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Radionuclide Separations Using Pillared Layered Materials

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Abstract

This is the final report of a two-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Pillared Layered Materials (PLMs) are layered inorganic ion exchangers propped apart by metal oxide pillars. PLMs have been synthesized to sorb strontium from liquid nuclear wastes. A study that compared over 60 sorbers for their ability to sorb strontium from Hanford simulants showed that PLMs were the best sorbers; strontium distribution coefficients ($^{\text{Sr}}K_d$) > 20000 mL/g were obtained. In addition, PLMs showed a high degree of selectivity for strontium over cesium, transition metals, lanthanides and actinides. The sorption of strontium is, however, inhibited by complexants (EDTA); $^{\text{Sr}}K_d$ values drop to < 20 mL/g when they are present. The most promising PLMs were the Cr, Ti, Zr, and Si pillared tantalum tungstate. The K_d values for Sr^{2+} and Ba^{2+} show a strong pH dependence; K_d values increase to $> 10^4$ above pH 12. The general surface complexation mechanism explains the sorption of these cations on PLMs.

Background and Research Objectives

The goal of this Laboratory Directed Research and Development (LDRD) research was to develop porous Pillared Layered Materials (PLMs) to efficiently sorb radionuclides from liquid nuclear wastes stored in underground storage tanks at Department of Energy (DOE) sites (Hanford, Oak Ridge, Savannah River) and from Los Alamos National Laboratory (LANL) mixed wastes. Our initial objective was to develop sorbers to remove ^{90}Sr . This target radionuclide was chosen because (1) separation of strontium from the bulk waste constituents would significantly lower the radiological hazard of low level waste forms¹, and (2) a study of 60 sorbers for radionuclides in Hanford-type wastes concluded that an efficient strontium sorber needed to be developed.² Some of the better sorbers in this study had high selectivities but low capacities for the target radionuclides and have not proven to be regenerable. Sorbers lacking these attributes would contribute significantly to the cost of remediating these wastes.

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PLMs are layered inorganic materials propped apart by metal oxide pillars. The selectivity of these natural ion exchange materials are tailored by the type and extent of the pillaring process. Theoretically, PLMs can be designed to selectively sorb specific metal cations. Originally, pillaring research centered on smectite clays pillared with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ for application as hydrocracking catalysts.³ Pillaring is a technique that exchanges the clay's naturally occurring interlayer cations, such as Na^+ or Ca^{2+} ions, with large metal oxohydroxide cations as shown in Figure 1. Subsequent calcination drives off water to create metal oxide pillars; protons released from the cations remain in the cavities to balance the layer charge. The result is a greatly expanded clay structure with large channels and cavities of fixed size and a reservoir of exchangeable protons. This morphology permits substrates such as petroleum feed stocks and metal ions to enter the material to undergo either a catalytic reaction or ion exchange. It is this latter property that was exploited by this research.

Many other classes of layered compounds have exchangeable cations and are, therefore, candidates for pillaring. The layered materials that were of primary interest in this work were $K_2Ti_4O_9$ (Ref. 4), $Na_2Ti_3O_7$ (Ref. 5), $KTiNbO_5$ (Ref. 6), $CsTi_2NbO_7$ (Refs. 6,7), $LiTaWO_6$ (Ref. 8), $Na_4Mn_{14}O_{26} \cdot H_2O$ (Ref. 9), and $K_3Sb_3O_3(PO_4)_2$ (Ref. 10). The structures of these compounds are shown in Figure 2. The criteria used in choosing these materials were (1) their potential for strontium selectivity, (2) stability in highly acidic and alkaline solutions, and (3) layer structures that can be pillared to create unique chemical environments.

Pillaring these layered materials with polyoxocations of Cr, Ti, Zr, and Si would create unique morphologies. Pillars distributed between the layers balance the layer charge; thus more highly charged pillars will be spaced further apart leaving larger cavities. More or less of this cavity space may be taken up by the pillar itself depending on its size, shape and positioning. Elongated pillars that position orthogonal to the layers will create larger cavities than those that have their long axis parallel to the layer plane. The preparative method affects the size, shape, and positioning of the pillars. Factors such as concentration, amount of pillar relative to layered material, pH, reaction temperature and time are important in designing the PLM. In summary, the selectivity of the resulting PLM was expected to be controlled both chemically and sterically by the choice of the layered compound, pillaring oxohydroxide cation, and the preparative method.

The scientific impact of this research was expected to give a greater understanding of the interactions of solid state sorbers with cations and anions. Like layered inorganic materials, the sorption sites in PLMs would have chemical environments similar to simple metal complexes. The PLMs, however, have an extended and repetitious molecular

framework. Understanding the influence of this framework on the sorber/ion interactions adds to the basic understanding of "metal-ligand" bonding in the solid state.

