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Evaluation of Solid-Based Separation Materials for the Pretreatment of Radioactive Wastes

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May 1993

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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MASTER

Summary

Separation science will play an important role in pretreating nuclear wastes stored at various U.S. Department of Energy Sites. The application of separation processes offers potential economic and environmental benefits with regards to remediating these sites. For example, at the Hanford Site, the sizeable volume of radioactive wastes stored in underground tanks could be partitioned into a small volume of high-level waste (HLW) and a relatively large volume of low-level waste (LLW). After waste separation, only the smaller volume of HLW would require costly vitrification and geologic disposal. Furthermore, the quality of the remaining LLW form (e.g., grout) would be improved due to the lower inventory of radionuclides present in the LLW stream.

In FY 1992 Pacific Northwest Laboratory evaluated the use of solid-based separation materials in the pretreatment of Hanford tank wastes. This work was not intended to exhaustively survey extraction chromatography materials, but rather to determine if use of extraction chromatography in the pretreatment of Hanford tank wastes warranted further investigation. Three commercially available chromatographic materials, Tru•Spec™, Sr•Spec™, and SuperLig™ 601, were tested in a column mode for use in separating Am, Pu, and Sr from actual neutralized cladding removal waste (NCRW) taken from a Hanford waste tank. For these experiments, the NCRW was dissolved in HNO₃/HF solutions. TRU•Spec™ was evaluated for the separation of transuranic elements, while Sr•Spec™ and SuperLig™ 601 were evaluated for the separation of Sr. Due to the limited amount of dissolved NCRW solution available, only the removal efficiencies in the early stages of loading could be evaluated.

The results indicated that Am and Pu can be separated from dissolved NCRW with TRU•Spec™, although the decontamination factor^(a) achieved was two orders of magnitude less than that obtained in previous experiments with the TRUEX^(b) solvent extraction process. The low DF achieved with TRU•Spec™ was likely due to loading of the column with U. For wastes with high U content, removal of U before the application of TRU•Spec™ may be necessary.

Sr•Spec™ performed very well in the separation of Sr from NCRW sludge. Sr could not be detected in the column effluent when a dissolved NCRW solution was passed through a column containing the Sr•Spec™ material, even after 6 bed volumes of feed had gone through the column. The Sr was eluted quantitatively from the loaded column with water. Because Sr•Spec™ is simple to use, it is an attractive candidate material for the separation of ⁹⁰Sr from Hanford tank wastes. Further investigation of this material is warranted.

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- (a) The decontamination factor (DF) for species x is defined as the quantity of x originally in solution divided by the quantity of x in solution after a given treatment.
- (b) Transuranic extraction.

SuperLig™ 601 was found to separate Sr, but the Sr was not removed to levels considered acceptable under the conditions of the experiment performed. Because a relatively high flow rate was used in this SuperLig™ 601 experiment, it was hypothesized that the low DF achieved resulted from slow kinetics of absorption on the column. An experiment conducted with simulated dissolved NCRW solution indicated that the separation performance could be dramatically improved by lowering the flow rate through the column. A "second generation" SuperLig™ 601, having a higher binding constant for Sr might also achieve adequate removal of Sr. One advantage of SuperLig™ 601 is that the macrocyclic ligand responsible for the separation of Sr is covalently attached to the solid support. Thus, the loss of column capacity due to solubilization of the ligand would not be significant. Furthermore, the silica gel support used in the SuperLig™ materials is likely to have good radiolytic stability. Given these advantages, further investigation of the SuperLig™ material(s) is warranted.

In addition to the evaluation of TRU•Spec™, Sr•Spec™, and SuperLig™ 601, a series of new inorganic ion exchange materials was tested for potential use in pretreating HLW. Three different "pillared" materials, IP-4, AC2, and 3PS-2, were examined to determine their affinities for Cs. Test results indicated all three pillared materials exhibited high distribution ratios (K_d)^(a) for Cs over a wide range of pH conditions.

The affinity of IP-4 for Cs was examined under highly acidic conditions. The K_d for Cs decreased with increasing acidity, but remained high enough for a workable process even at 3 M HNO₃. The K_d for Cs also decreased with increasing Na concentration, but it appears that under certain pH conditions a workable Cs separation process might be designed, even at 5 M Na. 3PS-2 was tested for the sorption of Sr from solutions with varying pHs. As with Cs, large K_d s were observed over a wide pH range.

Attempts to use IP-4 in a column mode did not succeed due to very low flow rates. In order to design a practical system, the preparation of these pillared materials must be modified so that the physical properties of the materials are amenable to use in a column.

In summary, depending upon pretreatment system requirements, chromatographic systems might serve as the primary separation method, or they could be used to polish waste streams arising from other separation methods (such as solvent extraction). The results of this work suggest that in depth studies should be conducted on the application of chromatographic separations to pretreat Hanford wastes.

(a) The batch distribution coefficient (K_d) for a species x is defined as the quantity of x sorbed (per gram of sorbent) divided by the quantity remaining in solution at equilibrium (per mL of solution).

Acknowledgments

This research was conducted by Pacific Northwest Laboratory, which is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Funding was provided by the U.S. Department of Energy, Office of Technology Development.

The authors would like to thank L. Ballou, D. M. Camaioni, B. P. Hay, J. L. Ryan, and J. L. Swanson for their many helpful suggestions. The new pillared inorganic ion exchange materials investigated in this work were donated by A. Clearfield of Texas A & M University.

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1.0 Introduction

Methods are currently being developed to treat and dispose of large volumes of radioactive wastes, such as those stored in underground tanks at the U.S. Department of Energy's (DOE) Hanford Site. The current baseline scenario for the treatment and disposal of these wastes involves partitioning the wastes into a small volume of high-level waste (HLW) and a relatively large volume of low-level waste (LLW). The HLW will be vitrified into borosilicate glass and disposed of in a geologic repository, while the LLW will be converted to grout and disposed of by shallow burial on the Hanford Site.

