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SNL-1, A HIGHLY SELECTIVE INORGANIC CRYSTALLINE ION EXCHANGE MATERIAL FOR Sr^{2+} IN ACIDIC SOLUTIONS

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ABSTRACT

A new inorganic ion exchange material, called SNL-1, has been prepared at Sandia National Laboratories. Developmental samples of SNL-1 have been determined to have high selectivity for the adsorption of Sr from highly acidic solutions (1 M HNO_3). This paper presents results obtained for the material in batch ion exchange tests conducted at various solution pH values and in the presence of a number of competing cations. Results from a continuous flow column ion exchange experiment are also presented

INTRODUCTION

At the Hanford Reservation in Washington state, 177 underground storage tanks are currently being used to store approximately 65 Mgal of radioactive waste containing more than 165 million curies of radioactivity. Much of the radioactivity in the waste is due to the presence of isotopes of cesium and strontium. Similar wastes are stored at DOE facilities at Savannah River, Oak Ridge, and Idaho. The waste in the Hanford tanks includes a mixture of sludge, salt cake, and alkaline supernatant liquids. The majority of these wastes resulted from the dissolution of irradiated fuel elements and the extraction of these feeds to recover the plutonium and uranium. The resulting acid waste was neutralized with caustic solutions and placed in underground storage tanks. The insoluble sludge fraction of the waste consists of metal oxides and hydroxides and contains the bulk of many radionuclides including strontium. The DOE is committed to the remediation and stabilization of the wastes stored at the Hanford site.

Recent negotiations relating to the Tri-Party Agreement (involving the DOE, the EPA, and the Washington State Department of Ecology) have resulted in a shift to vitrification as the final processing step for both the high-level waste (HLW) and low-level waste (LLW) fractions of Hanford's underground storage tanks. Accordingly the Tank Waste Remediation System (TWRS) pretreatment activities focused on a strategy to remove radionuclides from aqueous streams to an extent that would make the streams suitable for LLW vitrification. A major planning assumption for the TWRS emphasized the development of enhanced sludge washing (washing and/or selective leaching of sludges) to further reduce the volume of waste that will require HLW disposal. [1] A persistant treatment scheme is the dissolution of washed sludge with nitric acid followed by ^{90}Sr recovery from the acid waste. Thus there is a need for adsorbents that are selective for strontium in highly acidic solutions. Effective methods for removing Sr^{2+} from Defense Waste have been previously demonstrated. [2,3] The potential problems associated with implementing these materials arise from (1) the incompatibility of high levels of phosphorus with the vitrification process and (2) the inherent instability of organic based materials at high temperatures, elevated radiation exposures, and over multiple use cycles.

At Sandia, we have focused on developing titanate ion exchange materials for radwaste applications. We report herein an inorganic sodium titanate that provides the complement for acid side strontium processing to the class of titanates developed jointly at Sandia and Texas A&M University.[4,5] This new material has been tested for the selective removal of parts-per-million level concentrations of Sr^{2+} ions from solutions with a pH in the range of 1M HNO_3 to 5.7 M Na^+/0.6M OH^- (with the most important results in the highly acidic

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regimes). This novel material has been fully characterized with an array of techniques, including equilibrium distribution coefficient (K_d) determinations over a wide pH range, powder X-ray diffraction, TEM, BET, Direct-current plasma (DCP) and thermal analyses.

EXPERIMENT

Synthesis

SNL-1 (a hydrous sodium titanate) was prepared hydrothermally using titanium isopropoxide, sodium hydroxide, organic templates, dopant oxides and water as reactants. The reactants were mixed and reacted in an autoclave for an appropriate time. The product, a fine white powder, was recovered by filtration, washed with deionized water and air dried at ambient temperature. The details of the synthesis cannot currently be made public.

Characterization

Powder **X-ray** diffraction data were collected at room-temperature on a Siemens Model D500 automated diffractometer, with Θ-2Θ sample geometry and Cu K_α radiation, between $2\Theta = 5$ and 60°, step size 0.05°. **TEM** was performed on a Philips CM30 Transmission Electron microscope at 300 kV. **BET** measurements were performed on a Quantachrome Autosorb 6B automated gas sorption system, with adsorbed and desorbed volumes of nitrogen at relative pressures in the range 0.05 to 1.0. **TGA** measurements were collected on a DuPont 9900 system in air. The heating rate was 10°C/min from room temperature to 500°C.

