	4.2
Pb (M)	0.0012	0.0015	9.56E-4
SO_4 (M)	0.066	0.066	8.85E-3
Sr (M)	ND	6.3E-4	5.57E-3
Zr (M)	4.2E-4	0.0065	5.78E-4
Alpha (nCi/g)	506	NA	NA
^{241}Am (nCi/g)	34.9	NA	NA
^{238}Pu (nCi/g)	333.8	NA	NA
^{239}Pu (nCi/g)	123.3	NA	NA
U (mg/L)	114	NA	NA
^{237}Np (nCi/g)	$<$6.5	NA	NA
^{99}Tc (Ci/m^3)	0.036	NA	NA
^{137}Cs (Ci/m^3)	219	$\sim$100 dps/mL	$\sim$100 dps/mL
^{90}Sr (Ci/m^3)	201	NA	NA
density (g/mL)	1.25	ND	ND

ND = no data, NA = not applicable.

a simulant of waste stored in tank WM-183, designated as WM-183 Simulant, was also used. Compositions of each feed are shown in Table 1.

Each feed was filtered through a 0.45 micron filter prior to use. The simulants were spiked with ^{137}Cs prior to use in most cases, the only exception being 1 cm^3 and 10 cm^3 column tests performed with the Average Simulant. The feeds were spiked to approximately 100 dps/mL with a National Institute of Standards (NIST) ^{137}Cs tracer purchased from Isotope Products.

Experimental Equipment

Three different sized columns were used for these tests: 1 cm^3, 1.5 cm^3, and 10 cm^3. FS-2 and IONSIV IE-911 were tested using a 1 cm^3 with actual and sim-

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ulated waste. The column was made from stainless steel and was designed for downward flow through the column. The bed portion of the column is 35 mm high and 6.2 mm diameter. A 10 cm^3 column was also used for FS-2 testing. This column was also stainless steel, designed for downward flow, and had bed dimensions of 130 mm high and 10 mm diameter. The 10 cm^3 column had the same configuration and was made of the same material as the 1 cm^3 column.

AMP-PAN was evaluated in a 1.5 cm^3 column. The inlet, outlet, and base of the column were stainless steel while the bed portion of the column was made from Plexiglas. The column was designed for upward or downward flow. The bed portion of the column was 21 mm high and 9.5 mm diameter. The use of Plexiglas for the bed portion of the column was advantageous because it allowed for visual inspections to be made regarding bed disruptions, i.e. air bubbles or floatation in the bed, and potential AMP-PAN degradation.

Feeds, wash solutions, and eluents were pumped through the column using a valveless metering pump (FMI Lab Pump Model QVG-50). Flowrates were maintained by controlling the pump with a ten-turn potentiometer (FMI Stroke Rate Controller Model V100).

Column Preparation

A consistent procedure was used to load each column with one of the three sorbents. The top of the column was removed and the column was filled with deionized water prior to loading FS-2 and IONSIV IE-911 or with 1 M HNO_3 in 1 M $NaNO_3$ prior to loading the AMP-PAN. A piece of nalgene tubing was then attached to the top of the column and a funnel or large syringe was secured to the other end of the tubing which was also filled with water. A precisely measured dry FS-2 or CST sorbent weight or precise volume of wet AMP-PAN was slurried into the funnel or syringe, and allowed to gravity-settle into the column.. The column was gently massaged while the sorbent particles were dropping through the water into a uniform column bed. Dry sorbent weights and bed volumes for each column are shown in Table 2.

Table 2. FS-2, IONSIV IE-911, and AMP-PAN Dry Sorbent Weights and Bed Volumes for Each Column

Feed Tested	FS-2	IONSIV IE-911	AMP-PAN
WM-183	0.81 g/ 1 cm^3	1.02 g/ 1 cm^3	0.7 g/ 1.5 cm^3
WM-183 Simulant	0.80 g/ 1 cm^3	Not tested	Not tested
Average Simulant	0.80 g/ 1 cm^3 7.36 g/ 10 cm^3	1.05 g/ 1 cm^3	0.7 g/ 1.5 cm^3

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Quantitative sorbent transfer was attempted during each loading by inspecting the weighing dish, funnel or syringe, tubing, and water from the outlet to ensure all particles were transferred to, and remained in, the column. Verification of the AMP-PAN sorbent was performed by precisely marking the column at a height of 2.1 cm which is equivalent to 1.5 cm^3. A visual inspection of the column after AMP-PAN addition verified the bed height to be at 2.1 cm.