There are both economic and environmental reasons to separate various radionuclides from HLW. Because vitrification and disposal of HLW is considerably more costly than disposal of LLW, it is desirable to minimize the volume of HLW by removing radionuclides from the bulk waste material. Furthermore, maximum removal of radionuclides from the LLW stream would minimize leaching of these radionuclides from the grout matrix into the surrounding environment.

In recent years, highly selective extraction chromatographic materials have been developed in which ligands that have a high affinity for certain ions are covalently attached to solid supports (Bradshaw et al. 1988; Bradshaw et al. 1989a, 1989b; Izatt et al. 1988; Bruening et al. 1991) or sorbed onto solid supports (Horwitz et al. 1991a, 1992; Chiarizia et al. 1992). A number of such materials are now commercially available. The results of Barney and Cowan (1992) and Camaioni et al. (1992) suggest such materials might be used to separate key radionuclides from Hanford tank wastes. The work presented here is an evaluation of the potential of three such materials for the separation of radionuclides from Hanford tank wastes. This work is not meant to be an exhaustive survey of extraction chromatographic materials, but rather is intended to determine if extraction chromatography has applicability to pretreat Hanford tank wastes. TRU•Spec™ (EiChroM Industries, Inc., Darien, Illinois) was evaluated for the separation of transuranic elements, while Sr•Spec™ (EiChroM Industries, Inc., Darien, Illinois) and SuperLig™ 601 (IBC Advanced Technologies, Provo, Utah) were evaluated for the separation of Sr.

Actual Hanford neutralized cladding removal waste (NCRW) sludge was used to prepare feed solutions for testing these three materials. The primary constituents of this sludge waste are zirconium hydroxide and sodium fluoride. The waste also contains uranium, mixed fission products (e.g., ^{137}Cs and ^{90}Sr), and transuranic elements (Am and Pu; approximately 2000 nCi/g of dry sludge).

In addition to the testing of the commercially available materials, new inorganic ion exchange materials were tested for potential use in the pretreatment of high-level radioactive wastes. The affinities of three different "pillared" materials for Cs, and in some cases Sr, have been examined. These evaluations were conducted using simulated waste solutions.

2.0 Methods and Materials

The methods and materials that were used in the various experiments described in this report are detailed in this section.

2.1 Dissolution of NCRW Sludge

Before tests were conducted, the NCRW sludge samples were washed with water and dissolved in HNO_3/HF solution at ambient temperature. The concentration of HNO_3 was 2 M, and the ratio of $\text{F}/(\text{Zr} + \text{Al})$ ranged from 1 to 2.5 (0.1 to 0.4 M HF). The dissolved sludge solutions were clarified by filtration through a 0.2- μm membrane filter.

2.2 Separation of Am and Pu from NCRW with TRU•Spec™

TRU•Spec™ is a commercially available chromatographic resin that consists of octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and tributyl phosphate (TBP) sorbed onto Amberchrom™ CG-71. The material contains 13% CMPO and 27% TBP by weight (Barney and Cowan 1992)). Since CMPO is the extractant used in the TRUEX process (Horwitz et al. 1985), the separation properties of TRU•Spec™ are expected to parallel those observed with the TRUEX process.^(a)

TRU•Spec™ (500 mg) was wet-packed in a 5-mm-inside diameter (i.d.) glass column. The column bed volume was 1.44 mL. Before use the column was washed with 4 mL of 2 M HNO_3 . A total of 11 mL of feed solution 1 (see Table 2.1) was passed at room temperature through the column at a flow rate of 0.3 column volume (cv)/min. The effluent was collected in four fractions, 2, 3, 3, and 3 mL, respectively. The column was washed with 5 mL of 2 M HNO_3 , and then eluted with 1) 5 mL of 0.01 M HNO_3 , and 2) 5 mL of 0.01 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). Finally, the column was washed with 5 mL of water. The various solutions were collected and analyzed by alpha-energy analysis (following separation of Pu from Am by anion exchange) and by inductively coupled plasma atomic emission spectroscopy (ICP).

(a) The TRUEX process is a solvent extraction process in which TRUs are extracted from acidic solution using a solvent consisting of 0.2 M CMPO plus 1.4 M TBP in a normal paraffin hydrocarbon (Swanson 1991, Horwitz et al. 1985).

Table 2.1. Composition of Feed Solutions 1, 2, and 3 Used for TRU•Spec™, Sr•Spec™, and SuperLig™ 601 Evaluations, Respectively

Component	Feed Solution		
	1	2	3
	Concentration	Concentration	Concentration
Al	0.0041 <u>M</u>	0.0031 <u>M</u>	0.129 <u>M</u>
Ba	2.5×10^{-5}	2.0×10^{-5}	8.9×10^{-5}
Ca	0.0012	0.0010	0.0020
K	0.0042	0.0033	0.0077
La	2.4×10^{-5}	$< 2.2 \times 10^{-5}$	9.3×10^{-4}
Na	0.228	0.183	0.0587
Si	0.0011	0.0006	0.0019
Sr	6.3×10^{-6}	7.4×10^{-6}	9.9×10^{-6}
U	0.0066	< 0.001	0.0034
Zr	0.189	0.153	0.135
F ⁻	0.35	0.29	0.27
H ⁺	1.6	3.5	1.7
⁸⁵ Sr	--	0.427 $\mu\text{Ci/mL}$	0.604 $\mu\text{Ci/mL}$
Total alpha	0.120 $\mu\text{Ci/mL}$	n.a. ^(a)	n.a.
Pu	0.078	n.a.	n.a.
Am	0.042	n.a.	n.a.

(a) n.a. = not analyzed.