Ion Exchange

In order to quantitatively compare the various SNL-1 analogs against each other and against various sorbent materials, a standard set of conditions was chosen for measuring batch distribution coefficients, K_d. All distribution coefficient measurements (batch K_d's) reported here were obtained by contacting, with agitation, 0.1 g of SNL-1 with 10 ml of solution for approximately 24 hr. At the end of the contact period, the solution was passed through a 0.2 µm Whatman syringe filter. A sample of the solution was then diluted and analyzed by DCP. Distribution coefficients were calculated utilizing the measured mass of titanate material, and the initial and final concentrations of Sr in the solution. The values are reported for as-prepared materials; no attempt to account for the volatiles content (loss-on-ignition or LOI) of the material was made. K_d was calculated as follows:

$$K_d\ (\mathrm{ml/g}) = V(C_o - C) / (w \times C)$$

where V = volume of the solution used (in ml)
C_o = initial concentration of the Sr (in ppm)
C = concentration after equilibrium has been reached (in ppm)
w = mass of the sorbent used (in g).

RESULTS

The SNL-1 material is a dense, thermally stable (as indicated by TGA), microporous titanate material. Density was measured by water displacement to be approximately 1.5 g/ml. The multi-point BET surface area for this material is 28.4 m^2/g. The material appears to have an "ink-bottle" pore structure, as indicated by the shape of the closed hysteresis loop. (see figure 1) TGA data indicates an initial water weight loss at ≈ 100°C, with a gradual weight loss in the material until ≈ 180°C, after which point no weight loss is observed.

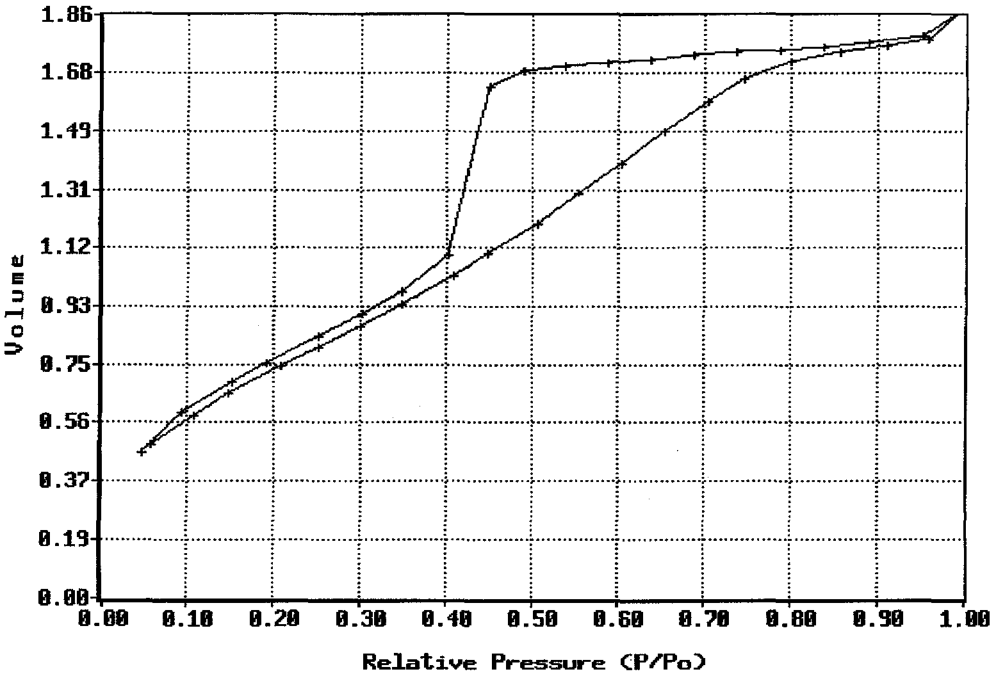

Figure 1: BET isotherm

Diffraction data indicate that this is a very fine particle material with a primary titanate phase and a minor sodium titanate impurity phase. Powder X-ray diffraction (see Table 1) shows that there is a layered phase present, however, the peaks are too broad to apply a crystallographic model for structure refinement. The broad peaks result from very small particle sizes. TEM data is complementary to the X-ray data by discerning a two phase system, with a dopant-titanate equiaxed phase whose particles are 10-30nm, and a flaked phase, whose particles are typically 5nm by 10's of nm across. (see figure 2)

d-spacing, Å	Relative Intensity
7.3888	100.0
5.9634	53.4
3.1032	56.2
2.9807	99.6
2.5767	36.4
2.0783	37.9
1.8232	46.2
1.7999	31.4
1.7393	25.7
1.5527	40.9

