

Research Activities at U.S. Government Agencies in Subsurface Reactive Transport Modeling

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REVIEW AND ANALYSIS

Vadose Zone Journal

The fate of contaminants in the environment is controlled by both chemical reactions and transport phenomena in the subsurface. Our ability to understand the significance of these processes over time requires an accurate conceptual model that incorporates the various mechanisms of coupled chemical and physical processes. Adsorption, desorption, ion exchange, precipitation, dissolution, growth, solid solution, redox, microbial activity, and other processes are often incorporated into reactive transport models for the prediction of contaminant fate and transport. U.S. federal agencies use such models to evaluate contaminant transport and provide guidance to decision makers and regulators for treatment issues. We provide summaries of selected research projects and programs to demonstrate the level of activity in various applications and to present examples of recent advances in subsurface reactive transport modeling.

ABBREVIATIONS: ARS, Agricultural Research Service; BTEX, benzene, toluene, ethylbenzene, and xylene; CNWRA, Center for Nuclear Waste Regulatory Analyses; DCE, dichloroethylene; DO, dissolved oxygen; DST, Drift Scale Test; EDTA, ethylenediaminetetraacetic acid; EM, Office of Environmental Management; EMSP, Environmental Management Science Program; ERD, Ecosystems Research Division; ERDC, U.S. Army Engineer Research and Development Center; ERSR, Environmental Remediation Science Program; GMS, Groundwater Modeling System; HE, high explosive; INL, Idaho National Laboratory; ISCMEM, Interagency Steering Committee on Multimedia Environmental Models; LBNL, Lawrence Berkeley National Laboratory; LLNL, Lawrence Livermore National Laboratory; NABIR, Natural and Accelerated Bioremediation Research; NTS, Nevada Test Site; OBER, Office of Biological and Environmental Research; ORNL, Oak Ridge National Laboratory; OST, Office of Science and Technology; PNNL, Pacific Northwest National Laboratory; RWMC, Radioactive Waste Management Complex; SCM, surface complexation model; TCE, trichloroethylene; USACE, U.S. Army Corps of Engineers; USDOA, U.S. Department of the Army; USDOD, U.S. Department of Defense; USNRC, U.S. Nuclear Regulatory Commission; WIPP, Waste Isolation Pilot Plant.

Subsurface reactive transport modeling may be defined as the use of mathematical models to simulate the fate and transport of dissolved species and particulates in groundwater as these species are transported through porous media and react with each other, with mineral surfaces, and with microbes associated with the porous media matrix. This type of modeling has evolved over the last 30 yr from a specialized research topic involving a dozen or so practitioners (with often large stacks of computer punch cards) to a common office tool found today on the personal computer (and occasional supercomputer) of many environmental chemists, geochemists, and soil scientists. The devel-

opment of theory, numerical methods, and computer code to monitor the evolution of reactive solids, aqueous solutions, and gases in complex systems has led to significant advances in our understanding of both natural and artificial systems. Reactive transport modeling provides the scientist with a convenient tool to sort out the myriad of individual reactions that contribute to various reaction pathways. Incorporation of multiple chemical, physical, and biological processes such as adsorption, desorption, ion exchange, precipitation, dissolution, growth, mineral solid solution, reduction–oxidation reactions (redox), and even microbial activity can modify the reactive pathways in numerous ways. The reactive transport model provides a basis for identifying the important reactions, the extent of reaction, and the resulting mineral assemblage and fluid composition of a particular pathway. The extrapolative nature of such models is the key factor in our understanding of natural geochemical and environmental processes where the evolution of reactive pathways ranges from minutes to millions of years. Therefore, reactive transport modeling of subsurface environments is a central component to our understanding the evolution of hydrothermal ore deposits, sediment diagenesis, acid mine drainage, petroleum reservoirs, carbon sequestration, transport of environmental pollutants, and radioactive waste isolation. In particular, such modeling provides a framework for performance assessment methods in the regulation of radioactive waste and other hazardous contaminants.

This contribution provides a description of current research activities at several U.S. federal agencies relating to subsurface reactive transport modeling. Among the most active agencies involved in this research are the USEPA, USDOE, USDA, U.S.

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Department of Defense (USDOD), USGS, and U.S. Nuclear Regulatory Commission (USNRC). In addition to their analysis, regulatory, protection, and development activities, these agencies provide much of the scientific and technical understanding of geochemical reactions and reactive transport modeling. We provide research summaries for several ongoing research projects at each of the agencies, with particular emphasis on field applications, variety of contaminants, active geochemical processes, reactive transport models, parameter selection, associated laboratory research, and characterization studies. The summary often includes a description of the reactive transport code used in the application. Tables of chemical and radionuclide contaminants and critical geochemical processes are also provided. Although not all details of each project can be easily summarized, the interested reader can pursue further information using the cited references and associated Web pages.

Much of the content of this paper has been derived and expanded from interactions and collaborations among members of a Federal Working Group on Subsurface Reactive Solute Transport Modeling sponsored by the Federal Interagency Steering Committee on Multimedia Environmental Models (ISCMEM; <http://www.iscmem.org>). A 2004 workshop titled "Conceptual Model Development for Subsurface Reactive Transport Modeling of Inorganic Contaminants, Radionuclides, and Nutrients" involving working group members and leading reactive transport modelers from government, university, and industry provided additional insights on critical and limiting technical issues. Davis et al. (2004b) and Cygan et al. (2006) provide excellent summaries and reviews of the workshop and joint efforts in research among the working group members and workshop participants. Lastly, consider the schematic presented in Fig. 1 (from Davis et al., 2004b), which captures the complexity of interactions involving contaminants, chemistry, geology, mineralogy, hydrology, and microbiology. Understanding the nature and evolution of the contaminant plume, be it arsenic or uranium in this example, will depend on the success of reactive transport models to accurately incorporate the complex and collective behavior of these phenomena. The success of these modeling efforts depends not only on the development and validation of numerical codes but also on conceptual model development, including site characterization and parameterization of the reaction model.

U.S. Environmental Protection Agency

In keeping with the USEPA's overarching mission to protect human health and the environment, its research programs address a broad range of environmental contaminants and stressors. Research projects with a reactive transport modeling component have addressed organic contaminants such as pesticides, petroleum hydrocarbons, fuel oxygenates, and solvents. Inorganic contaminants of concern to these USEPA research projects include arsenic, cadmium, chromium, copper, lead, mercury, nickel, perchlorate, selenium, and zinc. The selection of these contaminants is based on their toxicity, industrial use, and frequency of occurrence at Superfund sites. Radioactive con-

taminants are also of interest to the USEPA and the Monitored Natural Attenuation project. Of most concern among the radionuclides are various isotopes of cesium, cobalt, curium, neptunium, strontium, plutonium, uranium, technetium, tritium, thorium, radon, americium, radium, and iodine.

The USEPA provides a variety of models and tools for subsurface fate and transport modeling through the Center for Subsurface Modeling Support (<http://www.epa.gov/ada/csmos/models.html>) and the Center for Exposure Assessment Modeling (<http://www.epa.gov/ceampub/>). A number of research projects involving the development or application of subsurface reactive transport models are underway at the USEPA Office of Research and Development Divisions in Ada, OK, and Athens, GA.

National Risk Management Research Laboratory in Ada, Oklahoma

Framework Document on Monitored Natural Attenuation of Inorganic Contaminants

Ten USEPA researchers and five external experts have been involved in an effort to provide a framework document for the application of monitored natural attenuation of inorganic contaminants at hazardous waste sites. The first two volumes of the

