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The Chemical Forces and Mechanisms for Radiological Selectivity in Nanoporous Materials

Topic M: Nano-Structured Porous Materials

HDTRA1-08-10-BRCWMD-Service Call

Sandia National Laboratories

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1. Introduction:

Identification of the research: Topic M "Nano-structured Porous Materials".

The ability to predict and design separations materials with high selectivity in extreme environments is of importance for applications involving separation and removal of specific actinides and fission products for sensing, protecting and securing chemical warfare agents, Toxic Industrial -Chemicals and -Materials (TICs and TIMs). We are interested in applying our expertise to the fundamental understandings of chemical selectivity in multicomponent separations matrices. In particular, nanoporous inorganic ion exchangers are useful in the highly selective sequestration of actinides, lesser fission products and other radiological ions from extreme environments. Not only are they highly selective to ≈ 0.1Å size scale, they are also robust over a wide chemical and thermal range. It is particularly desirable to have the ability to predictably "tune" the selectivity of ion exchangers for a particular ion in extremely complex multicomponent streams. We will use our expertise in synthesis, materials characterization and modeling to address the underlying chemical mechanisms associated with "why" particular porous ion exchanger materials crystallize, and "how" ion exchange selectivity works on the nanoscale. We will have a particular emphasis on the competition between electrostatics, geometric constraints, and ion energetics (i.e., cation sphere of hydration).

2. Proposed Technical Approaches:

Exploratory research will be based on our combined years of experience in materials synthesis and characterization. Combining low temperature (RT-200°C) hydrothermal techniques for ion exchanger synthesis with structure identification techniques, we intend to determine which parameters are critical to the nanoscale formation of open structures and then pursue the synthesis of predicted selective ion exchanger materials. We will combine the synthesis with materials' characterization including electron microscopies (HRTEM, SEM/EDX), Magic Angle Spinning (MAS) NMR and thermal/elemental analyses. We will work to address a central hypothesis: that selectivity for high capacity frameworks is dictated by the geometry of ion exchange sites, the electrostatic energy at those sites, and the favorable energy of the ions.

Objectives: We propose a fundamental research program to answer the following questions:

- What chemical forces drive the operative reactions (i.e., crystallization) and can such understanding lead to the synthesis of other new classes of tailored separation materials?
- What chemical mechanisms are responsible for observed selective ion exchange? What are the atomic scale origins of selectivity in these materials?
- How will understanding nanoscale chemical mechanisms, such as binding energies, adsorption kinetics, and site selectivity lead to the synthesis of new separations media?

This program contains a two pronged approach. First we will use our experience and knowledge in the basic materials synthesis, characterization, and molecular simulation of ion exchangers to explore new materials phase spaces. Second, we will be using state-of-the-art crystallography techniques and facilities in our pursuit of understanding the mechanisms of nanoscale structure formation and structure/property relationships to ion exchange selectivity.

Gaining full understandings as to how their nanoscale structure affects their bulk properties and characteristics, we will employ a number of characterization techniques. We will test and amend this theory from nanoscale studies conducted on crystallizing reaction gels using *in situ* and time-resolved small angle neutron (SANS), X-ray scattering (SAXS) and traditional wide angle X-ray scattering (WAXS) techniques. [1-3] Furthermore, we will use inelastic neutron scattering (INS) techniques to study the role of H-bonding of water to ions in the pores.

In particular, we plan to leverage our earlier successes with ion exchange materials to develop new highly selective phases for the sequestration of actinides and other radiological ions from extreme environments. In particular, we will use our experience in synthesis and characterization of our SOMS system. [4] The novel niobate-based *Sandia Octahedral Molecular Sieves* (*SOMS*; Figure 1; $Na_2Nb_{2-x}M_xO_{6-x}(OH)_x{\bullet}H_2O$) were developed in an effort to discover micro- and nano-porous ion-exchangers suited to the selective removal of toxic cations from environmentally benign ones. [4-8] In particular, the SOMS has high selectivity toward divalent cations such as Sr^{2+}, Pb^{2+} and Cd^{2+}. Our recent INS studies results suggest that the selectivity of this material is derived from a combination of its unique structure **plus** the H-bonding relationship between ions and occluded water molecules in the pores. [6]

3. Potential Scientific Impact:

Our research approach to obtaining fundamental information on ion exchange selectivity builds on existing expertise and capabilities at SNL including:

Synthesis of known Highly Selective Ion Exchangers: Sandia has discovered highly selective ion exchangers for radioactive Cs^+ and Sr^{2+} sequestration, respectively. We have expertise for the synthesis of novel ion exchange materials and then fully characterizing them for structure / property relationships regarding selectivity for Hanford tank applications (see Figure 1). We will leverage our successes into studies of novel amorphous, 2D and 3D crystalline phases.

***Ion Exchanger Characterization*:** Structural Studies – a combination of multinuclear solid state NMR methods and structural characterization methods (TEM, XRD, BET, TGA/DTA) will be used to determine the structural characteristics of the framework materials. Structural Studies - These techniques include (1) powder and single crystal X-ray and neutron diffraction, (2) Transmission Electron microspcopy (HRTEM), (3) Magic-Angle Spinning (MAS) NMR, (4) *in-situ* synchrotron X-ray and neutron diffraction, and (5) inelastic neutron scattering (INS, fig. 1).

Molecular Simulation: Large-scale (>10,000 atoms) Molecular Dynamics modeling, based on codes we developed earlier [9], will be performed to predict selectivity and preferential diffusion of ions in Ion Exchanger materials. [10] We will also continue our research into the role of hydrogen-bonding for internal pore ion solvation by the use of accurate energy force field methods to characterize the interactions and disposition of exchangeable ions and water in the pores. [11] Exchange enthalpies, ion and water diffusion rates, and velocity autocorrelation-based power spectra will be derived for a suite of framework and exchangeable ion compositions with variable water content.