2.3 Separation of Sr from NCRW with Sr•Spec™

Sr•Spec™ is a commercially available chromatographic resin, which consists of a 1 M solution of di-t-butylcyclohexano-18-crown-6 (DtBC18C6) in 1-octanol sorbed onto Amberchrom™ CG-71 at a loading of 40% by weight (Horwitz et al. 1991a). Since DtBC18C6 is the extractant used in the SREX process (Horwitz et al. 1991b),^(a) the separation properties of this material are expected to parallel

(a) SREX is a solvent extraction process in which Sr is separated from acidic solutions by using a solvent consisting of 0.2 M DtBC18C6 in 1-octanol (Horwitz et al. 1991b).

those observed with SREX. The separation chemistry of Sr•Spec™ has recently been described in the literature (Horwitz et al. 1992; Chiarizia et al. 1992).

The effluent from the TRU•Spec™ column was spiked with ^{85}Sr ,^(a) then HNO_3 was added to raise the total acid content to 3.5 M. The composition of this feed solution is described in Table 2.1 as feed solution 2. Sr•Spec™ (494 mg) was wet-packed into a 5-mm-i.d. glass column. The column bed volume was 1.43 mL. After preconditioning the column with 5 mL of 3 M HNO_3 , 9.9 mL of feed was passed at room temperature through the Sr•Spec™ column at a flow rate of 0.1 cv/min. The first mL from the column was collected, then the remaining effluent was collected in one fraction. The column was washed with 3 mL of 3 M HNO_3 and eluted with three 3-mL portions of water. Each collected solution was analyzed by ICP and gamma-energy analysis (GEA).

2.4 Separation of Sr from NCRW with SuperLig™ 601

SuperLig™ 601 (0.407 g) was wet-packed into a 7-mm-i.d. plastic column. The height of the resulting column was 23.5 mm; thus, the bed volume was 0.90 mL. Three milliliters of 2 M HNO_3 was passed through the column to preequilibrate the SuperLig™ 601 with HNO_3 . Aluminum nitrate was added to the feed solution to lower the $F/(\text{Zr} + \text{Al})$ ratio to 1.0; this addition minimized the degradation of the silica gel support by the HF present in the dissolved NCRW solution. The feed solution was spiked with ^{85}Sr . The composition of the feed solution is shown in Table 2.1 as feed solution 3. Solutions were passed through the column in the following sequence: 1) 9 mL of feed solution, 2) 5 mL of 2 M HNO_3 , 3) 8 mL of 0.05 M Na_4EDTA , and 4) 5 mL of water. The maximum flow rate for this column was 1.7 cv/min, and the column was operated at room temperature. During the course of the column run, fractions were collected at 1-mL intervals. Selected fractions were analyzed by GEA and by ICP.

A second experiment with SuperLig™ 601 was conducted using a simulated dissolved NCRW solution. The 7-mm-i.d. column contained 0.5 g of SuperLig™ 601 and had a bed volume of 1.3 mL. The simulated NCRW feed solution consisted of 0.16 M $\text{ZrO}(\text{NO}_3)_2$, 0.19 M $\text{Al}(\text{NO}_3)_3$, 0.16 M NaNO_3 , 0.006 M $\text{UO}_2(\text{NO}_3)_2$, 1.3×10^{-5} M $\text{Sr}(\text{NO}_3)_2$, 5.2×10^{-5} M $\text{Ba}(\text{NO}_3)_2$, 0.25 M HF, 1.6 M HNO_3 , and was spiked with ^{85}Sr . Twenty-two milliliters of feed was passed through the column at a flow rate of 0.1 cv/min. The column was first washed with 3 mL of 1.5 M HNO_3 and then eluted with 5 mL of 0.1 M sodium citrate (NaCit) followed by 5 mL of 0.05 M Na_4EDTA .

-
- (a) The solutions were spiked with ^{85}Sr so that the behavior of Sr could be monitored by gamma-energy analysis. This method was used instead of analyzing for ^{90}Sr , due to the high cost of analyzing for this beta-emitting radioisotope.

2.5 Studies of New Inorganic Ion Exchange Materials

Three new inorganic ion exchange materials were investigated for their potential use in separating ^{137}Cs and ^{90}Sr from Hanford tank wastes. The chemical compositions of these materials are given in Table 2.2.

In order to quantitatively compare the various sorbent materials, a standard set of conditions was chosen for measuring K_d . These conditions were: 2 mL of test solution containing 0.0001 M CsNO_3 was contacted by shaking with 0.015 g of sorbent material^(a) for 24 h at ambient temperature. These batch contacts were performed using 4-mL capacity glass vials. The test solution was sampled for gamma counting before and after the contact. The samples were filtered prior to gamma analysis. The radionuclide concentration of interest in the starting test solution and in the solution after equilibration was determined by gamma counting using a sodium iodide detector. K_d was calculated as follows:

$$K_d = V(C_0 - C)/(w \times C)$$

where V = volume of the solution used (in mL)

C_0 = initial concentration of the radionuclide of interest (in cpm/mL)

C = concentration after equilibrium has been reached (in cpm/mL)

w = mass of the sorbent used (in g).

Table 2.2. New Inorganic Ion Exchange Materials Investigated for the Separation of ^{137}Cs and ^{90}Sr from Hanford Tank Wastes

Material	Composition
IP-4	$\text{Zr}(\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3)_{0.25}(\text{HPO}_4)_{1.5}$
AC2	SiO_2 , 53.55%; Al_2O_3 , 32.9%; Fe_2O_3 , 3.29%; MgO , 3.8%; CaO , 0.27%; K_2O , 0.17%; and Na_2O , 0.7%
3PS-2	$\text{Zr}(\text{O}_3\text{P}(\text{C}_6\text{H}_4)_3(\text{SO}_3\text{H})_y\text{PO}_3)_x(\text{HPO})_{2-2x}$

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- (a) The small amount of material chosen for the standard conditions was necessary because of the limited supply.

