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Selective Removal of Strontium and Cesium from Simulated Waste Solution with Titanate Ion-exchangers in a Filter Cartridge Configuration.

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LIST OF ACRONYMS

CST	Crystalline silicotitanate
D_F	Decontamination factor
MST	Monosodium titanate
PE	Polyethylene
PTFE	Polytetrafluoroethylene

Summary

This report describes experimental results for the selective removal of strontium and cesium from simulated waste solutions using monosodium titanate (MST) and crystalline silicotitanate (CST)-laden filter cartridges. Four types of ion exchange cartridge media (CST and MST designed by both 3M and POREX®) were evaluated. In these proof-of-principle tests effective uptake of both Sr-85 and Cs-137 was observed. However, the experiments were not performed long enough to determine the saturation levels or breakthrough curve for each filter cartridge. POREX® MST cartridges, which by design were based on co-sintering of the active titanates with polyethylene particles, seem to perform as well as the 3M-designed MST cartridges (impregnated filter membrane design) in the uptake of strontium.

At low salt simulant conditions (0.29 M Na^+), the instantaneous decontamination factor (D_F) for Sr-85 with the 3M-design MST cartridge measured 26, representing the removal of 96% of the Sr-85. On the other hand, the Sr-85 instantaneous D_F with the POREX® design MST cartridge measured 40 or 98% removal of the Sr-85. Strontium removal with the 3M-design MST and CST cartridges placed in series filter arrangement produced an instantaneous decontamination factor of 41 or 97.6% removal compared to an instantaneous decontamination factor of 368 or 99.7% removal of the strontium with the POREX® MST and CST cartridge design placed in series.

At high salt simulant conditions (5.6 M Na^+), strontium removal with 3M-designed MST cartridge only and with 3M-designed MST and CST cartridges operated in a series configuration were identical. The instantaneous decontamination factor and the strontium removal efficiency, under the above configuration, averaged 8.6 and 88%, respectively. There were no POREX® cartridge experiments using the higher ionic strength simulant solution.

At low salt simulant conditions, the uptake of Cs-137 with POREX® CST cartridge out performed the 3M-designed CST cartridges. The POREX® CST cartridge, with a Cs-137 instantaneous decontamination factor of 55 and a Cs-137 removal efficiency of 98% does meet the Cs-137 decontamination goals in the low salt simulant liquor. The Cs-137 removal with 3M-designed CST cartridge produced a decontamination factor of 2 or 49% removal efficiency. The Cs-137 performance graph for the 3M-designed CST cartridge showed an early cessation in the uptake of cesium-137. This behavior was not observed with the POREX® CST cartridges. No Cs-137 uptake tests were performed with the POREX® CST cartridges at high salt simulant conditions.

The 3M-designed CST cartridges, with an instantaneous Cs-137 decontamination factor of less than 3 and a Cs-137 removal efficiency of less than 50% failed to meet the Cs-137 decontamination goals in both the low and high salt simulant liquors. This poor performance in the uptake of Cs-137 by the 3M CST cartridges may be attributed to fabrication flaws for the 3M-designed CST cartridges. The reduced number of CST membrane wraps per cartridge during the cartridge design phase, from 3-whole wraps to about 1.5, may have contributed to Cs-137 laden simulant channeling/by-pass which led

to the poor performance in terms of Cs-137 sorption characteristics for the 3M designed CST cartridges.

The grinding of CST ion exchange materials, to reduce the particle size distribution and thus enhance their easy incorporation into the filter membranes and the co-sintering of MST with polyethylene particles, did not adversely affect the sorption kinetics of both CST and MST in the uptake of Cs-137 and Sr-85, respectively.

In general, the POREX® based cartridges showed more resistance to simulant flow through the filter cartridges as evidenced by higher pressure differences across the cartridges. Based on these findings we conclude that incorporating MST and CST sorbents into filter membranes represent a promising method for the semi-continuous removal of radioisotopes of strontium and cesium from waste solutions.

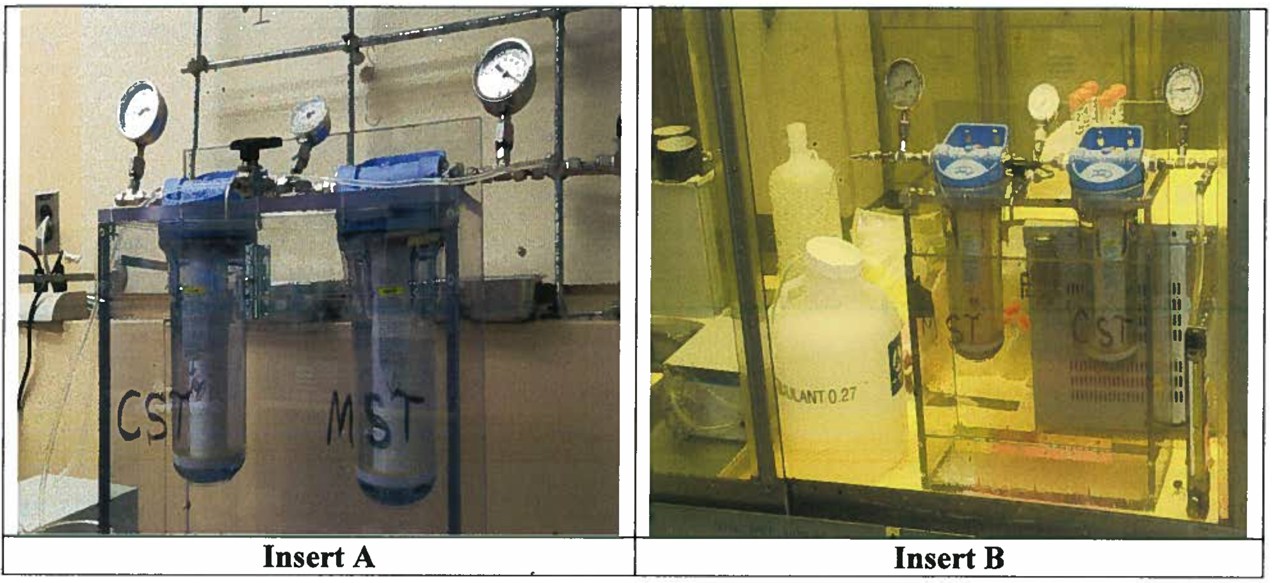
Based on findings from these feasibility tests we recommend the following:

- Perform additional tests with both the POREX® and 3M designed MST and CST cartridges to obtain cartridge saturation and thus allow the determination of the break through curves and loading capacities for these cartridges.
- Consult with 3M to determine the cause of the poor cesium removal performance by the CST cartridges and suggest alternate manufacturing techniques for improved performance.
- Perform additional tests with both the POREX® and 3M designed MST and CST cartridges to determine the influence of flow rates and flow rate variations on strontium and cesium removal performance.

1.0 Introduction

Commercial processes frequently use ion exchange materials in a continuous process featuring either a packed column or a cartridge filter configuration. To prevent hydraulic problems such as high pressure drops across the column, the particle size of the ion-exchanger must be relatively large, which reduces particle packing and, therefore, overall efficiency. In a cartridge filter design, the ion-exchanger is incorporated into an inert, porous material that allows faster solution flow. Relative to the packed column, the cartridge design can employ an ion-exchanger with much smaller particle size, which enhances denser particle packing. Given the smaller particle size and denser packing, the diffusion distances between particles is expected to be minimized leading to more efficient adsorption. The net effect is greater utility of the ion exchanger and higher throughput.

In an earlier study, membranes incorporating both MST and CST particles had been successfully produced and found to be capable of selectively decontaminating strontium and cesium from simulated radioactive waste stream.[1,2] The task involved incorporating MST and CST particles with acceptable particle size distribution into a porous membrane, passing a salt solution containing cesium and strontium through membrane discs having a diameter of 47 mm and thickness of 1.5-2.0 mm and analyzing the effluent. Because of the success attained in the initial phase with the MST and CST-impregnated membranes, SRNL decided to fabricate and test the performance of filtration cartridges incorporating membranes produced by both 3M and Porex Filtration Division. Figure 1 below provides photographs of the filter cartridge and associated equipment used to test the strontium and cesium removal performance.



Insert A **Insert B**

Figure 1. MST and CST filter cartridge configured in a Lexan® box. Insert A shows units in a non radiation laboratory and insert B shows unit inside a radioactive laboratory hood.

