ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

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EVALUATION OF NEW INORGANIC SORBENTS FOR STRONTIUM AND ACTINIDE REMOVAL FROM HIGH-LEVEL NUCLEAR WASTE SOLUTIONS

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Approximately 130 million liters of high-level nuclear wastes (HLW) are stored in 49 underground carbon steel tanks at the Savannah River Site (SRS). About 9% (11 million liters) of the waste consists of precipitated metal oxides and hydroxides resulting from caustic additions to acidic waste solutions produced from fuel reprocessing and other operations at the site. The precipitated solids, referred to as sludge, contain about 60% of the radioactivity and settle to the bottom of the HLW storage tanks. The remaining volume of HLW is stored as concentrated liquid and saltcake produced from evaporation of the waste solutions. This fraction of the HLW contains about 40% of the radioactivity and is comprised of principally ^{134,137}Cs with smaller amounts of ^{90}Sr and *alpha*-emitting isotopes of uranium, plutonium, neptunium and other actinide elements.

Processing facilities will disposition this waste by separating the dissolved radioactive components from the bulk wastes into a small volume fraction followed by vitrification in the Defense Waste Processing Facility (DWPF). Separation processes include settling, decanting the supernate and washing the sludge solids to reduce the soluble salt content. The washed sludge then transfers into the DWPF. Operations will retrieve the concentrated liquid and saltcake with the diluted alkaline salt solution (310 million liters) pretreated in the Salt Waste Processing Facility (SWPF) or the Actinide Removal Process Facility (ARP) to remove cesium, strontium and *alpha*-emitting isotopes of plutonium and neptunium. The separated radioactive components transfer into the

DWPF for vitrification with the sludge fraction of the HLW. The decontaminated liquid waste transfers into the Saltstone Facility for incorporation into a cement wasteform for onsite disposal as a low-level waste.

The baseline process for ^{90}Sr and actinide removal features batch adsorption with an inorganic sorbent referred to as monosodium titanate (MST). The MST contacts alkaline waste solutions diluted to 5.6M in sodium. After 24 hours of contact, crossflow filtration separates the MST containing the sorbed ^{90}Sr and actinides from the waste solution. The treated waste passes on to the caustic side solvent extraction process for separation of the ^{137}Cs from the bulk waste solution. After cesium removal the decontaminated waste solution passes to the Saltstone facility for disposal. The MST solids and concentrated ^{137}Cs fraction transfers to the DWPF for disposal in the borosilicate glass wasteform.

Crossflow filtration separates the decontaminated waste solution from the MST solids containing the sorbed radioactive components. Stainless steel filter elements planned for use feature nominal 0.1or 0.5-micron pore sizes. This filtration also captures any entrained undissolved solids associated with the salt solution retrieved from the high-level waste storage tanks.

Table 1 provides a listing of the current Saltstone waste acceptance criteria (WAC) for ^{90}Sr and selected *alpha*-emitting radionuclides. These limits establish the target concentrations that the process used in the SWPF for ^{90}Sr and actinide removal must meet. ^{90}Sr removal performance originally served as the chief criterion for selection of MST for use in radiochemical separations at the SRS. With increased characterization of SRS wastes, actinide removal performance has increased in importance.

Table 1. Saltstone Waste Acceptance Criteria for Selected Radionuclides

Radionuclide	Limit (nCi/g)	Limit (µg/L)
^{90}Sr	40	0.36
^{137}Cs	45	0.65
Total *alpha*	18	-
^{238}Pu	18	1.5
^{239}Pu	18	400
^{237}Np	0.03	53

Of the actinides present in SRS waste solutions, plutonium is the most prevalent contributor to *alpha* activity. Testing indicates that plutonium removal by MST serves as the rate-limiting step that sets the required process cycle time and equipment footprint in the SWPF. Significant savings in the capital and operating costs of the SWPF could occur from development of a new sorbent that exhibits greater actinide capacity and more rapid removal kinetics than that currently demonstrated by MST. Even greater cost savings would result if that sorbent removes cesium in addition to ^{90}Sr and actinides. This dual functionality would reduce or eliminate the need to use the CSSX process for ^{137}Cs resulting in even further capital and operating cost savings.

Synthesis efforts in this project to date focused on producing a sorbent with increased ^{90}Sr and actinide removal performance. Specific types of sorbents produced and evaluated for removal performance include sodium nonatitanate, metal-substituted sodium nonatitanates, crystalline silicotitanates, titanosilicates having a pharmacosiderite structure and heteropolyniobates. Table 2 provides a list of sorbent materials tested. Performance testing featured a simulated waste solution comprised of the major anionic components of SRS waste solutions as the respective sodium salts and specific amounts of strontium and actinide elements.