3.0 Results and Discussion

3.1 Separation of Am and Pu from NCRW with TRU•Spec™

The results of the TRU•Spec™ column run are summarized in Table 3.1. As expected, the TRU•Spec™ material displayed little affinity for bulk NCRW sludge components such as Zr, Na, or Al. The elements U, Pu, and Am were absorbed onto the column, but the decontamination factors (DF)^(a) for the transuranics (TRUs) were low. Although the DF for Am in the first fraction was greater than 250 (taking into account dilution from the interstitial solution initially on the column), the DF for Am was much lower in subsequent fractions. The average DF achieved for Am in the second, third, and fourth fractions was 2.4. In contrast the average DF for Pu in these three fractions was 180. The average DF achieved for the TRUs (Am + Pu) was 6.6. These DFs are much lower than those achieved with the TRUEX process for NCRW, in which DFs for TRUs of 900 have been reported (Swanson 1991).

Calculation of mass balance for the important NCRW sludge components indicated good recovery for each (see Table 3.1). In the cases of U and Am, the percentages of recovered materials were somewhat high. This is likely due to uncertainties in the analytical methods that were used.

The low DFs for Am in fractions 2, 3, and 4 can be attributed to the loading of the TRU•Spec™ column with U and Zr. According to the data in Table 3.1, U sorbed virtually quantitatively on the TRU•Spec™ column throughout the course of the column run, and a small amount of Zr also loaded onto the column during collection of the first fraction. In subsequent fractions, the amount of Zr in solution was slightly greater than that in the feed, suggesting that the loaded Zr was undergoing displacement (presumably by U).

The total amount of U sorbed during this experiment was 7.3×10^{-5} mole, which is enough to bind ~90% of the 1.6×10^{-4} mole of CMPO calculated to have been present, based on formation of a complex containing two CMPO ligands per U. This U, along with the Zr that was also loaded onto the column, presumably reduced the number of CMPO molecules available to bind Am, thus a large fraction of the Am was not retained on the column. Uranium was extracted in tests of the TRUEX solvent extraction processing on dissolved NCRW sludge, but the concentration of U in the organic phase was low enough that solvent loading did not occur (Swanson 1991).

The problem of Zr loading on the TRU•Spec™ column could likely be eliminated by adding fluoride ion to complex the Zr in the feed solution. The loading of U is a more serious problem. This loading would likely preclude the use of TRU•Spec™ as the primary actinide separations process for

(a) Decontamination factor is defined as the concentration in the feed solution divided by the concentration in the column effluent.

Table 3.1. Results from the TRU•Spec™ Column Run

Solution	Volume, mL	Concentration						
		Zr, <u>M</u>	Al, <u>M</u>	Na, <u>M</u>	U, <u>M</u>	Total α, dpm/mL	Pu, dpm/mL	Am, dpm/mL
Feed	11	0.189	0.0041	0.228	0.0066	2.67x10 ⁵	1.73x10 ⁵	9.38x10 ⁴
First Fraction	2	0.020	0.0016	0.078	<0.001	<200	<66	<130
Second Fraction	3	0.191	0.0040	0.230	<0.001	3.58x10 ⁴	844	3.50x10 ⁴
Third Fraction	3	0.198	0.0041	0.235	<0.001	4.36x10 ⁴	1070	4.26x10 ⁴
Fourth Fraction	3	0.197	0.0041	0.233	<0.001	4.36x10 ⁴	976	4.27x10 ⁴
Column Wash (2 <u>M</u> HNO ₃)	5	0.057	0.0013	0.062	<0.001	2.02x10 ⁴	6550	1.37x10 ⁴
First Elution (0.01 <u>M</u> HNO ₃)	5	0.001	<0.0006	0.003	0.0163	1.63x10 ⁵	1.59x10 ⁴	1.47x10 ⁴
Second Elution (0.01 <u>M</u> HEDPA)	5	<0.0002	<0.0006	0.003	0.0026	3.46x10 ⁵	3.55x10 ⁵	n.d. ^(a)
Third Elution (water)	5	<0.0002	<0.0006	0.003	<0.001	904	660	244
Mass Balance	In	2.08	0.0455	2.51	0.073	2.94x10 ⁶	1.91x10 ⁶	1.03x10 ⁶
	Out	2.09	0.0462	2.60	0.094	3.02x10 ⁶	1.90x10 ⁶	1.17x10 ⁶
	% recovered	101	102	104	130	103	99.5	113

(a) n.d. = not detected.

the treatment of dissolved Hanford tank wastes because U is a major constituent in these wastes. However, TRU•Spec™ might be effective in removing Am and Pu if the U is first separated by a different method. This possibility will be explored in future work.

3.2 Separation of Sr from NCRW with Sr•Spec™

The results of the Sr•Spec™ column run are summarized in Table 3.2. Very high DFs for Sr were achieved. No ⁸⁵Sr activity could be detected in the column effluent. Of the bulk components present, only a small amount of Na was eluted from the column along with the Sr; the separation of Sr from the other sludge components was virtually complete (except for Ba, *vide infra*). The mass determined by ICP for each element except Sr balanced within experimental error. The percent recovery for Sr appeared low according to the ICP data, but the counting data indicated complete recovery of Sr.

These results indicated that Sr•Spec™ has high potential for application in the removal of ⁹⁰Sr from HLW stored on the Hanford Site. Use of Sr•Spec™ offers the advantage that water alone (or dilute acid) is required to elute the Sr. (A complexant is required to elute Sr from SuperLig™ 601, *vide infra*).