Table 1: Powder X-ray diffraction data

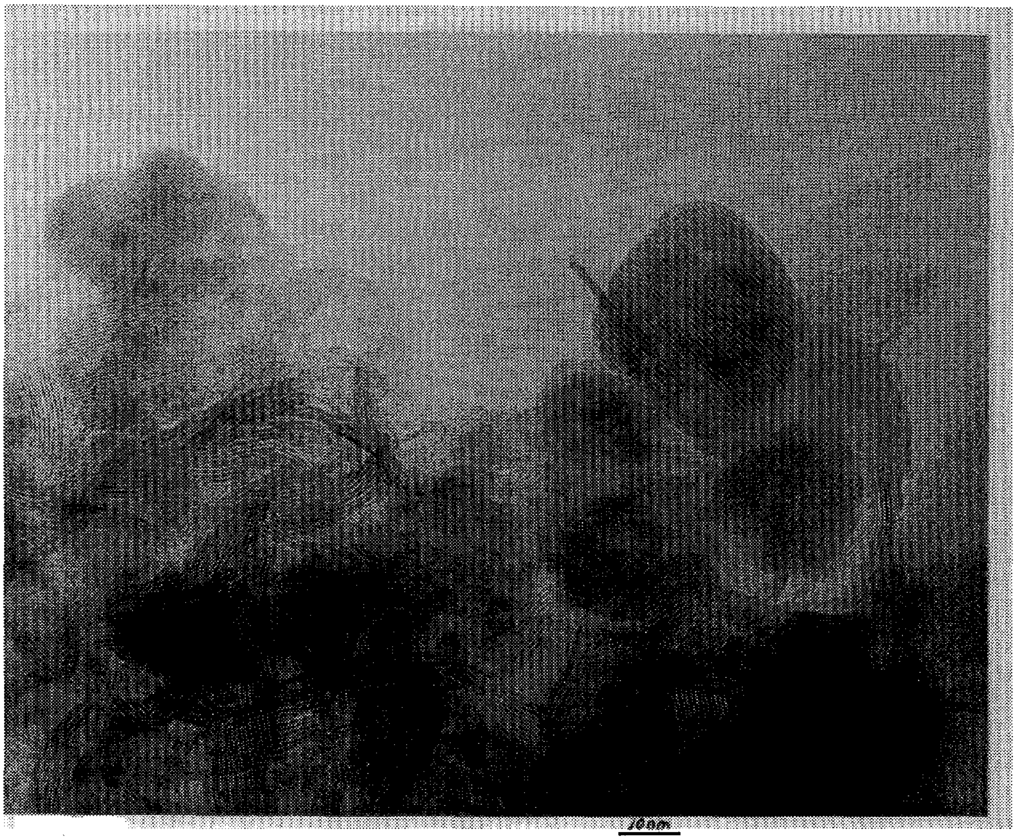

Figure 2: TEM (1,600,000 x)

This material has strong adsorption of Sr (as measured by K_d) over a broad range of pH. At neutral pH (DI H_2O, 100ppm initial Sr), Sr $K_d > 99{,}000$ ml/g. At basic pH (5.7 M Na^+/

Description	Amount
SiO_2	0.029 M
HNO_3	2.3 M
$Al(NO_3)$	0.013 M
$Ba(NO_3)$	3.3×10^{-5} M
$Bi(NO_3)_3{\bullet}5H_2O$	0.024 M
$Ca(NO_3)_2{\bullet}4H_2O$	5.3×10^{-3} M
$Cr(NO_3)_3{\bullet}9H_2O$	4.0×10^{-3} M
$Fe(NO_3)_3{\bullet}9H_2O$	0.092 M
$La(NO_3)_3{\bullet}6H_2O$	0.001 M
$Mg(NO_3)_2{\bullet}6H_2O$	1.8×10^{-3} M
$NaNO_3$	0.19 M
$NaH_2PO_4{\bullet}H_2O$	0.072 M
$Pb(NO_3)_2$	1.3×10^{-3} M
$Sr(NO_3)$	7.9×10^{-4} M

