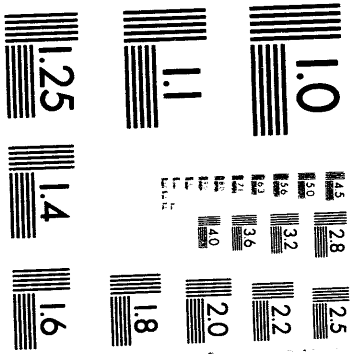
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TOWARDS A REALISTIC APPROACH TO VALIDATION OF REACTIVE TRANSPORT MODELS FOR PERFORMANCE ASSESSMENT

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ABSTRACT

Performance assessment calculations are based on geochemical models that assume that interactions among radionuclides, rocks and groundwaters under natural conditions, can be estimated or bound by data obtained from laboratory-scale studies. The data include radionuclide distribution coefficients, measured in saturated batch systems of powdered rocks, and retardation factors measured in short-term column experiments. Traditional approaches to model validation cannot be applied in a straightforward manner to the simple reactive transport models that use these data. An approach to model validation in support of performance assessment is described in this paper. It is based on a recognition of different levels of model validity and is compatible with the requirements of current regulations for high-level waste disposal. Activities that are being carried out in support of this approach include (1) laboratory and numerical experiments to test the validity of important assumptions inherent in current performance assessment methodologies, (2) integrated transport experiments, and (3) development of a robust coupled reaction/transport code for sensitivity analyses using massively parallel computers.

I. INTRODUCTION

The debate over the definition and feasibility of model validation continues to be spirited and dynamic. Most workers in the technical and regulatory branches of contaminant transport studies agree that greater confidence is needed in models that will be used to assess the performance of high-level waste (HLW) disposal sites. However, no consensus exists on what constitutes either reasonable goals or expectations in this area. Some segments of the general public may expect that accurate predictions of processes at potential repository sites for a 10,000-year time period will be made with *validated* models. Other workers suggest that the term *validation* should be abandoned completely because it implies an unattainable level of certainty.

Models of flow and contaminant transport in the unsaturated zone are an essential part of performance assessment calculations. Such calculations rely on simplified representations of complex chemical behaviors of aqueous radionuclides, hydrologic flow fields and material properties of the rock layers surrounding the repository. The structures of these models are strongly influenced by (1) current theories describing the transport and reaction of chemical species in natural systems, (2) the availability of data from both empirical and mechanistic studies of solute/rock/water interactions in the specific geochemical environments of interest, and (3) the costs associated with computer simulations of large-scale natural systems. The requirements for performance assessment (PA) model validation must recognize that limitations in these three areas will prevent the inclusion of all possible phenomena in any single analysis.

This paper describes a framework for the validation of reactive transport models that are used in support of performance assessment (PA). The approach is based on a recognition of different types of models, different levels of validity, and the requirements of current regulations for high-level waste disposal. Current studies that apply these general principles include experiments to test the validity of several assumptions inherent in the current PA methodology, integrated flow and transport experiments and development of a robust coupled reaction/transport code for sensitivity analyses using a massively parallel computer.

II. PRINCIPLES OF MODEL VALIDATION FOR PERFORMANCE ASSESSMENT

A. Model Validity: General Principles

Zeigler[1] describes several concepts that have been useful in traditional approaches to model validation. He identifies the following five distinct elements of a model:

(1) The *real system*, which is the source of **all** data;
(2) *Experimental frames,* which are subsets of data used in a particular application;
(3) The *base model*, which is a hypothetical model valid in all experimental frames;
(4) *Lumped models*, which are simple models designed for particular experimental frames; and
(5) The *computer codes,* which carry out the simulations.

Zeigler[1] defines three levels of model validation. A model is said to be *replicatively valid* if it matches data that have been previously acquired. A model is *predictively valid,* if it can match new data collected after formulation of the model. Finally, a model is *structurally valid,* if it accurately describes the underlying processes and operation of the *real system.*

The above definitions can be used to formulate precise descriptions of the process of model validation. Using Zeigler's concepts, the first step in model validation is to identify the appropriate experimental frames and the required level of validity. The validity of a model is then assessed relative to the particular experimental frame for which it is designed. The usefulness of alternative validation approaches proposed by different participants in HLW disposal research and regulation can be evaluated in light of these concepts. Unfortunately, as discussed below, the traditional approach to model validation cannot be applied in a straightforward manner to models for performance assessment. However, the above definitions are useful in developing realistic requirements for PA model validation.

B. Model Validation in a Regulatory Environment

The government agencies involved in performance assessment of potential HLW repositories have provided several definitions of the term *validation*. The U.S. Nuclear Regulatory Commission[2] (NRC) defined validation as "assurance that a model, as embodied in a computer code, is a correct representation of the process or system for which it is intended." The U.S. Department of Energy[3] (DOE) defined *model validation* as "a process whose objective is to ascertain that the code or model indeed reflects the behavior of the real world."

These definitions appear to require demonstration of *structural validity*. It is the opinion of some researchers[4,5] that proof of *structural validity* is not possible and runs counter to the accepted framework of scientific investigation. Models, like scientific hypotheses can only be *invalidated* or disproven.

