ZEOLITES AND FELDSPATHOIDS

Tuesday June 22, 2004

Zeolites and Feldspathoids Poster Session	
5:00p	**CANCRINITE AND SODALITE FORMATION IN THE PRESENCE OF Cs^+, K^+, Mg^{2+}, Ca^{2+}, or Sr^{2+} IN HANFORD TANK WASTE SIMULANTS.** Youjun Deng[1*], Markus Flury[1], James B. Harsh[1], and James S. Young[2] [1]Department of Crop and Soil Sciences, Center for Multiphase Environmental Research, Washington State University, Pullman, WA 99164-6420. [2] Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, Richland, WA 99352
	STABILITY OF INCORPORATED Cs IN FELDSPATHOIDS, ZEOLITES AND ALLOPHANE FORMED IN HANFORD TANK WASTE SIMULANTS. Youjun Deng[1], Nu Nu Wai[1*], Markus Flury[1], James B. Harsh[1], and James S. Young[2] [1]Department of Crop and Soil Sciences, Center for Multiphase Environmental Research, Washington State University, Pullman, WA 99164-6420. [2] Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, Richland, WA 99352

Wednesday June 23, 2004

Zeolites and Feldspathoids I	
9:00 – 9:40a	**CONVENTIONAL AND UNCONVENTIONAL ZEOLITES: THERMODYNAMICS OF FORMATION, HYDRATION AND ION EXCHANGE.** Alexandra Navrotsky Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, CA 95616, U.S.A.
9:40 – 10:00a	**MOLECULAR CHARACTERIZATION OF STRONTIUM UPTAKE AND TRANSFORMATION WITH KAOLINITE REACTED AT HIGH pH.** Sunkyung Choi*[1,2], Peggy O'Day[2], Mary Kay Amistadi[1], and Jon Chorover[1] [1]University of Arizona, Department of Soil, Water and Environmental Science, Tucson, AZ 85721; [2]University of California, School of Natural Sciences, Merced, CA 95344
Zeolites and Feldspathoids II	
10:20 – 11:00a	**OPTICAL, MAGNETIC AND ELECTRONIC PROPERTIES OF NATURAL AND SYNTHETIC FELDSPATHOIDS.** Mark T. Weller[*1], Tom A. Mayer[1], and Sandra E. Dann[2] [1]School of Chemistry, University of Southampton, Southampton SO17 1BJ UK; [2]Department of Chemistry, Loughborough University, Leicestershire, LE11 3TU
11:00 – 11:40a	**VOC SORPTION BY HYDROPHOBIC ZEOLITES, AND THE EFFECTS OF CONFINED WATER.** Robert W. Thompson[*1], Arjan Giaya[1], Mathieu Fleys[1], A. Bergendahl[1], John C. MacDonald[1], Aye Erdem-Enatalar[2] [1]Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609; [2]Department of Chemical Engineering, Istanbul Technical University, Istanbul, Turkey

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ZEOLITES AND FELDSPATHOIDS

POSTER SESSION

5:00PM

CANCRINITE AND SODALITE FORMATION IN THE PRESENCE OF Cs^+, K^+, Mg^{2+}, Ca^{2+}, or Sr^{2+} IN HANFORD TANK WASTE SIMULANTS

Youjun Deng[1*], Markus Flury[1], James B. Harsh[1], and James S. Young[2]

[1]Department of Crop and Soil Sciences, Center for Multiphase Environmental Research, Washington State University, Pullman, WA 99164-6420. [2] Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, Richland, WA 99352