2.0 Experimental

2.1 Cartridge design

The polytetrafluoroethylene (PTFE)-based and polyethylene (PE)-based membranes containing MST and CST particles were prepared by commercial partners using their proprietary fabrication technologies. Industrial partners included 3M for the PTFE membrane cartridges and Porex Corporation, Filtration Division, for the PE membranes and sintered cartridges. CST pellets having a particle size distribution of 300 to 500 microns were obtained from UOP (Des Plaines, Illinois). Since the working particle size range for the CST had to be less than 80 microns (3M manufacturing requirement), the CST material was ground and wet vacuum sieved by SRNL to obtain the desired particle size distribution between 45 and 75 microns. MST powder, having a particle size distribution of about 1 – 35 microns, was obtained from Optima Chemical Group, LLC (Douglas, GA) as a 15 wt% aqueous suspension. Additional details for preparing of the MST and CST materials for incorporating into porous membranes are presented in reference.[1]

After preparing the MST and CST particles to meet the required particles size distribution, SRNL shipped the processed ion-exchange materials to the commercial partners for incorporation into the PTFE and PE membranes. The POREX® finished product included both MST and CST membranes and MST and CST cartridge filters based on their patented "sintered" technology. The technology involves co-sintering polyethylene particles with the MST or CST ion exchange particles and forming a molded and structured porous matrix, which constitutes the cartridge filter as shown in Figure 2. The ion exchange materials tend to be fixed into place with minimal leaching/extraction. Because the polymer used is polyethylene, it has a wide range of chemical compatibility.

The 3M finished product included only the MST and CST membrane sheets. Pentair Water (Brookfield, WI) was provided sheets several meters in length of the impregnated MST and CST membranes from 3M, which they wound into filter cartridges (MST or CST cartridges). These filter cartridges were produced by wrapping the membrane sheets around a central core three times with specific lengths of each MST and CST membrane sheet and sealing the ends of the cartridge units as shown in Figure 3. These 3M and POREX® cartridges can be put into any commercially available cartridge housing and meet the following basic configurations:

- hollow perforated core- see Figures 2 and 3 below,
- capped ends – one closed, the other open – to form the final cartridge,
- direction of flow through the cartridge is designed to be from outside to inside (influent surrounds the cartridge in its housing, passes through two or three layers of membrane, through a perforated core, and then out the open end),
- typical cartridge designed to process liquid up to 1/2 gallon per minute,
- 5.0-7.6 cm in diameter by 25.4 cm in length, and contains approximately 522.6 cm^2 of membrane (two 22.86 by 11.43 cm membrane sheets per cartridge),
- at least two to three sheets of membrane per cartridge separated by an inert material and
- open ends of the cartridges are fitted with O-rings that adapt to any industry-standard receptacles for filters and modified as necessary.

The dimensions of these cartridges (length, inner diameter and outer diameter) were standard values which fit into any Pentair Water's commercial filter housing with end-caps. The nominal dimensions of the cartridges along with weight percent and actual weights of the active ion exchange materials per cartridge are shown in Table 1.

Figure 2. Photo of a typical POREX® "sintered" cartridges (7.0cm diameter x 25.4 length).

Representative MST and CST cartridges from both 3M and POREX® were dismantled and the weight of the active titanates determined based on the weight percent information of the MST and CST active sorbent materials as provided by 3M and POREX®. These values are summarized in Table 1. The number of active membrane wraps for the 3M products (MST and CST cartridges) were also ascertained. POREX® products, as mentioned earlier, were based on sintering of the active titanates with the polymeric support and, thus, did not require wrapping.

2.2 Filter cartridge unit configuration and testing methodology

The experimental configuration is shown previously in Figure 1. The unit consists of a transparent box (45.72 cm x 30.48 cm x 20.32 cm) made of Lexan® polycarbonate sheets containing two transparent filter housing units connected in series. Each filter housing unit contains one filter cartridge. Thus, two filter housing units contains two filter cartridges in series with the MST cartridge the lead cartridge followed by the CST cartridge. The lead MST cartridge sees the incoming feed solution delivered by the peristaltic pump before the CST cartridge. The system contains three pressure gauges; one at the influent, the other between the two cartridge units and the last one placed after the CST cartridge, just before the effluent line. The unit was equipped with two valve sampling ports. The first sampling port valve was located between the two cartridges and the last one after the CST cartridge (effluent end).

The simulated waste solutions used for these tests featured salt solutions having two different ionic strengths and spiked with known levels of Sr-85, Cs-137 and Np-237. The simulated waste did contain uranium and plutonium, but the concentrations of these components were not measured in these tests. The lower ionic strength simulant featured a total sodium concentration of 0.29 M (derived from a simple dilution of the 5.6 M Na^+ simulant), while the second simulant, known as the high-salt simulant, featured a total sodium concentration of 5.6 M. These solutions were chiefly comprised of sodium salts of nitrate, hydroxide, nitrite, aluminate, sulfate and carbonate. The simulant composition for all other constituents and radionuclide compositions are shown in Tables 2 and 2b. Reagent grade chemicals (Fisher Scientific) and in-house ultra pure water (MilliQ Element) were used in the preparation of the simulants. After the simulant preparations, the resulting solutions were stirred at ambient laboratory temperature for about three weeks, filtered through 0.45-micron disposable Nalgene® filters, and filtered solutions stored in tightly-capped polyethylene bottles until use.

The salt solution was pumped through the filter cartridges using a peristaltic pump at a flow rate of 80 ± 1 mL/min for the 3M cartridges and a flow rate of 67.0 ± 1 mL/min for the POREX® cartridges. Simulant flow through POREX® cartridges were maintained at lower flow rates to reduce pressure differences across the filter cartridges in series. For the 3M cartridges and the 0.29 M Na^+ simulant, it took 26 ± 1 minute for the simulant to completely fill the lead cartridge housing. After this time the effluent from the lead MST cartridge started flowing into the second cartridge housing containing the CST cartridge. At this time, sampling at the sampling port located between the two cartridge housings was initiated to determine the performance of the lead cartridge. It took another 19 ± 1 minutes or a total of 45 ± 1 minutes from when the pump was first turned on to have the second cartridge housing (CST cartridge) completely filled. Sampling of the effluent after the CST cartridge occurred using the second port. The pressure difference between the cartridges, at this flow rate, was less than 2.5 psi. The tests were repeated with the 3M cartridges using the 5.6 M sodium salt solution.

Tests with the POREX® cartridges were carried out with both types of simulants at the same flow rates. The POREX® cartridges are more densely packed and, therefore, required a higher operating pressure of approximately 7 psi to obtain reasonable flow of 67 ± 1 mL/min. Thus, a time of 45 minutes was required to fill the lead MST cartridge housing and a total of 85 minutes to fill the second CST cartridge before sampling from the second or effluent sampling port could be started.

The sampling sequence included collecting two aliquots immediately after the solution came out of the lead MST cartridge and then two additional aliquots after the solution exited the CST cartridge. Thereafter, additional samples were collected after every five minutes of simulant flow through the cartridges at each of the two sampling ports. Only one of the duplicate samples was analyzed while the second was held in reserve in case of discrepancies.

Figure 3. Photo of typical 3M membrane cartridges (7.0cm [diameter] x 25.4 length).

To determine the average sorbate (Sr-85 or Cs-137) picked up by the cartridge during each sampling time, the corresponding measured activity for that sorbate was subtracted from the initial sorbate concentration in the simulant solution. This difference was normalized to give the average activity per gram sorbate [(dpm/mL)/g] using the weight of the sorbate per cartridge. Similarly, the normalized processed simulant volume was determined by dividing the volume of simulant in mL which had gone through each cartridge at each sampling event (using the liquid flow rate through the cartridge) by the total volume of simulant in the cartridge and cartridge housing (1, 500 mL). Thus, the adsorption performance graph presentations are based on a plot of the product of the average activity per gram sorbate and simulant flow rate in mL per minute (adsorption rate [dpm/min].g) versus the normalized processed volume. The sorbate activity changes with processed simulant volume are shown as plots of sorbate permeate activity (concentration at any time divided by initial sorbate concentration) versus normalized processed volume.