Current HLW regulations require calculations of integrated radionuclide discharge to the accessible environment over a 10,000-year period and radioactive contamination of certain sources of groundwater for 1,000 years following waste emplacement. Demonstration of *predictive validity* for the models used in these calculations is difficult because comparisons of predictions and experimental results cannot be made *within the same* temporal, spatial, and physicochemical *experimental frames*. Model predictions (long-term/large-scale) can only be compared against experimental results or field observations collected over relatively short time periods and at discrete sampling points, rather than from large volumes of geomedia. In addition, the empirical nature of laboratory methods, used to provide geochemical data for transport codes, prevents demonstration that the data have been collected in the correct physicochemical experimental frame.

Recently, several researchers[5,6] have recognized the special requirements of models for performance assessment. They have concluded that ultimately, assessment of model validity may require a significant amount of *subjective* judgment. According to this view, *model validation* involves convincing the regulatory and scientific communities that the model is *adequate and appropriate* for the intended use (i.e., demonstration of compliance with regulatory standards), that it has been developed in a *logical manner* with the *best available* technology, and that model predictions agreed with *high quality* experimental and observational data within *acceptable* limits in a *sufficient* number of tests.

Unfortunately, precise definitions for many of the terms in the above description of model validation are not available. Because specific requirements for model validation have not been defined, numerical acceptance criteria for validation tests have not been defined by either the scientific or regulatory communities.

The lack of clear definitions for basic terms and lack of acceptance criteria have impeded progress towards obtaining consensus on an acceptable approach to model validation. The model validation approach described in this paper uses several different methods of analysis to reconcile the requirements of regulations for HLW disposal with elements of traditional approaches to model validation. This paper attempts to show a correspondence between the different types of models and different levels of validity defined by Zeigler[1] previously, and specific issues and phenomena important to reactive transport in PA calculations.

III. PROPOSED VALIDATION APPROACH

In the approach proposed here, ***validation* is defined as an ongoing process to obtain reasonable assurance that models can be used to calculate realistic bounds for appropriate performance measures.** For high-level waste disposal, these measures are the calculated integrated radionuclide discharges and groundwater contamination levels. The *reasonable assurance* can be gained by disproving a *null hypothesis* for performance assessment[3]. For the Yucca Mountain Site Characterization Project, this hypothesis is: *It is likely that conditions or processes at Yucca Mountain will lead to radionuclide discharges that are significantly greater than those predicted with simple performance* *assessment codes, using data collected in laboratory or field studies.*

The proposed approach to **disprove** this null hypothesis includes (1) demonstration that the results of model validation tests, carried out under the spatial, temporal and physicochemical experimental frames accessible to researchers, can be extrapolated to the experimental frames relevant to the U.S. Environmental Protection Agency (EPA) Standards[7] for HLW disposal, (2) demonstration that the assumptions used in PA calculations are applicable under site-specific conditions (i.e., at Yucca Mountain for HLW disposal) and (3) methods to define numerical criteria for adequate agreement between model predictions and experimental or observational data.

At the heart of the approach defined in this paper is the relationship between *robust models* and *lumped models*. The most robust model possible corresponds to the *base model* defined by Zeigler[1] in Section II.A. above. Model robustness can be described in terms of the *intrinsic* and *conditional* constants required by the model. *Conditional* constants are used in lumped models and are valid only for very specific experimental conditions; *intrinsic* constants are used in more robust models and are valid over a wider range of conditions. It is proposed here that models that use intrinsic constants should be used to extrapolate results obtained in laboratory or field experiments to experimental frames relevant to the HLW regulations

The distinction between robust models and more lumped models can be made clearer by considering two types models for equilibrium sorption used in transport calculations and laboratory studies:

1. Retardation factors calculated from linear (K_d) or non-linear sorption (Freundlich and other) isotherms and
2. Surface-complexation models such as the triple-layer model (TLM)[8].

The simplest model (linear sorption or K_d) requires a single constant that is *conditional* with respect to a large number of variables. Even if a batch K_d experiment is carefully carried out to avoid introduction of extraneous effects such as precipitation, the K_d that is obtained will at best describe equilibrium sorption only for the particular conditions of the experiment. The radionuclide concentration, pH, major and minor element composition, Eh, temperature, rock mineralogy, particle size, and solid surface-area/solution volume ratio must be specified for each K_d; there is no way to extrapolate a K_d obtained under one set of conditions to another.

In contrast, the more robust triple-layer model contains seven adjustable parameters and is one of the most complex models used in contaminant transport studies. The TLM constants are valid over the ranges of pH, ionic strength, solution composition, specific surface areas and site densities used to extract the constants. An important advantage of the triple-layer model is that it provides a structured way to examine experimental data obtained in batch sorption studies. Application of such a model can ensure that extraneous effects will not be introduced into the sorption experiments.

The comparative adantages and disadvantages of the TLM and K_d in reactive-transport modeling and PA can be summarized as follows. Use of a robust model such as the TLM requires greater understanding of chemical processes than does use of a K_d. It is the opinion of the author that this greater level of understanding leads to greater confidence that the model does accurately describe some aspects of the *real system.* Although *structural validity* has not been established for the TLM, ongoing research suggests that the model is *predictively valid* within the experimental frame used to obtain the surface complexation constants (see Section IV.C. below and cited references). A great deal of experimental and theoretical work is required to obtain surface complexation constants, however, ultimately, these constants could be used to predict sorption within experimental frames that span laboratory and field conditions.

