ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

Organized by

T. Zachry

Symposia Papers Presented Before the Division of Environmental Chemistry
American Chemical Society
Anaheim, CA March 28 – April 1, 2004

ORIGIN OF SELECTIVITY IN TUNNEL TYPE INORGANIC ION EXCHANGERS

Abraham Clearfield[1], Akhilesh Tripathi[1], Dmitri Medvedev[1],
Jose Delgado[1] and May Nyman[2]
[1]Department of Chemistry, Texas A&M University,
P.O. Box 30012, College Station, TX 77843-3255
Clearfield@mail.chem.tamu.edu, fax 979-845-2370, atripathi@mail.chem.tamu.edu,
medvmitr@cedar.tamu.edu, akira5284@neo.tamu.edu
[2]Sandia National Labs, P.O. Box 5800, MS 0755, Albuquerque, NM 87185-0755
mdnyman@sandia.gov

The removal of highly radioactive species ^{137}Cs and ^{90}Sr from Weapon's grade Tank Waste is a daunting task. The tanks normally are 5-7M in Na^+, 1-3M in NaOH but only ~10^{-5}M in the targeted species. Nevertheless several sorbents and ion exchangers have been found that are sufficiently selective to be considered for remediation purposes. We are involved in a collaborative study, joint with personnel at the Westinghouse Research Center, Sandia National Laboratory and University of Notre Dame to uncover the origins of this selectivity in these compounds. The presentation will be concerned with the framework titanium silicates with the sitinikite and pharmacosiderite structures.

Synthetic sitinikite has the ideal formula $Na_2Ti_2O_3(SiO_4)\bullet 2H_2O$ and was first prepared at Sandia National Laboratory. The crystals are tetragonal *a* = 7.8082(2), *c* = 11.9735(4) Å with four formula units per unit cell. The titanium atoms occur in clusters of four grouped about a 4_2 axis, two up and two down rotated by 90°. Each titanium is octahedrally coordinated, sharing edges in such a way that an inner core or four oxygens and four Ti atoms form a distorted cubane-like structure[1]. These cubane-type structures are bridged to each other through silicate groups along the *a*- and *b*-axis directions. The titanium-oxygen clusters are 7.81 Å apart in both the *a*- and *b*-axis directions with the Si atoms at Z = ¼, ¾. In the *c*-axis direction, the Ti atoms are bridged by oxo-groups. The *c*-axis is approximately 12 Å long, which is twice the distance from the center of one

cubane-like cluster to its neighbor in the *c*-axis direction. This arrangement produces tunnels parallel to the *c*-axis direction. Perpendicular to the tunnels are vacancies in the faces or four sides enclosing the tunnel. Half the Na^+ are held in these cavities and the remainder reside in the tunnels. Cs^+ can readily exchange for Na^+ within the tunnel but not Na^+ in the framework sites. The cesium ions are eight coordinated at distances from the framework oxygens approximately equal to the sum of the Cs-O ionic radii.

The K_d values for Cs^+ -Na^+ exchange are extraordinarily high but fall off to very low values under conditions simulating those in Nuclear Tank Wastes. However, substitution of 25 mol% Nb(V) for Ti(IV) eliminates half the Na^+ from the tunnels. The Cs^+ in the Nb substituted framework forms a twelve coordinate compound[2], with eight framework oxygens and four water molecules. Because of this high coordination number the selectivity for Cs^+ is sufficiently enhanced to remove Cs^+ from nuclear waste solutions.

In exchange reactions for Sr^{2+} the reverse is true. The Nb containing phase forms a seven coordinate complex whereas the non-Nb form gives a ten coordinate Sr^{2+} complex.

Pharmacosiderite is the name of a natural mineral of composition $K(FeOH)_4(PO_4)_3 \bullet H_2O$. The titanium silicate analog is $K_3H(TiO)_4(SiO_4)_3 \bullet 4H_2O$. It has the same cluster of four TiO_6 octahedra bridged by silicate groups but it is cubic. As a result it has three intersecting tunnels perpendicular to each other. Exchange of Cs^+ and Sr^{2+} in these and Ge substituted forms will be described[3].

ACKNOWLEDGEMENTS
This research was supported by the U.S. Department of Energy's Environmental Management Science Program grant no. DE-FG07-01ER6300 with funds supplied through Westinghouse Savannah River Technology Center. Research carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory is supported by the U.S. DOE, Division of Materials Sciences and Division of Chemical Sciences, under contract no. DE-AC02-98CH10886.

REFERENCES
1. D. M. Poojary, R. A. Cahill and A. Clearfield, *Chem. Mater*. **6** 2364 (1994).
2. A. Tripathi, D. G. Medvedev, M. Nyman and A. Clearfield, *J. Solid State Chem*. **175**, 72 (2003).
3. A. Clearfield, *Solid State Sci*. **3**, 103 (2001).