Table 1. A summary of 3M and POREX® filter cartridge properties

	3M		*POREX®*	
	MST	CST	MST	*CST*
Absorbent weight per cartridge (Average), g*	7.99 (32 wt %)	28.76 (85 wt %)	60.4(32 wt %)	74.17(40 wt %)
Cartridge height (cm)	25.4	25.4	25.4	25.4
Cartridge diameter (cm)	5.715	5.715	5.715	5.715
Membrane length (cm)	10.16	10.16	NA	NA
Membrane thickness (cm)	4.57E-02	5.08E-02	NA	NA
Number of membrane wraps per cartridge	3	1.5	NA	NA
Average total weight of filter and active IX materials, g	24.96	33.84	188.74	185.41

NA: Not applicable. POREX® cartridges were based on sintered design.

* PTFE and PE used as filler. Vendor cartridges did not contain the same total mass of absorbent.

Table 2. Recipe for 5.6 M Sodium Simulant Composition.

Component	**Target Concentration, M**
Free NaOH	1.33 E+00
Total $NaNO_3$	2.60E+00
$NaAl(OH)_4$	4.29E-01
$NaNO_2$	1.34E-01
Na_2SO_4	5.21E-01
Na_2CO_3	2.60E-02
Total Na^+	**5.6E+00**

Table 2b. Analytical Result for Simulant Composition

Analytes	**0.29 M Na^+ solution**	**5.6 M Na^+ solution**	**Units**
Al	1.26E+02± *8.49E-01*	1.16E+04± *4.24E+01*	mg/L
B	<9.2E+00	3.07E+01± *7.50E+00*	mg/L
Ca	3.07E+00± *1.94E+00*	9.23E-01± *8.34E-02*	mg/L
K	<1.20E+00	8.85E+01± *2.69E+00*	mg/L
Mg	5.06E-01± *0.00E+00*	1.78E-01± *6.22E-03*	mg/L
Mo	<5.34E+00	<5.34E-01	mg/L
Na	6.64E+03± *2.83E+01*	1.28E+05± *5.66E+02*	mg/L
S	<2.70E+01	1.93E+04± *3.96E+02*	mg/L
Si	<1.19E+01	2.32E+01± *8.49E-01*	mg/L
Zn	<1.06E+00	1.66E-01± *2.31E-02*	mg/L
Cs-137	1.30E+05±*1.13E+03*	3.59E+05 ± *2.97E+04*	dpm/mL
Sr-85	1.00E+05±*7.07E+02*	9.65E+04± *2.69E+03*	dpm/mL
Pa-233	3.31E+02±*7.07E+00*	4.95E+02± *9.19E+01*	dpm/mL
Np-237	8.21E+02 ± *4.38E+01*	1.05E+03± *1.13E+02*	dpm/mL

2.3 Batch Contact Test

A batch contact test was also performed with the "as-received" and ground CST materials used in the fabrication of the CST cartridges. In this batch experiment, about 0.1 grams of the respective sorbent samples were contacted with 10 mL of a 5.6 M Na^+ salt solution containing Sr-85, Cs-137, Np-237, U-235/238 and Pu-239/240 for 24-hours at ambient laboratory temperature. The CST solids were removed by filtration and the filtrate analyzed by gamma spectroscopy to determine Sr-85, Cs-137 and Np-237 activities. The results are summarized in Table 3. The concentrations of U and Pu were not measured in these batch contact tests.

Table 3. Batch Contact Experimental Results using the "As-Received" and Ground CST.

Section A- Experimental Results

	Concentration in simulant	Concentration after passing through "As-Received" CST	Concentration after passing through Ground CST
	dpm/mL	dpm/mL	dpm/mL
Cs-137	1.97E+05 ± *9.85E+03*	1.12E+04 ±*5.60E+02*	9.59E+03 ±*4.80E+02*
Sr-85	1.24E+04 ±*6.20E+02*	5.32E+02 ±*2.66E+01*	1.29E+02 ±*8.37E+00*
Np-237	1.79E+03 ± *9.76E+01*	4.32E+02 ±*2.81E+01*	6.07E+02 ±*4.30E+01*

Section B-Calculated D_f

		"As-Received" CST	Ground CST
Cs-137 D_F values	NA	17.6 ± *0.92*	20.5 ± *1.08*
Sr-85 D_F values	NA	23.3 ± *1.2*	96.1 ± *5.2*
Np-237 D_F values	NA	4.14 ± *0.24*	2.95 ± *0.18*
% Cs-137 Removed	NA	94.3%	95.1%
% Sr-85 Removed	NA	95.7%	99.0%
% Np-237 Removed	NA	75.9%	66.1%

Section C-Calculated K_d

		"As-Received" CST	Ground CST
Cs-137 K_d values, mL/g	NA	1.65E+03 ± *8.67E+01*	1.92E+03 ± *1.01E+02*
Sr-85 K_d values, mL/g	NA	2.22E+03 ± *1.17E+02*	9.34E+03 ± *5.07E+02*
Np-237 K_d values, mL/g	NA	3.13E+02 ± *1.84E+01*	1.91E+02 ± *1.14E+01*
Batch contact time, h.	24	24	24

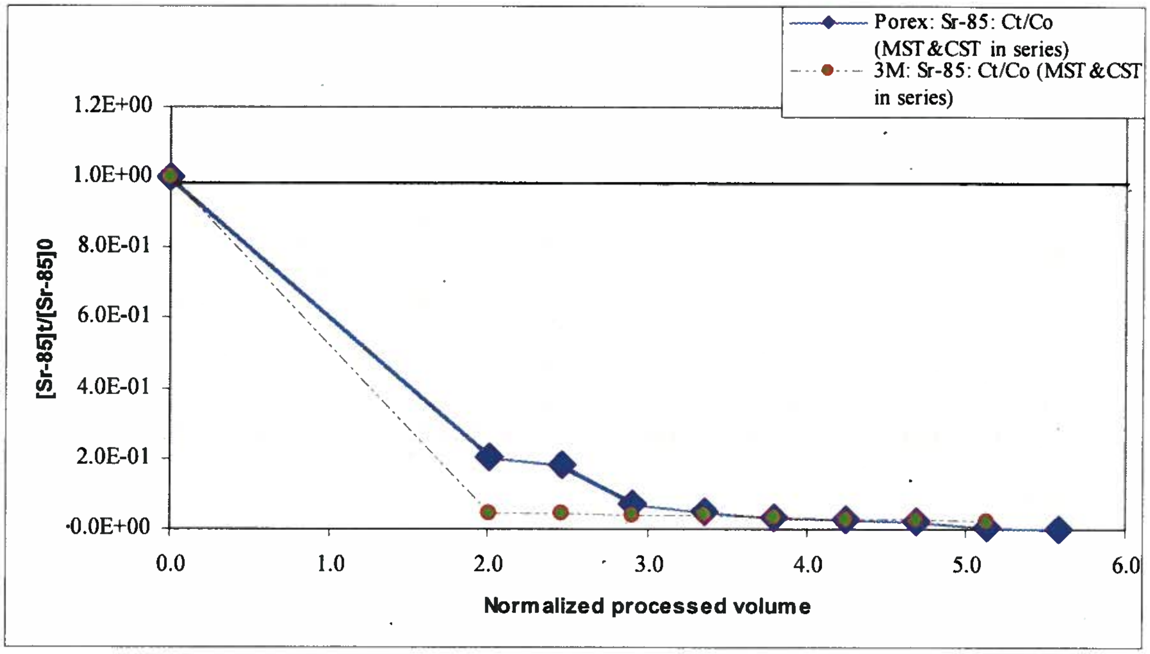
3.0 Results and Discussion

Filtration cartridges incorporating titanate ion-exchange sorbents, MST and CST, respectively, were fabricated using two different porous matrices and their performance for the removal of strontium and cesium were evaluated in low (0.29M Na^+) and high (5.6M Na^+) ionic strength salt solutions. The PTFE-based cartridges were assembled by Pentair Waster using sheets comprised of PFTE impregnated with MST or CST produced by the 3M Corporation. The PE-based cartridges were produced by the Porex Corporation. Characteristics of the filter cartridges are summarized in Table 1.