PLMs should offer several advantages over organic exchange resins and organically pillared inorganic materials: (1) enhanced selectivity, controlled by the creation of fixed pore sizes and by the chemical composition of the materials, (2) greater stability to radiation and to attack by acids and bases making regeneration by elution viable, (3) the possibility of being hot pressed to form a ceramic-like, stable waste form and also better compatibility with hydrated cement-based matrices,¹¹ and (4) low material cost and no need for highly hazardous materials or organic solvents in their preparation or utilization.

Importance to LANL's Science and Technology Base and National R&D Needs

This research fell under the broad Laboratory mission assignments of performing environmental R&D, basic research in chemistry and materials science, and had an applied science component. This work contributed to the Laboratory's development of a core competency in advanced materials. Application of these radionuclide sorbers for tank waste remediation programs would have required an industrial partner to synthesize large quantities of the materials. Potentially, the dual use of these materials as catalysts would have offered additional possibilities of technology transfer to industry. The university collaboration helped the Laboratory ensure a continuous and adequate supply of technical personnel to contribute to future DOE programs. Research into Pillared Layered Materials helped increase LANL's competitive position in separations technology and in the chemical and materials sciences. This work was in an area where the Laboratory could help the U.S. regain a research area that it started but has since lost to Japan and the European Community. Besides the separation application, this area of research has cross-cutting applications that address other issues that are important to LANL, such as environmental stewardship, nonproliferation, and technology transfer. These applications could help diversify the Laboratory's programmatic opportunities and funding base and help in attaining its missions.

This research attempted to help DOE solve one of its major environmental problems, the safe pretreatment and stabilization of the Hanford Tank waste. There is a need to safely manage and immobilize for disposal the highly radioactive waste stored at various DOE sites. For example, Hanford has 177 underground storage tanks containing 65 M gallons of caustic waste. Remediation of this waste will involve separation of the waste into high-level waste (HLW) and low-level waste (LLW) streams. Partitioning ⁹⁰Sr and ¹³⁷Cs from the LLW stream and vitrifying them with the HLW would significantly lower the biological

hazard of the LLW form. Research has yielded some successful ^{137}Cs sorbers; however, separation technologies for strontium have been less successful. This is due in part to organic complexants in the waste competing with strontium separations. Proposed technologies therefore need to be highly efficient to work in this environment. Inorganic layered materials have shown very high affinities (K_d values up to 10,000) for cesium. This technology needed to be applied to strontium. Pillaring inorganic layered materials was expected to increase their capacities and selectivities and make them useful for remediation of Hanford and other DOE nuclear wastes.

Scientific Approach and Accomplishments

PLMs were prepared through a series of similar steps: (1) high-temperature solid-state synthesis of the layered material, (2) exchange of the charge-balancing interlayer cations for protons under acidic conditions, (3) intercalation of polar molecules to spread apart the layers, (4) exchange of the protonated form of these polar molecules as cations with the metal oxohydroxide cations, and (5) calcination to form the metal oxide pillars and to bind them to the layers.

For example the preparation of a chromium pillared tantalum tungstate material began with the preparation of HTaWO_6 . The lithium salt was first prepared from stoichiometric proportions of Ta_2O_5 , WO_3 , and Li_2CO_3 at 900°C for 12 hours.¹² The LiTaWO_6 product was converted to acid form by stirring in 3 M HCl and then intercalated with propylamine (PA) by stirring a suspension of the acid form in an aqueous solution of the amine. The amine intercalated tantalum tungstate, PAHTaWO_6 was then pillared by stirring it with an aqueous solution of $(\text{CH}_3\text{CO}_2)_7\text{Cr}_3(\text{OH})_2$ at a set temperature for a certain period of time. The material was then dried, ground, and calcined at 400°C under N_2 for 9 hours. Factors such as concentration, molar ratio of pillar to layered material, pH, reaction temperature and time were manipulated to vary the nature of the product.

The PLMs were characterized by X-ray powder diffraction patterns (XRD), fourier transform infrared spectra (FTIR), thermal gravimetric analysis (TGA), surface area (SA), Eu(III) luminescence, electron spin resonance (ESR), and elemental analysis.

The PLMs were evaluated for their ability to remove strontium from simple well defined solutions and from Hanford waste simulant solutions. This test measured the strontium batch contact distribution coefficient ($^{\text{Sr}}K_d$) between the solution and the PLM. Addition of ^{85}Sr tracer ($t_{1/2} = 64.8$ d, $\gamma = 514$ keV) to the solutions facilitated these measurements by allowing the pre-contact and post-contact solutions to be counted using gamma-ray spectrometry. The difference between the pre-contact activity and post-contact

activity of the supernate gives the activity on the PLM. The $^{87}\text{SrK}_d$ is then determined from the following equation:

$$^{87}\text{SrK}_d = \frac{(^{87}\text{Sr}_{(\text{pre-contact})} - ^{87}\text{Sr}_{(\text{post-contact})})}{^{87}\text{Sr}_{(\text{post-contact})}} \times \frac{\text{mL of contact solution}}{\text{g of PLM}}$$

For comparison, K_d values were obtained for many other radionuclides including cesium, barium, calcium, transition metals, lanthanides and actinides. These were measured from Hanford simulants and/or simple well defined solutions.