Table 2. List of Sorbent Materials Evaluated for Strontium and Actinide Removal

Sorbent	Composition
Sodium Nonatitanate (SnT)	$Na_4Ti_9O_{20}{\cdot}xH_2O$
Niobium-Substituted SnT (Nb-SnT)	$Na_{4-x}Ti_{9-x}Nb_xO_{20}]{\cdot}zH_2O$
Crystalline Silicotitanate (CST)	$Na_2Ti_2O_3(SiO_4){\cdot}2H_2O$
Niobium-Substituted CST (Nb-CST)	$Na_{2-x}Nb_xTi_{2-x}O_3(SiO_4){\cdot}2H_2O$
Titanosilicate Pharmacosiderite (TSP)	$K_3H(TiO)_4(SiO_4)_3.4H_2O$
Heteropolyniobates (IPX)	$M_{12}[Ti_2O_2][SiNb_{12}O_{40}]{\cdot}16H_2O$

Table 3 provides a summary of the simulated waste solution used to evaluate new sorbent materials. Testing also featured actual tank waste material diluted to the same sodium concentration (5.6 M) as that provided by the simulated waste solution in Table 3. The actual waste solution, however, contains a different salt composition than that of the simulated waste.

Table 3. Composition of Simulated and Actual Tank Waste Solutions

Component	Simulant	Tank Waste
NaOH	1.33 M	3.7 M
$NaNO_3$	2.60 M	0.86 M
$NaNO_2$	0.134 M	0.58 M
$NaAl(OH)_4$	0.429 M	<0.20 M
Na_2SO_4	0.521 M	0.0040 M
Na_2CO_3	0.026 M	<0.20 M
Sr	6.8 µM	0.068 µM
Pu	0.84 µM	5.0 µM
Np	2.1 µM	0.65 µM
U	42 µM	33 µM

We evaluated removal performance by contacting a weighed amount of the sorbent with a measured volume of solution in a shaker bath at 25 $\pm$ 2 °C. For titanium-containing sorbents, we add the sorbent to provide the equivalent amount of titanium as that from

0.4 g/L MST. For non-titanium materials, we added the sorbent to provide the same number of equivalents as that provided by 0.4 g/L MST. Typically, we sampled the batch-contact test bottles after 4, 24 and 168 hours and measured solution phase strontium and actinide concentrations after removing sorbent solids by filtration.

Figures 1 and 2 provide graphs of strontium and plutonium concentrations, respectively, versus time of contact of the simulated waste solution with selected sorbent materials. Included in each graph is the performance of the baseline MST sorbent for comparison. Testing indicates that sodium nonatitanates, pharmacosiderite and the heteropoly-niobates materials exhibit strong affinity for strontium and actinides and in some cases higher capacities than MST. Thus, these materials appear promising candidates for use in treating high-level nuclear waste solutions. In general crystalline silicotitanate and germanium-substituted pharmacosiderites exhibited poor actinide removal and, therefore, do not appear to be promising materials for treating nuclear waste solutions.