In addition to Sr, Sr•Spec™ is reported to remove Pu(IV) from acidic solution (Horwitz et al. 1992). Because most of the Pu had been removed from the feed solution during the preceding TRU•Spec™ column run, the behavior of Pu during the Sr•Spec™ column run could not be accurately assessed. However, information regarding Pu was obtained from this experiment. The feed solution contained 1.1 nCi of ^{239,240}Pu/mL. ^{239,240}Pu was undetected in the column effluent and in the column wash solution. The first fraction from the elution with water contained 1 nCi of ^{239,240}Pu/mL. ^{239,240}Pu was undetected in the second and third fractions from the elution with water. The fact that the amount of ^{239,240}Pu found was not well balanced could be due to counting errors at this low level of activity or to incomplete elution of Pu from the column. However, it does appear that Pu is significantly retained on the Sr•Spec™ material.

The Sr•Spec™ material displayed no affinity for Am(III). The feed solution contained 13 nCi of ²⁴¹Am + ²³⁸Pu/mL, whereas the column effluent (second fraction) contained 12 nCi of ²⁴¹Am + ²³⁸Pu/mL.^(a) Thus, very little Am was retained on the Sr•Spec™ column.

The behavior of Ba during the Sr•Spec™ column run was of interest because the separation of Ba from Sr is difficult to achieve. The concentration of Ba in the second fraction collected from this column run was 1.1×10^{-5} M, which is approximately half of that present in the feed solution (2×10^{-5} M). Thus, Sr•Spec™ does have some affinity for Ba, but it is much less than that for Sr. This trend is opposite of that seen with SuperLig™ 601 which has a higher affinity for Ba (*vide infra*).

(a) ²⁴¹Am and ²³⁸Pu could not be distinguished by the alpha energy analysis method used.

Table 3.2. Results from the Sr•Spec™ Column Run

Solution	Volume, mL	Concentration						
		Zr, <u>M</u>	Al, <u>M</u>	Ba, <u>M</u>	Na, <u>M</u>	Sr, <u>M</u>	⁸⁵ Sr, <u>μCi/mL</u>	¹³⁷ Cs, <u>μCi/mL</u>
Feed	9.9	0.153	0.0031	2.0x10 ⁻⁵	0.183	7.4x10 ⁻⁶	0.427	0.097
First Fraction	1	0.029	n.d. ^(a)	6.1x10 ⁻⁶	0.001	<2.6x10 ⁻⁶	n.d.	0.000
Second Fraction	8.9	0.150	0.0031	1.1x10 ⁻⁵	0.174	<2.6x10 ⁻⁶	n.d.	0.094
Column Wash	3	0.065	0.0015	6.4x10 ⁻⁶	0.091	<2.6x10 ⁻⁶	n.d.	0.047
First Elution	3	<0.0002	<0.0006	2.9x10 ⁻⁵	0.001	2.0x10 ⁻⁵	1.391	n.d.
Second Elution	3	<0.0002	<0.0006	<3.3x10 ⁻⁶	0.001	<2.6x10 ⁻⁶	0.031	n.d.
Third Elution	3	<0.0002	<0.0006	<3.3x10 ⁻⁶	0.000	<2.6x10 ⁻⁶	n.d.	n.d.
Mass Balance		In	1.515	0.031	2.0x10 ⁻⁴	1.812	7.3x10 ⁻⁵	0.964
		Out	1.560	0.032	2.1x10 ⁻⁴	1.830	6.0x10 ⁻⁵	0.974
% recovered			103	105	105	101	82	101

(a) n.d. = not detected.

Based on data in the literature (Horwitz, Chiarizia, and Dietz 1992), improved Ba/Sr separation could likely be achieved if the loading cycle was conducted at higher HNO_3 concentration.

3.3 Separation of Sr from NCRW with SuperLig™ 601

The results of the separation of Sr from dissolved NCRW solution with SuperLig™ 601 are summarized in Figure 3.1. The analytical results obtained from GEA agreed quite well with those obtained by ICP. The data showed that Sr did indeed load onto the SuperLig™ 601 column; however, the separation was not efficient enough to achieve a high DF under the conditions of this experiment. The final fraction taken during the passing of the feed solution through the column contained $0.118 \mu\text{Ci/mL}$ of ^{85}Sr , compared to $0.604 \mu\text{Ci/mL}$ in the feed solution; thus, the DF for that fraction was only 5.1.

According to the manufacturer, SuperLig™ 601 is selective for Ba as well as Sr. Figure 3.2 shows the behaviors of Ba (determined by ICP) and Cs (determined by GEA) in the experiment. Barium loaded onto the SuperLig™ 601 column and was eluted with $0.05 \text{ M Na}_4\text{EDTA}$. In contrast, Cs was not retained on the column.

Figure 3.1. Behavior of Sr in the SuperLig™ 601 Column Test with Actual Dissolved NCRW Solution. C/Co is the concentration of Sr in the column effluent divided by the concentration of Sr in the feed solution.

Figure 3.2. Behavior of Cs and Ba in the SuperLig™ 601 Column Test with Actual Dissolved NCRW Solution. C/C_o is the concentration of Cs or Ba in the column effluent divided by the concentration in the feed solution. The concentration of Cs was determined as the concentration of ^{137}Cs by gamma counting techniques, whereas the concentration of Ba was determined by ICP analysis.

The performance of the SuperLig™ 601 material in separating Ba from the solution was better than that for Sr. This would be expected given the larger binding constant for Ba (*vide infra*).

According to our results, the SuperLig™ 601 showed high selectivity for Sr and Ba. In particular, the bulk elements that were present (Zr, Al, and Na) were not retained on the column. There was no apparent breakdown of the silica gel support during the column run; however, the material was not in contact with the feed solution for as long a period of time as would be encountered in a large-scale process.

