Environmental Management Science Program

Project ID Number 54735

Development of Inorganic Ion Exchangers for Nuclear Waste Remediation

Abraham Clearfield
Texas A&M University
P.O. Box 300012
College Station, Texas 77842-3012
Phone: 409-845-2936
E-mail: pjf2434@acxrd.chem.tamu.edu

B. Zane Egan
Oak Ridge National Laboratory
MS 6223
P.O. Box 2008
Oak Ridge, Tennessee 37831-2008
Phone: 423-574-6868
E-mail: eganbz@ornl.gov

A. I. Bortun
Texas A&M University
P.O. Box 300012
College Station, Texas 77842-3012
Phone: 409-845-2936

L. N. Bortun
Texas A&M University

S. Khainakov
Texas A&M University

P. Sylvester
Texas A&M University

June 1, 1998

Development of Inorganic Ion Exchangers for Nuclear Waste Remediation

Abraham Clearfield, Texas A&M University

B. Zane Egan, Oak Ridge National Laboratory

A. I. Bortun, Texas A&M University

L. N. Bortun, Texas A&M University

S. Khainakov, Texas A&M University

P. Sylvester, Texas A&M University

Research Objective

To expand our efforts to provide families of inorganic ion exchangers useful on a global scale. In carrying out this objective, we will synthesize a variety of ion exchange materials, determine their structures and where necessary alter these structures to build in the desired properties. The underlying thermodynamic, kinetic and molecular basis of ion exchange behavior will be elucidated and their suitability for nuclear waste remediation will be assessed.

Research Progress and Implications

As of September 1, 1996, we have synthesized a number of highly selective inorganic ion exchangers, determined their crystal structures and elucidated the mechanism of exchange for a number of these exchangers.

1. $\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ (CST). This compound is the most highly selective Cs^+ exchanger known and is also selective for Sr^{2+} . The structure of this compound was solved from powder data¹ and found to have a framework structure enclosing unidimensional tunnels. For alkali metals the exchange sites were found to vary depending upon the size of the cation. Li^+ and Na^+ are small enough to fit into framework sites which accommodate half the required cations. The remainder lie within the tunnels. The larger Cs^+ cannot fit into the framework sites and can occupy only half the tunnel sites. Thus, only 25% of the total exchanger sites is available to Cs^+ . However, the Cs^+ -O bonds that form are exactly equal to the sum of the radii for Cs^+ and O^{2-} . All other cations have a poorer fit and tend to be displaced for Cs^+ . In the presence of Na^+ dual exchange occurs simultaneously³ as Na^+ fills the framework sites and a second site inside the tunnels. As the sodium ion concentration increases the uptake of Cs^+ decreases and is only 0.05-0.1 meq/g in simulants of Hanford Tank Waste Solutions.

We have recently carried out a neutron diffraction study of $\text{H}_2\text{Ti}_2\text{O}_3\text{SiO}_4$. All the protons reside on the oxygens bonded to titanium. Addition of water results in about half the protons forming hydronium ion within the tunnels.² This highly acid character of the protons we attribute to the fact that the OH oxygens are each bonded to three Ti^{4+} ions. This results in a very high repulsion towards the protons resulting in a high ionization constant. Addition of Cs^+ to this protonated form at pH2 results in saturation of the Cs^+ site to form $\text{Cs}_{0.5}\text{H}_{1.5}\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot 2\text{H}_2\text{O}$.

Planned Activities

Implications and Planned Activities. We now understand how this (misnamed) crystalline silicotitanate (CST) is able to take up Cs^+ from highly acid and basic solutions containing high levels of electrolyte. We are obtaining thermodynamic data and obtain kinetic data. This combination of

structural, thermodynamic and kinetic data will allow engineers to apply this exchange to a variety of remediation problems. Structural studies relevant to Sr^{2+} exchange are planned for the near future. Substitutions within the framework will also be carried out.

