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# WORK PLAN FOR HYDROGEOCHEMICAL MODELING OF RADIONUCLIDE TRANSPORT

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## WORK PLAN FOR HYDROGEOCHEMICAL MODELING OF RADIONUCLIDE TRANSPORT

### 1.0 INTRODUCTION

In order to maintain public health and safety, the ability of the proposed high-level waste (HLW) repository at Yucca Mountain to isolate the waste is of critical importance. For the proposed multiple-barrier design, a key measure of repository performance is the degree of attenuation of radionuclide transport provided by water/rock interaction along flow paths to the accessible environment. An important part of this retardation is sorption of radioelements on the geologic media. Typical approaches to modeling repository performance have tended to use a retardation factor ( $R_r$ ) to represent attenuation. In turn,  $R_r$  is often based on a discrete sorption coefficient ( $K_d$ ) which assumes that retardation occurs by equilibrium adsorption/desorption alone. While this treatment is computationally simple, it is empirical in nature and has no theoretical basis for extrapolation beyond experimental conditions. Additionally, it cannot discriminate between the contributions of the various processes (e.g., sorption, precipitation/dissolution) involved in retardation.

Geochemical equilibrium codes have been used for many years to calculate different aspects of geochemical systems, such as speciation and chemical saturation. Hydrogeochemical codes that couple geochemistry and transport have been used as tools for evaluating retardation processes, and predicting the nature and extent of contaminant transport. Development of such comprehensive codes is being actively pursued by several research groups [e.g., Los Alamos National Laboratory (LANL), Commission of the European Communities (CEC), Lawrence Berkeley Laboratory (LBL), Pacific Northwest Laboratory (PNL), Harwell Laboratory, Electric Power Research Institute (EPRI), Stanford] using a variety of approaches. To find the appropriate balance between completeness and applicability, a hydrogeochemical code should be considered with respect to accuracy, efficiency, flexibility, and computational requirements, among other characteristics.

Task 2 of the Sorption Modeling for High-Level Waste Performance Assessment Research Project is the use of hydrogeochemical models to model radionuclide transport in the Yucca Mountain environment (Pabalan, 1991a). The geochemical code MINTQA2 (Allison et al., 1990), and the hydrogeochemical code CTM (Erikson et al., 1990) are both able to model sorption processes using one of several models and evaluate other retardation mechanisms. Results are highly dependent on the completeness and quality of the input data, making database development and adaptation an important aspect of hydrogeochemical modeling. As a means of validating the model, the results of simulations can be compared with a number of available or planned experimental and field studies. More complete code descriptions and a list of code selection criteria are available in Turner (1991).

## 2.0 TECHNICAL BACKGROUND

### 2.1 SORPTION MODELS

Equations relating solute concentrations in coexisting solid and liquid phases can be generated through curve-fitting to observed data and deriving empirical coefficients (Ames et al., 1983a,b). A drawback common to all empirically-derived sorption models (e.g.,  $K_d$ , Freundlich, Langmuir) is the inability to discriminate between different retardation mechanisms (Reardon, 1981; Miller and Benson, 1983; Kelmers et al., 1987). Extrapolation of isotherms beyond the experimental conditions used to derive the necessary coefficients is generally not theoretically justified. Empirical models are therefore largely unsuited to rapidly changing systems, and necessarily limited to restricted ranges of conditions (Miller and Benson, 1983; Parker and Jardine, 1986; Kent et al., 1988). Also, because aqueous speciation cannot be addressed by empirical approaches, these methods may be inadequate to model the interactions that occur during multispecies transport. Therefore, in order to evaluate the adequacy of an empirical approach, it is critical to have an understanding of the physicochemical conditions along likely flow paths, and the magnitude of changes anticipated in the system (Turner, 1991).

Mechanistic approaches to sorption have been developed to provide flexible, robust models that are applicable to the variety of conditions likely to be encountered in the subsurface (Turner, 1991). These include ion exchange (e.g., Pabalan, 1991b), and surface complexation models (Davis et al., 1978; Davis and Leckie, 1978; 1980; Kent et al., 1988). Based on theoretical considerations, these models are able to address changing conditions (e.g., pH, temperature) through the use of a set of equations and experimentally-derived parameters. Unlike empirical models, these approaches are designed to discriminate between different retardation mechanisms, and justifiable extrapolation beyond experimental conditions is possible. Unfortunately, these models have only been applied in a relatively limited number of cases, and the necessary input parameters, particularly for radioelements, are largely unavailable. In the absence of experimentally-determined parameters, it is possible to use either estimation techniques such as those of Smith and Jenne (1988; 1991) and Dzombak (1986), or curve-fitting techniques to derive the parameters that best fit the observed data. While it is perhaps sufficient to fit observed solute distributions in this fashion despite the lack of "hard" data, it is less satisfactory in that it introduces a new element of uncertainty; "Are the estimating or curve-fitting techniques appropriate?". An additional source of uncertainty is the parameters needed for the estimation models. Also, curve-fitting approaches compromise the theoretical justification of model extrapolation, subjecting mechanistic models to many of the same limitations as empirical approaches. The large number of parameters in most mechanistic models may lead to the additional drawback of a nonunique fit to the data.