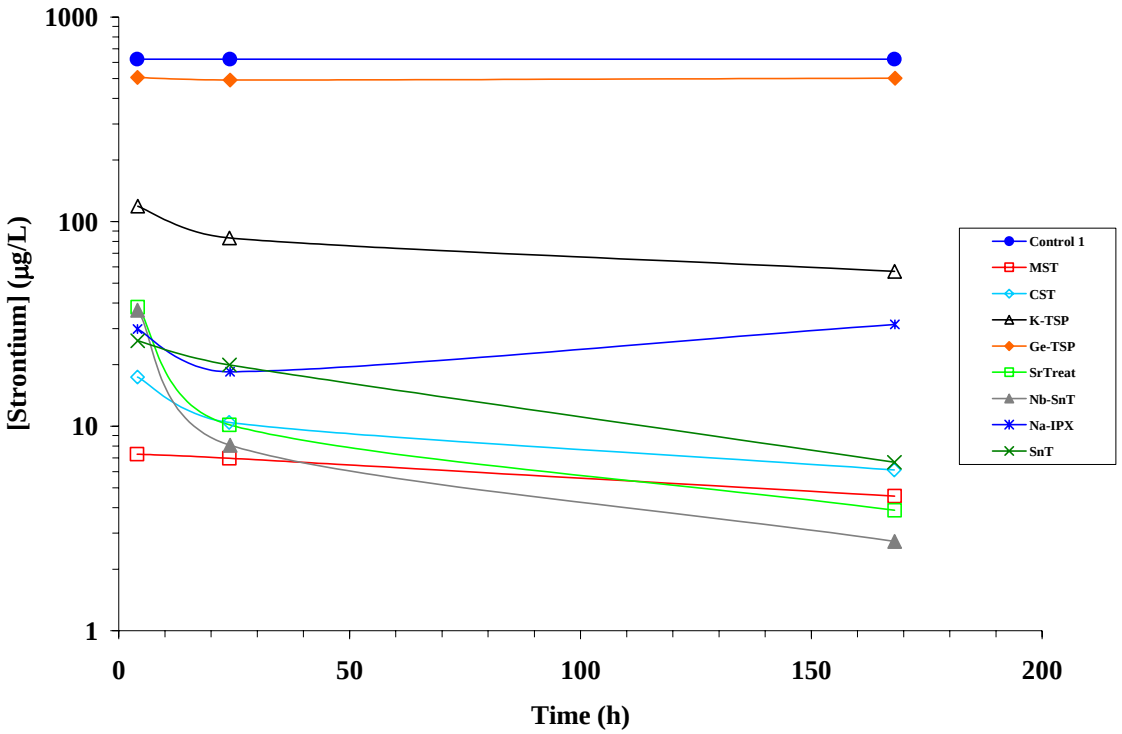

Figure 1. Strontium Removal Performance with Various Sorbents

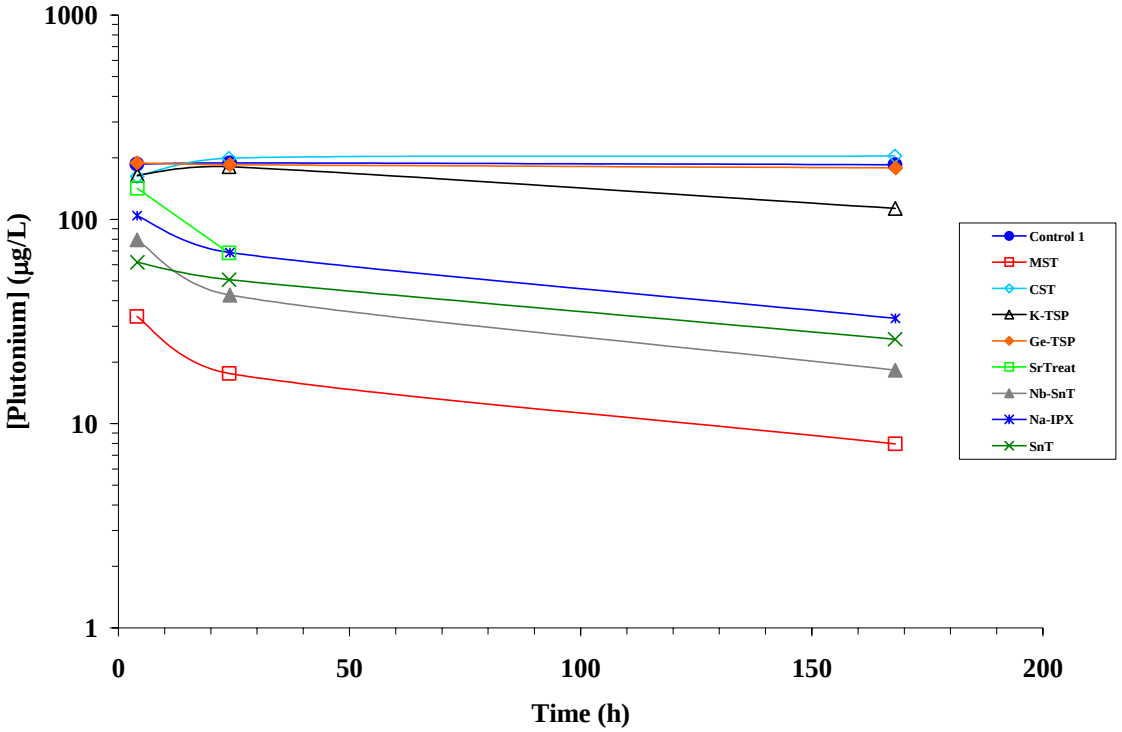

Figure 2. Plutonium Removal Performance with Various Sorbents

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