Robust models can be used to demonstrate that the assumptions used in PA calculations are applicable under site-specific conditions. Simplified (lumped) models used in performance assessment calculations do not include descriptions of many potentially important phenomena. Model validation in support of PA involves showing that the effects of these *missing* phenomena on the regulatory performance measures are advantageous, nonexistent or relatively small under site-specific conditions. This can be accomplished by demonstrating that the errors in the regulatory performance measures, due to the use of lumped geochemical models, are acceptable when compared to other errors in the total systems PA calculations. The errors are calculated by comparing the results of simulations carried out with simplified PA models to those of robust reactive-transport models or exact analytical solutions. Criteria for adequate agreement between the robust and lumped models can be based on the numerical criteria in the U.S. Environmental Protection Agency (EPA) Standard[7] and other requirements for HLW disposal.

In the following section, the general concepts outlined above are applied to specific subjects in radionuclide transport. The treatment described below is not intended to encompass all aspects of reactive transport; the studies discussed are used to illustrate the proposed approach to model validation.

III. METHODS FOR VALIDATION OF REACTIVE TRANSPORT MODELS FOR PERFORMANCE ASSESSMENT

A crucial element in the design of the reactive models used in PA calculations is the validity of the simplifying assumptions used to describe radionuclide retardation. Lumped retardation models used in PA calculations often include the following assumptions:

Assumption (1) Radionuclide retardation can be described by reversible, linear sorption isotherms involving a single aqueous species in equilibrium with the substrate.

Assumption (2) Local equilibrium exists between fluids in fractures and in adjacent rock matrix in porous fractured media.

Assumption (3) The intensity of sorption (moles radionuclide sorbed /moles substrate) is independent of hydraulic saturation.

Assumption (4) Compositions of the rock and solution along fluid flow paths are the same as those used in the K_d experiments.

The following methods can be used to test the validity of the assumptions:

(1) Solution of inverse problems for PA performance measures,
(2) Derivation of numerical criteria for site-specific applicability of lumped models used in PA models,
(3) Experimental studies to test predictive abilities of alternative models for solute-rock interactions, and
(4) Integrated flow and transport experiments to compare the predictive abilities of simple transport models and complex hydrogeochemical transport models.

Examples of previous and current work illustrating these methods are given below.

A. Solutions of Inverse Problems

Siegel and Erickson[9] demonstrated an inverse method that addresses part of the above Assumption 1. The analysis identifies conditions wherein lack of chemical equilibrium leads to significant underestimation of radionuclide releases, if K_ds, measured using standard techniques, are used in PA calculations. In the hypothetical scenario that was examined (Figure 1), laboratory K_d measurements are dominated by a strongly sorbing radionuclide species (species A). However, during transport, this species converts to poorly sorbing species (species B) that is not detected in the laboratory experiments. Clearly, the total integrated discharge of the radionuclide species A and B will be greater than the discharge calculated assuming that all the nuclide exists as species A. The magnitude of the error will depend on the relative mobilities of species A and B as well as the rate of transformation A->B.

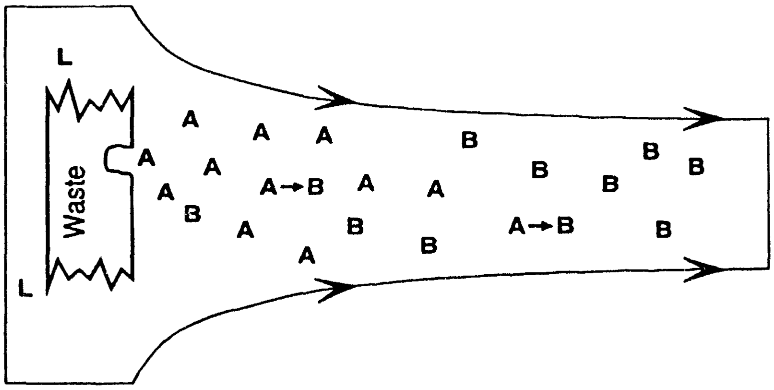

Figure 1. Scenario for inverse problem solution. Species A is a hypothetical sorbing species studied in batch sorption experiments that converts during transport to a hypothetical nonsorbing species B. Adapted from Reference 9.

Critical combinations of values of geochemical and hydrological parameters that would lead to violations of the remanded EPA Standard[7] for the scenario illustrated in Figure 1 were identified by Siegel and Erickson[9] in the following way. Terms for homogeneous and heterogeneous chemical reactions were incorporated into individual radionuclide transport equations for species A and B. The equations were simplified, using conservative assumptions that calculate an upper bound for radionuclide discharge; the integrated discharge was then calculated for the 10,000-year EPA regulatory period. The discharges of species A and species B were summed and the resultant expression was set equal to a specific release limit (the EPA radionuclide release limit or some fraction thereof). Finally, the resulting equation was solved numerically to determine combinations of the parameters (K_ds for A and B, reaction rate, groundwater travel times, etc.) that caused radionuclide releases greater than the specified release limit.

