This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors. Development of prototype titanate ion exchange loaded-membranes for strontium, cesium and actinide decontamination from aqueous media.

L. N. Oji*, K. B. Martin and David T. Hobbs Savannah River National Laboratory Savannah River site Aiken, SC 29808

E-mail: lawrence.oji@srnl.doe.gov

WSRC-MS-2008-00097

Abstract

We have successfully incorporated high surface area particles of titanate ion exchange materials (monosodium titanate and crystalline silicotitanate) with acceptable particle size distribution into porous and inert support membrane fibrils consisting of polytetrafluoroethylene (Teflon[®]), polyethylene and cellulose materials. The resulting membrane sheets, under laboratory conditions, were used to evaluate the removal of surrogate radioactive materials for cesium-137 and strontium-90 from high caustic nuclear waste simulants. These membrane supports met the nominal requirement for nonchemical interaction with the embedded ion exchange materials and were porous enough to allow sufficient liquid flow. Some of this 47-mm size stamped out prototype titanium impregnated ion exchange membrane discs was found to remove more than 96% of dissolved cesium-133 and strontium-88 from a caustic nuclear waste salt simulants. Since in traditional ion exchange based column technology monosodium titanate (MST) is known to have great affinity for the sorbing of other actinides like plutonium, neptunium and even uranium, we expect that the MST-based membranes developed here, although not directly evaluated for uptake of these three actinides because of costs associated with working with actinides which do not have "true" experimental surrogates, would also show significant affinity for these actinides in aqueous media.

It was also observed that crystalline silicotitanate impregnated polytetrafluoroethylene or polyethylene membranes became less selective and sorbed both cesium and strontium from the caustic aqueous salt simulants.

Keywords: Monosodium titanate, crystalline silicotitanate, ion exchange membranes.

Introduction

Over the years, several types of ion exchange materials ranging from organic ion exchange resins, to inorganic ion exchange materials like zeolites and potassium cobalt hexacynoferrate (KCOHEX) have been incorporated into membranes used in filtration and solid phase extractions to remove undesired heavy transition metals and radionuclides from various types of aqueous media^{1, 2, 3, 4}. However, the application of these ion exchange sorbent-loaded membranes, in most cases, have always been limited to those environments with low activity as in the case of radionuclide decontamination or near neutral pH conditions for fear of poor performance results due to low or very high caustic conditions, which is typical of nuclear waste streams in various Department of Energy (DOE) facilities here in the USA.

One of the unique properties of titanates as ion exchange materials lies in the ability of this class of materials to function in a wide range of pH conditions without falling apart as in the case of potassium cobalt hexacynoferrate^{5, 6}, which performs beautifully at near neutral pH conditions for Cs-137 removal, but disintegrates in high pH environments. Titanate ion exchange materials also perform well in the presence of competing ions like sodium, calcium and potassium, which are always present in caustic nuclear waste streams and thus are able to enhance the decontamination of α and β -emitting radionuclides present in nuclear wastes at ppm levels^{7, 8, 9,10}.

Current separation applications of most titanate ion exchange materials (monosodium titanate [MST] and crystalline silicotitanate [CST]) involves the traditional use of packed column beds through which liquid media containing soluble species to be removed or decontaminated is passed through the packed column. In the case of these titanates several non traditional packed column problems do develop. Some of these problems include the following:

- Excessive radiolytic heating due to efficient loading of radionuclides like Cs-137 on the packed column,
- Leaching of ion exchange components such as the leaching of silicon from CST, which in the presence of aluminum ion leads to the precipitation of aluminosilicate minerals, which may eventually contribute the plugging of the packed columns with the minerals and fines, and
- Direct and prolonged exposure of the whole titanates particles (CST) to a caustic environment which would enhance more leaching of the ion exchange components.