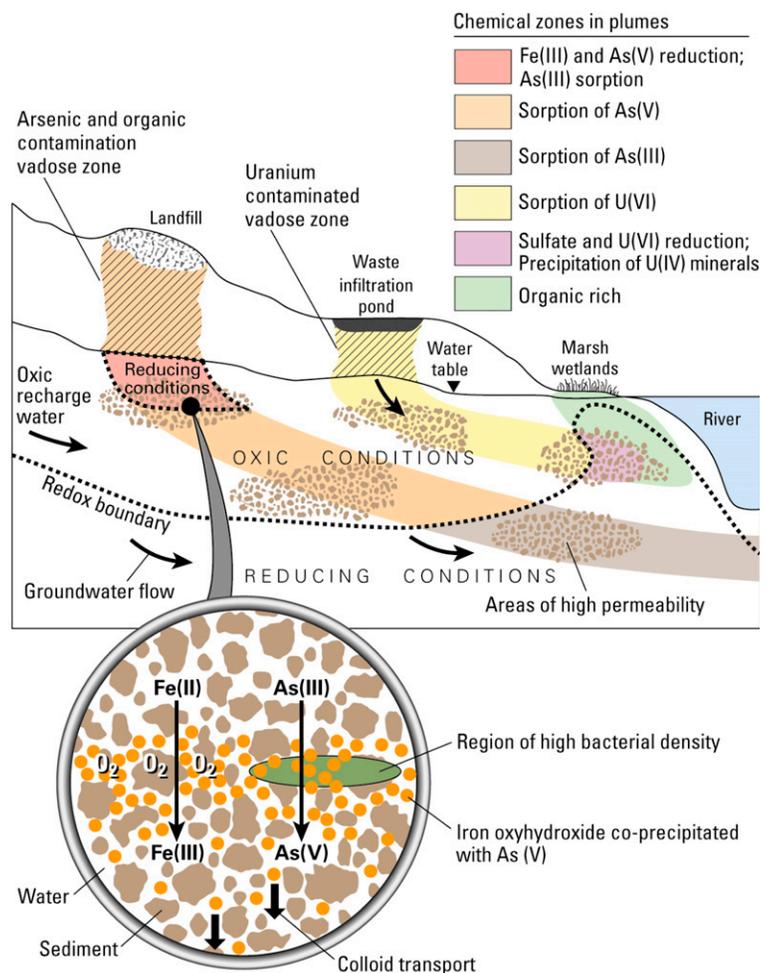


FIG. 1. Schematic illustrating the complex behavior and transport of arsenic and uranium contaminants in changing sediment and redox environments. From Davis et al. (2004b), copyright 2004 American Geophysical Union; reproduced by permission of American Geophysical Union.

document are targeted for completion in November 2007 and will be available at www.epa.gov/ada/pubs/reports.html. The document focuses on the groundwater pathway but includes information on the unsaturated zone as source zones for contaminant migration. The document addresses radioactive and nonradioactive elements. The first volume provides the underlying framework for the assessment of natural attenuation, including important processes and characterization and monitoring methods. The second volume addresses specific nonradioactive elements of concern to most government agencies, and the third volume address specific radioactive elements. Similar guides have been published for chlorinated solvents (Wiedemeier et al., 1998) and volatile organic compounds (Pope et al., 2004). In these documents, reactive transport models are identified as a tool to design monitoring networks and estimate attenuation rates for contaminant plumes. Additional reports associated with monitored natural attenuation are also available on the USEPA report Website.

Natural Attenuation of Inorganics during Metal Sulfide Formation

Researchers at the USEPA Office of Research and Development in Ada, OK, are investigating metal fixation during iron sulfide formation, a key environmental process that governs the distribution and mobility of metal contaminants in sediments and soils. Iron sulfide minerals are especially common components of soil-sedimentary environments, and reactions at the surfaces of iron sulfides play pivotal roles in metal retention, mobility, and bioavailability. Although essential for predicting the fate of metals in specific environmental realms, the details of reaction mechanisms, geochemical cycling pathways, and the limiting factors that govern metal uptake by iron sulfides are incompletely understood. This research involves experimental studies that explore mechanisms and limitations of metal uptake during iron sulfide formation. Examples of research in this area include Wilkin et al. (2003) and Wilkin and Ford (2002).

Attenuation or Stabilization of Arsenic by Iron (Hydr)oxides in Soils and Sediments

The attenuation or stabilization of arsenic in soils and sediments is often controlled by partitioning reactions to mineral oxides. Iron oxide minerals play a major role in arsenic cycling in these environments due to scavenging reactions that occur during iron precipitation from ground and surface waters. Initially precipitated iron (hydr)oxides are rarely the most stable form, and transformation to more crystalline (or stable) products occurs with time. As a consequence of this transformation, coprecipitated arsenic could potentially be immobilized within crystalline iron (hydr)oxides. The purpose of the study by Ford et al. (2006) was to provide baseline rate data on the long-term stabilization of arsenic associated with iron (hydroxides) under controlled laboratory and field conditions. These data aid assessment of the attenuation/stabilization potential for arsenic in soils and sediments with a significant iron (hydr)oxide mineral component.

Natural Attenuation of Arsenic in an Urban, Industrialized Watershed

The potential natural attenuation of contaminant metals within a watershed is controlled by processes that sequester the metal from solution to immobile soil or sediment solids.

Observation of arsenic cycling in natural systems suggests that partitioning to iron (hydr)oxide minerals may immobilize arsenic within soils and sediments. The research explores the extent of this attenuation process within an industrialized watershed impacted by arsenic contamination from historical industrial activities. The research combines field and laboratory studies designed (i) to determine the geochemical processes that control aqueous and solid phase arsenic speciation, and (ii) to evaluate the most reliable methods and practices for sample collection, preservation, and characterization. The results of this research will aid in the overall development of assessment criteria and practices for determining the potential for attenuation of arsenic via partitioning to soil and sediment matrices. An example of research in this area is provided by Lin and Puls (2000, 2001).

Monitoring Oxidation-Reduction Processes in Groundwaters, Sediments, and Soils

Oxidation and reduction processes play major roles in the mobility, transport, and fate of inorganic and organic chemical species in natural waters. Consequently, field characterization of redox chemistry is an integral component of evaluating the geochemical and microbiological cycles of chemical contaminants, as well as evaluating the performance of remedial technologies, such as monitored natural attenuation, permeable reactive barriers, in situ reactive zones, and anaerobic bioremediation. The overall purpose of this research is to identify the best field practices for characterizing redox chemistry. The overall goal of the project is to develop recommendations and technical guidelines for evaluating redox processes in contaminated groundwater, sediment, and soil systems. One specific goal is to evaluate existing methodologies for determining dissolved oxygen (DO) concentrations and to document appropriate field practices for obtaining accurate and repeatable DO measurements. Additional studies are being performed to establish useful methods for characterizing redox processes in suboxic (no free oxygen, no free hydrogen sulfide), and anoxic systems (sulfide- or methane-rich). Examples of studies in this area include Liang et al. (2000), Su and Puls (2001a,b), and Lien and Wilkin (2002).

National Exposure Research Laboratory and Ecosystems Research Division in Athens, Georgia

Fate and transport research at the USEPA Ecosystems Research Division (ERD) in Athens, GA, is primarily focused on organic contaminants, nutrients, and pathogens in surface water; however, several ERD research projects are investigating the subsurface fate of contaminants. The PRZM-3 model was developed to simulate pesticide and nitrogen fate in the crop root zone and the unsaturated soil zone (Suárez, 2005). The OnSite online calculators, which are available on the ERD Website (<http://www.epa.gov/athens/onsite/>), provide simple subsurface contaminant transport models, as well as model parameter estimates, focused on the issue of fuel contamination from leaking underground storage tanks (Weaver, 2004). The need for input parameters for fate and transport models has been further addressed through the development of the SPARC calculator for estimating physicochemical properties and rate constants for organic chemicals (Hilal et al., 2003, 2004).

In addition to model development programs for the subsurface fate of contaminants and stressors, the ERD has an ongoing research project to investigate nitrogen transport and transformation in agricultural watersheds. This research project consists of laboratory studies, field sampling, and reactive transport modeling. It has been established that biologically mediated transformation is the dominant sink for excess nitrogen in the environment; however, controls on reaction kinetics and speciation during these transformations are poorly understood. In this project, the primary objective of the laboratory studies is to quantify nitrogen transformation kinetics and product distributions as a function of measurable geochemical properties. The primary objective of the field sampling program is to explore the extent and mode of coupling of the oxidation state of nitrogen with other redox-sensitive solutes in the subsurface environment (Washington et al., 2004, 2006). The results of the laboratory studies and data collected during field sampling are used to parameterize a reactive transport model of nitrogen fate in the shallow subsurface. An important goal of the modeling effort is to determine the minimum level of model complexity that is needed to simulate observed chemical behavior in the field. The field site for this project is a USDA Agricultural Research Service (ARS) research watershed used for cattle grazing and located near Athens.

U.S. Department of Energy

Field-Scale Reactive Transport Issues at USDOE Waste Sites

The Office of Environmental Management (EM) is one of several organizations in the USDOE that perform subsurface reactive transport analyses to accomplish their mission goals (e.g., Defense Programs, Environmental Management, Fossil Energy, Science, Civilian Radioactive Waste Management, Energy Efficiency, and Nuclear Energy). The EM is responsible for the assessment and cleanup of legacy waste sites from the nuclear weapons production complex. While most of the resources have been directed at characterization and engineering activities performed by consulting engineering companies, there have historically been research and development programs that addressed reactive transport issues. In particular, the EM Office of Science and Technology (OST) has been tasked to bridge the gap between broad fundamental research, such as that performed in the USDOE Office of Science (see below), and needs-driven applied technology required for waste-site cleanup and closure. The OST previously managed the Environmental Management Science Program (EMSP) involving researchers at universities, USDOE laboratories, other government agencies, and two private institutions. The program portfolio included a number of projects with geochemical and reactive transport issues (e.g., the characterization of tank waste chemistry, tank waste-sediment interactions, and hydrogeochemical interactions with sediments).