The fraction (f) of sites on the SuperLig™ 601 material that are occupied by a given metal, M , at full loading is given by the following equation:

$$f = \frac{K[M]}{1 + K[M]}$$

where K is the binding constant for the metal M , and $[M]$ = molar concentration of M (Bruening et al. 1991). The SuperLig™ 601 material is reported to have $\log(K) = 2.7$ for Sr and 3.8 for Ba. Thus, for the concentrations of Ba ($8.9 \times 10^{-5} \text{ M}$) and Sr ($9.9 \times 10^{-6} \text{ M}$) in the feed solution, $f = 0.005$ for Sr and 0.36 for Ba. Given an overall capacity of 0.3 mmole/g for SuperLig™ 601, the total possible loading for Sr at equ librium should have been 0.0006 mmole and that for Ba should have been 0.045 mmoles under the conditions of this experiment. The feed solution represented 15% of the capacity for Sr and 2% of the capacity for Ba.

Clearly, considerable amounts of Sr passed through the column (Figure 3.1) even though the capacity of the column for Sr was not exceeded. One possible explanation is that the feed solution was passed through the column too quickly. If the sorption kinetics of Sr on the SuperLig™ 601 are diffusion controlled, then a longer residence time for the solution on the column might improve performance.

This hypothesis was tested by passing a simulated dissolved NCRW solution through a SuperLig™ 601 column at a lower flow rate (0.1 cv/min). The results of the loading cycle are shown in Figure 3.3. Much higher DFs for Sr were achieved in this experiment in which a lower flow rate was used. The overall DF for ^{85}Sr during the loading cycle (18 bed volumes) was 250.

Figure 3.3. Loading Cycle for the Separation of Sr from Simulated Dissolved NCRW Solution Using SuperLig™ 601 at a Flow Rate of 0.1 cv/min. The quantity C/Co is $[\text{Sr}]$ in the column effluent divided by $[\text{Sr}]$ in the feed solution.

These results indicated the importance of absorption kinetics on SuperLig™ 601. This material is quite effective at separating Sr from HNO₃ solution, but further work is needed to optimize the conditions (especially flow rate) under which the separation is performed.

The results of the elution cycles (Figure 3.4) indicated that Sr and Ba can be separated by selective elution. The Sr was eluted from the column with 0.1 M NaCit, while the Ba was eluted with Na₄EDTA. Quantitative separation of Sr from Ba was achieved.

Another possible means to improve the performance of the SuperLig™ material would be to use a macrocyclic ligand that has a higher affinity for Sr. Under the conditions of this experiment, only 0.5% of the macrocyclic ligand sites on the SuperLig™ 601 would bind Sr at full loading. To increase the fraction of sites available for binding Sr, the binding constant for Sr must be greater. For example, for 10% of the ligand sites to be occupied by Sr at full loading from a feed solution containing 10⁻⁵ M Sr, the log(K) for Sr must be 4, as dictated by the above equation. According to the supplier (IBC Advanced Technologies), a new SuperLig™ product with a higher K for Sr will be available after patent applications have been filed. This product will be tested when it is available.

Figure 3.4. Behavior of Sr and Ba in the Loading and Elution Cycles of the SuperLig™ 601 Experiment with Simulated Dissolved NCRW Solution. The quantity C/Co is [Sr] or [Ba] in the column effluent divided by the concentration in the feed solution.

3.4 Studies of New Inorganic Ion Exchange Materials

A series of experiments was conducted to test new inorganic ion exchange materials for potential application in pretreating HLW. In particular, three pillared compounds like those described by Kullberg and Clearfield (1989, 1990) and Clearfield (1992)^(a) were evaluated to determine their affinity for Cs and Sr. These materials, designated as IP-4, AC2, and 3PS-4, were supplied by Abraham Clearfield of Texas A & M University.

The affinities of these materials for Cs and Sr were determined by batch distribution measurements. Tests were conducted to ensure that the contact times were adequate to attain equilibrium. A set of "standard conditions" was defined so that meaningful comparisons could be made between the various distribution ratios measured. The affinity of these materials for the various ions of interest were studied as a function of pH, Na concentration, and HNO₃ concentration.

3.4.1 Sorption of Cs on IP-4: Kinetics

An experiment was conducted to determine if equilibrium was attained after contacting the sorbent material with the test solution for 24 h. The test solution used in this experiment consisted of 0.0001 M CsNO₃ and 0.1 M NaNO₃ at an initial pH of 7.54. One portion of this solution was contacted with IP-4 at ambient temperature for 24 h, while another portion was contacted with IP-4 at ambient temperature for 117 h. In both cases, the solution-to-sorbent ratio was 130 mL/g. The distribution ratios (K_ds) were found to be 354 and 343 mL/g for the 24-h and 117-h contacts, respectively. The final pH of the solutions was 4.41 for the 24-h contact and 4.45 for the 117-h contact. Clearly, equilibrium had been reached after 24 h. In subsequent experiments, the sorbent materials were shaken with the test solutions for about 24 h.

3.4.2 Sorption of Cs on IP-4: Dependence on the Amount of Material Used

An experiment was conducted to determine if the measured K_ds varied with the amount of sorbent material used (at constant volume of test solution). In this experiment a test solution, identical to the one used in the kinetic experiment described above, was contacted with IP-4 at a solution-to-sorbent ratio of 65 mL/g. The K_d (720 mL/g) was approximately twice that found at a solution-to-sorbent ratio of 130 mL/g (i.e., in the contacts described in the previous paragraph).

One likely explanation of this is that the capacity of the material for Cs has been exceeded in the experiment where the solution-to-sorbent ratio was at least 130 mL/g. According to capacity data supplied by Clearfield, the ion exchange capacity of the material was not exceeded. It could be that

(a) Clearfield, A. 1992. "New Ion Exchange Materials and Their Potential Use for Nuclear Waste Treatment." In *Proceedings of the First Hanford Separation Science Workshop*. Manuscript in preparation. Pacific Northwest Laboratory, Richland, Washington.

there is more than one type of ion exchange site on this material, and that only a small percentage of these display high affinity for Cs. Further work is needed to more fully understand these systems, including the effect of Cs concentration.