Table 2: B-110 simulant composition

0.6M OH^-, 50ppm initial Sr), Sr $K_d > 50,000$ ml/g. At acidic pH (1 M HNO_3 and 0.1 M HNO_3, 50ppm initial Sr) $K_d = 62$ ml/g and 157 ml/g, respectively. As a method for determining the effects of competing cations in acidic conditions, a batch K_d (run for 16 hours) was run for this material in Hanford B-110 dissolved sludge simulant (see table 2) with a resultant $K_d = 15$ ml/g. [6] Both calcium and magnesium are known to interfere with the selective adsorption of strontium in solution. It is probably their presence in the B-110 simulant which caused the substantial drop in K_d value. Furthermore, increased equilibration time (24 hours and beyond) will probably lead to an increased K_d value.

Ion Exchange Column Run

The kinetic behavior of the SNL-1 material was assessed using a laboratory-scale column. The 7 mm x 4 cm column was completely filled with +40 mesh SNL-1. The feed consisted of 50 ppm Sr in 0.05M HNO_3 (resulting pH = 1.8). The experiment was carried out downflow at 10 column volumes/hour flowrate and 25°C. Effluent samples were analyzed by DCP. For SNL-1 in HNO_3, 10% breakthrough ($C/C_o = 0.1$) occurred at about 70 column volumes, and 50% breakthrough occurred at about 95 column volumes (see figure 3).

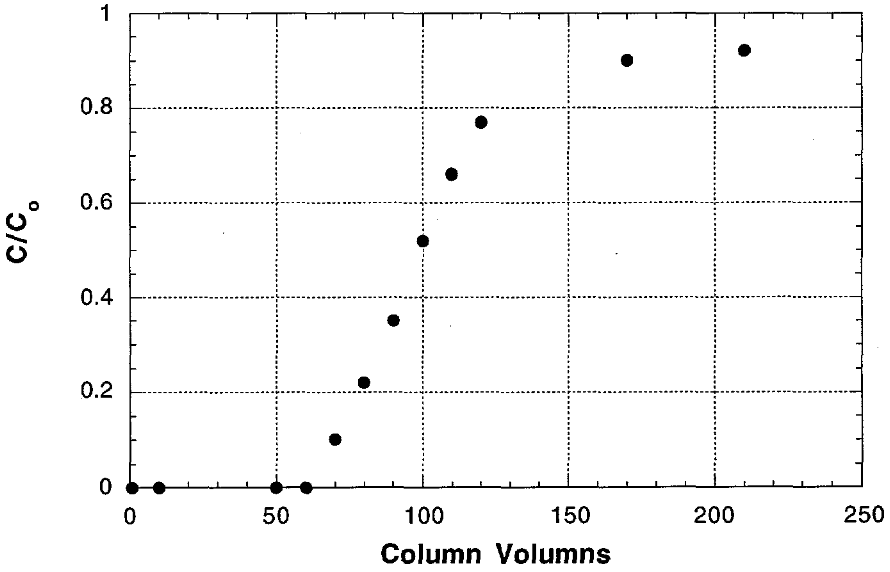

Figure 3: Column experiment at pH ≈ 1.8 (HNO_3) for Sr^{2+} removal

CONCLUSIONS

At Sandia, we have focused on developing titanate ion exchange materials for radwaste applications. The SNL-1 material is a developmental microporous titanate material that potentially offers significant advantages for use in strontium separations from wastes such as acid washed sludge. Unlike phosphates and organic ion exchangers, titanates will be compatible with vitrification processes and chemically, thermally and radiation stable.

The current SNL-1 formulation exhibits high distribution coefficients for Sr in acidic solutions, and in a preliminary ion-exchange column study exhibited rapid kinetics. We are attemping to optimize the performance of the material in the presence of competing cations by refining the synthesis and dopant chemistry.

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