2. Trisilicates: $\text{M(II)}_2\text{M(IV)} \text{Si}_3\text{O}_9\text{H}_2\text{O}$, ($\text{M(II)} = \text{Na}^+, \text{K}^+$, $\text{M(IV)} = \text{Ti, Sn, Zr, Ce}$). We have prepared a family of trisilicates and solved the crystal structures of three of them.^{4, 5} These compounds have framework structures enclosing alternating large and small cavities. The cavity sizes vary with the size of the M(IV) cation. For example, the Ti phase does not take up Cs^+ but the Zr phase exhibits very high K_d values for Cs^+ (10^5 ml/g in groundwaters) and is even 1500 ml/g in 6M NaOH . The mixed phase $\text{Na}_2\text{Zr}_{0.75}\text{Sn}_{0.25}(\text{Si}_3\text{O}_9)\text{H}_2\text{O}$ shows even higher K_d values. The interchangeability of the M(IV) ion changes the size of the cavities and governs the selectivity. This is an excellent example of crystal engineering. The mechanism of exchange is complex involving both cavities.

Implications and Planned Activities This family of exchangers can be prepared hydrothermally and should not be too expensive (\$5 - \$10 per lbs.). It can be utilized for groundwater remediation and process waters which are alkaline. We plan to analyze the wealth of structural data we have accumulated in the light of the ion exchange behavior and to examine their behavior towards divalent metals. We have already shown that we can remove Pb^{2+} and Cd^{2+} from contaminated effluents. Further structural work will be carried out to elucidate the exchange mechanism (siting of ions) prior to thermodynamic and kinetic studies.

3. Pharmacosiderites: We have prepared a family of compounds based on the pharmacosiderite mineral structure⁶ solved their structures and determined the ion siting. The titanium silicate version, $\text{K}_3\text{H}(\text{TiO})_4(\text{SiO}_4)_3\text{H}_2\text{O}$ has a structure that is similar to that of the CST compound. It exhibits a high affinity for both Cs^+ and Sr^{2+} .⁷ The K_d values have been considerably improved by partial substitution of Ge for Ti.⁸ The structure of the Sr^{2+} phase is under investigation.

Implications and Planned Activities This study is another example of crystal engineering and we will continue to make additional substitutions by a computer modeling procedure to arrive at the best structure for exchange of Cs^+ and for Sr^{2+} . We will also probe the acidity of the proton form to compare with the CST. We have made a start on developing a theory of ion exchange behavior in tight tunnel structures and will use it as a guide in understanding the effect of different electrolytes on the selectivity in this and other similar exchangers.

Summary of Additional Studies

4. We have developed a simple technique to remove Sr^{2+} from tank wastes that contain high levels of complexants. The scheme is to add a cation that is preferentially complexed and so releases the Sr^{2+} to the solution that is readily removed with our strontium selective sodium nonatitanate.
5. We have prepared sodium micas and zirconia pillared clays that exhibit extremely high K_d values ($>10^5$) for Cs^+ in contaminated groundwater. They are superior to zeolites for Cs^+ removal and because of their low cost may be used as a barrier to Cs^+ movement in soils.
6. We have prepared a sodium niobium silicate that appears to have a pyrochlore structure. It is highly selective for Sr^{2+} in the presence of Ca^{2+} , Mg^{2+} and Na^+ .

Implications and Planned Activities Nuclear waste systems are highly diverse and one remediation process will surely not suffice for this diversity. Hence our global approach. In process and testing are four more families of exchangers.

Other Access To Information

Publications

1. D.M. Poojary, R.A. Cahill and A. Clearfield, Chem. Mater. 6, 2364 (1994).
2. D.M. Poojary, A.I. Bortun, L.N. Bortun, A. Clearfield, Inorg. Chem. 35, 6131 (1996).
3. A. Clearfield, A.I. Bortun, L.N. Bortun, Ion Exchange Developments and Applications, Proc. IEX '96, Royal Soc.

- Chem., London 182, 338 (1996).
4. A.I. Bortun, L.N. Bortun and A. Clearfield, Chem. Mater. 9, 1854 (1997).
 5. D.M. Poojary, A.I. Bortun, L.N. Bortun and A. Clearfield, Inorg. Chem. 36, 3072 (1997).
 6. E.A. Behrens, D.M. Poojary, and A. Clearfield, Chem. Mater. 8, 1236 (1996).
 7. E.A. Behrens and A. Clearfield, Microporous Mater. 11, 65 (1997).
 8. E.A. Behrens, D.M. Poojary and A. Clearfield, Chem. Mater., 10,, 959 (1998).