

EMSP Project No. 54735
Development of Inorganic Ion Exchangers for Nuclear Waste Remediation

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Number of Graduate Students: Currently 1, Total 3;
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One of the most compelling environmental problems facing our nation is the remediation of enormous stocks of nuclear waste that exists throughout the land. The waste takes many forms, high level waste (HLW) stored in tanks, contaminated groundwater and soils and as solid sludge. We have attempted to address each of these problems. One of the major techniques considered for remediation is the judicious use of ion exchange processes. We have concentrated on inorganic materials because they exhibit high selectivities for specific ions and because they are stable to the effects of radiation. In the past seven years we have received support from DOE initially through Battelle PNNL, then INEEL-Oak Ridge and through the EMSP. During that time we have synthesized about 50 ion exchange materials and characterized their ion exchange properties. In addition we have solved the crystal structures of the most crystalline exchangers and tracked the ion exchange processes by solving the structures of the partially and fully exchanged phases. This has led to a fundamental understanding of the exchange mechanisms from which we developed a theory that the selectivity for a particular ion is a function of ion size relative to the size of the tunnel or cavity present in the framework type exchangers. A prime example is that of sodium titanosilicate.

Research Progress and Implications

1. $\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot 2\text{H}_2\text{O}(\text{CST})$. 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 data 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 are 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 by Cs^+ . In the presence of Na^+ dual exchange occurs simultaneously as Na^+ fills the framework sites and a second site inside the tunnels. As the sodium ion concentration increases the uptake of Cs^+ site decreases to 0.05 - 0.1 meq/g in tank waste simulants.
2. Trisilicates: $\text{M(I)}_2\text{M(IV)}\text{Si}_3\text{O}_9 \cdot \text{H}_2\text{O}$, ($\text{M(I)} = \text{Na}^+, \text{K}^+$, $\text{M(IV)} = \text{Ti, Sn, Zr, Ce}$). We have prepared a family of trisilicates and solved the crystal structures of three of them. 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 $\text{Na}_2\text{Zr}_{0.75}\text{Sn}_{0.25}(\text{Si}_3\text{O}_9)\cdot\text{H}_2\text{O}$ shows even higher Kd 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 where substitutions within the framework change selectivities.

3. **Pharmacosiderites:** We have prepared a family of compounds based on the pharmacosiderite mineral structure, solved their structures and determined the ion siting. The titanium silicate version, $\text{K}_3\text{H}(\text{TiO})_4(\text{SiO}_4)_3\cdot n\text{H}_2\text{O}$ 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 Kd values have been considerably improved by partial substitution of Ge for Ti, another example of controlling selectivity. The structure of the Sr^{2+} phase is under investigation.

Sodium Nonatitanate: This compound, of composition $\text{Na}_4\text{Ti}_9\text{O}_{20}\cdot n\text{H}_2\text{O}$ is layered and the interlayer spacing varies with the water content. It is selective for Sr^{2+} in highly alkaline systems and the strontium is easily eluted with mild acid solutions. It works well under column flow conditions and is stable to irradiation. The main interference is Ca^{2+} .

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 or CST. This really works!

5. We have prepared sodium micas and alumina and zirconia pillared clays that exhibit extremely high Kd values ($>10^5$) for Cs^+ in contaminated groundwater. They are superior to zeolites for Cs^+ removal and may be used as a barrier to Cs^+ movement in soils. The sodium mica traps the Cs^+ permanently.

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 Future Work: A major failing of the EMSP program is a lack of focus on actual remediation. We had almost no contact with people involved in the actual remediation. Although, we published more than thirty papers we received no inquiries or comments from any DOE personnel. Since we were not refunded, we cannot follow through on our theory of how to improve selectivity for targeted ions. Also, my team of post-docs and graduate students all left due to lack of funding.

In the interim we submitted a proposal on sludge treatment in collaboration with a team at CSIRO, Australia and phytoremediation with the Institute for Sorption and Problems of Endoecology (ISPE) in the Ukraine. Both were rejected. ISPE has demonstrated a 2-4 fold increase in radionuclides removal from contaminated soil at Chernobyl and CSIRO has shown that their process removes radioactive ions from heavy metal minerals. Unless some interest is shown in our work, I plan to move on to greener pastures such as nuclear medicine.