## 2.2 GEOCHEMICAL CODES

To address the relative contributions of different chemical processes to radionuclide retardation, a computer code must have the capability of modeling these processes. Furthermore, the code must offer the user the option of choosing among different sorption models in order to address their suitability. The MINTEQA2 geochemical equilibrium code (Allison et al., 1990) uses the mathematical approach of the MINEQL code (Westall et al., 1976), and the thermodynamic database of the U.S. Geological Survey WATEQ3 code (Ball et al., 1981). In addition to modeling equilibrium precipitation/dissolution, MINTEQA2 (and earlier versions) is currently the only widely available geochemical code that has the ability to model sorption processes. Seven different sorption models are available, including empirical isotherms ( $K_d$ , Freundlich, and Langmuir), ion exchange, and surface complexation (diffuse-layer, constant capacitance, and triple-layer). In addition, many key variables can be externally fixed in the MINTEQA2 code [e.g., pH,  $P(\text{CO}_2)$ , etc.], avoiding problems such as "pH drift" (Read and Broyd, 1989). Elevated temperatures up to 100° C can be modeled, either through the use of the Van't Hoff equation or using a power function where available. Data input is formatted, but an interactive input program, PRODEFA2 is available to construct input files.

Morrey et al. (1986) determined that if the thermodynamic data are similar, MINTEQ (an earlier version of MINTEQA2) provided results similar to those obtained from the EQ3NR/EQ6 code (Wolery, 1979). In test cases where the thermodynamic data differed significantly, however, divergent results were obtained. Calculated mineral saturations also differed slightly; this is likely a function of differences between included values and the relative completeness of the two databases. While MINTEQ (and MINTEQA2) are limited to equilibrium calculations, the authors concluded that it would be easier to add reaction-path modeling to MINTEQ than to modify EQ3NR/EQ6 to include adsorption. Similar differences occurred in the CHEMVAL validation exercise (Read and Broyd, 1989) which compared the PHREEQE code (Parkhurst et al., 1980) and MINEQL. Read and Broyd (1989) note that differences between thermodynamic databases is the largest single cause of discrepancies between speciation and precipitation results. As with EQ3NR/EQ6, PHREEQE is subject to pH drift, and lacked the ability to model sorption.

Thermodynamic data are of critical importance in modeling any geochemical system. Validation exercises such as the CHEMVAL exercise (Read and Broyd, 1989) are an attempt to test a database for accuracy and internal consistency. Additionally, the database should be broad enough to include a relatively complete set of species, minerals, and complexes that are likely to be encountered in the geologic environment of interest (Kincaid et al., 1984; Krupka et al., 1988). The database should be able to incorporate both updated information and additional data as needed for a given system. A readily available, public domain database has the advantage of being tested through application to a wide variety of problems, and will also benefit from a general interest on the part of the research community in keeping the database consistent, accurate, and current.

### 2.3 REACTIVE TRANSPORT APPROACHES

Two approaches have been used commonly to couple geochemical equilibria and transport models. Direct (one-step) coupling (Rubin and James, 1973; Valocchi et al., 1981a,b) involves insertion of the nonlinear, algebraic equations describing equilibrium geochemistry into the partial differential equations that describe transport. The resulting set of nonlinear partial differential equations are solved simultaneously for geochemistry and transport for a given set of dependent variables. For the second method, geochemistry and mass transport equations are posed independently, and solved sequentially rather than simultaneously. This two-step approach has been used successfully in several studies (Walsh et al., 1982; Cederberg et al., 1985).