Loss of the FS-2 and CST material was prevented by placing a plug of glass wool at the bottom of the column prior to sorbent addition. The plug of glass wool helped to "fix" the bed and to prevent loss of material. A fiberglass frit was inserted at the bottom of the AMP-PAN column prior to sorbent addition and another plug was inserted at the top at the completion of bed addition. The particle sizes of the sorbents tested were as follows: FS-2 0.25-0.75 mm; IONSIV IE-911 0.1-0.4 mm; and AMP-PAN <0.3 mm.

Dilute nitric acid was pumped through the column to rinse/flush the bed after it had been "fixed" with either glass wool or fiber glass frits. The column effluent was inspected for bed material.

EXPERIMENTAL PROCEDURES

Feed Adjustments

Each feed used in FS-2 testing was adjusted with hydrazine nitrate prior to initiating flow through the column. A minimum hydrazine nitrate concentration of 0.05 M in the feed was used [15]. Hydrazine is a nitrite scavenger which prevents the nitric acid waste from oxidizing Fe^{+2} in the sorbent to Fe^{+3}. The cyanoferrate sorbent will only sorb cesium when iron is in the divalent oxidation state, while cesium is desorbed from the sorbent by oxidizing the iron to the trivalent oxidation state.

Hydrazine nitrate was prepared by neutralizing 13 mLs of 3.5 M HNO_3 with 3 mLs of 99 % $N_2H_4 \cdot H_2O$. A pH~7 was verified with litmus paper after neutralization. The resulting solution was approximately 16 mL of 2.8 M $N_2H_4 \cdot HNO_3$ which was used to adjust 800 mLs of feed. However, the feed was adjusted in 400 mL batches because hydrazine is consumed as nitrite is scavenged, and must be replenished to prevent oxidation of iron in the sorbent. Care was taken when neutralizing nitric acid with hydrazine, which is a highly exothermic reaction, by adding the hydrazine very slowly with an automated pipet/titrator (Rainin Model EDP-Plus Pipette 1000 μL) and by constantly and vigorously swirling the solution. The feed was hand mixed after the addition of 8 mLs of hydrazine nitrate was added for homogeneity, then pumped through the column.

Feeds used in the IONSIV IE-911 and AMP-PAN tests were not adjusted and used directly after filtration.

Experimental Reagents and Parameters

Reagents and flowrates used for each of the sorbents tested are shown in Table 3. All feed, and wash flows were downward through the column for FS-2 and IONSIV IE-911 (up flow was used for AMP-PAN). The elution flow for all FS-2 tests was downward, but the elution flow for all AMP-PAN tests was reverse or downward through the column. The eluent used to remove cesium from the AMP-PAN also regenerated the column; therefore, a separate regeneration step was not performed with this material. Cesium is not readily removed from IONSIV IE-911, and no attempts to elute cesium from this material were made.

Sampling and Analysis

Column effluents from the test using actual SBW from tank WM-183 were collected in a glass beaker approximately every 3 to 5 hours. The effluent volume of each sample fraction was measured by pouring the sample into a clean graduated cylinder. The sample fraction was then poured into an unused polyethylene bottle, the beaker and graduated cylinder were thoroughly rinsed with DI water and inverted to dry. Two beakers were used during actual waste testing, one of which was drying while the other was being used to collect effluent fractions. Each sample fraction required dilution with 3 % nitric acid prior to removing a sample aliquot from the shielded (hot) cell for ^{137}Cs analysis to reduce the radioactivity in the sample to safe handling limits. Each sample had to be diluted to

Table 3. Flowrates and Reagents Used for Each Sorbent Tested

Reagents and Parameters	FS-2	IONSIV IE-911	AMP-PAN
Feed Flowrate (BV/hr)	6-7	5-6	26-27
Superficial Vel. (cm/hr)	23.3 (1 cc col.) 89.1 (10 cc col.)	20.0	56.3
Wash Reagent	0.5 M HNO_3 or Water	Not needed	0.1 M KNO_3 in 0.1 M HNO_3
Wash Flowrate (BV/hr)	6-7	Not needed	26-27
Eluent Reagent	8 M HNO_3	Not needed	5 M NH_4NO_3 in 0.1 M HNO_3
Eluent Flowrate (BV/hr)	1-2	Not needed	3-4
Regeneration Reagent	0.6 M $KC_2H_2O_2$ in 0.3 M $NaNO_2$	Not needed	Not needed
Regeneration Flowrate (BV/hr)	1-2	Not needed	Not needed

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less than 100 millirem total dose before it could be transferred from the hot cell. Typically, a 0.1 mL to 20.1 mL dilution was used. A 1 mL aliquot of the diluted fraction was taken with a 1 mL Eppindorf pipettor and dispensed into a 5 dram glass vial for ^{137}Cs analyses.