High-level radioactive tank waste solutions at the U.S. DOE Hanford Site, Washington, have complex chemical compositions. Some of the tank waste leaked into the subsurface. It was reported that under simulated laboratory conditions, two feldspathoids, cancrinite and sodalite, formed when tank waste solutions contacted sediment minerals. Here, we investigated the effect of different cations, Cs^+, K^+, Sr^{2+}, Ca^{2+}, and Mg^{2+}, on mineral formation and transformation pathways under conditions mimicking Hanford tank leaks. We used sodium silicate to represent the dissolved silicate from sediments. We prepared a series of simulants that contain 0.5 M of aluminate, 1 M or 16 M NaOH, and the nitrate salts of the cations. The precipitates were monitored by X-ray diffraction, scanning electron microscopy, and X-ray energy dispersive spectroscopy. In the 1 M NaOH simulants, low concentration of Cs^+ (< 100 mM) did not affect the formation of lepispheric cancrinite and sodalite, whereas only highly crystalline cancrinite formed when Cs^+ was >250 mM. An unidentified feldspathoid or zeolite intermediate phase was observed in the presence of high concentration of Cs^+. The presence of K^+ did not alter but slowed down the formation of cancrinite and sodalite. The presence of divalent cations can lead to the formation of intermediate or stable silicates, aluminates, hydroxides or even aluminosilicates. Formation of these intermediate phases slowed down the formation of cancrinite and sodalite by consuming OH^-, silicate or aluminate. Compared with the concentrations used in this study, radioactive Cs^+ and Sr^{2+} in the tank solutions are much smaller than those used in our experiments, and released divalent cations from sediments likely precipitate out as hydroxides, silicates, or aluminates. Therefore, we do not expect that these monovalent and divalent cations affect the formation and transformation pathways of cancrinite or sodalite in the sediments underneath the leaked waste tanks.

STABILITY OF INCORPORATED Cs IN FELDSPATHOIDS, ZEOLITES AND ALLOPHANE FORMED IN HANFORD TANK WASTE SIMULANTS

Youjun Deng[1], Nu Nu Wai[1*], Markus Flury[1], James B. Harsh[1], and James S. Young[2]

[1]Department of Crop and Soil Sciences, Center for Multiphase Environmental Research, Washington State University, Pullman, WA 99164-6420. [2] Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, Richland, WA 99352

Cesium-137 is the major radioactive element in the high-level radioactivity waste tanks at the U.S. DOE Hanford site. Cancrinite and sodalite have been found as the neoformed stable mineral phases when Hanford sediments contacted the waste simulants. Allophane, Linde Type A (LTA) zeolite, and a 3-dimension-cross shaped feldspathoid or zeolite have been observed as the intermediate phases in our previous simulation experiments. We investigated the incorporation of Cs^+ and the stability of the incorporated Cs^+ in these metastable and stable minerals and short-range ordered materials. These materials were synthesized in the presence of $CsNO_3$, CsCl, or CsOH according to previous experiment results. Mineral phases were verified with X-ray diffraction and electron microscopic analyses. The incorporated Cs^+ was quantified by atomic absorption spectroscopy after digestion in 1 M HCl. Four hundred milligram of each mineral or short-range ordered material was exchanged three times with 0.25 M Ca^{2+}, 0.5 M K^+ or 0.5 M Na^+ at 80 °C, and three times with water at room temperature. For each time of ion exchange treatment, the solid and cation solution were in contact for 24 hours with 20 minutes shaking for every two hour interval. The solid was separated by centrifugation and mixed with fresh solutions. No morphology changes were found after the ion exchange treatment, yet crystal expansion by K^+ was detected by XRD on lepispheric sodalite and cancrinite. Very little (<2%) of the incorporated Cs^+ was replaced by the cations in a highly-crystalline cancrinite formed in the presence of CsCl, whereas 57% of Cs^+ was replaced by K^+ in another highly-crystalline cancrinite formed in the presence of $CsNO_3$. Cesium in lepispheric sodalite showed strong resistance to cation exchange, and less than 15% of the incorporated Cs^+ was replaced by the cations. Cesium in LTA zeolite, the 3-dimensional cross-shaped fledspathoid or zeolite, and allophone were rapidly replace by the cations, more than 98% of the incorporated Cs^+ was replaced by K^+ or Na^+ in LTA zeolite and the unidentified fledspathoid or zeolite. Potassium showed the strongest ability of replacing Cs^+, whereas Ca^{2+} showed stronger ability than Na^+ in lepispheric cancrinite and sodalite, but weaker ability than Na^+ in LTA zeolite, the 3-dimension-cross shaped feldspahtoids or zeolite, and allophane. Elemental mapping data support the ion exchange reaction and also indicate that ion exchange reaction occurred homogeneously in the bulk of the small particles. The stability of Cs^+ in the minerals more likely depends on the size of the apertures of the channels and cages in the feldspathoids and zeolites. Transmission electron microscopic analysis indicates structural stacking fault was not an important factor in controlling the stability of incorporated Cs^+.

WEDNESDAY JUNE 23, 2004

ZEOLITES AND FELDSPATHOIDS I

9:00AM

CONVENTIONAL AND UNCONVENTIONAL ZEOLITES: THERMODYNAMICS OF FORMATION, HYDRATION AND ION EXCHANGE

Alexandra Navrotsky

Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, CA 95616, U.S.A.