3.4.3 Sorption of Cs on IP-4, AC2, and 3PS-2: Function of pH

A series of batch contacts was performed with the three materials to determine the affinity for Cs ion as a function of pH. The results are summarized in Table 3.3 and Figure 3.5. All three materials displayed a high affinity for Cs in the pH range studied (pH 1 to 13). 3PS-2 had the highest affinity for Cs in acidic solutions, but the lowest in highly alkaline solution. The data suggest that 3PS-2 would be the best material to use for an acid-side Cs removal process, while either IP-4 or AC2 could be used for removing Cs from alkaline solution.

Table 3.3. Sorption of Cs on Pillared Clay Materials as a Function of pH

<u>Material</u>	<u>[Cs], M</u>	<u>[Na], M</u>	<u>Initial pH</u>	<u>Final pH</u>	<u>Kd, mL/g</u>
IP-4	0.0001	0.1	12.95	12.70	3,020
AC2	0.0001	0.1	12.95	12.73	3,110
3PS-2	0.0001	0.1	12.95	12.01	99
IP-4	0.0001	0.1	10.44	4.50	809
AC2	0.0001	0.1	10.44	6.30	703
3PS-2	0.0001	0.1	10.44	4.27	14,900
IP-4	0.0001	0.1	8.47	4.50	717
AC2	0.0001	0.1	8.47	5.72	523
3PS-2	0.0001	0.1	8.47	4.23	11,400
IP-4	0.0001	0.1	8.36	4.51	649
AC2	0.0001	0.1	8.36	5.66	482
3PS-2	0.0001	0.1	8.36	4.30	11,500
IP-4	0.0001	0.1	1.67	1.32	177
AC2	0.0001	0.1	1.67	1.81	89
3PS-2	0.0001	0.1	1.67	1.30	2,770
IP-4	0.0001	0.1	5.38	4.47	610
AC2	0.0001	0.1	5.38	5.31	348
3PS-2	0.0001	0.1	5.38	4.25	7,380
IP-4	0.0001	0.1	8.33	4.48	711
AC2	0.0001	0.1	8.33	5.70	522
3PS-2	0.0001	0.1	8.33	4.30	11,400

Figure 3.5. Cs Kd as a Function of pH for the Pillared Ion Exchange Materials. The curves correspond to a second-order regression.

3.4.4 Sorption of Cs on 3PS-2: Function of Nitric Acid Concentration

The high affinity of 3PS-2 for Cs in the pH range 1 to 5 indicated that 3PS-2 may be applicable for removing Cs from strongly acidic solution. A series of batch contacts was performed to determine the affinity of this material for Cs as a function of HNO_3 concentration. In this experiment, the sodium nitrate concentration was held at 0.1 M , while the nitric acid concentration was varied from 0.1 to 3 M . The initial Cs concentration in the test solutions was 0.0001 M . The results are shown in Figure 3.6. The K_d for Cs decreased with increasing concentration of HNO_3 ; however, even at 3 M HNO_3 , the 3PS-2 displayed good affinity for Cs. The utility of this material for removing Cs from acidic waste solutions, such as dissolved tank sludges, should be investigated further.

Figure 3.6. Cs Kd for Pillared Ion Exchange Material 3PS-2 as a Function of HNO₃ Concentration

3.4.5 Sorption of Cs on 3PS-2: Function of Sodium Nitrate Concentration

The dependence of the Cs Kd for 3PS-2 on sodium nitrate concentration is shown in Figure 3.7 for test solutions with initial [HNO₃] = 1 M or initial [NaOH] = 0.001 M. (Although pH was not measured for these solutions after equilibration, it is likely that in the cases in which the initial [NaOH] = 0.001 M, the final pH was in the range 4 to 5; see Table 3.3.) The general trend observed was that Kd decreased with increasing sodium nitrate concentration. Interestingly, for the test solution with initial [NaOH] = 0.001 M, the Kd remained above 100, even at 5 M NaNO₃. Thus, it appears that under the proper pH conditions, 3PS-2 (and likely IP-4 and AC2) should be capable of separating Cs from aqueous solution even in the presence of a large excess of Na.

3.4.6 Sorption of Sr on 3PS-2: Function of pH

3PS-2 was reported to have high affinity for Sr by Clearfield (private communication). Using 3PS-2, Kd for Sr was measured at several different pHs. The results are presented in Table 3.4. Except for pH > 12, the measured Kd values were an order of magnitude less than expected based on Clearfield's results (private communication). This discrepancy may have been due to the different conditions under which measurements were taken compared to Clearfield (e.g., Na concentration). For solutions in which the initial pH was between 5.8 and 10.2, the final pH was found to be around 4.6. In these cases the Kd fell to the range between 945 and 1,120 mL/g. Under slightly more acidic

Figure 3.7. Cs K_d for Pillared Ion Exchange Material 3PS-2 as a Function of NaNO₃ Concentration

Table 3.4. Sorption of Sr on 3PS-2: Function of pH

[Sr], M	[Na], M	Initial pH	Final pH	K _d , mL/g
0.0001	0.1	12.79	12.25	24,300
0.0001	0.1	10.19	4.63	1,120
0.0001	0.1	8.81	4.60	1,010
0.0001	0.1	8.66	4.60	1,070
0.0001	0.1	3.64	3.75	192
0.0001	0.1	5.81	4.50	945
0.0001	0.1	8.60	4.66	1,100

solutions (final pH = 3.75), the K_d was much less (192 mL/g). For strongly alkaline media (pH > 12), a very high K_d of over 24,000 mL/g was measured. It is likely that the high K_d in this case was not due to an ion exchange process but rather resulted from precipitation of strontium phosphate. Clearfield (private communication) reported that at high pH the phosphate groups on these materials are solubilized. The presence of phosphate ions would then induce precipitation of strontium phosphate.