Column effluents from tests using simulated SBW were collected in polyethylene bottles at specified time intervals. Sampling times changed during testing because continuous testing was attempted; therefore, the operation was not always attended. Those samples that were collected in the morning, after the experiment had been operating all night, were larger than those samples collected during the day and evening. Sampling frequency was also decreased during weekends, and the columns had to be shut down for the weekend occasionally. Each effluent fraction was sampled for ^{137}Cs analysis by taking a 1 to 125 mL sample. The total effluent fraction was used as the sample in those tests in which the feed was not spiked with ^{137}Cs (1 cm^3 and 10 cm^3 FS-2 tests).

Samples from actual waste and tracer tests were analyzed by gamma spectroscopy for ^{137}Cs, while samples from the two non-traced tests were analyzed for non-radioactive cesium by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

FS-2

Tests were performed with the FS-2 sorbent and actual WM-183 and Average Simulant wastes. The 1 cm^3 column was used in the actual WM-183 test and in one of the Average Simulant tests, while the 10 cm^3 column was used in the other Average Simulant test. Cesium breakthrough data from these tests are shown in Figure 1.

A direct comparison of the breakthrough curves obtained with actual and simulant wastes may not be valid because the different compositions of these two wastes may cause different cesium sorption characteristics. A 20 % ^{137}Cs breakthrough was observed after 775 bed volumes (BV) of actual waste were processed through the column. A 20 % cesium breakthrough occurred after 1800 bed volumes using the Average Simulant and the 1 cm^3 column, while 20 % breakthrough occurred after 1300 bed volumes using the 10 cm^3 column. The discrepancy between the 1 cm^3 and 10 cm^3 column tests, both of which used the Average Simulant, is not fully understood. Residence time was approximately equal for both columns, however, the superficial velocity in the 10 cm^3 was considerably higher than in the 1 cm^3 column.

Tracer tests performed with spiked WM-183 simulant were also performed in the 1 cm^3 column. Cesium breakthrough data for two loading cycles are shown in Figure 2. Cesium-137 breakthrough (50 %) occurred at approximately 2000 BV

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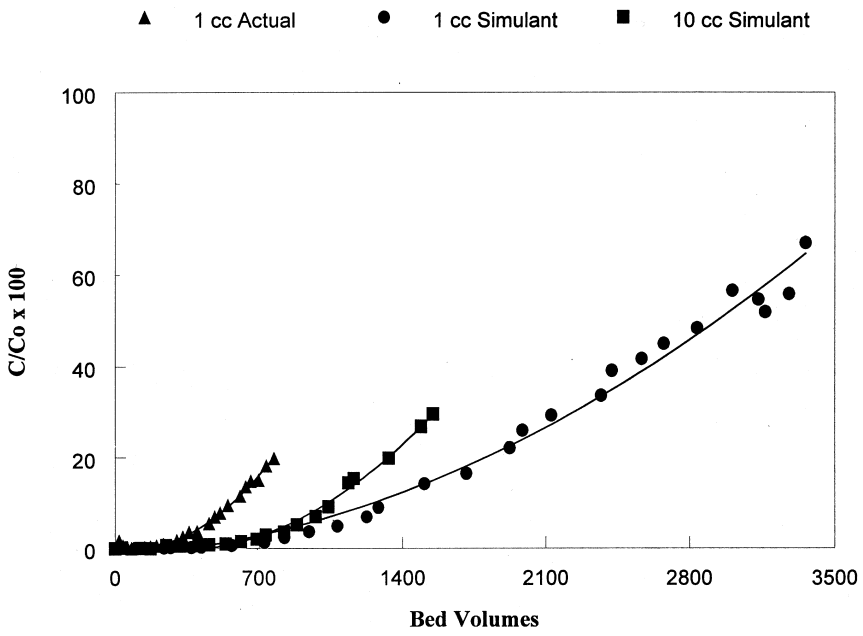

Figure 1. FS-2 breakthrough for Cs using actual WM-183 feed in a 1 cm^3 column and the Average Simulant feed in the 1 cm^3 and 10 cm^3 columns.