Microporous molecular sieves, including zeolites sensu stricto, are important in nature and technology for catalysis, ion exchange, and water retention. Natural zeolites (clinoptilolite and others) are important in backfill and surrounding strata for nuclear repositories such as Yucca Mountain. Synthetic silicotitanate and niobate molecular sieves have been designed to have high selectivity of cesium over sodium and of strontium over calcium. Liquid tank wastes at Savannah River and Hanford sites, rich in sodium, aluminum, silicon, and nitrate, precipitate sodalite and cancrinite phases as unwanted products. The thermodynamics of these three classes of systems have been studied by high temperature oxide melt solution calorimetry. The interplay of thermodynamic and kinetic factors in the formation of these materials, in ion exchange, and in their calcination to dense ceramics is summarized.

MOLECULAR CHARACTERIZATION OF STRONTIUM UPTAKE AND TRANSFORMATION WITH KAOLINITE REACTED AT HIGH pH

Sunkyung Choi*[1,2], Peggy O'Day[2], Mary Kay Amistadi[1], and Jon Chorover[1]

[1]University of Arizona, Department of Soil, Water and Environmental Science, Tucson, AZ 85721; [2]University of California, School of Natural Sciences, Merced, CA 95344

Microscopic and molecular-level spectroscopic investigations were conducted to elucidate the chemical behavior of Sr in reacted purified specimen kaolinite (KGa-1) under extreme geochemical conditions at the Hanford Site in WA (0.05 M Al_T, 2 M Na^+, 1 M NO_3^-, pH~14, Cs^+ and Sr^{2+} present as co-contaminants). Time series batch experiments were conducted from 0 to 190 days, with initial Cs^+ and Sr^{2+} concentrations ranging from 10^{-3} to 10^{-5} M.

Chemistry, X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) and diffuse reflectance infrared Fourier transform spectra (DRIFT) data revealed a pronounced reactivity and secondary phase precipitation during the reaction time. Dominant secondary phases identified in the kaolinite system after 190 days were cancrinite, sodalite and chabazite.

Synchrotron-based extended X-ray absorption fine structure (EXAFS) was used to characterize the local coordination environment of strontium in reacted bulk kaolinite samples. Strontium K-edge measurements were performed with sample loadings of 10^{-3} M Cs and Sr at room temperature and compared with published data.

Fitting results of kaolinite samples reacted for 1 and 7 days show that the local atomic structure around strontium is similar to the structure of crystalline $SrCO_3$, which was not detected by XRD or SEM. Results may imply small particle size for the $SrCO_3$ precipitate or a small amount of $SrCO_3$ that is below detectionwith XRD. Kaolinite samples reacted for 33 days indicate that the $SrCO_3$ phase is transient and is replaced by another secondary phase. Fitting results of kaolinite samples reacted for 93 and 190 days indicate that strontium mainly is associated with zeolite phase(s). These results suggest that strontium uptake from solution may occur initially by formation of a transient carbonate phase, followed by localization into secondary zeolite phases that form at later reaction times.

Present findings are of importance with respect to reliable risk assessment of contaminants under the leaking tanks, as well as for the development of sustainable environmental management and protection strategies. Furthermore, the knowledge gained of the chemical behavior of strontium at high pH and high ionic strength have implications for the development of future ^{90}Sr waste treatment technologies and in-situ remediation schemes.

WEDNESDAY JUNE 23, 2004

ZEOLITES AND FELDSPATHOIDS II

10:20AM

OPTICAL, MAGNETIC AND ELECTRONIC PROPERTIES OF NATURAL AND SYNTHETIC FELDSPATHOIDS

Mark T. Weller[*1], Tom A. Mayer[1], and Sandra E. Dann[2]

[1]School of Chemistry, University of Southampton, Southampton SO17 1BJ UK; [2]Department of Chemistry, Loughborough University, Leicestershire, LE11 3TU