On the other hand, the incorporation of these titanates into a membrane and eventually into a cartridge will not only eliminate standard packed column problems such as channeling effects but minimize radiolytic heating as a result of limited heat build up and the presence of inert fibrils and continuous aqueous layer which tends to enhance heat transfer and distribution. In a membrane-based ion exchange titanate sorbent, the leaching of titanate components would be minimized because the solution, in this case caustic sodium hydroxide solution, would not be in direct contact with the ion exchange particles alone. It would be in contact with both the IX particles and the membrane support fibrils. With this minimization of heat build up in the membrane as well reduction of leaching of IX components the formation of clogging aluminosilicate minerals would certainly be minimized if not eliminated.

For the first time, ion exchange membrane sheets loaded with CST and MST titanate materials have been made to evaluate the performance of such self supporting membrane disc at removing unwanted radionuclide from aqueous media. We are here reporting the performance results of our prototype membranes with each of the three support materials. The eventually goal is to use this class of membrane sheets or filter cartridge based on these membranes to enhance a variety of applications including medical isotope production, treatment of aqueous nuclear waste and mining operations for heavy metal removal and recovery and basic laboratory analytical applications.

Experimental

Membrane selections were based on the ability to incorporate high surface area particles of the titanium-based sorbents with particle sizes ranging from about 5 to 80 microns and provide a sturdy, yet porous membrane. Other considerations included using support materials with good radiation resistance (for radioactive applications) and chemical stability over a wide pH. Ideally, the particles were incorporated into an inert matrix that does not interfere with the activity of the sorbent material, retains the sorbent particles and allows rapid passage of liquids through the membrane with low pressure drop. We targeted the sorbent loading at a minimum of 40-90 wt% to minimize inert components.

From a review of commercially available filter membranes and discussions with membrane manufacturers, three membrane matrices, cellulose (pulp and paper), polytetrafluoroethylene (PTFE) and polyethylene (PE) were selected. Cellulose-based membranes find wide use in applications at near neutral conditions including medical applications such as dialysis. PTFE is a fluorocarbon polymer that offers exceptional chemical stability over a very wide pH range and temperatures. PE-based materials also offer good chemical stability over a wide pH range and generally better radiation resistance than PTFE polymers.

The cellulose-based MST and CST membranes were prepared in house at SRNL, while the PTFE, and PE based MST and CST membranes were prepared by commercial suppliers using their fabrication technology. Industrial partners included 3M for the PTFE-based membrane and Porex for the PE-based membrane.

Granular and engineered crystalline silicotitanate CST (particle size distribution of 300 to 500 microns) were obtained from UOP-Des Plaines, Illinois and monosodium titanate (MST) from Optima. Since the working particle size range for the CST had to be less than 80 microns, the CST material had to be ground and wet vacuum sieved to obtain the desired particle size distribution between 45 and 75 microns.

Cellulose impregnated titanate membranes

Two types of cellulose pulp materials from Augusta Print were used; yellow and grey pulp material with different pH values. The yellow and grey pulp had water contents of 96% and 91%, respectively, with pH values of 4.3 and 7.5.

Self supporting, 43 ± 1 mm cellulose membrane discs impregnated with granular CST, MST or CST/MST blends were prepared by blending wet pulp with these titanate sorbents. The resulting wet pulp-titanate mixture was converted into disc by pouring the blend into a metal cylinder containing retaining screens and forcing the bulk of the water out with the application of pressure though a stainless steel piston of about equal diameter. The membranes were then placed in an oven at 100 °C for twenty minutes to drive off excess water. The ratio of the wet pulp to titanates, by weight, was approximately 1:1 in most of the cases. After preparing the discs, the cellulose–based membrane discs appeared loosely compact and visibly porous.

The diameter and thickness of a typical self supporting cellulose disc loaded with CST, MST and CST/MST discs ranged, respectively, from 42-44 mm and 3.2-4.5 mm. The performance of these cellulose discs for cesium and strontium removal using distilled and de-ionized water solution containing 25 ppm of Cs and 12.5 ppm of Sr with cesium nitrate and strontium nitrate as precursors, respectively, was tested. For these tests, each cellulose disc or combination of two discs (double passes) was placed in a standard 45 mm filter holder housing and approximately 250 mL of the Cs and Sr simulant salt solution was passed through the membrane discs at a flow rate of 4.5 ± 1 mL/min using a peristaltic pump to push the liquid through. These tests were run in triplicate. The resulting filtrate samples were analyzed for Cs and Sr by Inductively Coupled Plasma Mass Spectroscopy (ICPMS).