Derivation and presentation of the equations, given in Siegel and Erickson[9], are beyond the scope of this paper. Figure 2 provides an example of the results of this parametric analysis. Combinations of values of k^*, the rate of A->B conversion, and R_B,, the retardation factor for species B, which lead to discharges of ^{237}Np equal to 20 curies over a 10,000-year period are shown for two values of groundwater travel time to the accessible environment. Combinations of k* and R_B that lie below the curve for a specified groundwater travel time lead to discharges greater than the release limit. A retardation factor for species A ($R_A = 200$) was assumed, and it was also assumed that after an initial 1,000-year isolation period, 1 mole ^{237}Np per year was released from the waste form.

Siegel and Erickson[9] show that the above method of analysis can be used to determine minimum rates for speciation reactions that need to be considered for PA calculations. The analysis can also be used to determine the duration of kinetic and sorption experiments required for quantitative observation of the effects of potential speciation reactions that could disguise violations of the remanded EPA Standard[7]. In the context of a model validation strategy, inverse solution methods can help identify conditions under which simplified lumped models are invalid for PA calculations.

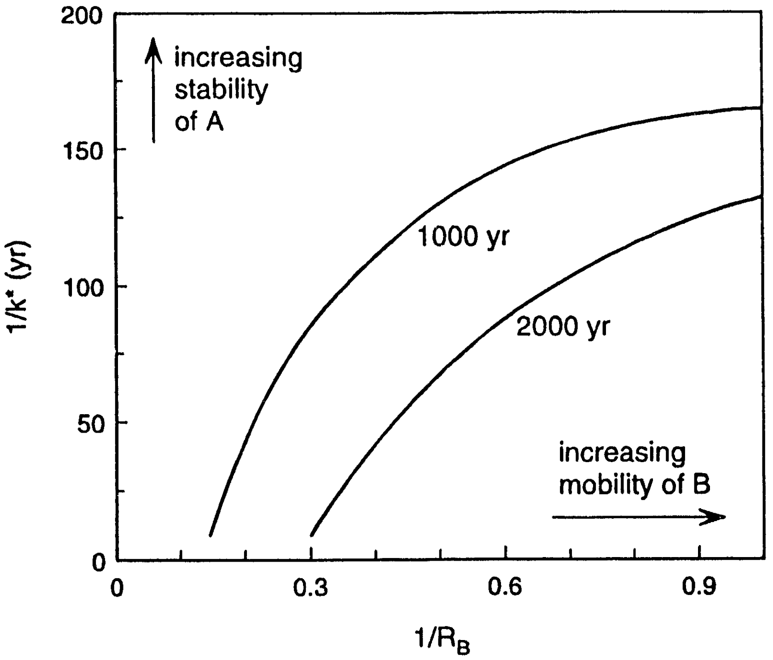

Figure 2. Combinations of reaction rate k* and retardation factor R_B that lead to ^{237}Np discharges of 20 Curies for 1000 yr and 2000 yr groundwater travel times in the scenario described in Figure 1. See text for values of other parameters assumed in calculation. From Reference 9.

B. Derivation Of Numerical Criteria For Site-Specific Applicability Of Lumped Models Used In PA Models

Erickson et al.[10] demonstrated a method to test the validity of Assumption 2 above under site-specific conditions. They evaluated three approximate models commonly used in PA calculations to describe matrix diffusion in fractured, porous rock. The analysis was designed to determine if the errors in the calculated integrated discharge due to the use of the lumped transport models are acceptable when compared to other errors in the total systems calculations. In the context of model validation, this is equivalent to formulating numerical criteria which define the experimental frame within which the lumped models are valid for their intended use (i.e. demonstration of compliance with regulatory standards).

The models evaluated were: (1) a semi-infinite-medium approximation (SIM), where radionuclide diffusion rates are calculated assuming a semi-infinite matrix; (2) a linear-driving-force model (LDF), where radionuclide diffusion rates are assumed to be proportional to the difference between radionuclide concentrations in the fracture fluid and in the matrix pore fluids; and (3) an equivalent-porous-medium model (EPM), where radionuclide diffusion rates into the matrix are proportional to depletion rates in the fracture fluids.

An analysis of the models was made by considering one-dimensional transport of a single radionuclide species with linear sorption in saturated porous rock containing uniform fractures. Criteria for the validity of each model were derived in terms of fundamental physicochemical parameters from consideration of the fluid residence times in the fractures and relaxation times for chemical gradients in the matrix. The respective errors in radionuclide discharge over a 10,000-year period, calculated using the approximate models, were examined by comparing those discharges with discharges calculated using exact solutions to rigorous convection-diffusion radionuclide transport equations. A model was considered to be valid if errors in calculated radionuclide discharge were less than 30% when compared to the exact solution. The numerical criterion was arbitrarily chosen, but reflected a subjective assessment of uncertainties in other system parameters used in the calculation.