A variety of PLMs were prepared and submitted for batch testing using Hanford Doubled-Shell Slurry Feed (DSSF) and Neutralized Current Acid Waste (NCAW) waste simulants. The results are shown in Table 1. Four general types of layered materials were tested: titanates, smectite clays, antimony phosphate, and tantalum tungstates. As a class, the tantalum tungstates were the most successful; the Zr, Ti, and Cr PLM classes had samples that had $^{87}\text{SrK}_d$ values $> 13000 \text{ mL/g}$. In comparison, the $^{87}\text{SrK}_d$ value for the unpillared tantalum tungstate was only 93 mL/g , which illustrates the dramatic effect the pillaring process had on this material. The surface area of the PLMs derived from tantalum tungstate are significantly larger than the parent material. The PLM "d spacings", the distance between the layers of tantalum tungstate, are also greater than the parent compound.

It should be noted that the PLM materials had the highest $^{87}\text{SrK}_d$ values of the more than 50 types (i.e. cation resins, etc.) of sorbers tested. The study involved not only strontium but cesium and 12 other radionuclides. The selectivity of the PLMs for Sr over Cs was very high from the DSSF simulant; the $^{137}\text{CsK}_d$ values were < 150 for all the classes of PLMs (Table 2). The selectivity for strontium over other metal cations was very good; at least 10 over Fe^{3+} , Mn^{2+} and > 100 over other transition metals, lanthanides and actinides. The pertechnetate anion (TcO_4^-) had no affinity for the PLMs. The results for the DSSF simulant were quite encouraging. However, this simulant is quite simple and does not contain complexants. When the complexant concentrate (CC) simulant is used, the results were not encouraging. The EDTA type complexants compete strongly against the PLMs for the strontium, the $^{87}\text{SrK}_d$ values drop to $< 20 \text{ mL/g}$. The Cr and Ti pillared HTaWO_6 PLMs were also tested with actual Hanford waste from tanks 101-SY and 103-SY. Since these wastes contain complexants also, it was not unexpected that the results would be disappointing; the $^{87}\text{SrK}_d$ values were 0 mL/g .¹⁵

The presence of complexants in the waste presents a significant separation problem. Strontium stability constants with EDTA type ligands are quite high. Separation of strontium from these matrixes will require sorbers with $^{87}\text{SrK}_d$ values $> 10^6 \text{ mL/g}$. In order to obtain distribution coefficients of this magnitude we began to investigate what factors

contributed to the high $^{87}\text{K}_d$ values we had achieved in the absence of complexants. Understanding these factors would help us design more efficient PLM sorbers.

A set of Cr, Ti and Zr pillared tantalum tungstate was prepared from the same batch of LiTaWO_6 . The $^{87}\text{K}_d$ values were measured as a function of pH and ionic strength; the effect of carbonates on these measurements was prevented by doing them under nitrogen. Figure 3 and 4 are plots for the chromium pillared compound, $\text{Cr}_1\text{Ta}_1\text{W}_1\text{O}_6 \cdot \text{H}_2\text{O}$. Similar plots were obtained for all the PLMs. The $^{87}\text{K}_d$ values increased dramatically with pH; the curve fits in the figure are for illustrative purposes only. These sorptions are often described by a surface complexation mechanism:¹⁷

This is consistent with what we observe for the PLMs. It also explains the large pH changes we observe on doing the contacts with solutions containing 1M sodium. Although most of the contact solutions were initially at a pH >11, only those that were initially at pH 14 were able to maintain a basic pH in the presence of the high $[\text{Na}^+]$.

This tantalum tungstate series of PLMs attempted to correlate the $^{87}\text{K}_d$ values with the physical characteristics of the PLMs. Unfortunately, there were few correlations, even with compounds with the same pillaring species. Surprisingly, materials with greater surface areas and more extensive pillaring generally had smaller $^{87}\text{K}_d$ values. For example, the PLM in Figure 3 has a $^{87}\text{K}_d$ of 230000 mL/g (pH 13.5) while a $\text{Cr}_2\text{Ta}_1\text{W}_1\text{O}_6$ PLM's $^{87}\text{K}_d$ value is only 50000 mL/g (pH 13.5). The corresponding surface areas for these two materials were 53 and 180 m^2/g , respectively. We speculate that the pillaring process is exposing more of the TaWO_6 exchange site but the extent of pillaring may limit access to some of the sites.