Several policy changes have occurred at the USDOE in recent years, including the transfer of the EMSP out of the EM to the Office of Science and in 2005 the merger of EMSP with the Natural and Accelerated Bioremediation Research (NABIR) program to form the Environmental Remediation Sciences Program (ERSP). These changes are consistent with a de-emphasis of dedicated support for subsurface science from the EM and an increased

emphasis on such research by the Office of Science. There is ongoing involvement of scientists (primarily from the USDOE national laboratories) in reactive transport analyses at waste sites at Hanford, WA, Idaho National Laboratory, Oak Ridge, TN, and Savannah River, SC. The following summaries are intended to be examples, not a representative summary, involving field-scale reactive transport issues from each of these sites.

Hanford Site

During the 1950s and 1960s, waste in the SX tank farm at the Hanford Site in Washington State had the highest radiation, highest pH, highest ionic strength, and highest aluminum waste of that stored in Hanford single-shell tanks (Freeman-Pollard et al., 1994). Leaks from one or more of these tanks resulted in high concentrations of cesium-137 over 40 m deep in the vadose zone, challenging commonly held views of cesium mobility. To elucidate the properties and mechanisms controlling the mobility of cesium-137, a comprehensive program of investigation was undertaken that included the emplacement of vertical and angled boreholes for sampling of contaminated sediments, a wide variety of laboratory studies, field studies of liquid migration in Hanford sediments, and various hydrologic and reactive transport modeling. The finding that high free sodium concentrations in the high temperature tank waste could suppress cesium sorption to exchange sites in the sediments was tested and confirmed in the field through a history matching modeling study beneath tank SX-115 (Liu et al., 2003a,b, 2004, 2006; Steefel et al., 2003).

Savannah River Site

From 1955 to 1998, shallow, unlined seepage basins in the F and H areas of the Savannah River Site in South Carolina received acidic (pH = 2.4) radioactive process water containing tritium, other radioactive isotopes, and metals (Cummins et al., 1991). While the tritium poses a long-term chronic situation controlled principally by decay, the persistence of elevated metal concentrations is primarily a result of acidic groundwater conditions (metals from process water and metals dissolved from the formation materials). A groundwater remediation system consisting of extraction wells, a treatment system, and upgradient reinjection became operational in 1999. Under the present treatment scenario, the system would have to operate for 90 yr (until tritium decays to drinking water standards), resulting in life-cycle costs of \$1 billion. In addition to operating costs, the treatment system generates approximately 850 m³ of low-level solid radioactive waste each year that must be transported off-site for disposal. The Savannah River Site is currently evaluating in situ base injection technology as an alternate remedial strategy to control metal releases to surface water. Precipitation of aluminum hydroxides during base injection has the potential to locally alter permeability of the formation. Consequently, a coupled framework for integrating and fusing geological, hydrological, geochemical, and remedial data is being pursued to understand the complex system dynamics. Of interest is the optimization of base injector placement and injection rates to maximize chemical effects while minimizing adverse physical effects. In related research, Ekechukwu et al. (2001) have suggested the use of limestone as a treatment medium for increasing the pH to cause direct precipitation, coprecipitation, and enhanced adsorption of radionuclides. Dai et al. (2002) provides

a discussion of recent transport of actinide contaminants from the F and H areas at the Savannah River Site. Additionally, the treatment of organic solvent contaminants such as trichloroethylene (TCE) in the groundwater at the site have generated significant research efforts (Brigmon et al., 1998; Kirtland et al., 2003).

Idaho National Laboratory

From 1954 to 1970, mixed transuranic and organic waste primarily from Rocky Flats was uncontrollably released to pits and trenches in the Subsurface Disposal Area within the Radioactive Waste Management Complex (RWMC) at the Idaho National Laboratory (INL), west of Idaho Falls, ID. This 97-acre area is now an active shallow land burial site for the permanent disposal of solid low-level radioactive waste. The USDOE, in cooperation with the USEPA and the state of Idaho, is investigating the risks to the sole source aquifer, which lies more than 180 m below ground surface in a fractured basalt formation. Extensive monitoring of the groundwater and vadose zone (including 8.5 m of surficial sediments) is underway to learn more about current and potential contaminant migration under the arid (~ 20 cm precipitation yr^{-1}) hydrologic regime. Predictions of contaminant migration must consider dense, nonaqueous phase liquid (carbon tetrachloride) behavior in unsaturated fractured basalt. Laboratory experiments have identified the importance of carbon tetrachloride interaction with calcium carbonate minerals in controlling the wetting state of the three-phase system. Active gas, multiphase fluid flow with phase change is currently accounted for in a dual porosity modeling approach that includes mass transfer between fractures and the matrix. Engineered bioremediation has been employed in the past at another INL organic waste site, Test Area North, where TCE was the targeted contaminant (Sorenson, 2003). For more information, see the following Websites: www.inl.gov/subsurface/environmentalissues/burialgrounds.shtml and www.inl.gov/subsurface/environmentalissues/plumes.shtml.

Oak Ridge Site

Abetted by high rainfall rates (~ 1.4 m yr^{-1}) and shallow groundwater, radionuclides, toxic metals, and organic contaminants in shallow burial grounds, ponds, and lagoons are readily transported to groundwater at the Oak Ridge National Laboratory (ORNL) and associated facilities (Y-12 Plant, East Tennessee Technology Park, Portsmouth, and Paducah Gaseous Diffusion Plants) in Tennessee. The geology at ORNL consists of interbedded fractured weathered shales and limestone. Extreme preferential flow results in physical, hydraulic, and geochemical nonequilibrium conditions between fast-flowing pathways and the surrounding soil matrix. Contaminant migration rates can be extremely rapid along preferred flow paths, and sources dissipate very slowly (naturally or with conventional remediation technology) due to the significant inventory of contaminant in soil and bedrock matrices and diffusion-limited mass transfer rates between matrix and fracture zones. A series of multiscale experimental campaigns have led to a mechanistic understanding of the rapid mobility of water and solutes in preferential flow paths and the simultaneous slow movement of water and solutes within the soil and rock matrix (Wilson et al., 1998; Jardine et al., 1998, 1999, 2000, 2001). Advanced numerical models for predicting contaminant transport with complex biogeochemical interactions in fractured and macroporous media (Gwo et al., 1995, 1999,

2001) have been developed to assess long-term risk reduction and uncertainty associated with alternative remedial actions.

Parameter Estimation for Reactive Transport Models

A large number of activities related to parameter measurement and estimation for reactive transport models are currently underway in the USDOE. The parameters, in turn, feed into a variety of models, ranging from multicomponent, multispecies “mechanistic” models for reactive transport to more standard “performance assessment”-type models based on linear sorption and simplified reaction networks. Several examples are listed below.

Waste Isolation Pilot Plant

Accurate estimates of radionuclide sorption coefficients are essential for forecasting the long-term performance of the Waste Isolation Pilot Plant (WIPP), located east of Carlsbad, NM; however, there is no active program to measure sorption coefficients for WIPP. Data are based either on literature values or on data collected about 5 yr ago. At that time, linear partition coefficient K_D values (ratio of equilibrium amount of contaminant sorbed to equilibrium amount of contaminant in solution, mL g^{-1}) were measured for the shallow aquifer consisting of Culebra Dolomite overlying the WIPP site. Previous work also included actinide complexation with organics and humic substances. More recently, experimental work on the hydration rate and uptake of carbonate by magnesium oxide has been performed. Some examples of the significance of sorption at WIPP and the evaluation of sorption parameters are provided by Ostensen (1998) and Brady et al. (1999).

Yucca Mountain Unsaturated and Near Field Zone

In support of modeling efforts to predict the long-term viability of Yucca Mountain in Nevada as a repository for nuclear waste, a set of equilibrium constants for aluminosilicate reactions based on modeling of chemical data has been collected from the vadose zone at the Yucca Mountain Project. These data have been used to carry out long-term infiltration calculations and to model the Drift Scale Test (DST). In the DST, Lawrence Berkeley National Laboratory (LBNL) researchers successfully applied an active fracture model to describe an interfacial area limitation on chemical exchange between fractures and matrix (Xu et al., 2001; Spycher et al., 2003). The active fracture model expresses the amount of wetted fracture as a function of the saturation in the fractures. From a chemical point of view, this governs both exchange between the fracture and the matrix and the amount of reactive surface area available. This model was necessary to produce reasonable results—otherwise, the extent of reaction was greatly overestimated. The LBNL workers were able to extract field rates based on matching of chemical analyses from DST waters. The data indicated that aluminosilicate reactions are relatively minor in terms of their effect on the water chemistry.

