

# **Environmental Management Science Program**

**Project ID Number 54735**

## **Development of Inorganic Ion Exchangers for Nuclear Waste Remediation**

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June 1, 1998

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## Development of Inorganic Ion Exchangers for Nuclear Waste Remediation

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### 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  $\text{Cs}^+$  exchanger known and is also selective for  $\text{Sr}^{2+}$ . The structure of this compound was solved from powder data<sup>1</sup> 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.  $\text{Li}^+$  and  $\text{Na}^+$  are small enough to fit into framework sites which accommodate half the required cations. The remainder lie within the tunnels. The larger  $\text{Cs}^+$  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  $\text{Cs}^+$ . However, the  $\text{Cs}^+$ -O bonds that form are exactly equal to the sum of the radii for  $\text{Cs}^+$  and  $\text{O}^{2-}$ . All other cations have a poorer fit and tend to be displaced for  $\text{Cs}^+$ . In the presence of  $\text{Na}^+$  dual exchange occurs simultaneously<sup>3</sup> as  $\text{Na}^+$  fills the framework sites and a second site inside the tunnels. As the sodium ion concentration increases the uptake of  $\text{Cs}^+$  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.<sup>2</sup> This highly acid character of the protons we attribute to the fact that the OH oxygens are each bonded to three  $\text{Ti}^{4+}$  ions. This results in a very high repulsion towards the protons resulting in a high ionization constant. Addition of  $\text{Cs}^+$  to this protonated form at pH2 results in saturation of the  $\text{Cs}^+$  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  $\text{Cs}^+$  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  $\text{Sr}^{2+}$  exchange are planned for the near future. Substitutions within the framework will also be carried out.

2. Trisilicates:  $\text{M(I)}_2\text{M(IV)}\text{Si}_3\text{O}_9\text{H}_2\text{O}$ , ( $\text{M(I)} = \text{Na}^+, \text{K}^+$ ,  $\text{M(IV)} = \text{Ti, Sn, Zr, Ce}$ ). We have prepared a family of trisilicates and solved the crystal structures of three of them.<sup>4, 5</sup> These compounds have framework structures enclosing alternating large and small cavities. The cavity sizes vary with the size of the  $\text{M(IV)}$  cation. For example, the Ti phase does not take up  $\text{Cs}^+$  but the Zr phase exhibits very high  $K_d$  values for  $\text{Cs}^+$  ( $10^5$  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  $\text{M(IV)}$  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  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  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 structure<sup>6</sup> 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  $\text{Cs}^+$  and  $\text{Sr}^{2+}$ .<sup>7</sup> The  $K_d$  values have been considerably improved by partial substitution of Ge for Ti.<sup>8</sup> The structure of the  $\text{Sr}^{2+}$  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  $\text{Cs}^+$  and for  $\text{Sr}^{2+}$ . 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  $\text{Sr}^{2+}$  from tank wastes that contain high levels of complexants. The scheme is to add a cation that is preferentially complexed and so releases the  $\text{Sr}^{2+}$  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  $\text{Cs}^+$  in contaminated groundwater. They are superior to zeolites for  $\text{Cs}^+$  removal and because of their low cost may be used as a barrier to  $\text{Cs}^+$  movement in soils.
6. We have prepared a sodium niobium silicate that appears to have a pyrochlore structure. It is highly selective for  $\text{Sr}^{2+}$  in the presence of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ .

**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 few families of exchangers.

## Other Access To Information

### Publications

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