While one-step coupling yields a more exact solution, the coefficient matrix must be reformulated for each iteration, leading to extensive computer calculation time and large memory requirements (Cederberg, 1985). Alternatively, two-step coupling solves equations in sequence, and uses computer resources much more effectively. Cederberg (1985) calculated that a two-step coupling approach was more than 30 percent faster than direct coupling in solving the same problem. In addition, several studies (Morrey et al., 1986; Yeh and Tripathi, 1989) suggest that only a two-step approach will be able to model larger two- and three-dimensional problems, given likely limits on computational speed and memory storage in the foreseeable future. Storage and run costs can amount to many thousands of dollars for a single 10,000-year simulation on a scale similar to Yucca Mountain (Siegel et al., 1989), and efficient numerical solutions are necessary to minimize run costs (Yeh and Tripathi, 1989). In addition, because a transport code is envisioned as a part of an interactive approach to performance assessment, codes requiring extensive supercomputer time are at a distinct disadvantage (de Marsily, 1990). This will become increasingly apparent in a stochastic approach that relies on performing large numbers of calculations to develop adequate statistics. Elaborate, computationally slow codes become the rate-limiting step in performing these calculations, making a stochastic approach untenable without invoking significant (perhaps unrealistic) advances in computer technology.

### 2.4 HYDROGEOCHEMICAL CODES

As described in the Task 1.1 literature review (Turner, 1991), the CTM code (Erikson et al., 1990) has been initially chosen for further investigation. Its relative simplicity makes it attractive for use in the multiple runs under a variety of conditions that will be required in performance assessment. Based on the two-step coupling approach, the CTM code solves for reactive solute transport more efficiently than the one-step coupling approach. Because the code has been adapted to the IBM PS/2 Model 70 personal computer system, computer costs are minimal, although more powerful computer capabilities will be necessary for future extension into two- and three-dimensions. Also, since the hydrological approach used by CTM only requires a velocity flow field, it is not, in theory, specific to any particular flow code. This flexibility offers the possibility for adapting the CTM model to more sophisticated transport codes in the future. The current database is based on the 1990 version of PHREEQE, extended

to include the uranium data of Tripathi (1984). Data format is based on a modified (Krupka et al., 1988) version of MINTEQ, and several sorption mechanisms are available for evaluating sorption processes. The thermodynamic database is extensive and does not require either the extensive formatting of input or the development and construction of a run-specific database like the CHEMTRN and CHMTRNS codes. Interactive preprocessing will simplify modification of the conceptual model and allow for flexible application. Post-processing capabilities permit a variety of data display options. Although the code only considers equilibrium geochemistry, kinetic data are currently limited or nonexistent for most of the radioelements, and under certain conditions (e.g., long residence time), an equilibrium treatment may be adequate to model sorption and retardation for performance assessment (Valocchi, 1985).

### **3.0 WORK PLAN**

#### **3.1 OBJECTIVES-TASK 2**

The overall objective of this study (Pabalan, 1991a) is to develop a methodology for the application of coupled hydrogeochemical models to Yucca Mountain performance assessment. Since the geochemistry is the most computer intensive aspect of hydrogeochemical modeling (Liu and Narsimhan, 1989), the geochemical model must be streamlined wherever possible. This objective can only be reached through a series of steps designed to: (i) identify important radionuclides; (ii) provide the thermodynamic and sorption databases necessary to evaluate the relative importance of sorption and other retardation mechanisms for these key radioelements; (iii) check the codes, process models, and data against laboratory and field results in well characterized systems, (iv) identify key solids and solution species for which sorption and thermodynamic data are needed, and; (v) use the validated geochemical models to determine the simplest model that is adequate to address critical sorption processes applicable to the Yucca Mountain environment, probably through examining relatively well characterized radioelements.

Once the geochemical modeling of static systems has identified critical parameters, suitable models, and appropriate simplifications with respect to geochemical processes, it will be possible to couple the streamlined geochemistry with transport. In a manner similar to that outlined for modeling geochemical equilibrium, the immediate objective with hydrogeochemical transport will be to work from simple, well characterized systems to gradually more complex natural systems, with the ultimate goal of modeling radionuclide transport for performance assessment in the Yucca Mountain environment.

Because sorption and hydrogeochemical modeling are dynamic areas of research, it is expected that new data will continue to become available throughout the duration of this study. For this reason, a review of the pertinent literature, and technical exchanges with the research community will be an ongoing objective. Technical exchange will be especially critical as site characterization proceeds at Yucca Mountain and mineralogies, water chemistries, and physicochemical conditions are defined along likely flow paths.

## 3.2 GEOCHEMICAL MODELING

### 3.2.1 Identify Important Radionuclides

Modeling efforts will focus on those elements, which have been identified as important and abundant based on criteria of the anticipated composition of the high-level waste, and the NRC and EPA standards outlined in 10 CFR Part 60 and 40 CFR Part 191, respectively (Kerrisk, 1985; Oversby, 1987). These include U, Th, Np, Am, and Pu. The radioelements Tc, and I were also identified as being of concern due to possibly high solubility and low sorption, and will also be considered.