4. Potential Team and Management Plan:

The Sandia team includes Nenoff (synthesis), Cygan (simulation), Alam (NMR), Huang (TEM). Sandia principal investigators (PIs) and project managers. The project will be structured, as delineated by a work breakdown structure. Project milestones will be established, with deliverables specified for each phase of the project. Quarterly and annual reports will be used to formally document and update project team members on the status, milestones and successes. **Yearly breakdown plan: Yr1** – Identification of needed ion exchange material based on targets (size, charge, elemental soft/hard), synthesis and predictive modeling of interactions; **Yr2**- fully characterization of materials plus pure component ion exchange studies; **Yr3**- validation of models by optimized synthesis and characterization, plus complex stream ion exchange studies.

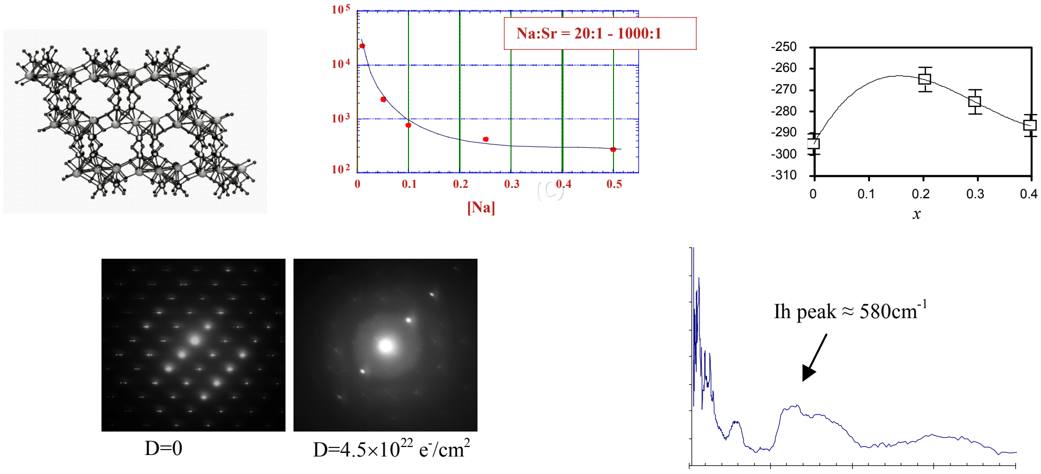
5. Summary of Estimated Costs:[1]

FY09 - $350K
FY10 - $375K
FY11 - $400K

References:

[1] Cahill, et.al, *Chem. Geo* **2000**,*167*, 53. [2] Parise, J.B.; Cahill, Lee, *Can. Mineral*., **2000**, *38*, 777. [3] Lee, et.al. *Proc. 12th Int. Zeolite Assoc.,* MRS, 1999, IV, 2401. [4] Nenoff, T. M., etal., *JACS.*, **2001**, *123*, 1529; (b) Nenoff, T. M., Parise, J.B.; et.al.; *JACS*, **2002**, *124*, 1704; (c) Nenoff, T. M.; Nyman M. US Patent # 6,596,254, 7/22/03; (d) Nenoff, T. M., et al; *J. Mater. Res*., **2005**, *20*, 618; (e) Nenoff, T.M., et al; *Chem. Mater*., **2005**, *17*, 950; (f) Nenoff, T. M.; Navrotsky, A., et.al.; *Chem. Mater*., **2004**, *16*, 2034; (g) Nenoff, T. M.; etal, US Patent #7,122,164, 2006. [5] a) Nenoff, T.M., et.al. *Chem. Mater.* **2000**, *12*, 3449; b) Nenoff; T. M., et al., *Chem. Mater*., **2002**, *13*, 4603. (c) Nenoff, etal. US Patent # 6,482,380, 2002. [6] Nenoff, T.M., et.al. J. Phys. Chem. C, **2007,** *111*(35), 13212. [7] Navrotsky; Nenoff, et.al., *J. Mater. Res*., **2000**, *15*(3), 815. [8] Parise, et.al, *JACS,* **2000**, *122*, 11023. [9] Cygan, R.T., etal. *J. Phys Chem B* **2004**, 108(4), 1255. [10] Cygan, R.T., et.al., *Chem. Mater.* **2004**, *16*(11), 2121. [11] Ockwig, N.W., Nenoff, TM; et.al. *J Phys Chem C*, **2008**, *10*, 800.

Figure 1 [4,6]: 1) SOMS structure, 2) selectivity for Sr^{2+}, 3) thermodynamics vs. dopant (x=Ti) level, 4) radiation stability, 5) INS data of ice-like water formation inside pores of SOMS x=0



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[1] As a DOE/NNSA government owned, contractor operated national laboratory and Federally Funded Research and Development Center (FFRDC), Sandia is required to achieve full cost recovery on any work for others efforts in accordance with DOE policy. As a result, Sandia cannot accept the 35% cap on indirect costs as set forth in Pub. L. No. 110-116, §8115 if such 6.1 funds (DoD Basic Research FY08 Funding) are awarded. DOE General Counsel is addressing this issue with DoD since it's believed the intent of the legislation was NOT to preclude DOE/NNSA FFRDCs from providing their unique capabilities in support of efforts that benefit both DoD and DOE/NNSA. However, until this issue is resolved, Sandia will not be able to accept work awarded using the aforementioned funding source if the limitation on indirect is required.