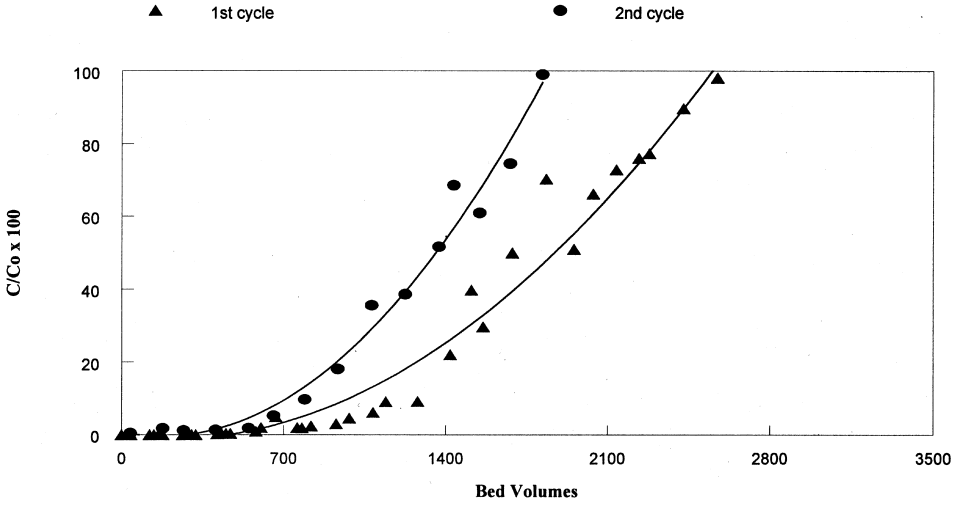

Figure 2. Cesium breakthrough for two loading cycles using WM-183 simulant and a 1 cm^3 containing FS-2.

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for the first loading cycle and at approximately 1300 BV for the second cycle. Reasons for the apparent decrease in cesium capacity between the first and second cycles are being investigated at this time. It is known that approximately 10-15% of the cesium sorbed in the first cycle, will remain on the column, and lower the capacity for subsequent cycles.

Cesium was eluted with 8 M HNO_3 from the 10 cm^3 column test, where the Average Simulant was used (Figure 1), and after the first cesium loading cycle with the WM-183 Simulant (Figure 2). The FS-2 sorbent manufacturer claims that the sorbent is stable in high nitric acid concentrations, and no apparent physical degradation of the sorbent was noted. The elution mechanism is a simple oxidation/reduction of the iron component of the sorbent. Loading is accomplished by reducing the feed and ensuring the iron in the sorbent is in the divalent state, allowing cesium to be exchanged with potassium. During elution, the iron is oxidized to the trivalent form, and cesium is given up to maintain charge neutrality. Elution results from the 1 cm^3 column test are shown in Figure 3. Only 81% of the cesium loaded onto the 1 cm^3 was eluted in 28 BV. Very little cesium eluted from the 1 cm^3 column after 18 BV. Higher cesium elution percentages were achieved in the 10 cm^3 column which was loaded with the Average Simulant.

The two simulants have approximately the same cesium concentration (Table 1); therefore, another constituent in the simulants, other than cesium, may have been sorbed by the column which decreased the cesium capacity and pre-

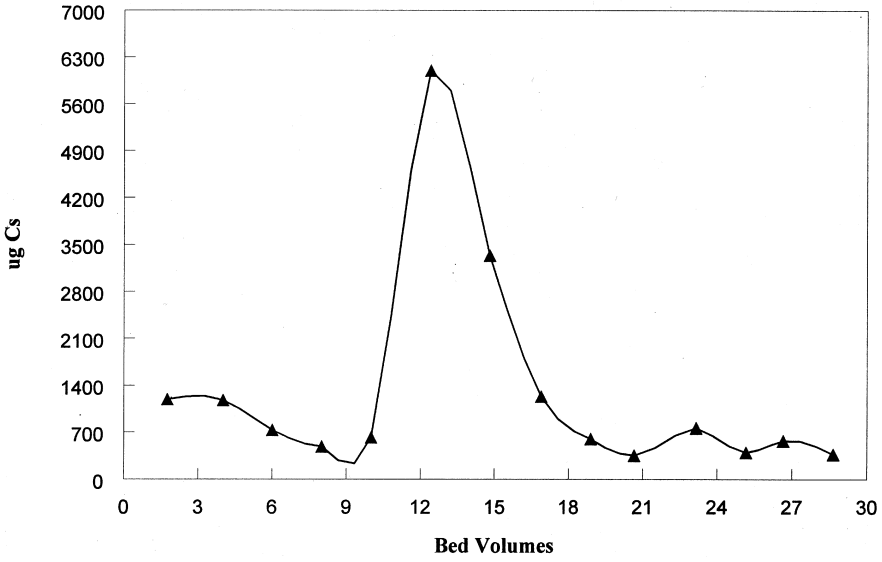

Figure 3. Cesium elution curve from 1 cm^3 FS-2 column loaded with WM-183 simulant.