The use of two membrane discs (double pass) in some cases was designed to mimic the eventual design of filter cartridges from these membranes where a minimum of two membranes sheets would be wound around a center perforated core to produce a filtration cartridge. It was also deemed necessary to use two membrane discs instead of one to ensure reasonable decontamination values, especially in the presence of competing ions or low titanate loadings on a membrane as was the case with the cellulose –based membranes.

PE and PTFE titanate impregnated membranes

MST and CST-impregnated membrane sheets based on PE and PTFE supports were manufactured by 3M and Porex corporations. Representative titanate materials (MST [14.8 wt% suspension, Optima Chemical Group LLC [Lot # 00-QAB-417], and CST (UOP LLC, Ionsive IE-911, Lot #899902081000009]) of given particle size distributions were provided to these two commercial companies to prepare these membranes based on PTFE and PE supports, respectively. These commercial versions of the titanate impregnated membranes could be used as rolled inserts for filter cartridges or cut into self supporting disks.

The CST IE-911 average particle size was about 360 micron and in order to achieve the desired particle size of 45 - 75 micron, the CST was ground and separated by dry sieving using an IKA A10 Grinder and a Gilson Wet Vacuum Sieve Unit (Model WV-3). A constant vacuum was applied from below the 8" diameter sieve stacks along with controlled vibration amplitude to facilitate flow through the screens. The MST materials shipped to both 3M and Porex had lot of fines (<5 micron) which needed to be removed to prevent formation of a brittle membranes. The preferred way to remove fines from larger particle batches was attained by sedimentation-filtration. Particles were mixed with deionized water and allowed to settle for 2 hours. Supernatant was removed and stored. Bottom 400-600 mL of suspension was filtered through #113 filters (Whatman) and the filter cake collected. The resulting filter cake was dried at 50 degrees Celsius over the weekend. 3M used their proprietary Empore® membrane technology in the design of these impregnated titanate membranes based on MST and CST. 3M provided polytetrafluoroethylene (PTFE) membranes loaded with 90% CST, 30% MST with 60% polypropylene filler. The filler was used because of insufficient MST raw materials and the fine particle size distribution for MST (between 1 and 10 microns). The sample strips were approximately 4 inches wide, 30 inches long, and 18-20 mils thick. The 3M membranes had relatively high particle loading for CST.

The membrane design technology from Porex involved sintering plastic particles, in this approach polyethylene particles were sintered with the MST or CST materials thereby forming a molded and structured porous membrane matrix. The MST or CST materials were thus fixed into place with minimal leaching/extraction and possibly minimal loss of active sites/areas due to the proximity of the plastic support particles to the ion-exchange particles. Polyethylene polymer used here as support for the materials by Pores is known to have a wide range of chemical compatibility, showing for instance an "A" rating with caustic soda.

Porex made these prototype polyethylene membranes impregnated with 40% CST, 40% MST, and 20% each of CST and MST mixture (titanate blends). The membranes were approximately 50 mm wide, 20 mm long and 1.8 mm thick. The samples appeared slightly rigid yet malleable and tightly compact. Several 47-mm size discs were stamped out and used for these tests.

Scanning electron microscope of these materials from 3M and Porex were taken. All the membrane sheets prepared by both 3M and Pores appeared tightly compact and pliable, with the 3M materials a little bit softer.

