CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: U.S. Federal Interagency Workshop on Conceptual Model Development for Subsurface Reactive Transport Modeling of Inorganic Contaminants, Radionuclides, and Nutrients

DATE/PLACE: April 20–22, 2004, in Albuquerque, New Mexico

AUTHORS: F.P. Bertetti, R.T. Pabalan, S. Painter, and D.R. Turner

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PERSONS PRESENT: F.P. Bertetti (CNWRA), R.T. Pabalan (CNWRA), S. Painter (CNWRA), and D.R. Turner (CNWRA) and about 70 invited scientists, engineers, and consultants from Federal agencies, universities, private industry, and other international agencies. See Attachment A for a meeting agenda and list of attendees.

BACKGROUND AND PURPOSE OF THE TRIP:

In 2001, the Memorandum of Understanding for the Federal Interagency Steering Committee on Multimedia Environmental Models was established. The agreement among eight Federal Agencies provided a framework for facilitating cooperation and coordination in research and development of multimedia environmental models, software and related databases, including development, enhancements, applications and assessments of site-specific, generic, and process-oriented multimedia environmental models as they pertain to human and environmental health risk assessment.

The Working Group on Subsurface Reactive Solute Transport presented a proposal to the Memorandum of Understanding steering committee in 2002 to facilitate developing a common understanding and technical framework for applying reactive solute transport models to field scale problems. Most of the participating agencies have programs that actively use or support the development of coupled hydrologic and geochemical models to simulate the transport of chemical contaminants in the subsurface environment. Members of the Working Group agreed that an effort to compare and contrast approaches used to develop and parameterize conceptual chemical reaction models in reactive solute transport models would greatly assist all of the Memorandum of Understanding participating agencies.

Specific goals of this Working Group include the following:

- Facilitate cooperation, communication and coordination among various federal agencies that are conducting research on the application of reactive transport models
- Assess of the current state of reactive transport models
- Identify scientifically credible approaches to developing conceptual models for simulating reactive transport
- Recommend research efforts to bridge gaps in the knowledge base for simulating reactive transport

At the recommendation of the Memorandum of Understanding steering committee, the focus of this workshop was on processes that affect the transport of inorganic contaminants. The Working Group on Subsurface Reactive Solute Transport is planning to have a second workshop related to organic contaminants and biological processes.

The workshop was attended by about 70 invited participants from the Nuclear Regulatory Commission (NRC), U.S. Department of Energy (DOE), U.S. Geological Survey, U.S. Army Corps of Engineers, National Oceanic and Atmospheric Administration, Environmental Protection Agency (EPA), Department of Agriculture, and Department of Homeland Security. In addition to agency representatives, consultants, contractors, and university researchers were also invited to attend.

MEETING SUMMARY

The following is a brief summary of presentations made by the meeting participants. The authors of this trip report have copies of the materials presented by the participants in the workshop.

Plenary Session 1: Overview of Modeling Issues

T. Appelo (Hydrochemical Consultant) provided an overview of field simulations using the geochemical code PHREEQC. Rather than using a traditional retardation factor based on a linear sorption coefficient (K_d), Appelo noted that a flushing factor based on the slope of the sorption isotherm is a more appropriate representation for reactive transport modeling. Using examples of uranium/zinc transport in acid mine drainage at the Konigstein uranium mine (Germany), he demonstrated that use of the flushing factor can produce significantly different predictions of uranium/zinc distributions as the acid plume moves through the simulation and pH changes. In particular, the uranium front will sharpen as a function of pH. For the example of arsenic transport in Bangladesh groundwaters, Appelo noted that the sorption of bicarbonate (HCO_3^-) displaces arsenic from iron oxhydroxides. Because of enhanced bicarbonate production by the oxidation of organic matter, neglecting HCO_3^- uptake in the sorption reaction models may limit the ability to simulate arsenic release.

M. Hill (U.S. Geological Survey) presented an overview of the impact of uncertainty in affecting simulation accuracy. She identified contributors to parameter uncertainty and described different methods to use for parameter importance determination. She also discussed that uncertainty analysis needs to consider the end use of the model results (scientific simulations, stakeholder confidence, decision-making). The analyst also needs to consider trade-offs between model complexity and model predictive capability. An overly complex model may do a good job of fitting observations, but this may come at the cost of the prediction accuracy. Dr. Hill recommended that generally, an analysis should start with a simple model and build in complexity as it is justified by additional data.