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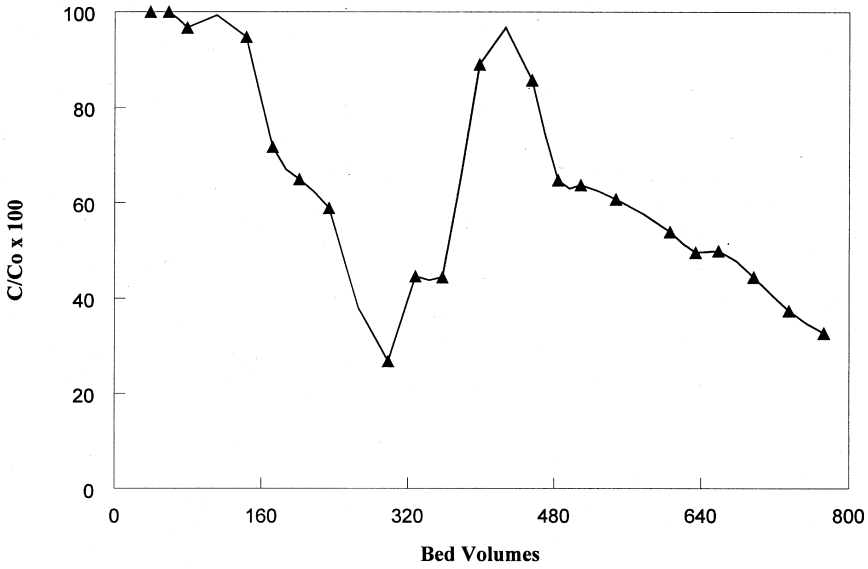

Figure 4. Mercury breakthrough from actual WM-183 tank waste test using a 1 cm^3 column containing FS-2.

vented cesium desorption. There are many factors which may contribute to the differences in breakthrough and elution between the experiments, but the one element in the waste which is suspected to be the primary contributor to sorbent behavior is mercury. Ferrocyanide compounds are known to sorb mercury [16-18]; therefore, a potential mercury interference with both cesium loading and desorption may be expected.

The two simulants also have comparably close mercury concentrations, but the WM-183 Simulant has approximately one third the chloride concentration of the Average Simulant. The FS-2 sorbent may sorb ionic mercury differently than mercury chloride and the mercury speciation is very dependent on the chloride to mercury molar ratio. WM-183 Simulant has a chloride to mercury molar ratio of 8, while the Average Simulant has a molar ratio of 20. Even though both ratios are > 2, more mercury may be present as $HgCl_2$ in the Average Simulant which resulted in higher cesium loading (i.e. less Hg sorption).

Mercury interference was evaluated in the 1 cm^3 column test using actual WM-183 waste and the mercury breakthrough curve is shown in Figure 4. Mercury did not sorb significantly during the first 175 BV, but mercury breakthrough of $\sim$25 % was observed at 300 BV. A fresh bottle of feed was started at 358 BV, after which mercury did not significantly sorb again. However, just as with the first batch of feed, mercury slowly began sorbing on the column through completion of

the test at 773 BV. This pattern of mercury sorption may be attributed to Hg^{+2} being reduced to Hg^{+} by the hydrazine nitrate added to the feed just before that feed is used for testing. Monovalent mercury, which is not stable, is oxidized back to Hg^{+2} as the hydrazine is depleted over time. The Hg^{+2} is then either sorbed by the column or complexed with chloride which sorbs differently or not at all. Thus two mechanisms may influence the Hg^{+2} concentration and eventual sorption: 1) the chloride concentration, which impacts mercury's initial speciation (Hg^{+2} or $HgCl_2$), and 2) the reduction of Hg^{+2} by hydrazine. The mechanism of Hg^{+2} sorption on the FS-2 material is not completely understood, but is being investigated.

AMP-PAN

AMP-PAN tests were performed with actual waste from tank WM-183 and the Average Simulant. Both tests were performed in a 1.5 cm^3 column. Cesium was eluted from AMP-PAN using 5 M NH_4NO_3 in 0.1 M HNO_3 after the column was loaded with cesium from the actual or simulated waste.

Cesium breakthrough results from the actual waste test are shown in Figure 5. No feed adjustments were required prior to testing AMP-PAN. All the fractions