The performance of these PE and PTFE discs for cesium and strontium removal using simulant salt solution containing 25 ppm of Cs-133 and 12.5 ppm of Sr-88 with cesium nitrate and strontium nitrate as precursors, respectively, was tested. This base simulated salt solution liquor contained 6 M sodium with 4 M total free-hydroxide ion, 1 M nitrate, 1 M nitrite ions, 0.3 M aluminum and 0.025M silicon. For these tests, each PE and PTFE or overlay combination of two discs (double passes) was placed in a standard 45 mm filter holder housing and approximately 250 mL of this initial concentration Cs-133 and Sr-88 simulant salt solution was passed through the membrane discs at a flow rate of 4.5 ± 1 mL/min using a peristaltic pump to push the liquid through. The resulting filtrate

samples were analyzed for Cs-133 and Sr-88 by Inductively Coupled Plasma Mass Spectroscopy (ICPMS).

Result and discussions

The double pass decontamination factor (D_f) results obtained for the cellulose impregnated membranes (CST_{-yellow}, CST_{-gray}, CST-MST_{-gray} and MST_{-gray}) for the removal of both strontium-88 and cesium-133 from a solution of distilled and de-ionized water are summarized in Table 1. Here "double pass" is defined as the passing of the solution through two identical membrane discs placed inside the sample holder. Both yellow and gray cellulose membranes without impregnated titanates showed no affinity for either Sr-88 or Cs-133 (Same order of magnitude as the initial Cs-133 and Sr-88 concentrations). The Cs-133 D_f with both the yellow and gray cellulose-CST impregnated membranes at, respectively, 17 (5) and 22 (3) were about the same order of magnitude. Both the yellow and gray cellulose-CST impregnated membranes, in this aqueous media, showed no measurable uptake for Sr-88 [Numbers in bracket represent standard deviations]. Likewise, the gray cellulose MST-impregnated membranes with a Sr-88 decontamination factor of 41 (2), as expected, showed no measurable uptake of Cs-133. As expected, the CST/MST impregnated cellulose membrane also showed appreciable uptake of both CS-133 and Sr-88 at, respectively, 25 (4) and 30 (3).

Overall, the cellulose-based CST disc membranes removed more than 90% of the Cs-133 in solution while the cellulose-based MST disc membranes removed more than 95% of the Sr-88 in solution. On the other hand, these cellulose-based titanate membranes did not perform well in a typical salt laden simulant. For both CST and MST-cellulose membranes the Sr-88 and Cs-33 decontamination factors in the salt simulant were less than 3. These poor performances were attributed to the low loading of the titanates onto the cellulose, high porosity of the resulting membrane and possibly some interaction between the support and the titanates in the presence of competing ions in the nuclear waste salt simulant.

In comparison to the cellulosed-based data presented above, Table 2 summarizes the uptake of both cesium-133 and strontium-88 from a similar distilled water based matrix in a single pass for CST/MST–impregnated PE (40% loading). It is worth noting that the cellulose membranes were made in-house while these PE and PTFE based membranes were made, respectively, by our commercial partners Porex and 3M. The decontamination factor for both cesium and strontium were in the thousands; respectively, about 4,800 and 337,000 and the removal efficiencies were better than 99%.

The same experiments, with membrane combination of CST/MST–impregnated PE (20% loading of each titanate per membrane), was repeated but this time the salt simulant with competing ions was used instead of distilled and de-ionized water. The double pass results are summarized in Table 3. Here the decontamination factors for Sr-88 and Cs-133 were significantly lower, respectively, at 34 and 8, with a removal efficiency of 97 and 88%. The reasons for these very low D_f values is attributed to the effect of competing ions present in the salt solution and possibly the lower loading of the titanate blends at

20% each. The initial concentration of Sr-88 and Cs-133 in these runs were, respectively, 12 and 25.3 mg/L. The final concentration for these species in these salt simulants, after passing the salt simulant through a PE and PTFE support membrane not impregnated with any of the titanates (blank samples), were 12.3 and 25 mg/L, respectively. These values are not significantly different from the initial concentration as cited above for Sr-88 and Cs-133. Thus, we conclude that the blank samples, that is PE or PTFE membranes without ion exchange materials, did not pickup measurable amounts of Cs-133 or Sr-88.