D. Parkhurst (U.S. Geological Survey) presented the results of simulations of three field sites: naturally occurring groundwater arsenic in Oklahoma, phosphorous transport at Cape Cod, Massachusetts, and aquifer storage and recovery simulations at Charleston, South Carolina. For the simulations of arsenic transport at Oklahoma, simulations of ion exchange and complexation generally agreed with the field observations, indicating that arsenic could be a problem in the water supply, depending on the degree to which calcite/dolomite dissolves in the

system. If mineral dissolution is suppressed, arsenic release is decreased, but the discrepancies in the simulation suggest that the flow model needs refinement. The simulations were more accurate for the simulations of water quality and recovery in the aquifers at Charleston, South Carolina, but highlighted the need for better estimates of dispersion.

Plenary Session 2: Overview of Agency Applications and Modeling Needs

This plenary session was intended to outline agency approaches to reactive transport modeling, and identify agency needs to improve the use of models. Speakers from the DOE presented an overview of unsaturated zone flow and transport at Yucca Mountain, and remediation activities at Hanford. The EPA is increasing funding priorities related to contaminated sediments, brownfields, waste management, and risk/hazard assessment. The focus at EPA is moving away from individual sites towards so-called "mega-sites". W. Ott (NRC) described the NRC Office of Research approach to focus on more realistic radionuclide transport modeling, including laboratory, modeling, and field activities. The Agricultural Research Service has focused its research efforts on the near surface environment, including the effect of variable major ion chemistry, nutrient cycles, and toxicity. With regard to reactive transport modeling, the Army Corps of Engineers is most focused on military-unique remediation activities, including unexploded ordnance, solvent contamination, and lead cleanup (bullets, old paint). To aid in this, the Corps has developed the GMS software, a high-order executive that provides common pre- and post-processing GUI options for groundwater modeling codes developed by different Federal agencies. The Corps has also announced a new initiative in Environmental Modeling and System-Wide Assessment to develop a modular toolbox to evaluate large-scale contamination problems.

Plenary Session 3: Physical Properties and Coupling with Reactive Processes

C. Harvey (MIT) presented results of laboratory experiments designed to address basic questions about solute mixing and reactions at the core scale. New methods for imaging changing concentrations during reactions in porous media experiments allowed reactants and products to be distinguished and quantitatively tracked by different light adsorption. In some of the experiments, incomplete mixing segregated the reactants, which caused the conventional coupling of transport with chemical reaction parameters to over predict the reaction rates.

J. Gwo (University of Maryland) presented a calibrated site-scale model of the Waste Area Group 5 site at Oak Ridge National Laboratory. The highly heterogeneous site includes confined fractured aquifers, partially weathered shale bedrock, and saprolite near ground surface. A dual-permeability model was constructed and calibrated hydraulically. Tracer breakthrough curves were also used to calibrate non-reactive transport including matrix diffusion. Once calibrated the model was used to study movement of metals and metal-EDTA chelates.

Plenary Session 4: Sorption Processes

R. Pabalan (CNWRA) presented "Radionuclide Sorption in High-Level Waste Performance Assessment: Abstraction of Results from Experiments and Surface-Complexation Models", co-authored by R.T. Pabalan, D.R. Turner, and F.P. Bertetti. The presentation described the role of sorption in performance assessments of nuclear waste repositories, discussed CNWRA experimental and modeling studies that helped identify the key geochemical parameters

controlling sorption of radionuclides onto mineral surfaces, and summarized the approach used in the NRC Total-system Performance Assessment (TPA) Version 5.0 code for abstracting sorption processes based on experimental and modeling studies combined with Yucca Mountain site-specific geochemical and hydrologic information.