Sorption at Yucca Mountain

The USDOE has developed a set of K_D values for the important radionuclides at Yucca Mountain by fitting experimental data using the USGS model, PHREEQC. A nonelectrostatic model was used to obtain the fits, and the results were then converted into linear distribution coefficients suitable for the chemical conditions expected at Yucca Mountain. The assump-

tion is that most of the sorption can be described as occurring on silica since iron hydroxide is minor at Yucca Mountain. A series of probability density functions are then generated using the K_D values, and these are then used in the Total System Performance Assessment model at Yucca Mountain. Also underway is an effort to develop sorption coefficients for individual rock types at Yucca Mountain. Some effort toward expanding the thermodynamic and adsorption property database for radionuclides as applied to waste isolation at Yucca Mountain has been funded through the USDOE Office of Science and Technology and International source term and natural barriers programs. These projects have led to significant advances in our understanding of phase stability and radionuclide attenuation (e.g., Kubatko et al., 2003, 2006; Pepper et al., 2006).

Colloids at Yucca Mountain

Researchers at Argonne National Laboratory are studying the degradation of spent fuel. The types and quantities of colloids that form as the glass and/or spent fuel degrades are being quantified. Smectite appears to be the dominant silicate phase. In the case of commercial spent fuel, Argonne is trying to determine the amount of colloids generated when small amounts of water are squirted onto the spent fuel. Sorption is based on previous studies that indicated some irreversible sorption (especially for plutonium) and some reversible (Kaminski et al., 2005).

Solubilities of Radionuclides

New radionuclide solubility databases are being developed for the Yucca Mountain project. One database is based on a new formulation for Pitzer coefficients as a function of temperature that was developed at Lawrence Livermore National Laboratory (LLNL). A second non-Pitzer database is also being developed. The Pitzer database is used to predict evaporation-driven reaction paths and to predict deliquescence on dust and salt particles expected to fall on the Yucca Mountain waste packages. Additionally, some experiments on neptunium have been performed to determine whether it is incorporated as a pure phase or in solid solution with uranyl minerals (Rai et al., 2001).

Nevada Test Site

A set of nonelectrostatic surface complexation constants has been developed for iron oxide, calcite, and the aluminosilicates smectite and kaolinite used in reactive transport modeling of sites at the Nevada Test Site (NTS). These constants are for the radionuclides plutonium, neptunium, uranium, cesium, strontium, and the lanthanides. The fits are based on literature data and some unpublished experimental data. The surface complexation constants are used directly in multicomponent reactive transport models like CRUNCH and are also used to generate K_D s for incorporation into particle tracking-based reactive transport codes. Some validation is provided by flow-through experiments using alluvium from NTS. In addition, some validation of the parameters (and calibration) is done at the field scale by comparing model results with observed radionuclide concentrations in wells at NTS.

Hanford Site Transport

Starting with a series of batch experiments investigating binary exchange in the cesium–sodium and cesium–potassium

and cesium–calcium system performed by Zachara et al. (2002), a set of cation exchange coefficients was generated to describe cesium exchange on sediment at the Hanford Site. These selectivity coefficients were then used to try to match the results of column experiments. The column experiments actually showed greater retardation than was predicted by the batch experiments. The classical cation exchange model for cesium and sodium, however, worked very well to 5 mol L⁻¹ NaNO₃. In addition, column-derived parameters were used to match chromatographic front separations at the one of the leaks in the SX tank farm (SX-115). This match was performed without any scaling procedure, suggesting that laboratory experiments on composite sediments were capable of predicting field-scale transport at the Hanford SX tank farm. More recently, transport experiments involving strontium and sodium have been performed at the LLNL. These experiments show a strong ionic strength effect, particularly between about 0.1 and 1 mol kg⁻¹ NaNO₃. The result is that strontium is more retarded at 1 mol L⁻¹ NaNO₃ than would be predicted with an unmodified ion exchange model. A summary report on the Hanford work is available (Certa, 2003). In addition, there are numerous articles on more specific issues (Fredrickson et al., 2004; Liu et al., 2003a,b, 2004, 2006; Pruess et al., 2002; Steefel et al., 2003; Yabusaki, 2002; Yabusaki and Gamedainger, 2002; Zachara et al., 2002).

Office of Science, Office of Biological and Environmental Research

The new Environmental Remediation Sciences Division in the Office of Biologic and Environmental Research (OBER) originally had two major programs that involved subsurface reactive transport—the Natural and Accelerated Bioremediation Research Program (NABIR) and the Environmental Management Sciences Program (EMSP). In 2005 NABIR and EMSP were combined to create the Environmental Remediation Sciences Program (ERSP) to support innovative, fundamental research investigating the coupled physical, chemical, and biological processes affecting the transport of subsurface contaminants at USDOE sites. The Office of Biologic and Environmental Research has an annual budget of approximately \$54 million to fund the ERSP research projects.

The Environmental Remediation Sciences Program and the Natural and Accelerated Bioremediation Research Program

The NABIR program (now part of ERSP) is developing a scientific basis for the use of subsurface microorganisms to immobilize uranium, technetium, and chromium in groundwater plumes on USDOE lands. The goal is to stimulate subsurface microorganisms, primarily metal-reducing bacteria, through electron donor addition to lower redox potential and to generate adsorbed and precipitated iron(II) for heterogeneous redox reaction with the noted contaminants. While the program has strong biological emphasis, approximately 35% of the programmatic support is directed toward biogeochemical research and subsurface reactive transport. The ERSP research is divided into approximately six elements. Three of these (the biogeochemistry element, the biotransformation element, and the Field Research Center) involve reactive transport modeling.

Reactive transport modeling is used by approximately four projects in the biogeochemistry and biotransformation section

to describe coupled microbiologic and geochemical reactions controlling uranium and technetium migration in laboratory columns of mineral material and sediments with single or mixed culture microbial inocula. The modeling challenges are to identify the reaction networks and to model the involved redox reactions, parameterize complex kinetic phenomena, and rationalize changes in system geochemistry with microbial growth and turnover. The projects typically use dual Monod-type kinetic models linked with kinetic geochemical models. The primary research is being performed at the Pacific Northwest National Laboratory (PNNL), LLNL, Princeton University, and Pennsylvania State University.

The NABIR program had originally established a field research center at a uranium- and technetium-contaminated site at ORNL. The present ERSP program supports approximately four to five field injection projects at this site focused on biostimulating subsurface microorganisms to reduce mobile uranium and technetium in groundwater (e.g., Wu et al., 2006). The ORNL researchers have assembled a reactive transport simulator for the field test cells to support the research effort at that site.

The Environmental Remediation Sciences Program and the Environmental Management Sciences Program

The original goal of the EMSP was to develop fundamental science and technology information and knowledge in support of USDOE site remediation. Now merged into ERSP, a large component of the program emphasizes subsurface science focused at issues of (i) geochemical fate and transport, (ii) physical heterogeneity and scaling, and (iii) geophysical imaging and characterization. While reactive transport modeling exists as a supporting component to some projects in the portfolio, the primary focus of ERSP research has been the development of improved conceptual models of hydrologic and geochemical processes controlling contaminant migration on USDOE lands.

The Hanford Science and Technology Program and Groundwater Protection Program is unique to Hanford and is supported by site restoration dollars from the Office of Environmental Restoration within the EM. The program was originally intended to augment the EMSP effort. The goal is to develop and apply fundamental science in support of high-visibility clean-up decisions at the Hanford Site, such as the high level waste tank farms, and the strontium-90 and uranium groundwater plumes that discharge directly to the Columbia River. The program is developing improved Hanford-specific geochemical reaction (for cesium, uranium, strontium, and other contaminants) and vadose zone transport models. The research team applies reactive transport modeling for history matching and future migration projections at key Hanford sites. The team has tackled complex issues such as elevated temperature (up to 100°C), high solution densities, extreme ionic strengths (>10 mol kg⁻¹), and high reactant concentrations (e.g., uranium, hydroxide).