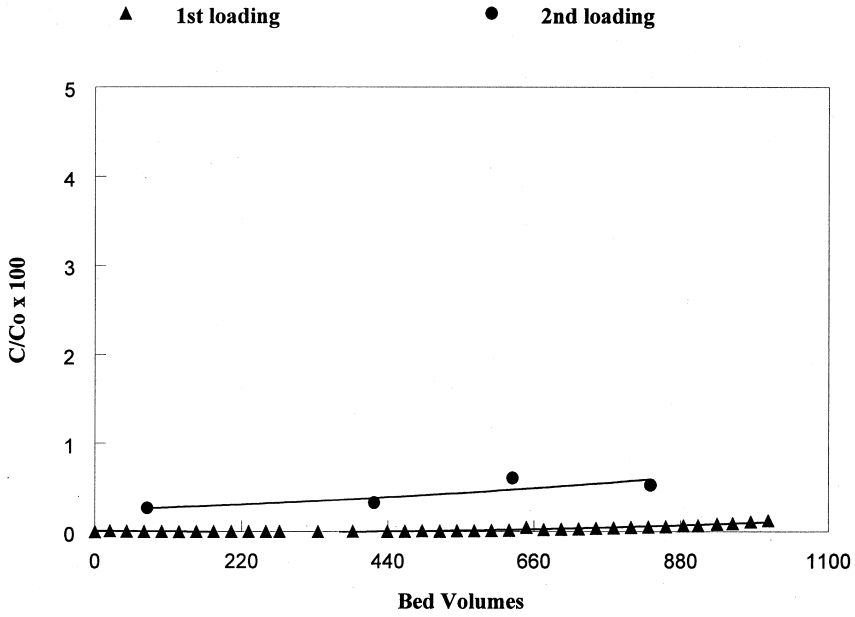

Figure 5. Cesium breakthrough from actual waste from tank WM-183 using a 1.5 cm^3 column containing AMP-PAN.

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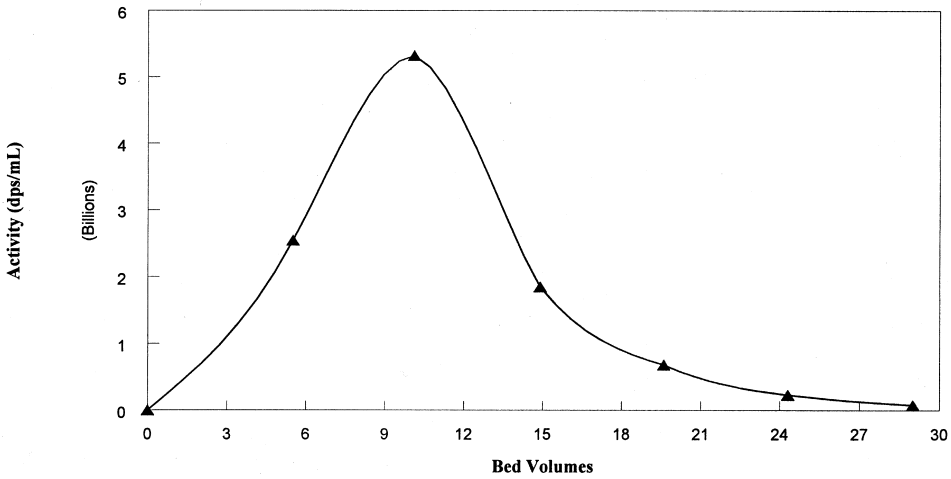

Figure 6. Cesium elution curve from AMP-PAN loaded with actual waste from tank WM-183.

collected from the column, plus the unused feed, were re-combined after being processed and re-run through the column. Cesium breakthrough of 0.15 % was reached after 1000 BV (1500 mLs) of waste were initially processed through the column. A cesium breakthrough of 0.53 % was observed after 830 BV (1245 mLs) of recombined waste was processed, which results in a total cesium decontamination factor of >3000. Sorption characteristics may be different between the first and second loading because of the lower cesium concentration in the second feed batch and loading of non-elutable cesium from the first test, reducing the sorbent capacity.

Cesium was eluted from the AMP-PAN after both the first and second loading cycles with actual waste. Elution results from the first loading are shown in Figure 6. Greater than 83% of the cesium was removed in less than 30 BV.

An overall ^{137}Cs material balance of 87 % was obtained from the AMP-PAN test with actual waste. The AMP material was dissolved by pumping 1.0 M NH_4OH through the column at a rate of 7 mL/hour for 3 hours.

Two loading and elution cycles were also performed with AMP-PAN and the Average Simulant. Cesium breakthrough curves for the first and second loading are shown in Figure 7, and elution curves are shown in Figure 8. Fresh feed was processed for each loading cycle for this test, unlike the actual waste test.