G. Curtis (U.S. Geological Survey) presented a summary of about four years of work at the Naturita, Colorado uranium mill tailings site. He described the hydrologic characterization of the site. Uranium concentrations have been measured for ground water, and hydraulic conductivity has been determined based on several methods, including ground-water age dating, chloride migration, slug tests, and tracer tests. Curtis presented batch sorption results using natural materials from the site, showing the significant effects of pH, uranium concentration, and CO_2 partial pressure on uranium sorption. He also summarized information regarding techniques of measuring *in situ* K_d values through field-based experimentation and assessing the "true"sorption capacity of mineral grains through measurements of isotopic exchange. A non-electrostatic surface complexation model was calibrated to the batch sorption data and used to investigate the key geochemical parameters controlling uranium sorption at Naturita. Calculated *in situ* K_d values showed good agreement in pH space (over a range of CO_2 partial pressures) with the range of surface complexation model results. Because of the limited pH range of Naturita waters, calculated K_d showed correlations only with uranium concentration and alkalinity, and model sensitivity to pH was not really tested. Point-to-point comparisons between calculated K_d and measured in situ K_d were not shown, but would provide another good test of both models and experimental approaches.

C. Steefel (Lawrence Berkeley National Laboratory) described reactive transport studies incorporating multicomponent ion exchange models. The key advantage of ion exchange models over phenomenological models such as linear, Langmuir, or Freundlich isotherms, is that it captures competitive adsorption behavior. Steefel described efforts to model Cs-Na exchange in column experiments involving Hanford sediments, and emphasized that selectivity coefficients derived from batch experiments under predicted retardation in flowthrough column experiments. He showed that the selectivity coefficients deduced from the column experiments could be used in field-scale reactive transport models to successfully reproduce aqueous geochemical measurements taken below a waste tank that had leaked in 1965.

Plenary Session 5: Discussion of Breakout Session Objectives

The participants were divided into four working groups to discuss specific aspects of reactive transport modeling. The working groups topics included (i) Coupling to Field Scale Physical Properties; (ii) Sorption; (ii) Precipitation/Dissolution, and; (iv) Redox/Microbiology. The results of the working group discussions are summarized below.

Plenary Session 6: Nucleation, Precipitation, and Dissolution Processes

N. Sahai (University of Wisconsin-Madison) summarized the molecular level controls on mineral nucleation and precipitation. She described the use of molecular orbital calculations and experimental spectroscopy for estimating nucleation reaction mechanisms, rate determining steps, and reaction rates. Phenomenological models of nucleation were also discussed. Challenges in scaling the microscopic models for use in field-scale simulations were recognized.

A. Blum (U.S. Geological Survey) discussed dissolution, precipitation, and nucleation rates in natural systems. He notes that laboratory determined rate laws for sparingly soluble salts such as calcite are useful for field-scale reaction transport models. However, laboratory rates for the dissolution of feldspars and other alumino-silicates have little relation to the rates of these reactions in natural environments.

J. Apps (Lawrence Berkeley National Laboratory) and E. Sonnenthal (Lawrence Berkeley National Laboratory) discuss issues related to precipitation-front modeling, with emphasis on metastable precipitation. Apps presented the first part of the presentation, reviewing the Ostwald Rule of Stages and pointing out that the underlying chemical principles are generally not included in reactive transport simulations except through ad-hoc fixes involving the suppression of particular phases. In the second half of the presentation, Sonnenthal described the thermal-hydrological-chemical modeling of the potential repository at Yucca Mountain, and discussed metastable precipitation within a transient boiling zone near the emplacement tunnels.

Plenary Session 7: Redox Processes and Biologically Mediated Processes

Plenary Session 7 focused on biologically mediated processes. W. Burgos (Pennsylvania State University) described reactive transport modeling of biologic iron(III) reduction under varied hydrological conditions using HYDROGEOCHEM. E. Roden (University of Alabama) presented studies on surface chemical and thermodynamic controls on bacterial metal reduction. P. van Capellen (Utrecht University) described use of the Michaelis-Menton (Monod) rate expressions for geomicrobial activity within reactive transport models. The first application involved the anaerobic degradation of sedimentary organic matter, and the second involved the anaerobic oxidation of methane by sulfate.

Plenary Session 8: Complex Applications

J. Sampier (University of La Coruna, Spain) described coupled reactive and microbial transport modeling of two experiments conducted at the Äspö Hard Rock Laboratory in southern Sweden. The modeling provided plausible quantitative explanations for unexpected trends in bicarbonate and sulfate at the experiments.

