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CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: DOE Radionuclide Adsorption Workshop and NRC/DOE Technical Interchange Meeting (20-3702-001)

DATE/PLACE OF TRIP: September 11-13, 1990; Los Alamos, New Mexico

AUTHORS: William M. Murphy and Roberto T. Pabalan

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AUTHORS: William M. Murphy and Roberto T. Pabalan

NRC REPRESENTATIVES PRESENT:

CNWRA	NRC
W.M. Murphy	G. Birchard
R.T. Pabalan	J. Bradbury
	R. Codell
LBL (for ACNW)	W. Ford
J. Apps	K. Stablein

BACKGROUND AND PURPOSE:

The Los Alamos National Laboratory hosted a workshop on radionuclide adsorption for the Department of Energy Yucca Mountain Project upon the recommendation of the Nuclear Waste Technical Review Board (NWTRB) in its report to the U.S. Congress and the Secretary of Energy. The general objectives of the workshop were: (1) to determine the applicability of available radionuclide adsorption data on tuff and models for predicting such adsorption under existing and postclosure conditions at Yucca Mountain, and (2) to establish what additional radionuclide adsorption research and model development are needed. The workshop was held in Los Alamos on September 11 and 12, 1990, and a subsequent NRC/DOE Technical Interchange Meeting on Sorption was held the following day to discuss and/or clarify technical issues regarding DOE's research program on radionuclide adsorption. The workshop was attended by approximately 65 people representing the NRC, the NWTRB, the State of Nevada, Los Alamos National Laboratory, the U.S. Geological Survey, Sandia National Laboratories, Lawrence Livermore National Laboratory, and the Yucca Mountain Project Office. Approximately fifteen representatives from the NRC, DOE and the State of Nevada attended the NRC/DOE/State of Nevada interchange meeting.

CONCLUSIONS/OBSERVATIONS:

The workshop was well-organized, and provided a forum for wide ranging technical discussions regarding sorption among experts from various national laboratories, universities and other organizations.

The workshop organizers will publish at some future date the papers that have been presented at the workshop, as well as their observations/recommendations arising from the workshop regarding the Yucca Mountain Project's sorption program.

SUMMARY OF THE WORKSHOP:

A copy of the workshop agenda is attached as Appendix 1. A copy of the workshop abstract summaries and outlines is available in the CNWRA library.

The following are notes taken during the various workshop presentations:

'Radionuclide Sorption Database - Experiments and Integration of Relevant Sorption Models' - A. Meijer, LANL.

A. Meijer presented an overview of the LANL Yucca Mountain Sorption Program (1977-1990). The key radionuclides that were studied or are being studied are based on those identified by Kerrisk (1985). The strategy for sorption studies involves empiricism (e.g., crushed rock and single mineral sorption studies) and theory (e.g., geochemical modeling). Sorption mechanisms comprise cation exchange, surface (or near-surface) adsorption, surface-induced precipitation (e.g., cluster formation), and true precipitation and coprecipitation (e.g., carbonates). Controls on cation exchange are steric effects, competition among cations, ionic strength, site energies, temperature, etc. Cation exchange reactions are treated by thermodynamic mass action relations. Selectivity coefficients for clinoptilolite exchange were originally established by Ames. For Yucca Mountain conditions the selectivity is $Cs^+ > Ba^{2+} \approx Ra_2^+ > Sr^{2+} > Ca^{2+} > K^+ > Na^+ > Am^{3+}$. Rd's for Cs are 10^4 ml/g for zeolitic tuff, 10^3 ml/g for devitrified tuff, and 10^2 ml/g for quartz/glass. 10^2 ml/g can be taken as a conservative minimum value. The strong pH dependence of Np sorption suggests an adsorption edge due to the pH dependence of surface adsorption. Triple layer models for adsorption are presently descriptive but not predictive. There are many complications: multiple elements, multiple phases, aqueous solution speciation vs. surface speciation, clustering, defect effects, crystallographic effects, impurities, etc. Therefore, whole rock Rd studies are most appropriate for Yucca Mountain applications. Beal and Allard give Kd data as a function of pH for Am (Kd > 100 ml/g, probably surface adsorption), Pu (Kd $\approx$ 100-1000 ml/g, difficult to interpret) and Np (Kd < 30 ml/g). For uranium, carbonate complexes are important and ion exchange with clinoptilolite is possible. Tc, I, and C are difficult to evaluate. Tc Rd's decrease in the order goethite > montmorillonite > hematite > clinoptilolite. In the unsaturated zone there may be water/rock ratio effects. Kd may decrease with W/R; unsaturated water chemistry is unknown, H_2O activity may change. For transport calculations a minimum (conservative) Kd approach is advocated. Discussion focused on the effects of fracture vs. matrix hydrology on sorption. Everett Jenne made the comment that given Freundlich isotherm fits to Kd data with nonunit exponents and the strong pH dependence of sorption isotherms, Kd's can not be used generally.