Fifty percent breakthrough occurred after 3200 BV in the first loading cycle and at after 2700 BV in the second loading cycle. This decrease observed in the second cycle of the simulant test was also observed in the actual waste test. The reason for the decreased capacity is not fully known, but may be due to the effect

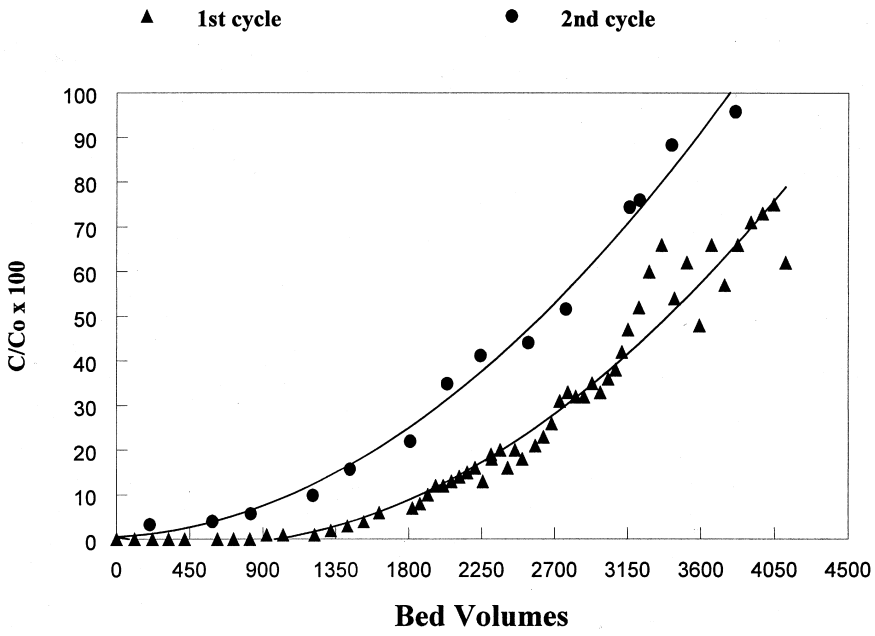

Figure 7. Cesium breakthrough curves using AMP-PAN and the Average Simulant.

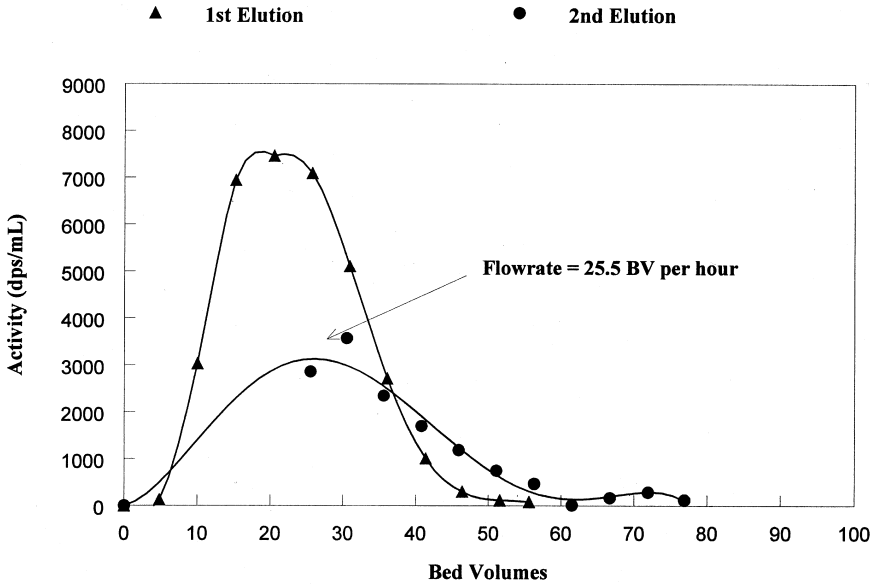

Figure 8. Cesium elution curves from AMP-PAN using 5 M NH_4NO_3 in 0.1 M HNO_3.

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of non-eluted cesium from the first sorption cycle remaining on the sorbent and reducing available exchange sites.

More than 70 % of the cesium loaded onto the AMP-PAN from the first loading cycle was eluted using 5 M NH_4NO_3 in 0.1 M HNO_3. No more cesium was eluted from the column after 50 BV. Only 48 % of the cesium loaded onto the column from the second loading cycle was eluted. A higher flowrate was used to collect the first fraction which caused a different shaped curve shape than that obtained from the first elution. Cesium elution stopped after 60 BV of eluent was collected.

An overall material balance of 59 % was obtained from this test, indicating 40 % of the cesium remained on the column.

IONSIV IE-911

IONSIV IE-911, a form of crystalline silicotitanate, was tested with actual waste from tank WM-183, and the Average Simulant. Cesium is not readily eluted from this material; therefore, no attempt to elute cesium was made.