P. Lichtner (Los Alamos National Laboratory) described ongoing work to model colloid-acilitated transport at the BENHAM test. The simulations focused on establishing the non-isothermal flow field and on non-reacting transport simulations. The simulations were used to estimate the mobile inventory of key radionuclides.

U. Mayer (University of British Columbia) described reactive transport modeling applied to two groundwater remediation problems: a permeable reactive barrier in North Carolina, and a permanganate injection applied to oxidation of chlorinated solvents in Connecticut. The focus was on evolving reactivity of the system, which manifests itself as changing reaction rates for the geochemical reaction rates within the aquifer.

Plenary Session 9: Spanning the Gap: Integration of New Research and Application Ideas for Reactive Transport Modeling at the Field Scale

In Plenary Session 9, representatives from each of the working groups summarized their findings and recommendations. Each of the four working groups independently recommended that a dedicated research field site was needed to test models, assumptions, and to generally move the process forward. CNWRA staff participated in the working group, Coupling to Field Scale Physical Processes, and the Sorption group.

The working group, Coupling to Field Scale Physical Properties, was concerned with the macroscopic representation of reaction processes at the field scale. The central issue for this working group is the scaling problem, wherein reaction parameters observed at the field scale appear to be different from those measured at the laboratory scale. The group discussed how the scale dependence arises from the combination of mass transfer limitations coupled with large-scale variations in velocity. The group concluded that field-scale calibration of reaction parameters using a limited set of tracer tests was necessary for applications, but that laboratory measurements should be used to provide the mechanistic understanding necessary to extrapolate limited tracer test data to different chemical or thermodynamical environments. The group recommended the establishment of a dedicated field research site where the upscaling issue could be studied by comparing reactivity measurements at different scales.

An early general conclusion from the Sorption group was that while the use of constant Kd models of sorption is typically inappropriate, available and well-developed surface complexation modeling approaches are underutilized. Furthermore, there are information needs that exist for potential users of surface complexation models. These include (i) no established source of parameters (i.e., complexation constants), (ii) no clear direction on how to develop those parameters, and (iii) no clear information on how much site characterization may be needed to implement such an approach. To address these and other needs, some preliminary recommendations were developed in the session:

- One or more dedicated field research sites should be identified and developed. The site(s) should be accessible to various research groups and funded to ensure continuity of work over periods pertinent to field-scale research. The site(s) would enable testing of modeling approaches and help to define the amount of characterization needed to support a given approach.

- A sorption parameter database or data clearing house should be developed to provide a comparison of parameters for different environmental settings and to provide users with a resource for application of surface complexation models.

- Additional research should be conducted to enhance knowledge of sorption processes in fractured rock and unsaturated conditions.

SUMMARY AND CONCLUSIONS:

On April 20–22, 2004, the Working Group on Subsurface Reactive Solute Transport organized a workshop on Conceptual Model Development for Subsurface Reactive Transport Modeling of Inorganic Contaminants, Radionuclides, and Nutrients in Albuquerque, New Mexico. R. Pabalan of the CNWRA presented an invited paper entitled "Radionuclide Sorption in

High-Level Waste Performance Assessment: Abstraction of Results from Experiments and Surface-Complexation Models," summarizing work done to incorporate sorption modeling results in the NRC TPA code.

All breakout sessions and much of the general discussion in the plenary sessions focused on information and research needs for reactive transport modeling. From a high-level waste management perspective, much of the discussion was directly applicable to performance confirmation activities for the potential repository at Yucca Mountain. For example, a primary recommendation independently put forward by each of the four breakout sessions was that a field-based study site was required to test models, assumptions, and move the modeling process forward. This strongly suggests that long term field-based testing should be a primary consideration for performance confirmation activities at Yucca Mountain.

PROBLEMS ENCOUNTERED:

NONE.

PENDING ACTIONS:

A meeting summary will be prepared and posted on the Memorandum of Understanding website (www.iscmem.org) and presented in an article submitted for publication in EOS. The Working Group on Subsurface Reactive Solute Transport will continue to plan a second workshop related to organic contaminants and biological processes. Both the NRC and CNWRA will continue to be involved in the working group.

SIGNATURE

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David R. Turner Assistant Director, Systems Engineering and Integration	05/21/2004 Date

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Attachment A

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