'Sorption and Porosity Heterogeneity: Effects on Radionuclide Migration' - Marilyn Bucholtz-ten Brink, LLNL.

Studies of actinide diffusion into tuff wafers analyzed by SIMS reveal a heterogeneous distribution exists at all scales associated with mineralogy and/or microporosity. Mercury porosimetry indicates a dual porosity: <0.1 micon and 10-100 microns. Calculated effective diffusion coefficients are 10^{-9} cm^2/sec for the fast path ($\approx$5%), 10^{-12} to 10^{-13} for the bulk (~95%), and 10^{-18} for grain boundaries ($\approx$0.1%). Dual porosity may lead to an apparent time dependence of dispersion. The experiments indicate that diffusion does not occur along a continuous front and occurs simultaneously at different rates due to different

mechanisms. Regions with greater concentrations of actinides are associated with greater porosity, microfractures, etc. Uranium sorptive capacity changes with composition of solution.

'Current Adsorption Models and Open Issues Pertaining to Performance Assessment' - Jeff Serne, PNL.

General and recent historical perspectives were given on retardation phenomena, noting NRC supported pronouncements from the mid-eighties, and references on saturated vs. unsaturated systems in Oblath (1989, Env. Sci. Tech, v. 23, p. 1098-1102) and Dougherty (1986, BNL52042).

'Modeling of Cation Exchange Processes Using EQ3/6' - Brian Viani, LLNL.

Clinoptilolite ion exchange modeling using an "exchanger" option for EQ6 makes use of two alternate exchange formulations: an ion reaction:

$$Na\text{-}Z + 1/2\ Ca^{2+} \Leftrightarrow 1/2\ (Ca\text{-}Z)_2 + Na^+$$

or an equivalent reaction:

$$Na\text{-}Z + 1/2\ Ca^{2+} \Leftrightarrow Ca_{0.5}\text{-}Z + Na^+.$$

The latter is equivalent to a solid solution equilibrium model. Na-Ca exchange data of Ames was modeled with 1 and 2 site exchange models. Yucca Mountain water and clinoptilolite data were matched using the exchange relations. K-clinoptilolite formed at high temperature may retain some K in low temperature exchange. Cs and Sr sorption data can be well explained using the exchange model. Calculated and measured Kd's for Yucca Mountain were compared.

'Sorption of Cesium and Strontium by Zeolite Single Crystals' - Roger Burns, MIT.

Experimental data show that sorption on the dominant (010) face of clinoptilolite is slow relative to sorption on other faces. Sorption decreased in $NaHCO_3$-rich waters. Daughters of Cs could affect sorption. Selectivity depends on the ionic radius of the species including its hydration sphere. 7 to 15 days are required to effect exchange with Cs in a 1 M CsCl solution.

'Sorption Model - Triple Layer Concepts' - Jim Leckie, Stanford.

Presented triple-layer adsorption model theory and data. Required data are acidity constants for surface species determined from titrations, the surface site concentration, the capacitance of the two adsorbed layers, aqueous speciation constants, and the equilibrium adsorption constant (for inner sphere or outer sphere bonding). The stoichiometry of surface complexes can be deduced from the pH dependence of sorption.

'Radionuclide Migration Studies for Validating Sorption Data - Past, Present, and Future' - Inez Triay, LANL.

Column transport experiments were modeled using batch Kd measurements. Sr, Cs, and Ba agree with Kd values. TcO_4^- and I^- show anion exclusion. Actinide speciation was important, and Pu(IV) eluted faster than conservative tracers due to size exclusion. Heterogeneities are important in intact tuff columns. Time-

dependent dispersion is required to rationalize constant batch Kd's. Diffusion tests confirm batch Kd's.

'Transport of Reactive Tracers by Unsaturated Flow Using Field and Column Experiments' - Peter Wierenga, LANL.

Discussed the use of mobile/immobile water and two-site models in the interpretation of experimental data. Large scale laboratory and field tests for low-level waste migration in unsaturated media show that small and large column tests give different results for Cr; the chemical sink may be different due to an oxidation state change (?). Differences in boron migration are due to dispersion effects.

'Transport in Unsaturated Flow Systems Using Centrifuge Techniques' - Jim Conca, Washington State University, Richland.

Studies of diffusion in unsaturated media and permeability of unsaturated media using ultracentrifugation show that the apparent diffusion coefficient is a strong function of volumetric water content due to a tortuosity effect. Measured permeabilities correspond very well to those measured by other techniques.

'Unsaturated Transport of Inorganic Cations in Undisturbed Soil Columns' - Phil Jardine, ORNL.

Presented trench and column experiments on soils from the ORNL.

'Radionuclide Transport and the Retardation Model' - Ken Eggert, LANL.

Presented three-dimensional models for flow and transport at Yucca Mountain using Kd's, and mineralogical and permeability heterogeneity. Advocated neglecting sorption in fractures in the unsaturated zone, and concentrating on retardation in the saturated zone.