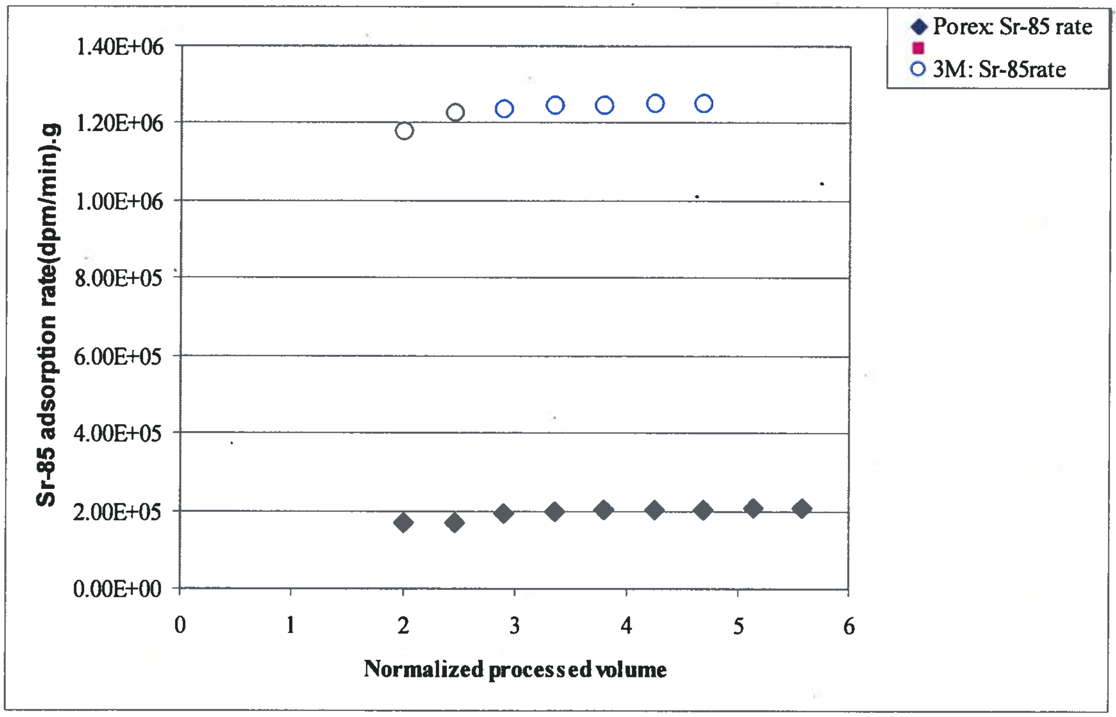
The strontium-85 permeate activity performance overlay graphs (effluent concentration profile) are shown in Figure 4 insert A for both POREX®-produced MST and 3M produced MST in a low ionic strength salt solution simulant. Both graphs indicate a steady decrease in the Sr-85 activity with increase in process volume for MST-CST in a series configuration. Figure 4 insert B shows the plot of Sr-85 uptake rate with both MST-loaded filter cartridges from the 0.29 M Na^+simulant. Both the 3M and POREX®-produced MST cartridges show a gradual and steady approach to steady-state adsorption of Sr-85 with increasing volume of simulant processed. The 3 M MST-cartridges exhibited a 96% removal efficiency for Sr-85 with an instantaneous decontamination factor of 26. The Sr-85 removal with POREX® cartridge exhibited a 97% removal efficiency with an instantaneous decontamination factor of 40.

Interestingly, the 3M-cartridge showed a remarkable large uptake rate of Sr-85 compared with the POREX®-based cartridge even though the 3M-cartridge contained only about 13% of the MST quantity found in the POREX®-cartridge. Since these tests were not carried out to full saturation, it is difficult to ascertain whether the POREX® -based MST cartridges, with significantly more MST sorbate than the 3M cartridges, would have processed more simulant without overloading of the active titanate in comparison with the 3M-based MST cartridges.

The strontium-85 permeate activity performance overlay graph is shown in Figure 5 insert C for both 3M produced MST and CST in a low ionic strength salt solution. This effluent concentration profile overlay graphs indicate a steady decrease in the Sr-85 activity with increase in process volume for MST only and CST as well. Thus, although CST is designed mainly for the uptake of Cs-137, the graph also shows that a measurable amount of Sr-85 is sorbed by CST. Figure 5 insert D shows the uptake rate of Sr-85 on the lead MST cartridge and the lagging CST cartridge (3M designed cartridges). As expected, the CST-cartridge removed additional Sr-85 that was not removed by the preceding MST cartridge. The uptake rate of Sr-85 by the CST-cartridge appeared to be constant with increase simulant volume treated. After passing through both cartridges, the overall removal efficiency measured 97.6% with an instantaneous decontamination factor of 41, which is significantly higher than immediately after the MST-cartridge (96% removal efficiency with instantaneous DF of 26. The increase in Sr-85 performance data is even much more pronounced with the POREX® MST and CST cartridges in series. After the lead MST-cartridge, the Sr-85 removal efficiency measured 97% (DF = 40). After passing through both cartridges, the Sr-85 removal efficiency measured 99.7% (DF = 368).

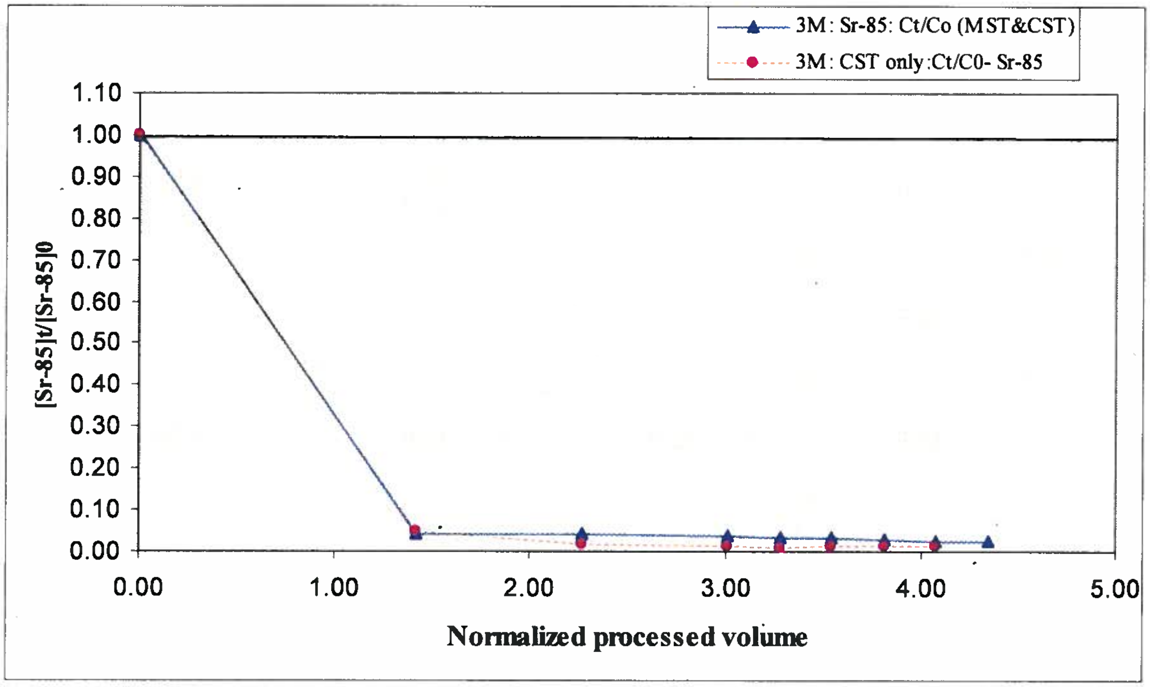


Insert A. Overlay plots for Sr-85 activity changes with respect to normalized volume of simulant processed (Porex and 3M MST cartridge designs).