Table 4 contains the summarized data obtained for the removal of C-133 and Sr-88 from the simulant salt solution using CST and MST impregnated PE and PTFE membranes on a double pass. This class of CST and MST impregnated PE and PTFE membranes had titanate loading for each ion-exchange material greater than 85%. The measured decontamination factor for Sr-88 on this CST-impregnated membrane on PE was about 11, while the decontamination factor for Cs-133 on this same CST-impregnated membrane on PE was only about 2.5 with a Cs-133 removal efficiency of only 58% (Table 4 columns 2 and 6).On the other hand, the decontamination factor for a CST-impregnated membrane on PTFE, columns 4 and 6 in Table 4, for both CS-133 and Sr-88 are relatively high at, respectively, 101 and 1369 with removal efficiency greater than 99% for each cation. Based on nuclear waste processing plant experience, it is worth mentioning that the desired nominal decontamination factor for these cations in a typical nuclear waste stream ranges only between 40 and 80. Hence, a decontamination factor greater than 100, even in a simulant solution, does meet the needs for cesium, strontium, plutonium and neptunium decontamination in a real nuclear waste stream^{11, 12, 13, 14}.

The measured decontamination factors for Sr-88 with MST impregnated PE and PTFE membranes, columns 3 and 5 in Table 4, were 49 and 120, respectively. In both cases the Sr-88 removal efficiencies were greater than 98%. The MST impregnated PTFE membranes showed a better affinity for Sr-88 than the PE-based membrane support for MST. As shown in Table 4, columns 3 and 5, MST impregnated PE and PTFE membranes showed no affinity for Cs-133; only Sr-88 was removed from the salt simulant.

On interesting observation is that both the CST impregnated membrane on PE and the CST impregnated membrane on PTFE, at this ion exchange loading, showed significant affinity for both CS-133 and Sr-88 (Table 4 columns 2 and 4), while the MST impregnated membranes on PE and the MST impregnated membrane on PTFE showed no measurable affinities for CS-133 (Table 4 columns 3 and 5) as mentioned above.

We speculate here that the reason for this less selective behavior by CST may be due to the grinding of the particles or "cold working" it to reduce the particles size of the CST from an average of 300 microns to a particle size distribution suitable for incorporation into the membrane (45-75 micron sizes). This "cold working" of the particles may have released sufficient amounts of the CST binders like zirconium and other impurities, which are normally amorphous with various phase change properties and known to exhibits general sorption properties for various types of transition metals cations^{15, 16}.

Figure 1, inserts A-E, show the scanning electron microscope (SEM) micrographs for the Porex (inserts A-C) and 3 M (inserts D and E) impregnated membranes, respectively, on polyethylene and polytetrafluoroethylene fibrils. Figure 1, inserts A, B and C show, respectively, the SEM micrographs for 40 wt.% CST (smallest non-uniform particles) on PE support, micron-size MST particles visible on larger diameter PE support, and 40 wt.% CST/MST blend (1:1) on PE support. Figure 1, inserts E and D show, respectively, MST suspended on PTFE fibrils with 60% polypropylene filler and CST particle suspended on PTFE fibrils. The MST and CST particles are the smallest particles in each SEM micrograph picture while the larger spherical particles are those of the PE or PTFE support fibrils.

From these SEM micrographs the 3M membranes, with higher titanate loadings, seem to have a better distribution of these CST and MST ion exchanges particles in the support fibrils when compared to the materials made by Porex. This may also explain why the membranes from 3M show a better Cs-133 and Sr-88 removal efficiencies and thus higher decontamination factors than the membranes based on Porex impregnation technology.

Conclusions

Data from this phase of our study to develop prototype crystalline silicotitanate (CST) and monosodium titanate (MST) impregnated membranes which could be eventually wound into cartridges for radionuclide decontamination and sorbing of heavy transition metals from aqueous media, has shown that these titanium-impregnated ion exchange membranes supported on inert fibrils can be effective in the removal of radionuclides like strontium and cesium from caustic aqueous nuclear waste environments. Since in traditional ion exchange based column technology^{12, 13, 14} MST is known to have great affinity for the sorbing of other actinides like plutonium, neptunium and even uranium, we expect that the MST-based membranes developed here, although not directly evaluated for uptake of these three actinides, would also show significant affinity for these actinides in aqueous media.