'Lessons in Applying Coupled Geochemical Transport Models' - V. Nguyen, EWA.

Presented a theory for scaling microscopic kinetic phenomena to macroscopic systems.

Speakers were asked to give their most important observations or note the most important issues; these are summarized below:

J. Conca: Matrix-fracture relations.

P. Wierenga: Integration of chemistry and physics; integration of modeling and experimentation; large-scale (field) experimentation.

J. Serne: No priorities are clear in the program.

A. Meijer: Saturated vs. unsaturated flow and fracture flow; integration of chemistry and hydrology; use of minimum Kd's is the first step.

I. Triay: Lab scale experiments can be controlled; unsaturated testing will be

conducted, although saturated and unsaturated sorption processes are likely to be the same; heterogeneities in the system are important; sorption processes along fractures need to be understood; modeling and experimentation need to be coupled; experiments must be well designed.

B. Viani: Need basic studies on sorption mechanisms; basic chemistry and modeling give credibility; need high temperature data on aqueous complexation, isotherms, and surface complexation.

K. Eggert: Well-designed experiments through integration with modelers; sorption in unsaturated fractures is a low priority.

M. Buchholtz-ten Brink: Need to understand microscopic processes and mechanisms in order to use macroscopic numbers; need to conduct single mineral studies; sensitivity of mobility to parameters; colloids may be important; need to study flow and sorption processes along saturated fractures.

R. Burns: Generalities need to be tested; need to study fracture mineralogy; pointed out the need for more communication between DOE researchers.

V. Nguyen: Need for more experiments to understand the kinetics of adsorption of actinides; need validation of models using field scale studies; need for long-term DOE financial commitment.

Max Blanchard from the DOE gave a brief presentation stating that funding stability is a GAO/Congress issue, not DOE. The role of geochemistry is retardation. Geochemistry is of secondary significance relative to hydrology. Geochemists should keep their program simple and within budget limitations.

NRC/DOE/STATE OF NEVADA TECHNICAL INTERCHANGE MEETING:

Technical discussions on sorption were held concerning issues that were either unclear or were not discussed previously in the workshop.

SIGNATURES:

William M. Murphy
Sr. Research Scientist

Roberto T. Pabalan
Research Scientist

CONCURRENCE SIGNATURES AND DATE:

John L. Russell
Manager, Geologic Setting

9/25/90
Date

Allen R. Whiting

Allen R. Whiting
Director, SE&I

9/25/90
Date

AGENDA

September 11, 1990

8:00 Welcome
R. Herbst, Los Alamos National Laboratory

8:10 Welcome
J. Whetten, Los Alamos National Laboratory

8:15 Welcome
D. Dobson, U.S. Department of Energy/Yucca Mountain Project

8:20 Introduction
J. Canepa, Los Alamos National Laboratory

8:30 *Radionuclide Sorption Data Base—Experiments and Integration of Relevant Sorption Models*
A. Meijer, Los Alamos National Laboratory

9:30 Discussion

10:15 Break

10:30 *Sorption and Porosity Heterogeneity: Effects on Radionuclide Migration*
M. Buchholtz-ten Brink, Lawrence Livermore National Laboratory

11:00 Discussion

11:30 *Current Adsorption Models and Open Issues Pertaining to Performance Assessment*
R. Serne, Pacific Northwest Laboratories

12:00 Discussion

12:30 Lunch

1:45 *Modeling of Cation Exchange Using EQ3/6 Processes*
B. Viani, Lawrence Livermore National Laboratory

2:15 Discussion

2:45 *Sorption of Cesium and Strontium by Zeolite Single Crystals*
R. Burns, Massachusetts Institute of Technology

3:15 Discussion

3:45 Break

4:00 *Sorption Model—Triple Layer Concepts*
J. Leckie, Stanford University

4:30 Discussion

5:00 Adjourn and Social (5:00 - 6:00)

AGENDA

September 12, 1990

8:00 *Radionuclide Migration Studies for Validating Sorption Data—Past, Present, and Future*
I. Triay, Los Alamos National Laboratory

8:30 Discussion

9:00 *Transport of Reactive Tracers by Unsaturated Flow Using Field and Column Experiments*
P. Wierenga, University of Arizona

9:30 Discussion

10:00 Break

10:15 *Transport in Unsaturated Flow Systems Using Centrifuge Techniques*
J. Conca, Washington State University

10:45 Discussion

11:15 *Unsaturated Transport of Inorganic Cations in Undisturbed Soil Columns*
P. Jardine, Oak Ridge National Laboratory

11:45 Discussion

12:15 Lunch

1:30 *Radionuclide Transport and the Retardation Model*
K. Eggert, Los Alamos National Laboratory

2:00 Discussion

2:30 *Lessons in Applying Coupled Geochemical Transport Models*
V. Nguyen, EWA, Inc.

3:00 Discussion

3:30 Workshop Summary

3:45 Adjourn