Cesium breakthrough curves obtained from the actual and simulated wastes are shown in Figure 9. Fifty percent breakthrough occurred at approximately 700

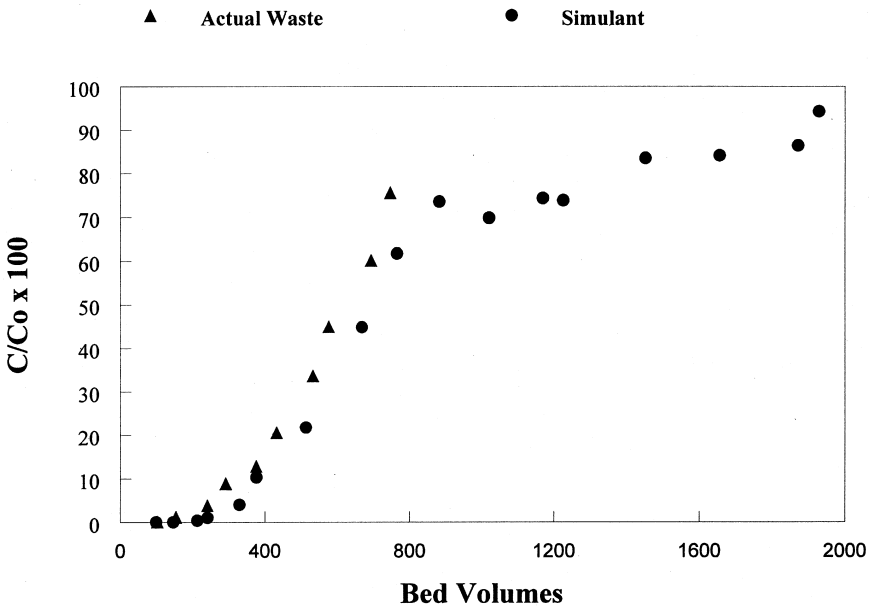

Figure 9. Cesium breakthrough curves using IONSIV IE-911, for actual and simulated wastes.

BV (700 mLs) for both wastes. The cesium breakthrough curve has a different slope beginning at 80% with the simulant, which cannot be explained at this time. One possible explanation is that the IONSIV IE-911 material, which exists as a mixture of sodium and H+ forms, underwent an alteration in form, resulting in different sorption characteristics.

CONCLUSIONS

AMP-PAN had the largest capacity for cesium of the three sorbents tested. However, the FS-2 material also had a high capacity, which may be improved with further feed adjustments that would prevent the sorption of mercury. IONSIV IE-911 had the lowest capacity, which is understandable considering this material is most effective in basic environments. Estimated BV at 20 % breakthrough for each of the sorbents for a given waste are shown in Table 4. Twenty percent was chosen as the point of comparison because most of the tests exceeded this breakthrough point, whereas 50 % breakthrough was not always achieved.

Cesium was elutable from the FS-2 and AMP-PAN sorbents. The 8 M HNO_3 used to elute cesium from the FS-2 is a more desirable reagent than the 5 M NH_4NO_3 used for the AMP-PAN because safety concerns with NH_4NO_3 may preclude it's use in a production process. Cesium was easily eluted from the AMP-PAN loaded with actual waste but poor cesium recovery was obtained when the Average Simulant was used. Cesium elution from AMP-PAN may not be necessary because of the high sorption capacity, and an alternative treatment method could be used by dissolving the AMP from the PAN binder using sodium hydroxide. Cesium was eluted from the FS-2 sorbent efficiently in the simulant waste tests, but was not evaluated in the actual waste test.

Chemical interferences, especially from mercury, effects cesium loading and eluting with FS-2. The cesium capacity appears to decrease in the second

Table 4. Approximate Bed Volumes of Waste Processed by Each Sorbent at 20 % Cesium Breakthrough

Sorbent	Actual WM-183	Average Simulant	WM-183 Simulant
FS-2	775	1300[3]	1,400[1]
		1800[4]	950[5]
AMP-PAN	>>1000[1]	2500[1]	Simulant not tested
	>>830[2]	1,800[5]	
IONSIV IE-911	425	500	Simulant not tested

1 = first loading cycle, 2 = breakthrough of re-combined fractions, 3 = 10 cm^3 column test, 4 = 1 cm^3 column test, 5 = second loading cycle with unused waste.

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loading cycle for all tests, while elution was sporadic (sometimes quantitative, and sometimes very poor). Cesium can not be eluted effectively from IONSIV IE-911.

Results from this work show that FS-2 and AMP-PAN should be considered as candidate technologies for removing cesium from INEEL acidic tank waste. Both sorbents have large cesium capacities, and are potentially regenerable. In addition, tests should be conducted with these sorbents using INEEL dissolved calcine. AMP-PAN is the preferred sorbent when treating wastes that contain chemical interferences, such as mercury, unless these interfering ions are removed prior to treatment.

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