In general, short contact times for some single and double passes resulted in fast decontamination of cesium and strontium by crystalline silicotitanate and monosodium titanate. Titanate loadings on these support fibrils worked best when the loadings were above 80% by weight.

Under traditional column operation conditions, CST ion exchange particles would normally have affinity for cesium only and not for strontium. However, in this CST impregnated study with aqueous nuclear waste simulant, we observed that CST supported on PTFE or PE fibrils had a significant affinity or uptake of both cesium and strontium. Thus, crystalline silicotitanate on these membrane supports became less selective. On the other hand, monosodium titanate supported on PTFE or PE had only affinity for strontium as expected and not for cesium. The mechanisms and reasons for this behavior of crystalline silicotitanate impregnated PTFE and PE membrane supports may need further investigations. PTFE supported titanate membrane seem to be better suited for the design of these types of ion-exchange loaded membranes because the uptake of radionuclide surrogates like cesium-133 and strontium-88 was more effective with PTFE based membranes since the magnitude of decontamination factors for these cations in the salt simulants was far above normal expectations.

	Sr-88	Cs-133
Sorbent/Membrane	$\mathbf{D_{f}}$	$\mathbf{D_{f}}$
CST-Yellow	-	17 (5)
CST -Grey	-	22 (3)
CST-MST-Grey	25 (4)*	30 (3)
MST -Grey	41 (2)	-

Table 1: Cellulose membrane-based titanate performance for Sr and Cs removal from distilled and deionized water matrix (double passes).

* Numbers in bracket represent standard deviations

	CST-MST-PE mg/L	Decontamination factor, D _f	% Removed	Initial conc. mg/L
Sr-88	0.0003	36,905 (2,473)	99.99	12.40
	(0.00002)*			
Cs-88	0.0052	4,847 (92.09)	99.98	25.30
	(0.0001)			

Table 2.	CST-MST on Polyethylene: Performance with cations dissolved in DI
	water at 20% loading for each titanate (single pass).

* Numbers in bracket represent standard deviations

Table 3. Polyethylene Membrane loaded with MST/CST blend: A typical performance in the presence of competing ions (6M Na+) at 20 each% loading for each titanate (double passes).

	CST-MST-PE	Decontamination	%	Initial conc.
	mg/L	factor, D _f	Removed	mg/L
Sr	0.3723	34 (1.70)	97	12.5
	(0.0186)*			
Cs	2.988	8.33 (0.582)	88	24.9
	(0.209)			

* Numbers in bracket represent standard deviations

	+CST-PE -ss	MST-PE-ss	CST-PTFE -ss	MST-PTFE -ss	D_{f}	%
	mg/L					Removed
Sr	1.131				11 (0.55)	91
	*(0.056)					
Cs	10.47				2.4	58
	(0.370)				(0.087)	
Sr	-	0.253	-	-	49 (3.43)	98
		(0.018)				
Cs		-			-	-
Sr	-	-	0.009		1369	99.9
			(0.0007)		(106.37)	
Cs	-	-	0.25 (0.007)	-	101 (2.83)	99.6
Sr				0.083	120.5	99.7
				(0.006)	(8.71)	
Cs				-		

Table 4. PE or PTFE support membranes loaded with either MST or CST. A typical performance in the presence of competing ion-6M Na+ (double passes).

+ All PE membrane materials were 40% IX loading and PTFE was > 85%.

*Numbers in bracket represent standard deviations.





Figure 1. SEM micrographs of PE and PTFE supported titanates.

References

¹ D. M. Beals, K. J. Hofstetter, V.G Johnson, G.W. Patton and D.C. Seely

J. of Radioanalytical and Nuclear Chemistry, Vol. 248, N0.2 (2001) 315-319.

²R.S. Herbst, K. N. Brewer, T. A. Todd, T. M. Kafka, and L. R. White," Decommissioning of Tan Injection Well Water Using 3M Web Technology." Report, November 1995, INEL-95\0589, Lockheed Idaho technologies Company, Idaho falls, ID.