Figure 3 shows how the appropriate experimental frame for each of these simple models can be defined. For systems consisting of parallel fractures having spacing 2B, matrix porosity ϕ_m, and fracture porosity ϕ_f, the SIM model is valid when:

$$x/v < B^2\alpha^2\phi_f/\phi_m D(1-\phi_f)\ ;$$

the LDF model is valid when:

$$x/v > 0.2B^2\alpha^2\phi_f/\phi_m D(1-\phi_f)\ ;$$

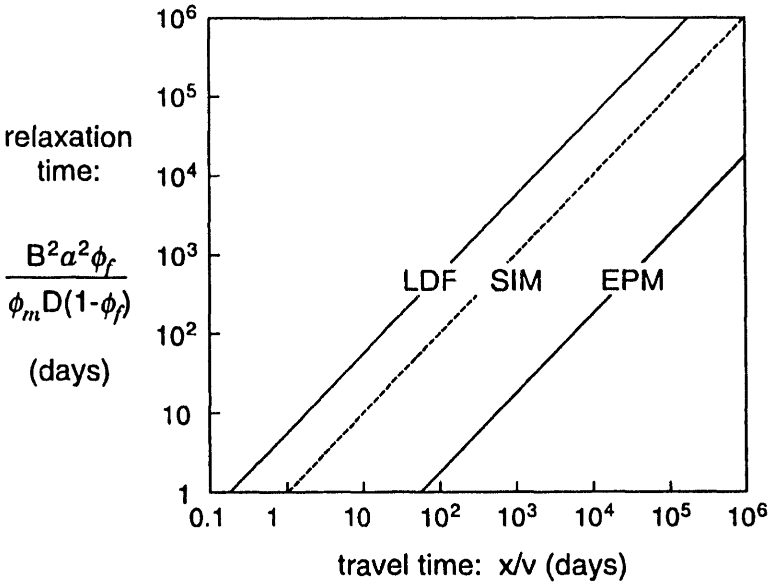

Figure 3. Criteria for application of approximations for calculations of radionuclide transport in fractured porous rock. Areas below lines marked 'LDF' and 'EPM' correspond to conditions under which linear driving force and equivalent porous media approximations, respectively apply. The semi-infinite medium approximation applies above the line marked 'SIM'. Adapted from Reference 10.

and the EPM model is valid when

$$x/v > 50B^2\alpha^2\phi_f/\phi_m D(1-\phi_f)\ .$$

Here, D is the radionuclide diffusion coefficient in the pore water, v is the average fluid velocity in the fracture, x is the radionuclide transport length, and α is a tortuosity/constrictivity factor for the matrix.

Derivation of the relevant equations is beyond the scope of this paper. Details can be found in Erickson et al.[10] where it is shown that the numerical criteria listed above can be used to determine the validity of lumped models of radionuclide transport under site-specific conditions. In the context of this proposed model validation approach, the lumped models are considered *valid for performance assessment calculations* if they can be used to calculate upper bounds for radionuclide discharges within acceptable limits of error under relevant experimental frames.

C. Experimental Studies To Test Predictive Abilities of Models For Solute-Rock Interactions

The proposed model validation approach includes development of tools to assess the applicability of lumped retardation models (e.g., K_ds obtained in saturated systems) to site-specific conditions. The comparative advantages and disadvantages of the TLM and K_d for reactive-transport modeling and PA were described in general terms in Section III. Batch sorption and transport experiments, involving a suite of tracers and solids, are currently being carried out to directly test assumptions of the lumped sorption models (e.g., Assumptions 1, 2, 3 above) and to develop more robust retardation models based on the TLM. The robust models will be used to support the application of the results of a relatively limited number of laboratory studies to a wide range of field conditions and reduce the dependence PA calculations on Assumption 4 above.

The tracers used in the experiments include: (1) bromide, a conservative tracer that can be used to track the movement of water in transport experiments, (2) lithium, a tracer that forms relatively weak surface complexes, (3) nickel, a transition metal that forms strong surface complexes with geologic materials and is representative of radionuclides released from the structural components of the spent fuel rods; and (4) uranium, an important component of high level waste and a chemical analog for several of the transuranics. The solids used in the experiments include minerals present in fractures in Yucca Mountain tuffs (quartz, calcite, clays and iron oxyhydroxides) and in the bulk matrix (zeolites).

1. Measurements of sorption under unsaturated conditions. Two techniques currently are being developed to carry out in-situ sorption studies in unsaturated media. One method measures the solute concentrations in moist sand using laser excitation and measurement of the resultant time-dependent fluorescence signal. Techniques to measure both

uranium concentrations and pH (via fluorescent dyes) are being developed. The technique is also being adapted to study the effects of fracture-surface coatings on the exchange of fluids and uranium between fractures and porous matrix. If successful, this work will allow evaluation of the validity of the local chemical equilibrium assumption in fractured tuff for uranium and other radionuclides (Assumption 2).

In the second method, sand-water systems at low degrees of saturation are equilibrated with enriched ^{235}U solution in a Turbula mixer and then flushed with enriched ^{238}U solution at a higher uranium content. With this technique it should be possible to extract the pore solution for analysis without causing the ^{235}U to desorb. The K_d of the unsaturated system can then be calculated from the ^{235}U/^{238}U ratio of the extracted solution. If successful, this work will allow evaluation of the effect of hydraulic saturation on sorption (Assumption 3 above).