3.4.7 Behavior of IP-4 in a Column

IP-4 was packed into a column to test its ability to separate ^{137}Cs from actual Hanford tank waste. When 0.5 g of IP-4 was packed into a 7-mm-i.d. column, the properties of the column bed prevented water from flowing through the column under the pull of gravity. Even when under vacuum, the flow of water through the column was slow. It was concluded that the physical properties of this batch of IP-4 are not conducive to use in a column mode.

3.5 Conclusions

Three chromatographic materials, TRU•Spec™, Sr•Spec™, and SuperLig™ 601, were tested for use in partitioning radioactive wastes. TRU•Spec™ was found to separate Am and Pu from dissolved Hanford NCRW, but the DF achieved was two orders of magnitude less than that obtained with the TRUEX solvent extraction process, apparently due to loading of the TRU•Spec™ column with U and Zr. Sr•Spec™ performed very well in the separation of Sr from dissolved NCRW sludge. SuperLig™ 601 was found to separate Sr, but the efficiency of Sr removal is dependent upon flow rate. Because the experimental conditions varied, Sr•Spec™ and SuperLig™ 601 were not directly compared.

A series of new inorganic ion exchange materials was also tested for potential use in the pretreatment of HLW. Three different pillared materials, IP-4, AC2, and 3PS-2, were examined to determine their affinities for Cs. All three ion exchange materials exhibited high Kds for Cs over a wide range of pH conditions. The affinity of IP-4 for Cs was examined under highly acidic conditions. The Kd for Cs decreased with increasing acidity, but remained high enough for a workable process even at 3 M HNO_3 . The Kd for Cs also decreased with increasing Na concentration, but it appears that under certain pH conditions a workable Cs separation process might be designed, even at 5 M Na. Another of these materials (3PS-2) was tested for the sorption of Sr from solutions with varying pHs. As with Cs, large Kds were observed over a wide pH range.

Attempts to use IP-4 in a column mode did not succeed because of very slow flow rates. In order to design a practical system, the preparation of these pillared ion exchangers must be modified so that the physical properties of the materials are amenable to use in a column.

In summary, the work described here demonstrates that new chromatographic materials have potential for the partitioning of nuclear wastes. Processes employing these materials may prove very useful in polishing the raffinates from solvent extraction systems before such LLW streams are disposed. Furthermore, a chromatographic method might be chosen over a solvent extraction process for a needed separation if the economics are favorable. The results of the initial screening tests described here indicate that further testing of these materials is warranted. Further testing will be conducted as appropriate tank waste samples become available.

4.0 References

- Barney, G. S., and R. G. Cowan. 1992. *Separation of Actinide Ions from Radioactive Waste Solutions Using Extraction Chromatography*. WHC-SA-1520-FP, Westinghouse Hanford Company, Richland, Washington.
- Bradshaw, J. S., R. L. Bruening, K. E. Krakowiak, B. J. Tarbet, M. L. Bruening, R. M. Izatt, and J. J. Christensen. 1988. *Journal of the Chemical Society, Chemical Communications* **1988**:812-814.
- Bradshaw, J. S., K. E. Krakowiak, B. J. Tarbet, R. L. Bruening, J. F. Biernat, M. Bochenska, R. M. Izatt, and J. J. Christensen. 1989a. *Pure and Applied Chemistry* **61**:1619-1624.
- Bradshaw, J. S., K. E. Krakowiak, B. J. Tarbet, R. L. Bruening, L. D. Griffin, D. E. Cash, T. D. Rasmussen, and R. M. Izatt. 1989b. *Solvent Extraction and Ion Exchange* **7**:855-864.
- Bruening, M. L., D. M. Mitchell, J. S. Bradshaw, R. M. Izatt, and R. L. Bruening. 1991. *Analytical Chemistry* **63**:21-24.
- Camaioni, D. M., N. G. Colton, and R. L. Bruening. 1992. *Investigation of the Potential of Silica-Bonded Macrocyclic Ligands for Separation of Metal Ions from Nuclear Waste*. PNL-7894, Pacific Northwest Laboratory, Richland, Washington.
- Chiarizia, R., E. P. Horwitz, and M. L. Dietz. 1992. *Solvent Extraction and Ion Exchange* **10**:337-361.
- Horwitz, E. P., D. G. Kalina, H. Diamond, G. F. Vandegrift, and W. W. Schulz. 1985. *Solvent Extraction and Ion Exchange* **3**:75-109.
- Horwitz, E. P., M. L. Dietz, and D. E. Fisher. 1991a. *Analytical Chemistry* **63**:522-525.
- Horwitz, E. P., M. L. Dietz, and D. E. Fisher. 1991b. *Solvent Extraction and Ion Exchange* **9**:1-25.
- Horwitz, E. P., R. Chiarizia, and M. L. Dietz. 1992. *Solvent Extraction and Ion Exchange* **10**:313-336.
- Izatt, R. M., R. L. Bruening, M. L. Bruening, B. J. Tarbet, K. E. Krakowiak, J. S. Bradshaw, and J. J. Christensen. 1988. *Analytical Chemistry* **60**:1825-1826.
- Kullberg, L. H., and A. Clearfield. 1989. *Solvent Extraction and Ion Exchange* **7**:527-540.

Kullberg, L. H., and A. Clearfield. 1990. *Solvent Extraction and Ion Exchange* 8:187-197.

Swanson, J. L. 1991. *Use of the TRUEX Process for the Pretreatment of Neutralized Cladding Removal Waste (NCRW) Sludge - Results of a Design Basis Experiment*. PNL-7734, Pacific Northwest Laboratory, Richland, Washington.

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