Contaminants of Interest at USDOE Facilities

Table 1 presents a comprehensive list of the inorganic contaminants associated with research activities at various USDOE facilities. Contaminants include metals, metal cations, volatile organic compounds, various hydrocarbons, high explosives, radionuclides, and oxyanions. The compilation includes site

totals for each contaminant and discriminates between vadose zone and groundwater contamination for many of the sites. The federal Agency for Toxic Substances and Disease Registry works with the USDOE in assessing the health effects associated with hazardous waste sites.

U.S. Department of Agriculture

The majority of USDA–ARS research on modeling reactive solute transport concerns nitrogen and phosphorus species. Nitrogen and phosphorus are major items of global commerce, and their application in vast quantities to agricultural lands as chemical fertilizers results in widespread enrichment of soil and water resources. Nitrogen and phosphorus are also generated as waste products in animal production, and manure is both a nutrient resource and a pollutant. Highly visible nutrient pollution issues such as *Pfisteria* infestations, Gulf hypoxia, manure lagoon failures, and nitrate in drinking water have generated demand for this research.

Nitrogen and phosphorus form a variety of reactive species in soil, water, and air. Their cycling in soils and water is mediated by soil properties, oxygen status, microbial activity, and plant utilization. Modeling of these cycles and application of the models to crop and animal nutrition and waste production has been a major focus of ARS natural resources conservation research. The primary inorganic contaminants associated with ARS research are phosphorus, nitrogen, arsenic, selenium, boron, and molybdenum. Additional contaminants include calcium, magnesium, sodium, potassium, and sulfate. In addition to research on nitrogen and phosphorus as inputs and waste products of agriculture, the ARS has a variety of other research on saline soils, application of urban solid and sewage treatment wastes, and other toxics, including metal, in those wastes. Among these projects are several involving subsurface reactive transport–irrigation effects on water quality, process modeling of pollutant movements in soils, modeling salt and toxic element subsurface flow at USDOE sites, and micronutrient and toxic metal behavior in soils. Details and additional projects can be found on the ARS Website (<http://www.ars.usda.gov>).

Research at the USDA in reactive transport modeling has concentrated mainly on the behavior and fate of pollutants in surface- and groundwater leaving agricultural operations such as crops and animal operations. However, runoff and leaching models examine contaminant transport across a wide range of spatial scales, from our traditional point (one-dimensional) or field-scale modeling to watershed and basin scale. The larger-scale modeling is currently receiving considerable attention because agriculture pollution prevention is being driven by consideration of Total Maximum Daily Loads.

Short summaries of various computer modeling tools for simulation of contaminant fate in the unsaturated zone that are actively used by USDA–ARS are presented below (Wauchope et al., 2003; Rien van Genuchten, personal communication). Summaries of environmental studies that use the software tools can be found in the provided references and the listed ARS Websites.

RZWQM

The Root Zone Water Quality Model (RZWQM) developed by the Great Plains Systems Research Unit of ARS located

phases, zero-order production, and two first-order degradation reactions. The program may be used to analyze water and solute movement in unsaturated, partially saturated, or fully saturated porous media. Recently, Simunek et al. (2006) integrated HYDRUS with PHREEQC (a biogeochemical model) to create the Hp1 code to enable the simulation of interactions between physical, chemical, and biological processes in soils and sediments. Numerous simulation studies involving the different versions of HYDRUS software have been published since 1993. Recent examples include Heistermann et al. (2003) in the analysis of pesticide sorption in soil columns, Pang and Simunek (2006) in the simulation of bacteria-assisted transport of cadmium in gravel columns, and Hanson et al. (2006) in the two-dimensional modeling of soil nutrients. For more information, see Skaggs et al. (2005) and <http://www.ars.usda.gov/Services/docs.htm?docid=8939>.

UNSATCHEM

Developed by the George E. Brown, Jr., Salinity Laboratory in Riverside, CA, UNSATCHEM is a software package for simulating water, heat, carbon dioxide, and solute movement in one- or two-dimensional variably saturated media. The major variables of the chemical system are calcium, magnesium, sodium, potassium, sulfate, chloride, nitrate, silicic acid, boron, alkalinity, and carbon dioxide. The model accounts for equilibrium chemical reactions between these components such as complexation, cation exchange, and precipitation–dissolution. The constant capacitance model is used to describe adsorption. Because the ionic strength of soil solutions can vary considerably with time and space and often reach high values, both modified Debye–Huckel and Pitzer expressions were incorporated into the model as options to calculate single ion activities. Recent examples of applications involving UNSATCHEM simulations include Vaughan et al. (2004), for evaluating the boron transport in the San Joaquin Valley, and Decker et al. (2006), to assess arsenic oxyanion transport in mine heap leaching. For more information, see Suárez and Simunek (1997) and Suárez (2005).

In addition to these vadose zone contaminant transport models, the USDA applies a variety of watershed and field-scale models for the simulation of water and nonpoint-source pollution loading to surface water bodies. These include the Agricultural Non-Point Source Pollution (AGNPS) model, the Soil Water Assessment Tool (SWAT), the Riparian Ecosystem Management Model (REMM), and the Water Erosion Prediction Project (WEPP).

U.S. Department of Defense: U.S. Army Engineer Research and Development Center

The U.S. Army Engineer Research and Development Center (ERDC) is a system of integrated laboratories that provide scientific and engineering technical support to the U.S. Army Corps of Engineers (USACE), the USDOA, and the USDOD. The ERDC conducts basic and applied research in a wide variety of disciplines with practical application to military and civil activities. Additional information can be found at the ERDC Website, <http://www.erd.c.usace.army.mil>.

Activities involving reactive transport modeling fall primarily within the ERDC Environmental Laboratory in Vicksburg,

MS, although other USDOD laboratories also develop or use such models. The majority of water-quality issues addressed by the ERDC involves either (i) eutrophication and the regulation of discharges to surface water, (ii) management of contaminated sediments in place or dredged from navigable waterways, (iii) restoration of soil and groundwater resources impacted by military activity, or (iv) minimization of environmental impact of current and future military activities. Research in reactive transport involves hazardous waste site restoration and contaminated sediment management. Within these areas, the emphasis has been in developing a broad range of modeling tools—from relatively simple screening level models to traditional groundwater transport models to research models using advanced computational resources. Several of the more relevant models or activities are described below and on the ERDC Environmental Laboratory Website, <http://el.erd.c.usace.army.mil/index.cfm>.

Groundwater Modeling System

The USDOD Groundwater Modeling System (GMS) is a centerpiece of groundwater modeling activity within ERDC and the USACE (<http://chl.erd.c.usace.army.mil/gms>). The GMS provides a common, graphical user interface to a suite of groundwater models and modeling tools. The commercial version of GMS includes interfaces to several groundwater flow and/or reactive transport models—FEMWATER, MODFLOW, MODPATH, MT3D-MS, RT3D, SEAM3D, UTCHEM, ADH, FACT, ART3D, SEEP3D, VS2D, and NUFT—most of which were developed by or for the agencies in the Federal Working Group on Subsurface Reactive Solute Transport Modeling (see Cygan et al., 2006). It also includes a variety of conceptualization, visualization, and data management tools (e.g., TPROGS, geostatistics, film loops). Capabilities of the GMS software can be found at the commercial Website, <http://www.ems-i.com>.

The reactive transport capabilities within the current suite of GMS models are focused primarily on relatively simple reactions, such as equilibrium or kinetic adsorption and first-order decay, although several models accommodate higher-order bioreactions and user-defined reaction modules. The strategy in GMS development has been to develop interfaces to the more commonly used, public domain models as well as for models useful in remediation design. An interface to a general, geochemical reactive transport model is anticipated. The preferred strategy is to enhance existing models where feasible. Development of new models requires a compelling rationale, such as the migration toward scalable, parallel codes for high-performance computational platforms, or fundamentally new approaches to issues such as scale-independent dispersion. Similar graphical interfaces are available for surface water models and watershed models, some of which involve contaminant transport processes (see Johnson and Gerald, 2006).

Surface Water Quality Models

The ERDC–Vicksburg (or Waterways Experiment Station) has been developing surface water–quality models for several decades. Many of these have become the model of choice for their respective niche. These include water-quality models for reservoirs (e.g., CE-QUAL-R1, CE-QUAL-W2, TWQM), wetlands (PREWET), rivers (CE-QUAL-RIV1), estuaries (CE-QUAL-ICM), contaminated sediments (RECOVERY, ICM/TOXI),

and landfill design (HELP, HELPQ). The aqueous geochemical processes described by these models tend to be fairly simple (equilibrium adsorption, first-order decay), consistent with the needs of the engineering community for whom they are developed. Additional information can be found at <http://el.ercd.usace.army.mil/products.cfm?Topic=model&Type=watqual>.