Synthetic semi-condensed zeolites or feldspathoids with compositions and structures based on naturally-occurring minerals provide a superb systems for controlling the key, application-oriented, electronic properties. Examples taken just from the sodalite system include pigments such as lapis lazuli / ultramarine, $Na_7[AlSiO_4]_6\{S_3\}$, photochromic materials such as hackmanite $Na_8[AlSiO_4]_6\{S, Cl\}$, magnetic properties, as in the transition metal based danalites, $M_8[BeSiO_4]_6.X_2$, M = Mn, Fe, Co, X = S, Se, Te, and electronic properties of the framework expanded semiconductors e.g. $Cd_8[AlO_2]_{12}.X_2$ X = S, Se, Te. Once materials such as the cancrinites, and other semicondensed zeolite topologies, such as the ABW and JBW types, are considered together with possible allied metal substitutions into the aluminosilicate frameworks, the range of feldspathoid-type materials with potentially useful applications grows very rapidly. This paper will initially discuss the properties of several naturally occurring feldspathoids/zeolites of this type and then show how chemistry can be used to improve upon Nature to control a specific optical, magnetic or electronic property of interest. So, for example, methods of producing improved synthetic ultramarines from natural and synthetic clays and zeolites will be discussed along with results of recent studies on synthetic photochromic hackmanites and danalites. The physical properties of these materials will be discussed in terms of the feldspathoid framework acting as “spacer” that controls the interactions between the embedded cations and anions, see Figure.

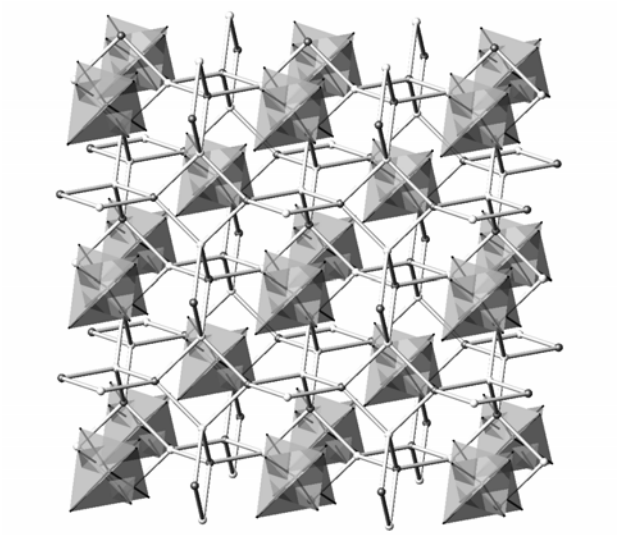

Figure. The structure of a sodalite of the type $M_8[TO_2]_{12}X_8$ shown as interpenetrating M_4X_4 blocks (polyhedra) separated by the TO_2 framework.

VOC SORPTION BY HYDROPHOBIC ZEOLITES, AND THE EFFECTS OF CONFINED WATER

Robert W. Thompson[*1], Arjan Giaya[1], Mathieu Fleys[1], A. Bergendahl[1], John C. MacDonald[1], Aye Erdem-Enatalar[2]

[1]Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609;
[2]Department of Chemical Engineering, Istanbul Technical University, Istanbul, Turkey

Volatile Organic Compounds (VOCs) can pose environmental problems in surface water and groundwater if left untreated. Recent studies of liquid and gas phase adsorption of VOCs (e.g., trichloroethylene [TCE] and methyl tertiary butyl ether [MTBE]) revealed some anomalous behavior in "hydrophobic" microporous zeolites. At very low concentrations the relatively small pore zeolite, silicalite-1, outperformed the larger pore material, a de-aluminated zeolite Y (DAY), even though both were about equally hydrophobic. It was speculated that the interference of water was responsible for the unexpected results.

The structure of water in confined spaces could be quite different from that of the bulk fluid. Therefore, a model for water confined in cylindrical micropores was developed, and will be discussed briefly. The equation of state accounts for fluid-fluid, fluid-wall, and hydrogen bonding interactions.

This model was used to analyze the density of water inside the micropores as a function of: a) the fluid density outside the pores, b) the pore radius, and c) the fluid-wall interaction affinity. The behavior of confined water in the presence of bulk <u>liquid</u> outside the pores was quite interesting: The model predicts that water should exist in a vapor-like state in the small pore silicalite, but could exist as a liquid phase in zeolite DAY.

More recent Molecular Dynamics calculations have provided supporting evidence for the existence of a liquid-like structure in zeolite Y, but a much less structured phase in the silicalite pore system. Therefore, the presence of a structured liquid-like water phase is predicted to disrupt the sorption of VOCs in some cases, but not in other cases.