2. Formulation of a sorption model for mineral mixtures and rocks. In heterogeneous groundwater systems, adsorption may be controlled by trace amounts of reactive minerals that are preferentially concentrated along flow paths or other structural features. Studies of metal adsorption by bulk rocks via traditional K_d measurements may not provide information about the most reactive adsorption sites. In order to determine if changes in mineralogy or solution composition along radionuclide transport paths will lead to radionuclide discharges substantially different than those calculated using K_d's obtained from the bulk rock, a model for mineral mixtures must be formulated and tested. Ultimately, the model developed in this study will be used to determine if Assumption 4 above is adequate for PA for site-specific conditions at Yucca Mountain.

Previous studies[8,11,12] attempted to formulate "linear adsorptivity models" (LAM), in which the adsorptive properties of mixtures are predicted from a weighted average of the adsorptive properties of the mineral components. In general, it was found that the LAM was not valid for the oxide-silicate and oxide-organic systems studied and that adsorption constants obtained in single-solute/single-sorbent systems could not be used in multi-solute/multi-site systems.

A review of the techniques and modeling approaches used in previous studies[8,11,12,13] suggests that a useful adsorption model for mixtures might be formulated if (1) the concentrations of component minerals are varied systematically over a wide range during adsorption studies of mixtures of minerals and (2) adsorption constants obtained in single mineral-single solute studies are used to model behaviors of mixtures and solids with multiple sites. Preliminary results[13] shown in Figure 4 indicate that the adsorption of Pb by simple synthetic clay-oxide mixtures, over a range of pH and solids concentration, can be predicted from the properties of the component minerals using surface-complexation models. The complexation constants obtained for individual minerals were used to model aqueous speciation and sorption properties of mineral mixtures with the HYDRAQL[14] computer code.

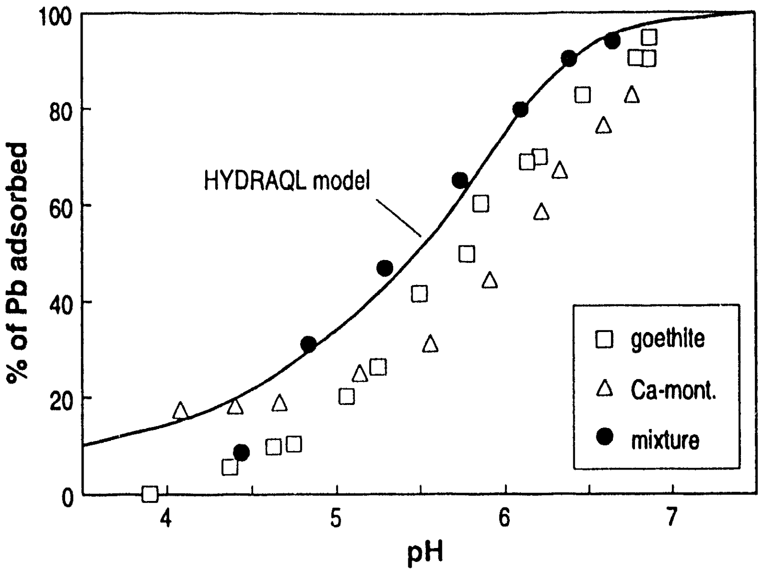

Figure 4. Adsorption of Pb (2.41×10^{-5} *M*) onto goethite, Ca-montmorillonite and mixtures containing 0.6 g/*l* goethite and 2 g/*l* Ca-montmorillonite in 0.1 *M* $NaNO_3$. Modeling results of HYDRAQL for the mixture are shown by the solid line. Adapted from Reference 13.

This approach is currently being tested with other mixtures of synthetic minerals and natural mineral mixtures. In these studies, the triple-layer surface-complexation model will be used to describe adsorption on surfaces with pH-dependent charge, and ion-exchange theory will be used for fixed-charge exchange sites. Surface hydrolysis constants will be measured by potentiometric titrations; specific adsorption constants for reactive tracers and background electrolytes will be obtained by batch sorption techniques. The predicted sorption properties of various synthetic mixtures and natural materials will be compared to those measured using certified K_d measurement techniques[15].

Studies of Ni sorption by a natural sand (Wedron 510) are being carried out in support of an integrated reactive transport experiment (described in the next section). According to its bulk chemistry and mineralogy, the sand is nearly pure quartz, but preliminary characterization suggested that it contains at least three other chemically reactive components: carbonate, iron oxyhydroxides, and kaolinite. Figures 5 and 6 compare the pH-dependent sorption of Ni by the raw sand and two model components of the sand (quartz and goethite) at similar surface area/solution volume ratios. The similarities in the location and shapes of the sorption curves for the raw sand and goethite (α-FeOOH) (Fig. 6) suggest that iron oxyhydroxide coatings may control Ni sorption by the sand. Collection of similar data for the kaolinite and calcite components of the sand will allow formulation of a more complete sorption model for transport modeling.