One particular focus will be sorption and transport modeling of uranium using the MINTEQA2 and CTM codes. Uranium is not only an important radioelement in high-level waste, but it is also believed to be a good analog to several actinides (e.g. Pu, Np) under Yucca Mountain conditions. Additionally, in comparison to the other actinides, uranium aqueous geochemistry is relatively well characterized. Many uranium sorption experiments have been conducted on oxide minerals (Tripathi, 1984; Hsi and Langmuir, 1985), allowing calibration of the computer models (see below; Section 3.2.4). Experimental and modeling studies of U-sorption which are currently being conducted at the Center for Nuclear Waste Regulatory Analyses (CNWRA) (Pabalan, 1991c) will provide insight into the sorptive behavior of clinoptilolite, a key adsorbent phase at Yucca Mountain. Data from research conducted at CNWRA will be incorporated and modeled as they become available.

### 3.2.2 Develop Radionuclide Thermodynamic Database

With respect to radioelements, the current MINTEQA2 database is largely limited to uranium, and contains no other actinide data. In order to construct a compatible thermodynamic database, data on the important radionuclides will be obtained from available sources. These include the EQ3/6 database (data0.com.r7, 29-Oct-90; Wolery et al., 1990), the CHEMVAL database under development by the CEC (Read and Broyd, 1989), and the tabulations of Benson and Teague (1980) and Phillips et al. (1988). Where possible, previously validated data will be used. For example, the NEA currently plans to develop thermodynamic databases for U, Am, Tc, and Pu; the uranium database is scheduled for release in March, 1992. In developing these databases, considerable effort has been made to provide a high-quality, internally consistent database, and poorly constrained data have been discarded (H. Wanner, Personal Communication). In a case such as the NEA effort, the database can be used with some degree of confidence. Where data quality is less certain, it is necessary to go to the original source and evaluate the experiments and techniques used to derive the data. Only adequately constrained data should be selected. In some cases, however, only one dataset may be available for a given species, and less well characterized data may be used for completeness. Such uses will be documented, and the results evaluated for consistency with other calculations where possible. With the exception of the CHEMVAL study, data are not generally in a format

that is usable by MINTEQA2; base components are also different. After selection, data sources data will be documented, and data for key radioelements will be formatted for use in the MINTEQA2 and CTM (modified MINTEQ format) codes where necessary.

### 3.2.3 Develop Radionuclide Sorption Database

To evaluate the suitability of different sorption models, sorption databases for the key radionuclides (U, Am, Th, Pu, Np) will be acquired (where available) or developed, and the quality of the data evaluated. Depending on the sorption model used, the number of adjustable parameters can range from one for a simple  $K_d$  approach to seven for the triple-layer surface complexation model (Kent et al., 1988). Sorption parameters have been compiled in a number of studies, although the exact experimental conditions are not always provided. New sorption data will be evaluated and incorporated as they become available.

#### 3.2.3.1 Empirical Sorption Data

Because of the uncomplicated nature of the empirical approach, and the apparent simplicity of the experiments, large numbers of batch experiments have been run to determine  $K_d$  values for a variety of radioelements and substrates. These values have been compiled in several computerized databases, including the NEA Sorption Database (Ticknor and Rügger, 1989), the Sandia Sorption Data Management System (SSDS) (Siegel et al., 1989), and the compilation of Yucca Mountain sorption data (Thomas, 1987; Beckman et al., 1988). To evaluate the  $K_d$  approach, these data compilations will be obtained; initial efforts should focus on relatively well characterized radioelements such as uranium or cesium. The computerized databases may not supply sufficient information about individual datasets, and original sources will be obtained where necessary. The data will be evaluated by examining the constraints on the experiments including: reproducibility of the results, water chemistry, particle size, water/rock ratio, whole rock vs. pure minerals (Beckman et al., 1988). A small dataset will be calibrated for the MINTEQA2 code and compared against other approaches to sorption modeling. Extrapolation to conditions outside of the experimental conditions will be a principal focus of these comparisons.