Adaptive Risk Assessment Modeling System

Efficient use of limited resources requires that cleanup activities be prioritized according to the magnitude of health or environmental risk posed by the situation. Toward that end, the U.S. Army has focused on developing methods to document exposure and impacts and to assess quantitatively any future risk. The Adaptive Risk Assessment Modeling System (ARAMS) serves as the modeling tool into which the risk and toxicological research can be integrated with multimedia fate and transport models to assess and prioritize risk. The Framework for Risk Analysis in Multimedia Environmental Systems (FRAMES), developed by the PNNL, provides the structure for linking disparate models and databases (Whelan and Castleton, 2006). Physicochemical properties required for reactive transport modeling are included in the ARAMS databases. The treatment of geochemical processes is constrained by the reaction package or model selected within ARAMS. Although the current options are rather limited, planned expansion includes, for example, the GMS models. Additional information can be found at <http://el.ercd.usace.army.mil/arams>.

Hazardous Waste Research

The primary focus of hazardous waste cleanup research within the ERDC laboratories relates to munitions constituents, such as explosives, energetics, and chemical agents, or contaminants associated with normal military activity, such as lead and depleted uranium. Brannon et al. (2002) discussed some of the sorptive capabilities of soils for the constituents of the explosive materials, and Rivera et al. (1998) included an analysis of remediation strategies for explosive-contaminated groundwater. The ERDC also has a substantial research program related to nonmilitary contaminants such as sediment-associated highly hydrophobic contaminants (e.g., polychlorinated biphenyl [PCB], polycyclic aromatic hydrocarbon [PAH]), solvents, hydrocarbons, and heavy metals. Remediation technology research includes monitored natural attenuation, bioremediation, in situ chemical oxidation, zerovalent iron, alkaline hydrolysis, electrokinetics, and others, again primarily, but not exclusively, targeted at munitions constituents. Additional information can be found at <http://el.ercd.usace.army.mil/research.cfm?Topic=envenv-cleanup&Option=List>.

Most of the engineered remediation methods of interest to the ERDC present interesting biogeochemical challenges in terms of identifying the critical products and in developing quantitative descriptions of reaction kinetics. The ERDC continues to support the enhancement and development of groundwater models as remediation design tools, with the GMS as the preferred vehicle for these enhancements. The primary inorganic contaminants associated with ERDC research include lead, depleted uranium, chromium, cadmium, and zinc.

U.S. Geological Survey

Summary of Reactive Transport Modeling Applications

The USGS has conducted a number of studies of reactive transport modeling in groundwater over the past 10 yr. The projects have used data collected in the laboratory and in the field. The scales of the field tests have ranged from meters to kilometers. The codes used to simulate reactive transport processes include NETPATH (Plummer et al., 1994), RUNSAT (Lahvis and Baehr, 1997), BIOMOC (Essaid and Bekins, 1998), PHREEQC (Parkhurst and Appelo, 1999), PHAST (Parkhurst et al., 2004), RATEQ (Curtis, 2005), and several other unpublished codes. Many of the applications have been conducted at sites supported by the Toxic Substances Hydrology Program. Research has also been conducted on U(VI) transport at a former uranium mill site in Naturita, CO. Results from these two programs are summarized below.

Toxic Substances Hydrology Research Sites

Bemidji, Minnesota

The Bemidji Toxic Substances Hydrology Research Site focuses on the fate crude oil spilled onto the ground as a result of a pipeline burst. Infiltration of crude oil to groundwater resulted in geochemical changes including the development of iron-reducing and methanogenic zones. The initial modeling efforts used the inverse model NETPATH, which identifies the dominant phase-transfer reactions that occur along a flow path from dissolved concentration data (Baedecker et al., 1993). Essaid et al. (1995) used the solute transport model BIOMOC to simulate hydrocarbon degradation coupled to the sequential use of multiple terminal electron acceptors and microbial growth and decay. Curtis (2003) illustrated that irreversible Monod kinetic models can force reactions to occur against the thermodynamic gradient and consequently developed an alternative approach that constrained kinetic parameters by reaction thermodynamics. Essaid et al. (2003) used the parameter estimation model UCODE (Poeter and Hill, 1998) to estimate rates of BTEX (benzene, toluene, ethylbenzene, and xylene) dissolution from the crude oil, first-order degradation rates, and hydraulic conductivity. It was found that despite having extensive historical data, it was not possible to distinguish between alternative conceptual models although long-term predictions obtained with the different conceptual models were significantly different. Bekins et al. (2005) presented a simple method that assumed benzene degradation was controlled by bioavailable, sediment-associated iron(III) to successfully describe the observed expansion of the benzene plume.

Cape Cod, Massachusetts

Transport of molybdate has been studied in a natural-gradient tracer test in an unconfined sand and gravel aquifer at the Massachusetts Military Reservation on Cape Cod, MA (Stollenwerk, 1995, 1998). Molybdate transport was controlled by adsorption that was sensitive to pH and competing solutes (phosphate and sulfate). Adsorption and its effect on transport were modeled using a one-site and a two-site diffuse-layer surface complexation model (SCM) that were calibrated in laboratory experiments. Both models simulated the travel distance of the molybdate

cloud to within 10% during the 2-yr tracer test; however, the two-site diffuse-layer model more accurately simulated the molybdate concentration distribution within the cloud. Kent et al. (2000) described a two-dimensional vertical cross-section model that was used to simulate the influence of pH on zinc adsorption and transport. Adsorption was described using semi-empirical SCM. The semi-empirical SCM assumed that the adsorption of zinc, which was dominated by interactions with complex surface coatings, could be described by equilibrium reactions and their associated mass action expressions. However, an electrical double layer was not included for simplicity, because double layer parameters are difficult to define for complex mixtures. The SCM parameters were determined in independent laboratory experiments. A 59-yr simulation with a one-site SCM described the influence of pH on zinc transport well, with greater mobility at the low pH values near the upper sewage plume boundary than at the higher pH values deeper in the sewage-contaminated zone. Simulation with a two-site SCM describes both the sharpness and approximate location of the leading edge of the zinc-contaminated region. Parkhurst et al. (2003) simulated the discharge of phosphorous to Ashumet pond using a three-dimensional reactive transport model that accounted for groundwater flow and a diverse set of chemical reactions, including phosphorus sorption on aquifer materials, dissolution, and precipitation of iron- and manganese-oxhydroxide and iron phosphate minerals, organic carbon sorption and decomposition, cation sorption, and irreversible denitrification. The simulations were consistent with both laboratory and field data and illustrated that although phosphorous discharge to the pond peaked in the mid-1990s, substantial discharge to the pond was predicted for at least 50 yr.

One-dimensional reactive transport simulations were conducted to study reactions of injected zinc, nickel, and calcium-ethylenediaminetetraacetic acid (EDTA) complexes during transport at the Cape Cod aquifer (Friedly et al., 2002). The system was dominated by dissolution of iron oxyhydroxides in the aquifer and the formation of iron-EDTA complexes. This dissolution was modeled with a single rate-controlled process calibrated from the field data and other EDTA complexation reactions were governed by equilibrium. Kent et al. (2002) conducted a field-scale transport experiment to examine the influence of variable pH on the transport of strongly adsorbing metal ions. The principal objectives of reactive transport modeling were to predict the influence of temporal variations in pH on Zn concentrations and transport using laboratory batch and column experiments for model calibration and to describe the behavior of other ions, including potassium and calcium, which varied in the experiment. Accounting for ion exchange reactions and surface buffering reactions was important for simulating the observed pH and zinc breakthrough. Friedly et al. (1995) modeled the reduction of chromium(VI) in observed batch and field studies. The reduction was assumed to be coupled to oxidation of iron(II) minerals and the accessibility of the iron(II) was limited by a diffusional resistance. The field-scale model included 21 parameters that ranged from readily measured values such as the volume and concentration of the injectant to estimated values such as the fraction of the porous media that was nonreducing. Both one- and two-dimensional reactive transport models for enhanced denitrification coupled to formate oxidation have been described (Smith et al., 2001; Killingstad et al., 2002). These models included microbial growth and decay, which

were simulated using the dual Monod formulation. The models accounted for the use of both nitrate and nitrite as terminal electron acceptors. The model consisted of 19 reaction parameters, which were estimated by calibrating the model to tracer test data. Peak rates of nitrate and nitrite reduction from the field model were about two orders of magnitude smaller than rates measured in laboratory batch studies, illustrating the limited value in this instance of laboratory batch studies to determine microbial reaction rate constants.