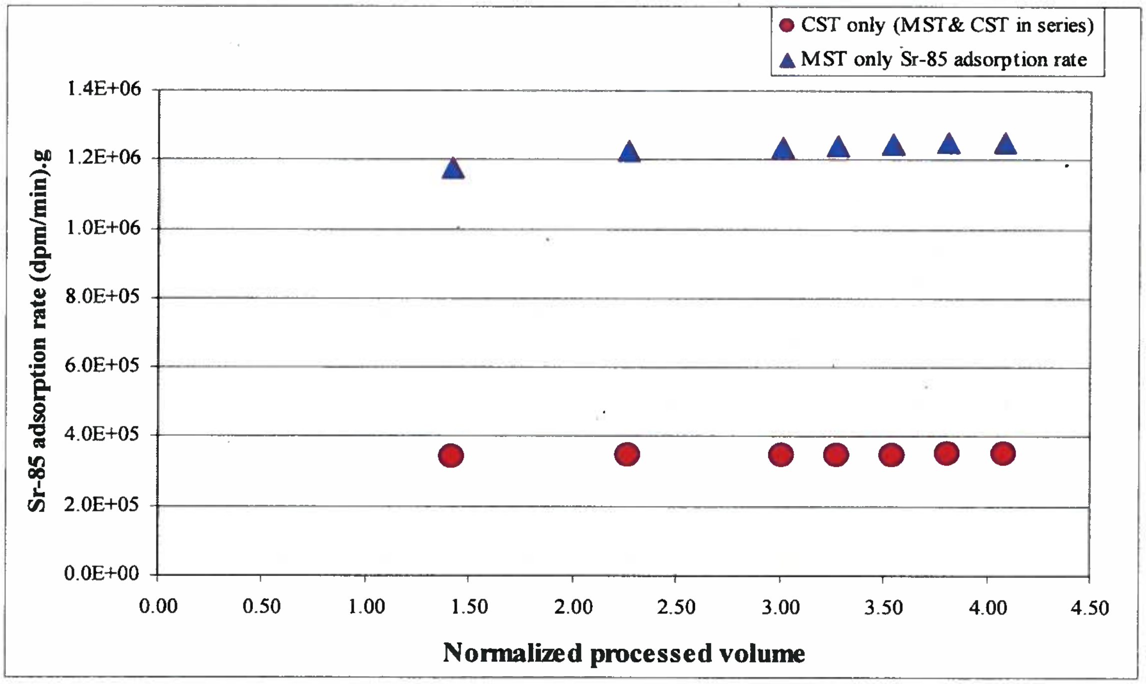


Insert B. Overlay sorption rate plots for strontium-85 removal with MST cartridges designed by 3M and POREX®.

Figure 4. Overlay plots for Sr-85 activity and sorption rate changes in a 0.29M Na^+ simulant with both Porex and 3M designed MST cartridges (MST and CST cartridges in series).



Insert C. Overlay plots for for strontium-85 removal with MST only and CST cartridge only (MST/CST cartridges in series-0.29 M Na^+ simulant.



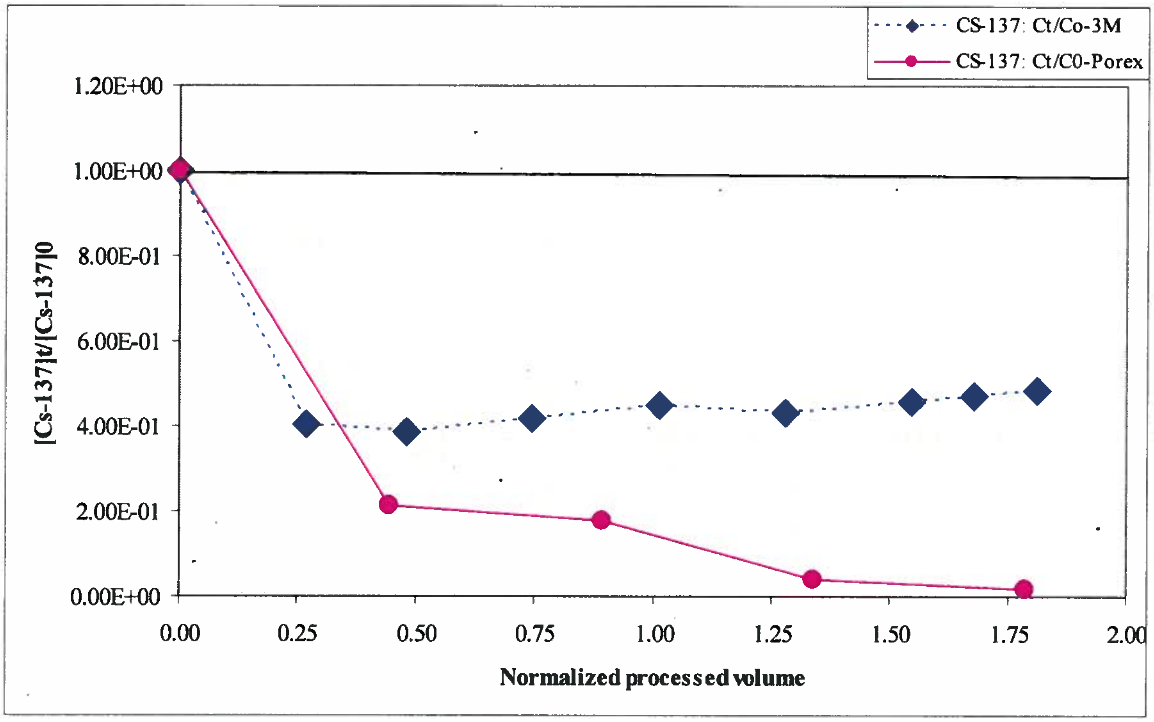
Insert D. Overlay sorption rate plots for strontium-85 removal with MST only and CST cartridge only (MST/CST cartridges in series-0.29 M Na^+ simulant).

Figure 5. Overlay plots for Sr-85 activity and sorption rate changes in a 0.29M Na^+ simulant with separate MST and CST cartridges only (Porex and 3M designs)

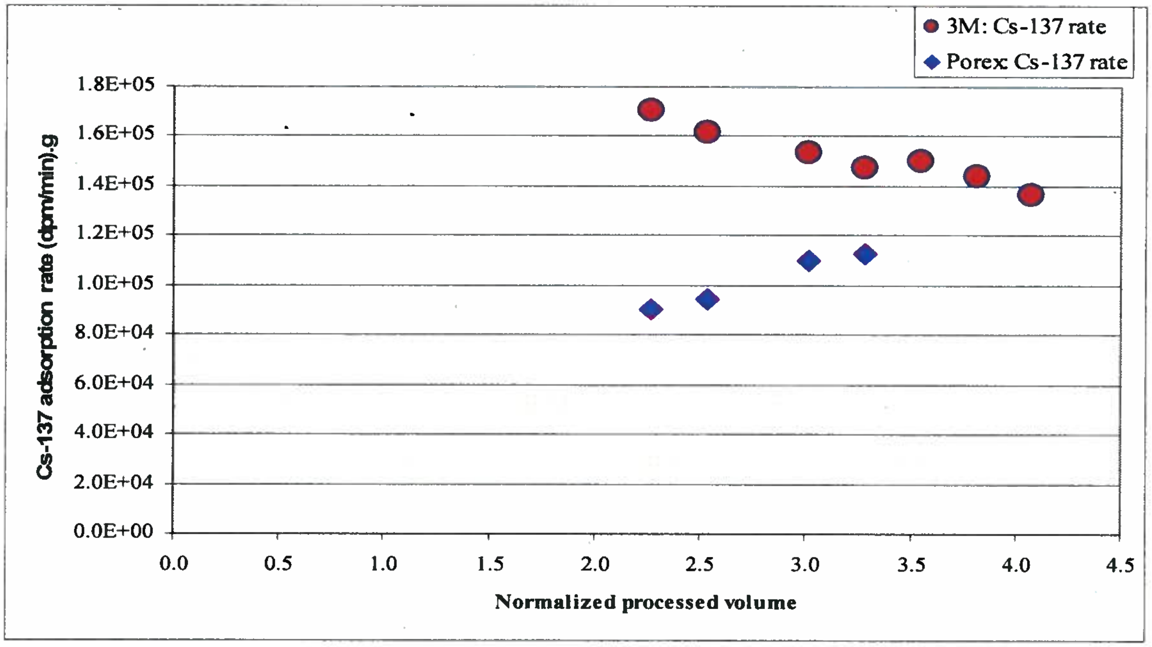
The cesium-137 permeate activity performance overlay graph is shown in Figure 6 insert E for both POREX®-produced CST and 3M produced CST in a low ionic strength salt solution. POREX®-produced CST graphs indicate a steady decrease in the Cs-137 activity with increase in process volume while the 3M- produced CST cartridge shows an early saturation in cesium as evidenced by the decrease in uptake of Cs-137 with an increase in simulant process volume. Figure 6 insert F shows the uptake rate of Cs-137 from the 0.29 M Na^+ simulant with the CST- cartridges prepared by both 3M and POREX®. Overall, the 3M cartridge exhibited a 49% removal efficiency with an instantaneous DF of 2. The POREX®-cartridge exhibited a much higher removal efficiency of 98% and instantaneous DF of 55. Note that the 3M-cartridge shows an early saturation in cesium as evidenced by the decrease in uptake rate of Cs-137 with an increase in simulant process volume just after a total flow of about 3 liters of the simulant. This is not the case with the POREX® CST cartridges. The Cs-137 uptake rate continued to increase steadily even after processing more than 7 liters of the simulant. The POREX® designed CST cartridge performance for the uptake of Cs-137 showed a steady increase with increase in processing simulant volume.