³ L. N. Oji, "Cesium Removal From R-Reactor Building Disassembly Basin Using 3M Empore[®] Web Membrane Filter Technology," Report, WSRC-RP-98-000, Rev 0.0 May 30, 1998

⁴ M.C. Thompson and L. N. Oji, "Advanced Chemical Separations at SRS," Report, WSRC-MS-98-001125, presented at the DOE Efficient Separations Mid-year review meeting, March 1998.

⁵ T. M. Kafka, L. R. White and G. N. Brown, "Removal of Radionuclides at the Hanford 105 N-Basin using 3M Separation Technology." American Nuclear Society Conference on Decommissioning, Decontamination and Reutilization of Commercial and Government Facilities, Knoxville, TN, September 7-12, 19997.0

⁶ D. M. Beals, W. G. Britt, J. P. Bibler and D.A. Brooks, J. of Radioanalytical and Nuclear Chemistry, Vol. 236, N0.1-2 (1998) 187-191.

⁷ R. G. Anthony, R. G. Dosch, D. Gu, and C. V. Philip, Use of Silicotitanates for Removing Cesium and Strontium from Defense Waste, *Ind. Eng. Chem. Res.*, 33, 2702-2705, 1994.

⁸ J. E. Miller, and N. E. Brown, Development and Properties of Crystalline Silicotitanate (CST) Ion

Exchangers for Radioactive Waste Applications, SAND97-0771, April 1997

⁹ Z. Zheng, et al., Ion Exchange of Group I Metals by Hydrous Crystalline Silicotitanates, *Ind. Eng. Chem. Res.*, 35, 4246-4256, 1996.

¹⁰ D. D. Walker, Cesium Sorption/Desorption Experiments with IONSIV IE-911 in Radioactive Waste, WSRC-TR-2000-00362, December 2000.

¹¹ Hunt, R. D.; Collins, J. L.; Adu-Wusu, K.; Crowder, M. L., Hobbs, D. T.; Nash, C. A. "Monosodium titanate in hydrous titanium oxide spheres for the removal of strontium and key actinides from salt solutions at the Savannah River Site," *Separation Science and Technology*, 2005, 40(14), 2933-2946. ¹² Duff, M. C.; Hunter, D. B.; Hobbs, D. T.; Fink, S. D.; Dai, Z.; Bradley, J. P.; "Mechanisms of Strontium and Uranium Removal from High-Level Radioactive Waste Simulant Solutions by the Sorbent Monosodium Titanate," *Environ. Sci. Technol.* 2004, 38(1), 5201 – 5207.

¹³Peters, T. B.; Hobbs, D. T.; Fink, S. D "Determination of actinide loadings onto monosodium titanate (MST) under conditions relevant to the Actinide Removal Process Facility,"., *Separation Science and Technology*, 2006 (41), 2447 – 246.0

¹⁴ D. T. Hobbs, M.d. Nyman and A. Tripathi, D. Medvedev, A. Clearfield. WM'05 Conference, February 27-march 3, 2005, Tucson, AZ

¹⁵ S. Frederic Marsh, Zita V. Svitra and Scot M. Bowen, "Distribution of 14 elements on 63 absorbers form three simulant solution (Acid-dissolved sludge, acidified supernate and alkaline supernate) for Hanford HLW tank 102-SY, LA-12654-Rev.0, UC-701, September 1994-Los Alamos technical report, Los Alamos laboratory, Albuquerque, N, Mex. (USA).

¹⁶ R.W. Lynch, R. G. Dosch, B. T. Kenna, J. K. Johnstone and E. J. Nowak, "The Sandia solidification process- Abroad range aqueous waste solidification method", IAEA-SM-207/75, IAEA Symposium on the management of radioactive waste, Management of radioactive waste from the nuclear fuel cycle, Vol.1 IAEA, Vienna, pg 36-0372 (1976).