Galloway, New Jersey

Aerobic biodegradation of gasoline hydrocarbons in the subsurface by indigenous microorganisms in the unsaturated zone was investigated at the Galloway, NJ, site. The R-UNSAT model was designed for quantifying the rates of diffusion, volatilization, and biodegradation of organic compounds above the water table. Calibration of the model to observed vertical gas concentrations and laboratory-determined diffusion coefficients gave estimates of the volatilization and biodegradation rates (Baehr and Baker, 1995). R-UNSAT was also used to simulate effects of vapor extraction, including rebound effects that occur when vapor extraction is terminated temporarily. By calibrating the R-UNSAT model to the rebound gas-concentration data, Lahvis and Baehr (1996) calculated an aerobic-biodegradation rate of approximately $0.061 \text{ L m}^{-2} \text{ yr}^{-1}$.

Pinal Creek, Arizona

Pinal Creek is in central Arizona, about 100 km east of Phoenix. Copper has been mined in the Pinal Creek basin since 1882, first in underground mines and, beginning in 1948, in open-pit mines. Contaminated acidic groundwater resulting from sulfide oxidation causes pH values of ~ 2 to 3 and large concentrations of sulfate, calcium, iron, manganese, copper, aluminum, and zinc. Acidic groundwater is neutralized mainly through reaction with calcium carbonate as the plume moves down gradient. The pH increases to between 5 and 6, and metals including iron, copper, and zinc precipitate or adsorb to mineral surfaces in the aquifer. Glynn and Brown (1996) used the inverse models NETPATH and PHREEQC to identify which reactions were responsible for the observed geochemical changes. Reaction parameters were all taken from tabulated thermodynamic data. The inverse modeling demonstrated that the principal reaction was the reductive dissolution of manganese(IV) solids by iron(II) and the consequent precipitation of iron(III) oxyhydroxides. Neutralization reactions in the carbonate aquifer slow the rate of advance of the plume's acidic front and most of the dissolved metals to about one-seventh of the rate of advective groundwater flow; this was simulated with PHREEQC. Field and modeling studies of calcite samples suspended in wells revealed that although the calcite dissolution rate in the field was approximately 10^3 times slower than that observed in laboratory studies, using a rate-controlled expression to simulate calcite dissolution did not improve model fit relative to an equilibrium model (Brown and Glynn, 2003).

USGS-USNRC Collaborative Research on Uranium(VI) Transport in Laboratory and Field-Scale Simulations

Transport of uranium(VI) and adsorption by quartz have been investigated in batch and column studies in the labora-

tory (Kohler et al., 1996). A nonelectrostatic SCM calibrated to three column experiments predicted transport in four other column experiments that had different chemical conditions. This included one experiment where a significant pH gradient developed as a result of adsorption involving high concentrations of uranium(VI). The calibrated-column SCM fit the batch data well. However, a SCM calibrated to batch data had column prediction errors of approximately 70%. This relatively large error resulted because the batch and column data were collected under different surface loading conditions.

Field studies were conducted at the site of a former uranium mill located along the San Miguel River approximately 3 km north of the town of Naturita, CO. A uranium mill that operated at the site between 1941 and 1961 processed uranium ores with both sodium carbonate and sulfuric acid. Mill tailings were deposited and remained on the site until they were removed in 1977. Davis et al. (2004a) developed a generalized composite SCM for describing uranium(VI) adsorption by Naturita aquifer background sediments under variable pH and $p\text{CO}_2$ in batch studies. The model consisted of four reactions and a total of three site types: weak, strong, and very strong. An electrical double layer was not included for simplicity. The model was calibrated to batch adsorption data collected under variable chemical conditions that nearly completely spanned the range of field conditions.

The applicability of the laboratory-derived model to simulate field conditions was evaluated in several closely related studies. Field K_D values were measured on fresh samples suspended in 17 43-cm (2-inch) wells that had variable alkalinity and uranium(VI) concentration. The field K_D values ranged from 0.5 to 9 mL g^{-1} , and the K_D values decreased with increasing groundwater alkalinity. The field K_D values were compared with model K_D values calculated from the laboratory-determined SCM. The field K_D values agreed with the model K_D values within a factor of two and explained the variable alkalinity at the site. The SCM also accounted for temporal changes of K_D values in three wells that resulted from variable chemical conditions in the groundwater (Curtis et al., 2004). The SCM was able to predict the adsorption of uranium(VI) onto contaminated sediments at the site (Kohler et al., 2004). Isotopic exchange experiments and carbonate extractions were conducted on contaminated sediments to determine the amount of labile uranium(VI) associated with the sediments. The labile uranium(VI) was assumed to represent adsorbed concentrations. K_D values measured by isotopic exchange methods were compared with model K_D values calculated from the SCM and the groundwater analysis obtained when the sediment samples were collected. The model and observed K_D values generally agreed within a factor of three or less.

The SCM was used in both one- and two-dimensional reactive transport models without any adjustment of the SCM parameter values. In small-scale tracer tests, one-dimensional model simulations predicted both increases and decreases in uranium(VI) concentration resulting from either increases or decreases in alkalinity (Curtis and Davis, 2006). At the plume scale, the model was matched to the observed existing conditions at the site (Curtis et al., 2006), although the source of the uranium(VI) was used as a calibration parameter. Simulations showed that the uranium(VI) K_D values in the field varied by approximately a factor of 20 and also illustrated a significant spa-

tial trend: the highest uranium(VI) concentration was associated with the smallest K_D values. This resulted primarily from the correlation between uranium(VI) and alkalinity. This distribution illustrates that performance assessment calculations should consider not only a range of K_D values but also the spatial structure of the K_D distribution. This could be difficult to do with look-up tables because the spatial structure is likely to change temporally and spatially.

Contaminants and Processes of Interest in USGS Research

Table 2 provides a listing of the contaminants associated with research efforts at the USGS. The primary chemical processes associated with each contaminant are indicated along with those that have been evaluated by reactive transport modeling and have been characterized through field testing. The compilation is primarily the result of the Toxic Substances Hydrology Program, which has brought together scientists with a broad range of expertise, including ecologists, geologists, chemists, hydrologists, geochemists, and biologists, to conduct long-term field studies. Important contaminants associated with joint projects between the USGS and either the USEPA or USNRC are also included.

U.S. Nuclear Regulatory Commission

The Center for Nuclear Waste Regulatory Analyses (CNWRA) is a federally funded research and development center located at the Southwest Research Institute in San Antonio, TX. The CNWRA was created to provide technical assistance to the USNRC in carrying out its licensing responsibilities for a potential high-level radioactive waste geologic repository. The CNWRA has developed its laboratory and modeling capabilities to focus on the role of reactive transport in repository performance. Laboratory studies include investigating the sorption behavior of neptunium and uranium on aluminosilicate minerals common to the Yucca Mountain, NV, environment, including quartz, montmorillonite, and clinoptilolite (Pabalan et al., 1998; Bertetti et al., 1998; Turner et al., 1998). Cesium and strontium uptake by ion exchange in the zeolite mineral, clinoptilolite, has been investigated in binary and ternary systems with sodium, potassium, and calcium (Pabalan and Bertetti, 2001). Current laboratory activities include studies of the sorption and coprecipitation behavior of neptunium and calcite (Bertetti, 2002). Precipitation and dissolution studies are underway to constrain the thermodynamics of the secondary uranium mineral, uranophane, and its potential role in limiting radionuclide release from spent nuclear fuel and other waste forms (Prikryl and Murphy, 2004). Extended X-ray absorption fine structure and molecular dynamic methods are used to investigate uranium sorption reactions at the mineral-water interface (Greathouse et al., 2002, 2005; Zaidan et al., 2003). The CNWRA has also investigated methods for using SCM with MINTEQA2 and PHREEQC to establish stochastic sorption parameter distributions for total system performance assessment calculations (Turner et al., 2002, 2006).

Metal sorption studies relating to the application of reactive transport models are also being performed at Sandia National Laboratories in Albuquerque, NM. The major objective of this work is to provide a defensible, science-based understanding of radionuclide migration and retardation for assess-

TABLE 2. Representative research studies on inorganic contaminants and processes conducted by the USGS.