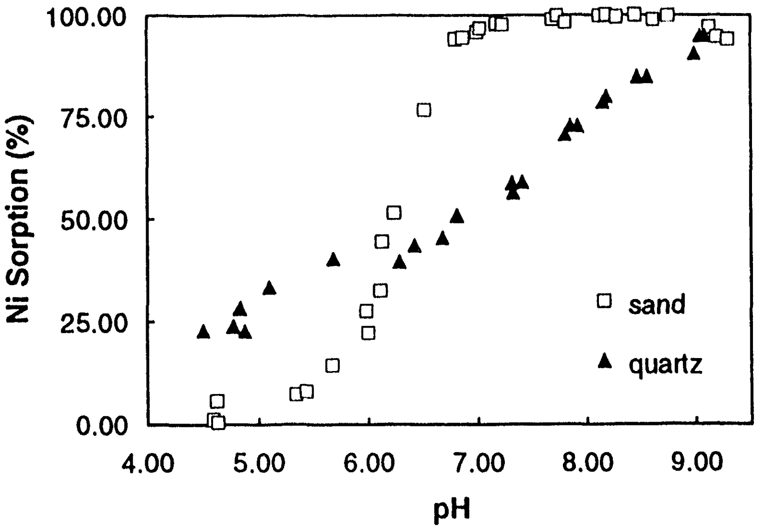

Figure 5. Ni Sorption Vs. pH for Wedron 510 sand and Min-U-Sil-5 quartz. The surface area of both types of systems was 0.12 m^2/ml.

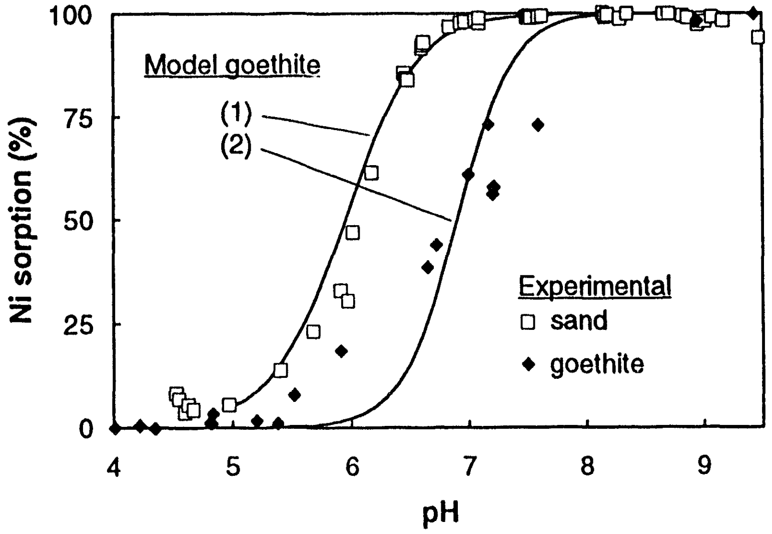

Figure 6. Comparison of Ni sorption by Wedron 510 sand (1 g/m*l*, CO_2-free conditions) to Ni sorption by goethite (0.12 mg/m*l*, atmospheric CO_2). Solid lines are calculated sorption curves for goethite using HYDRAQL: (1) 3 mg/m*l* goethite and 0.0001 *M* total CO_2, and (2) 0.13 mg/m*l* goethite under CO_2-free conditions.

D. Integrated Flow and Transport Experiments

The proposed model validation approach includes integrated flow and transport experiments to compare the predictive validities of simple transport models and coupled hydrogeochemical models. The experiments should provide an opportunity to test the ability of alternative geochemical models to predict reactive transport when used with different flow models. Major issues that will be addressed include: 1. What geochemical characteristics of the fractured and porous media will dominate chemical retardation of tracers? 2. What are the primary contributors to the uncertainty in the accurate detection of the tracers in transport experiments? and 3. Which geochemical models adequately describe tracer migration?

An intermediate-scale transport-model validation experiment is being carried out at the Experimental Engineered Test Facility at Los Alamos National Laboratory. The experiment involves the detection and prediction of the migration of fluid and tracers (Li, Br, Ni) through a 6-m high x 3-m diameter caisson filled with Wedron 510 sand, a commercially available silica sand described in the previous section (Wedron Silica, Wedron Ill. 60557). The overall objectives, experiment plan, and materials characterization studies are described in recent publications.[16,17,18]

Data, describing the interactions between each tracer and the sand, among the tracers, and among the tracers and the other solutes in the pore water of the sand are being collected to allow application of several models of geochemical retardation. K_d measurements are being carried out according to procedures developed by Los Alamos National Laboratory[15]; surface complexation constants are being obtained with methods developed at Stanford University[19] and Sandia National Laboratories. K_d data will be used to calculate tracer transport with the FEHMN[20] code; surface complexation constants will be used in the LEHGC version of the HYDROGEOCHEM[21] code.

The sorption studies indicate that an isotherm sorption model may be required to predict Li transport.

Additional data will be obtained to allow comparison of the validity of the Freundlich, Langmuir and other isotherm models for lithium transport. The data for Ni sorption suggest that a model describing the changes of pH and the concentrations of other solution species as a function of time and position within the caisson and the concomitant effects on Ni sorption may be required for accurate predictions of nickel transport.