After testing, a number of the MST and CST cartridges produced by 3M were dismantled and it was found that the CST cartridge had only 1.5 wraps of the membrane per cartridge versus the design specification of three wraps (see Figures 9 [inserts K, L, and M] and 10). Thus, the poorer performance of the 3M CST-cartridge compared to the POREX® cartridge is attributed to the reduced quantity of CST in the 3M cartridge.

Previous testing has shown that MST does not adsorb cesium in strongly alkaline salt solutions. Analysis of samples taken immediately after the MST cartridges confirmed no measurable uptake of Cs-137 by the lead MST cartridges produced by either 3M or POREX®.



Insert E. Overlay plots for Cs-137 activity changes with respect to normalized volume of simulant processed (Porex and 3M CST cartridge designs).

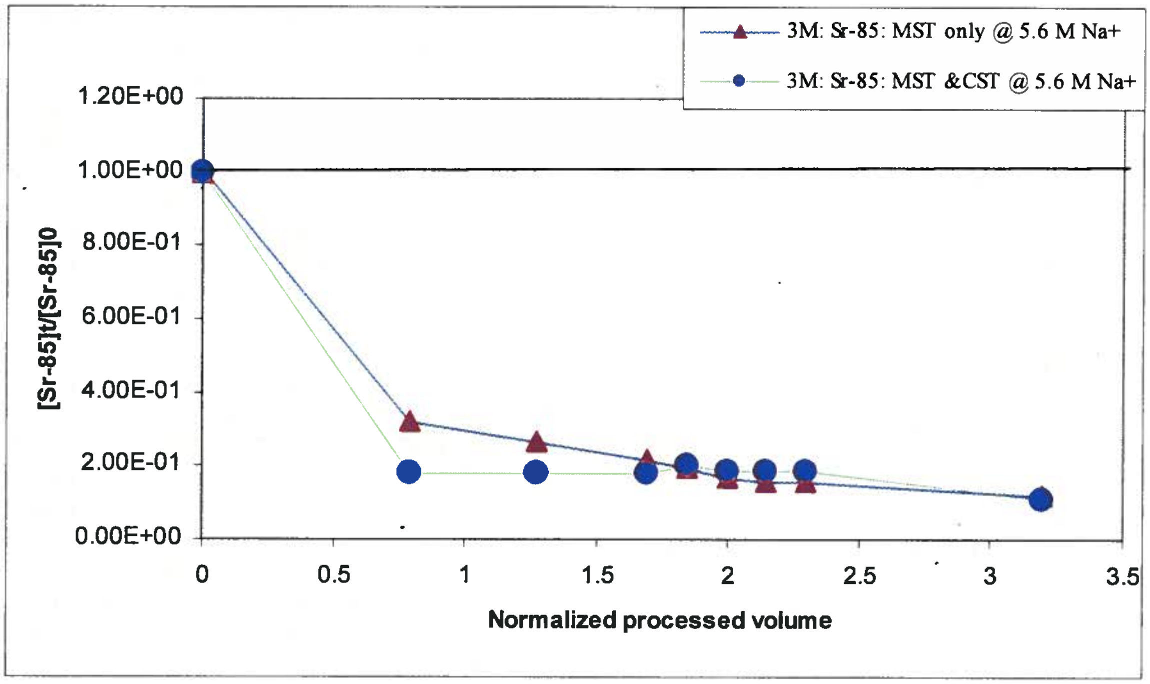


Insert F. Overlay sorption rate plots for cesium-137 removal with CST cartridge (3M and POREX® designs).

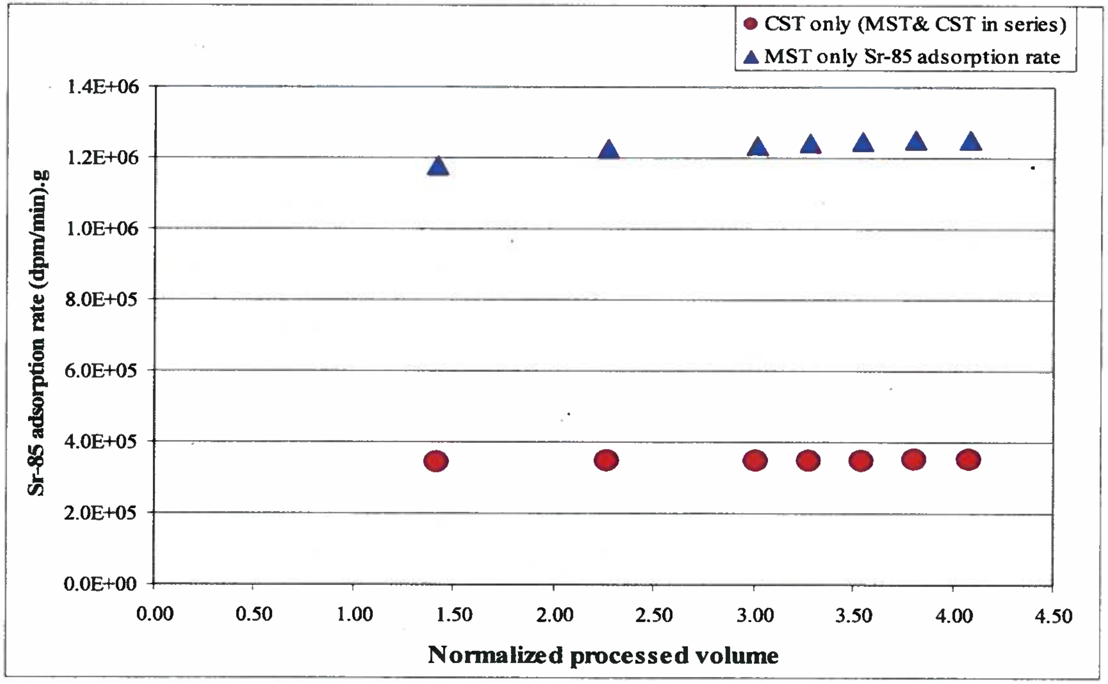
Figure 6. Overlay plots for Cs-137 activity and sorption rate changes in a 0.29M Na^+ simulant with both Porex and 3M designed CST cartridges

The removal of Sr-85 and Cs-137 from a much more concentrated salt solution containing 5.6 M in Na^+ was also tested. All experiments using the 5.6 M Na^+ solution were performed only with 3M-cartridges.

The strontium-85 effluent concentration profile overlay graphs are shown in Figure 7 insert H for both 3M produced MST only and MST-CST in series in a low ionic strength salt solution. The overlay graphs indicate a steady decrease in the Sr-85 activity with increase in process volume for MST only and MST-CST in series as well. Again, there is a measurable removal of Sr-85 when the permeate goes through the CST cartridge. Figure 7 insert G provides a plot of the uptake rate of Sr-85 with the MST-cartridge only and with the MST (lead) and CST (lag) cartridges in series. The Sr-85 removal efficiency with the MST cartridge only measured 89% with an instantaneous DF of 8.3. Again, as observed with previous experiments, the lagging CST cartridge also removed strontium-85: This Sr-85 uptake with the lagging CST cartridge remained fairly constant with increase in volume of simulant processed as shown in Figure 7 (insert H). The Sr-85 removal efficiency with 3M MST and CST cartridges operated in series (3M design) measured 89% with an instantaneous DF of 9.0.



Insert G. Overlay plots for Sr-85 activity changes with respect to normalized volume of simulant processed (Porex and 3M MST cartridge designs. 5.6 M Na$^+$ simulant).