Characterization of the sorbing sites was interesting but did not lend any greater insight into the sorption mechanism. FTIR studies of sorbed amines on the PLMs show that there are Bronstead and Lewis base sites on the PLMs. These are commonly observed with metal oxides that have limited exposure to water.¹⁷ The pillaring process did not appreciably change the surface acidity and distribution of acid types relative to the parent tantalum tungstate. Eu (III) luminescence indicated the presence of two major types of binding site. These may be related to the two major types of hydroxylated sites on a metal oxide surface after exposure to water, "type a" where the OH group is bound to one metal center and "type b" where there are multiple metal centers bound to the OH group.¹⁷

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Table 1. $^{87}\text{K}_d$ Values Between DSSF or NCAW Simulants and PLMs.¹³⁻¹⁵

Sample	Description ^a	$^{87}\text{K}_d$ (1 hr contact)
Si-pillared $\text{H}_x\text{Ti}_{2-x/4}\text{O}_4$ ^b	257 m ² /g; d=15.0 Å	4271
Si-pillared $\text{H}_2\text{Ti}_5\text{O}_{11}$ ^b	215 m ² /g; d=15.7 Å	12326
Al-pillared montmorillonite ^b	273 m ² /g; d=19.1 Å	971
Al-pillared saponite ^b	330 m ² /g; d=18.5 Å	834
Zr-pillared saponite ^b	252 m ² /g; d=21.5 Å	6767
Zr-pillared saponite ^b	278 m ² /g; d=25.4 Å	13564
Cr-pillared saponite ^b	123 m ² /g; d=21.3 Å	2231
Cr-pillared saponite ^b	78 m ² /g; d=24.2 Å	4290
Zr-pillared phlogopite ^b	115 m ² /g; d=14.9 Å	4534
Cr-pillared $\text{H}_3\text{Sb}_3\text{O}_6(\text{PO}_4)_2$	319 m ² /g; d=20.1 Å	3109
Cr-pillared $\text{HSb}(\text{PO}_4)_2$	328 m ² /g; d=27.8 Å	840
Si-pillared HTaWO_6	20.0 m ² /g; d=12.2 Å	1055
Zr-pillared HTaWO_6	65.8 m ² /g; d=11.4 Å	18107
Zr-pillared HTaWO_6	40.7 m ² /g; d=10.3 Å	4662
Ti-pillared HTaWO_6	42.1 m ² /g; d=10.1 Å	6121
Ti-pillared HTaWO_6	49.1 m ² /g; d=12.8 Å	13876
Ti-pillared HTaWO_6	62.7 m ² /g; d=14.5 Å	>61000
Cr-pillared HTaWO_6	227 m ² /g; d=19.6 Å	>26000
Cr-pillared HTaWO_6	148 m ² /g; d=amorphous	55000
unpillared HTaWO_6	2.9 m ² /g; d=9.2 Å	93

^aThe d spacings were determined prior to calcination.

^b Samples supplied by Abraham Clearfield, Texas A&M University.¹⁶

Table 2. Comparison of Sr and Cs K_d Values From DSSF and CC Simulants For a Variety of PLMs.

Sample	Sr K_d DSSF	Cs K_d DSSF	Sr K_d CC	Cs K_d CC
Si-pillared $H_xTi_{2-x/4}O_4$	4271	73	2	375
Si-pillared $H_2Ti_5O_{11}$	12326	148	1	157
Al-pillared montmorillonite	971	16	0.4	14
Al-pillared saponite	834	13	1	2
Zr-pillared saponite	13564	4	1	2
Cr-pillared saponite	4290	10	2	3
Zr-pillared phlogopite	4534	28	0	5
Cr-pillared $HSb(PO_4)_2$	840	0.1	---	---
Cr-pillared $HTaWO_6$	55000	0	15	0.3
Ti-pillared $HTaWO_6$	>61000	4	6	0
Zr-pillared $HTaWO_6$	18107	39	3	2
Si-pillared $HTaWO_6$	1055	0	0.1	0

Figure 1. A schematic showing the formation of a pillared clay.

Figure 2. Schematic of the structures of (a) $K_2Ti_4O_9$, (b) $Na_2Ti_3O_7$, (c) $KTiNbO_5$, (d) $CsTi_2NbO_7$, (e) $LiTaWO_6$, (f) $Na_4Mn_{14}O_{26} \cdot H_2O$, and (g) $K_3Sb_3O_3(PO_4)_2$.

Figure 3. Sr or Ba K_d values as a function of pH ($\mu = 1 \text{ M}$) for a chromium pillared tantalum tungstate.

Figure 4. Sr or Ba K_d values as a function of ionic strength (pH = 1.9) for a chromium pillared tantalum tungstate.