Validation of contaminant transport models involves comparison of calculated and observed tracer elution curves. The agreement between model predictions and experimental data will not be perfect because of uncertainties in tracer detection and the accuracy of model assumptions. Criteria for acceptable agreement are being formulated as part of model validation tests and will reflect various sources of uncertainty in the experimental and model designs. The caisson experiment was designed to provide well-controlled conditions and a well-characterized geomedia to allow separation of uncertainties due to chemical and physical processes.

E. Development of a Coupled Chemical Reaction/Transport Model

Complex chemical behaviors such as multiple dissolution-precipitation fronts, elevated releases of radionuclides from secondary enrichments and large variations in K_ds over time cannot be simulated by available performance assessment codes. PA models cannot be validated without an assessment of the potential importance of these phenomena under site-specific conditions. This requires demonstration that the effects of these phenomena on the regulatory performance measures are advantageous, nonexistent or relatively small. Simulations of radionuclide transport that include these phenomena on the time and spatial scales required for compliance assessments currently are not practical. For this reason, the proposed model validation approach requires development of a suitable coupled chemical reaction/transport code.

The LEHGC version of the HYDROGEOCHEM code[21] is a coupled chemical reaction/transport code which solves a set of linear partial differential equations

(PDEs) to describe hydrological transport of solutes and a set of nonlinear algebraic equations (AEs) to describe chemical speciation. The chemical processes, assumed to occur under conditions of local equilibrium, include aqueous complexation, adsorption (surface complexation), ion exchange, precipitation and dissolution. The code uses total analytical concentrations of components as the primary dependent variables and solves the PDEs and AEs as two coupled sequential sets of equations. The code uses a hybrid Lagrangian-Eulerian scheme which allows larger time steps to be used in advection-dominated calculations and causes less numerical dispersion than traditional Eulerian schemes.

This approach allows for efficient computations and implementation on a massively-parallel computing architecture. This will make possible two-dimensional (and ultimately, three-dimensional) simulations of radionuclide transport on a repository scale. The code is being adapted to Sandia National Laboratories' nCUBE computer which has 1024 processors. In the initial modifications to the code, the geochemical equilibrium calculations will be performed in parallel and the transport calculations will be carried out on a single node. When all the modifications are complete, the speed of the code could improve substantially.

Previously[22], HYDROGEOCHEM was used to simulate conditions and scenarios under which lumped sorption models using K_ds are invalid. These calculations did not examine scenarios that are relevant to Yucca Mountain. Determining whether or not similar scenarios exist that are relevant to conditions expected at Yucca Mountain or lead to extremely high radiological consequences are the roles of site characterization and performance assessment respectively. As part of the model validation approach described here, transport predicted by performance assessment codes using retardation factors measured on bulk mixtures will be compared to the tracer behavior predicted by LEHGC using surface complexation constants measured on the individual minerals and rocks. In this way, conditions relevant to Yucca Mountain, under which the use of a simple retardation factor to predict radionuclide transport are **not valid,** will be identified.

V. CONCLUSIONS

Within the technical and regulatory communities, expectations about model validation range from unrealistic requirements to suggestions that the term *validation* be abandoned. The thesis of this paper is that, although traditional approaches to model validation cannot be applied in a straightforward manner to performance assessment, a definition of validation appropriate to PA is both possible and useful. In this paper, validation is defined as a process to obtain reasonable assurance that PA models will bound the appropriate performance measures. The approach described here attempts to reconcile the requirements of current regulations for high-level waste disposal with elements of traditional approaches to validation by recognizing different types of models and different levels of validity.

The proposed approach for model validation will not lead to a rigorous proof that models reflect the behavior of the real world; in general, such proofs of *structural validity* are not possible. Proofs of *predictive validity* are also not possible for nuclear waste disposal because the spatial and temporal experimental frames accessible to experimentation and observation are much narrower than those relevant to the applicable regulations. At best, the approach described in this paper, can be used to disprove a *null hypothesis* for performance assessment: *It is likely that conditions or processes at Yucca Mountain will lead to radionuclide discharges that are significantly greater than those predicted with simple performance assessment codes, using data collected in laboratory or field studies.*

The methods proposed to test the null hypothesis involve a combination of numerical calculations comparing robust models to more lumped (simpler) models, and comparison of predictions made by the robust models to experimental results. Specific activities described in this paper include (1) calculation of critical combinations of values of geochemical and hydrological parameters that would lead to violations of the remanded EPA Standard[7], (2) derivation of numerical criteria for site-specific applicability of approximations used in PA models, (3) experiments to test the validity of assumptions inherent in the current performance assessment methodology, (4) integrated flow and transport experiments, and (5) development of a robust coupled reaction/transport code for sensitivity analyses using a massively parallel computer.

Although no single analysis will be sufficient to disprove the PA null hypothesis, the combination of techniques described above can be used to determine if the probable errors in the calculated regulatory performance measures (radionuclide discharge or groundwater contamination levels), due to the use of lumped geochemical models in performance assessment codes, are acceptable when compared to other errors in the total systems calculations. This information should be used by the regulators and public to determine if the performance assessment models are adequate and appropriate for demonstration of compliance with regulatory standards.

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