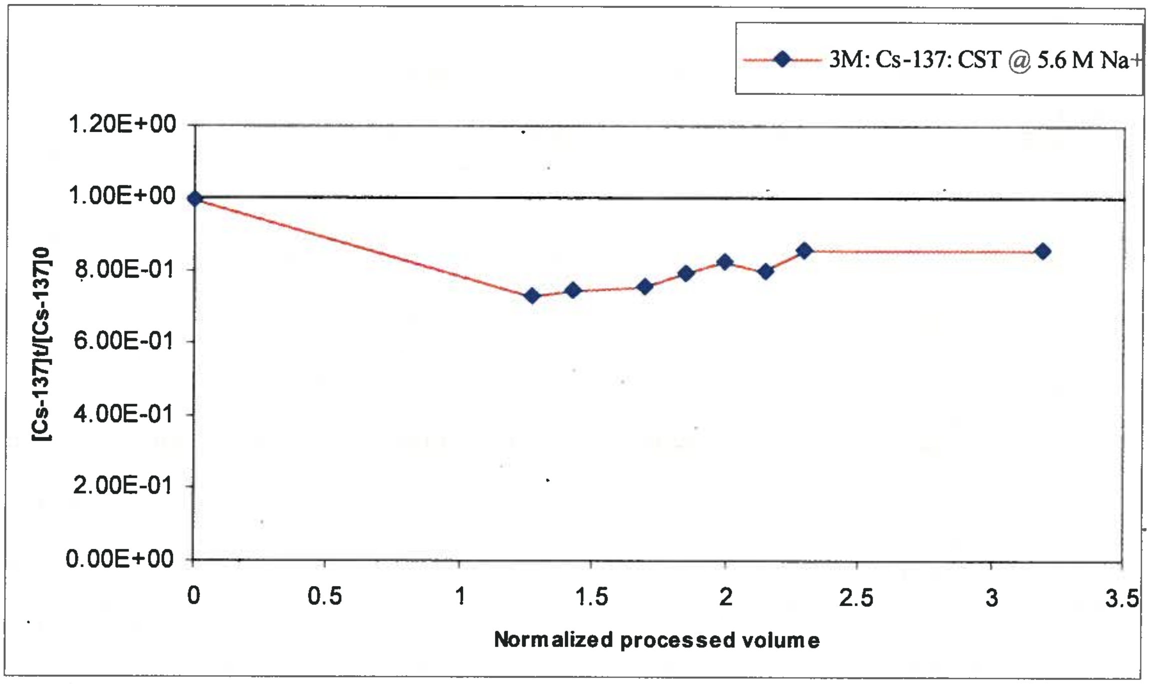


Insert H. Overlay sorption rate plots for strontium-85 removal with MST only and MST-CST cartridges in series (3M design) at 5.6 M Na$^+$ concentration).

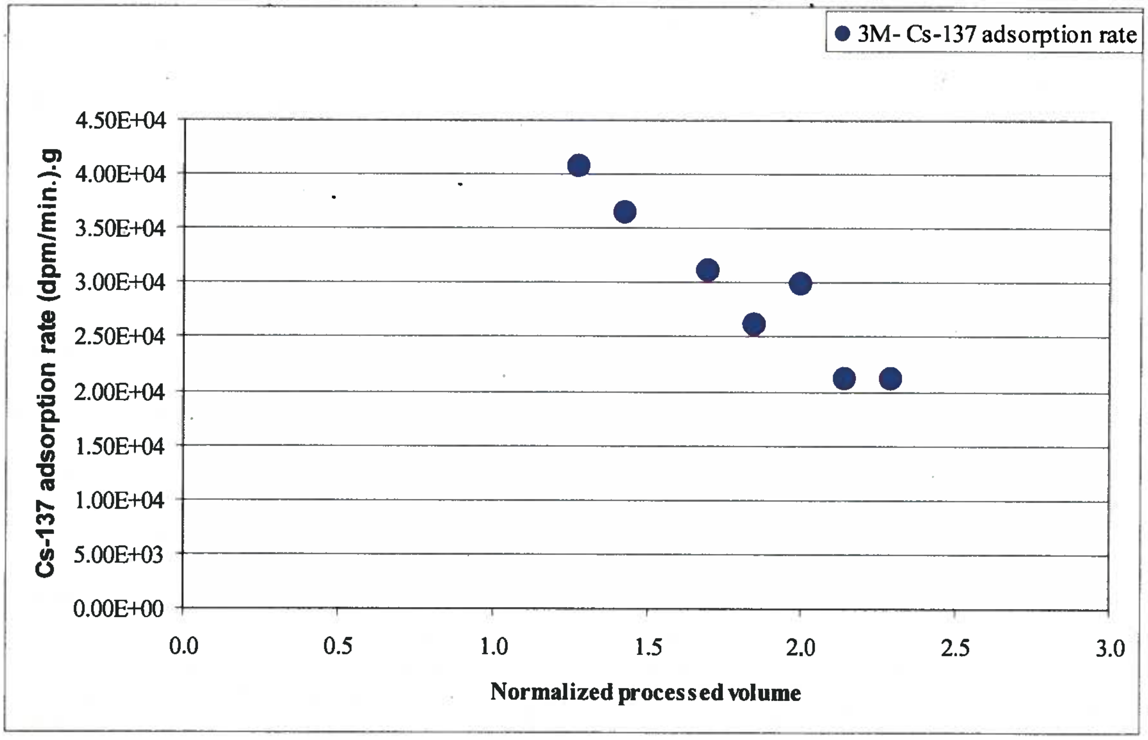
Figure 7. Overlay plots for Sr-85 activity and sorption rate changes in a 5.6 M Na$^+$ simulant with both Porex and 3M designed MST and CST cartridges.

As in previous low ionic strength salt solution experiments 3M-based CST cartridges exhibited low Cs-137 uptake. The cesium-137 permeate activity performance graph is shown in Figure 8 insert I for 3M produced CST in a high ionic strength salt solution. The 3M based CST cartridge shows a remarkable early saturation in cesium as evidenced by the decrease in uptake of Cs-137 with an increase in simulant process volume. Figure 8 insert J shows the Cs-137 removal rate with the 3M CST cartridge at a 5.6 M Na^+ simulant flow rate of 45 mL/min. The removal efficiency measured only 27% with an instantaneous DF value of 1.4. The cartridge appeared to stop sorbing Cs-137 within 20 minutes of operation, which represents less than 1.5 liters of simulant flowing through the cartridge.

The poor Cs-137 removal performance by the CST cartridge may be attributed to a number of factors including, (1) the high sodium ion concentration in the concentrated salt solution, (2) uneven distribution of CST particles in the membrane sheets, (3) the PTFE-CST media in the membrane may have lower porosity, (4) the PTFE may be blocking diffusion pathways to the CST, and (5) the particle morphology of the CST could have changed during the grinding of the original bead material to reduce the particle size distribution from an average of 300 microns down to 45-75 microns, and (6) the low quantity of CST in the cartridge. The high sodium ion concentration is not likely a significant factor since available batch distribution constant (K_d) data for CST with Cs-137 shows that the uptake of Cs-137 by CST powder is sufficiently high even in the presence of large competing ion like sodium.[2,3] Uneven distribution of CST, low porosity or blocking diffusion pathways due to the PTFE matrix are also not likely significant factors since the MST-cartridge did not show similar poor performance. On the other hand, if grinding altered the particle morphology, the sorption kinetics could be adversely impacted.



Insert I. Cs-137 activity changes with respect to normalized volume of simulant processed (3M CST cartridge designs 5.6 M Na^+ simulant).



Insert J. Sorption rate plot for cesium-137 removal with CST cartridge (3M design).

Figure 8. Overlay plots for Cs-137 activity and sorption rate changes in a 5.6 M Na^+ simulant with 3M designed CST cartridges

To ascertain if changes in particle morphology of the CST material occurred as a result of grinding a 24-hour batch contact test with the "as-received" and ground CST materials was conducted. The results, as shown in Table 3, indicate no difference in the removal of Cs-137 between the "as-received" and ground CST. Thus, it is concluded that grinding did not have any influence on the uptake of Cs-137. Note that the ground CST exhibited a slightly higher uptake of Sr-85, but lower uptake of Np-237 compared to the as-received MST.