	Adsorption–desorption; ion exchange	Precipitation–dissolution; coprecipitation	Redox	Modeling	Field tests
Alkali metals					
Lithium	X				X
Sodium	X			X	X
Potassium	X			X	X
Alkaline earth metals					
Magnesium	X	X		X	X
Calcium	X	X		X	X
Strontium		X			X
Radium	X				
Transition metals					
Chromium	X		X	X	X
Manganese		X	X	X	X
Iron		X	X	X	X
Cobalt	X	X			X
Nickel	X				X
Copper	X				
Zinc	X			X	X
Molybdenum	X			X	X
Technetium			X		
Silver					X
Cadmium	X	X			X
Mercury	X	X	X		X
Other metals					
Aluminum		X		X	X
Lead	X				
Metalloids					
Boron					X
Silicon		X			X
Arsenic	X	X	X	X	X
Nonmetal elements					
Hydrogen (pH)	X	X	X	X	X
Carbon	X	X	X	X	X
Nitrogen	NH ₄ ⁺		X	X	X
Oxygen			X	X	X
Phosphorus	X			X	X
Sulfur		X	X	X	X
Selenium	X	X	X	X	X
Noble gases					
Radon					X
Actinide series					
Uranium	X		X	X	X
Neptunium				X	
Plutonium				X	

ing contaminant transport in the environment. Performance assessment calculations are typically used to estimate radionuclide concentrations in ground and surface water, treat the uncertainty in those estimates, and evaluate the consequent dose impact to the public from USNRC licensed activities. Current performance assessment models use simplified conceptual models for radionuclide retardation that are based on linear and reversible partition coefficients (K_{Ds}) measured for a specific set of experimental conditions, which usually are laboratory measurements of soil samples. Unfortunately, experience shows that this approach often fails to correlate with field measurement of actual transport. The reason is that the experimental K_{Ds} represent localized properties and are sometimes not applicable over time and at other locations considering the range of nonlinear geochemical phenomena and chemical conditions that can significantly affect radionuclide transport. Therefore, it is critical to understand and model radionuclide retardation processes and mechanisms in soils. The Sandia project attempts to combine various state-of-the-art theoretical and analytical methods to evaluate these sorption concerns. The project objectives include the identification

of sorption-controlling soil minerals for selected radioactive waste sites (Jové Colón et al., 2006), determination of the extent of radionuclide retention on the sorption-controlling minerals using synchrotron-based microtomography (Altman et al., 2005), derivation of the theoretical limits on the range of K_D values for selected radionuclide-mineral pairs through molecular simulation (Teter and Cygan, 2002; Greathouse and Cygan, 2005, 2006), and the probabilistic analysis of sorption parameter uncertainty and the influence on radionuclide migration (Criscenti et al., 2006). Some of the characterization studies are being performed in collaboration with the USGS to better understand the nature of the soil phases at Naturita, CO.

A list of critical contaminants related to the USNRC research efforts is provided in Table 3. The contaminants are associated with decommissioning of mining and industrial sites, low-level radioactive waste sites, fuel cycle facilities, and uranium mill tailings sites. Most of these contaminants are controlled by adsorption–desorption and ion exchange processes in soil phases. The ultimate transport of contaminants through the environment is also related to redox fronts and complex dissolution–precipitation processes. Reactive transport modeling emphasizing surface complexation

has been completed by the USNRC in collaboration with the CNWRA, USGS, and Sandia.

Conclusions

The future success of subsurface reactive transport lies in the coordinated efforts of academic and government researchers in defining the limits and identifying the practical nature of using models and software tools for a variety of contaminant waste issues. Recent modifications of transport codes to include adsorption, surface complexation, ion exchange, redox, nucleation, precipitation, dissolution, fracture distributions, multi-scale heterogeneity, microbial activity, and other processes have made reactive transport models more general for a wide variety of environmental applications. With these advances in theory and conceptual models, however, the software and codes often become unwieldy and cumbersome. It is not uncommon that the software is limited to experienced practitioners and becomes impractical, if not dangerous, in the hands of the uninformed user. Moreover, the reactive transport modeler may be forced to ascertain whether a model is “good” or “good enough” to meet

TABLE 3. Representative waste sites and inorganic contaminants researched by the U.S. Nuclear Regulatory Commission.

Decommissioning	Location	U	Th	Am	Pu	Co	Cs	Ta	Nb	Sc	Tc	Ra	K	Sr
AAR Manufacturing Group, Inc.	Livonia, MI		X											
B&W Parks Operating Facility	Parks Township, PA			X	X	X	X							
B&W Parks Shallow Land Disposal Area	Parks Township, PA	X	X	X	X									
Cabot Performance Materials Inc.	Reading, PA	X	X											
DOW Chemical Company	Bay City, MI		X											
Fansteel Inc.	Muskogee, OK	X	X					X	X	X				
Heritage Minerals Inc.	Lakehurst, NJ		X											
Jefferson Proving Ground	Madison, In	X												
Kaiser Aluminum Specialty Products	Tulsa, OK		X											
Kerr McGee-Cimarron	Crescent, OK	X									X			
Kerr McGee-Cushing Refinery	Cushing, OK	X	X											
Kiski Valley Water Pollution Control Authority	Vandergrift, PA	X												
Mallinckrodt Chemical Inc.	St. Louis, MO	X	X											
Michigan Department of Natural Resources	Kawkawlin, MI		X											
Molycorp Inc	Washington, PA	X	X											
Molycorp Inc	York, PA	X	X									X		
Permagrain Products, Inc.	Karthus, PA					X								
Safety Light Corp.	Bloomsburg, PA			X			X					X		X
SCA Services	Kawkawlin, MI		X											
Sequoyah Fuels Corp.	Gore, OK	X	X									X		
Shieldalloy Metallurgical Corp.	Newfield, NJ	X	X											
Union Carbide Corp.	Lawrenceburg, TN	X												
Watertown GSA	Watertown, ME	X												
Westinghouse Electric Corp., Waltz Mill	Madison, PA						X							X
Whittaker Corp.	Greenville, PA	X	X									X		
Low-level waste (LLW)	Location	U	Th	H-3	C-14	Pu	Cs	Class A	Class B	Class C	Tc	Ra	K	Sr
Former LLW site	Beatty, NV	X												
LLW site	Barnwell, SC	X		X										
LLW site	Richland, WA	X												
Envirocare	Clive, UT	X												
Former LLW site	Sheffield, IL	X		X	X									
Former LLW site	Morehead, KY	X		X		X								
Former LLW site	West Valley, NY	X												
Fuel cycle facility	Location	U	Th	Am	Pu	Co	Cs	Ta	Np	Sc	Tc	Ra	K	Sr
US Enrichment Corp.	Portsmouth, OH	X												
US Enrichment Corp.	Padukah, KY	X	X	X	X				X		X			
Uranium mill tailings reclamation	Location	U	Th	Am	Pu	Co	Cs	Ta	Np	Sc	Tc	Ra	K	Sr
UMTRA†	Canonsburg, PA	X										X		
UMTRA	Burrell, PA	X										X		
UMTRA	Ambrosia Lake, NM	X										X		
UMTRA	Durango, CO	X										X		
UMTRA	Falls City, TX	X										X		
UMTRA	Green River, UT	X										X		
UMTRA	Gunnison, CO	X										X		
UMTRA	Lakeview, OR	X										X		
UMTRA	Lowman, ID	X										X		
UMTRA	Maybell, CO	X										X		
UMTRA	Mexican Hat, UT	X										X		
UMTRA	Naturita, CO	X										X		
UMTRA	Rifle, CO	X										X		
UMTRA	Salt Lake City, UT	X										X		
UMTRA	Shiprock, NM	X										X		
UMTRA	Slick Rock, CO	X										X		
UMTRA	Tuba City, AZ	X										X		
Mixed oxide fuels	Savannah River, SC	X	X		X									

†UMTRA, Uranium Mill Tailings Remedial Action site.

the needs of the application and remain consistent with the field observations. It is hoped that some of the practical examples provided here may assist the less-experienced user in choosing the appropriate conceptual model and understanding the limitations of the various software tools associated with subsurface reactive transport modeling.

This review provides many insights into the various approaches used by individual researchers and large research groups among the U.S. federal agencies involved in fundamental and applied research relating to the fate of contaminants in the environment. Although not an exhaustive review of reactive transport modeling (see Ghadiri and Rose, 1992), numerous

examples are provided of federally funded projects and programs that are of overriding interest to the federal government, and which require the coordination of several agencies. We hope that this concerted effort will continue to be supported and that several key technical issues will be addressed in the near future. Among the recommendations provided by Davis et al. (2004b), in their summary report for ISCMEM, is the support of long-term research at field sites specifically for conceptual model development for reactive transport simulation, with a balance between complexity and tractability. Such an approach is necessary to advance our understanding of the often-complex coupling of biogeochemical processes at various length scales to

better identify and accurately describe the controlling mechanisms in the reactive transport model. Laboratory and multi-scale field experiments are critical complements to the field-scale models and often provide the necessary parameterizations and independent constraints for the model inputs. Additionally, it is important that multiscale variability in subsurface properties be addressed through model calibrations against field observation.

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