As discussed earlier, the 3M CST cartridge had only about 1.5 wraps of the active CST membrane per cartridge resulting in a low quantity of CST in the filter cartridge and perhaps gaps in the membrane lining around the CST cartridges which may have resulted in by-pass flow of the simulant and, thus, reduced removal of Cs-137 for the 3M CST cartridges in both the low and high sodium ion salt solutions.

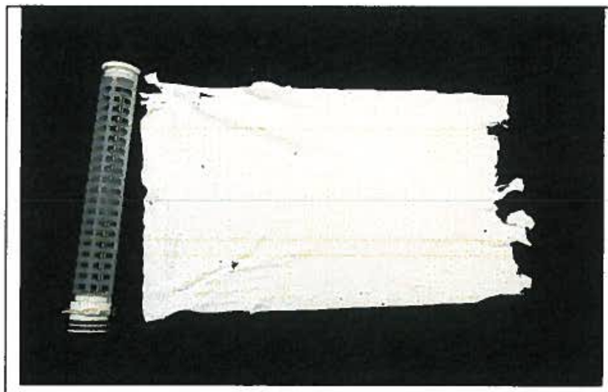
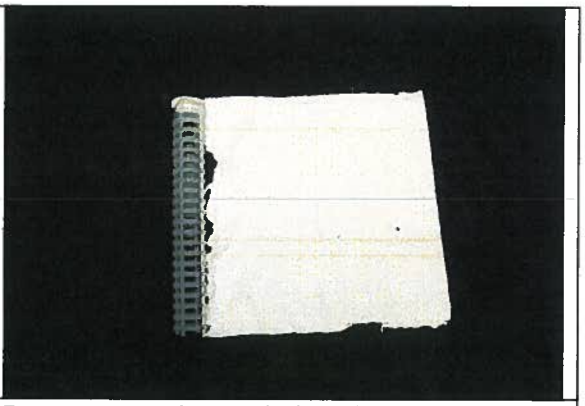
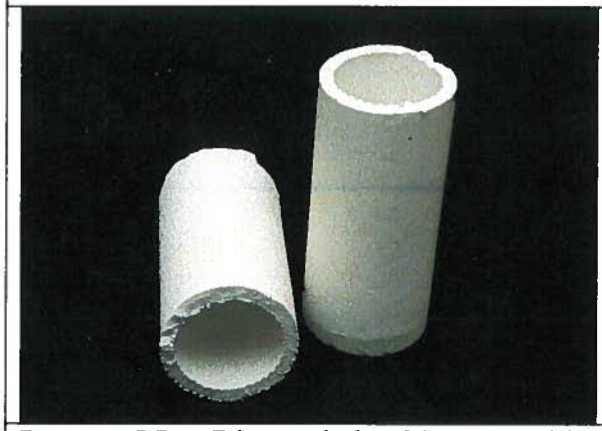
	
Insert K: Dismantled and unwound MST cartridge (3M design)	**Insert L:** Dismantled and unwound CST cartridge (3M design)
	No image here.
Insert M: Dismantled CST cartridge (POREX® design)	

Figure 9. Dismantled and unwound CST and MST Cartridges (3M design) and Dismantled CST Cartridge (POREX®).

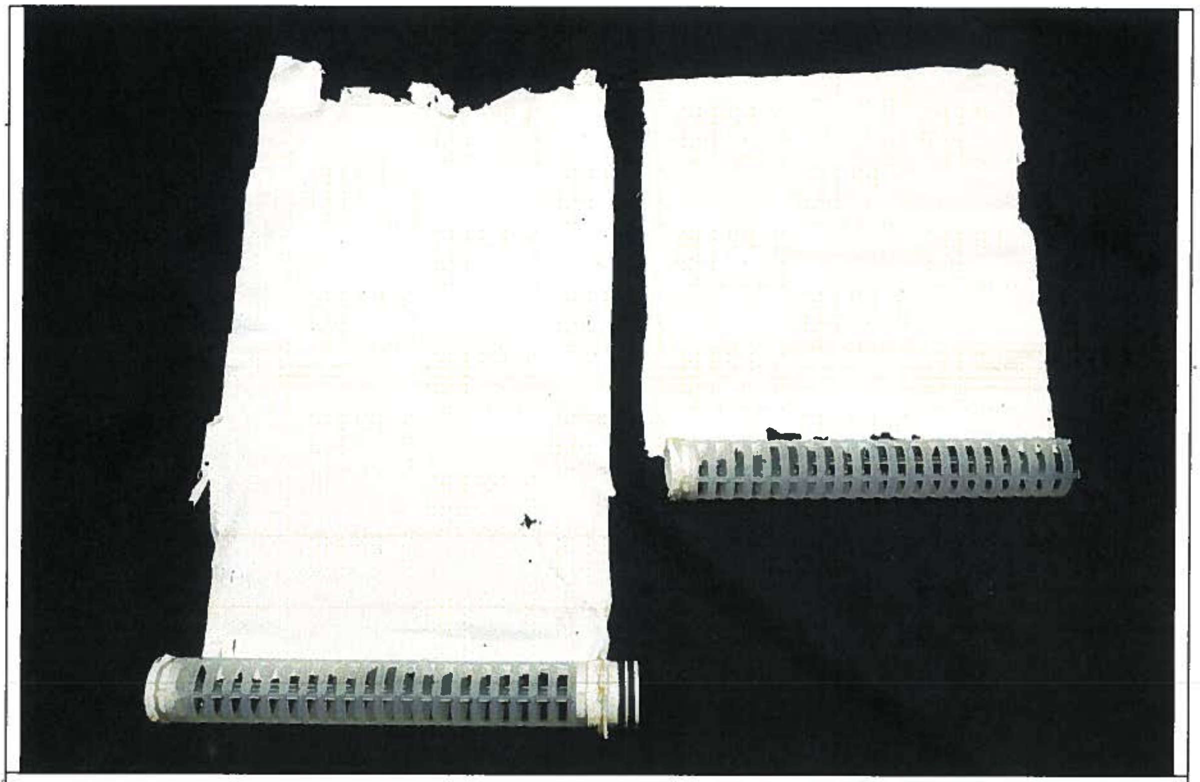


Figure 10. Dismantled and unwound MST (left image) and CST (right image) Cartridges (3M design). Design flaw seen in CST cartridges with double wraps instead of triple wraps as in MST cartridges.

4.0 Conclusions and Recommendations

Performance testing indicated that MST and CST sorbents embedded into inert PE and PTFE matrices and fabricated into filter cartridges effectively removed strontium and cesium from alkaline salt solutions at two different ionic strengths. The POREX® filter cartridges exhibited excellent removal of strontium and cesium from the dilute ionic strength solution. Due to funding constraints, no testing was conducted with the POREX® cartridges with the higher ionic strength solution.

The 3M filter cartridges exhibited excellent removal of strontium from both ionic strength solutions. However, the 3M CST cartridge exhibit relatively poor removal characteristics for cesium-137 with either salt solution. The relatively poor Cs-137 removal performance of the 3M cartridges is attributed to the cartridge having only about 50% of the targeted quantity of CST-impregnated membrane.

In general, the POREX® cartridges showed more resistance to flow of both salt solutions (0.29 M and 5.6 M Na^+) through the cartridges than that observed for the 3M cartridges.

Consequently, the test system operated at a higher pressure differential across the cartridges with the POREX® cartridges compared to that of the 3M cartridges to achieve flow rates of similar magnitude (67 mL/min for POREX® vs. 80 mL/min for 3M). Although POREX® cartridge designs involved the co-sintering of MST or CST with polyethylene particles at a temperature range of 240-340 °F (212-171°C), the performance of these ion exchange materials were not significantly degraded, if at all.

Based on these findings we conclude that incorporating MST and CST sorbents into filter membranes represent a promising method for the semi-continuous removal of radioisotopes of strontium and cesium from waste solutions. Although not demonstrated fully in these tests, the strontium-removal performance of the MST cartridges suggests that these cartridges would also be very effective for alpha-emitting radionuclides (e.g., Pu, Np, Am and U) since previous tests indicate that MST alone is an excellent sorbent for these sorbates. Given these findings, we recommend additional studies, which would include pre-wetting and pre-conditioning of the cartridges, to continue the development of this technology for treating radioactive waste solutions. Furthermore, given that MST effectively removed a variety of metal ions in weakly acidic and neutral solutions[4,5] filter cartridges containing MST may also find utility for the removal of metal contaminants from a wide variety of aqueous waste streams.

5.0 References

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