Where possible, data used to derive  $K_d$  will be considered using other sorption models (either empirical Freundlich, Langmuir isotherms or mechanistic models). From this comparison, the suitability of the  $K_d$  approach will be evaluated. It may also be possible to determine the contribution of other retardation mechanisms to the calculated " $K_d$ ". In addition, the relative importance of changing conditions [pH,  $P(\text{CO}_2)$ ] will be addressed. Isotherm data determined in the U-sorption studies of Task 3 (Pabalan, 1991c) will be incorporated as they become available. Data for Freundlich and Langmuir isotherms are generally only available on a case-by-case basis, and large tabulations are not widely available.

### 3.2.3.2 Mechanistic Sorption Data

In order to apply a surface complexation approach to model pH-dependent sorption, an initial step will be the development of a relatively complete database of the key radionuclides. Because the number of adjustable parameters is generally larger, and experiments are inherently more complex in terms of material characterization, tabulations of the parameters necessary for mechanistic sorption models are fewer, and reported data (e.g., Smith and Jenne, 1988) are not nearly as extensive as the large  $K_d$  databases. Where available and suitably characterized, parameters appropriate to a given model will be compiled (e.g., U - Hsi and Langmuir, 1985; Pu - Sanchez et al., 1985; Np - Girvin et al., 1991). Where necessary, codes such as FITEQL (Westall, 1982; Hayes et al., 1990) will be used to determine the required parameters from curve-fitting BET (specific surface area) and potentiometric titration (protonation/deprotonation) data.

In the absence of the required experimental data, estimation techniques such as those outlined for the diffuse-layer (Dzombak, 1986) and the triple-layer (Smith and Jenne, 1988; 1991) models will be used to provide the required parameters. A data estimation approach may be particularly appropriate for the actinides, where experimental data are frequently unavailable or poorly characterized. It may also be necessary to estimate data for less well characterized adsorbent phases such as zeolites and clays that are anticipated to be important at Yucca Mountain.

### 3.2.4 Validation of Results

Simulation results will be checked against well constrained experimental data in order to evaluate (validate) the suitability of any geochemical model under the selected conditions. This establishes confidence both in the data and modeling techniques employed, and in the ability to model more complex natural systems. This strategy will be used to point the way to justifiable simplifying assumptions as retardation processes are better understood. Geochemical modeling implies no transport mechanism, and comparison of MINTEQA2 results to batch equilibrium studies (e.g., Hsi and Langmuir, 1985; Sanchez et al., 1985; Payne et al., 1990) is appropriate. Batch studies planned at CNWRA (Pabalan, 1991c) will investigate the effects of pH, carbonate complexation, competing ions, and solid-mass/solution-volume ratios on U-sorption by zeolites. MINTEQA2 predictions will be compared with these results in order to provide insight into a potentially critical adsorbent barrier at Yucca Mountain. Other potential studies for comparison are listed in the Task 1.1 literature review (Turner, 1991).

On a limited basis, MINTEQA2 results will be compared with results from other codes. This will be useful in evaluating and developing confidence in the ability of MINTEQA2 to use the radioelement database constructed as a part of this project (see above, Section 3.2.3). While comparison does not prove that either code is "right", reasonably close

correspondence provides some additional degree of confidence in the results of both. Two of the most commonly used geochemical codes are PHREEQE (Parkhurst et al., 1980) and EQ3/EQ6 (Wolery, 1979). Both are codes currently in use at the Center. Since neither EQ3/EQ6 nor PHREEQE currently model sorption processes, direct comparisons of sorption results are not possible. It is possible, however, to compare the results of radioelement speciation calculations. Because these codes are constructed differently, it is somewhat difficult to develop problems where results can be compared directly. Several studies (Morrey et al., 1986; Read and Broyd, 1989) have constructed sets of test conditions that are appropriate for code comparisons. These problems will be adapted for critical radioelements where possible.

### **3.2.5 Comparison of Different Sorption Models**

Once confidence is developed in the ability of the MINTEQA2 code to handle radioelements reliably, it will then be possible to evaluate the suitability of different sorption models. Working first with experiments performed under simple, well characterized laboratory conditions (dilute simple solutions; 25°C, etc.), empirical and mechanistic models will be used to model sorption of critical radioelements. Goodness-of-fit will be monitored either through subjective analysis or statistical treatment. Sensitivity analyses will also be performed to describe the response of different models to changing conditions such as pH, temperature, P(CO<sub>2</sub>), and ionic strength (Hayes et al., 1990). For a given set of experimental conditions, it will also be possible to calculate speciation, and observe how sorptive behavior changes in response to species predominance.

There is concern about the inability of empirical methods to discriminate between solute uptake due to sorption or precipitation/dissolution (Kelmers et al., 1987). The ability of MINTEQA2 to handle sorption and precipitation simultaneously will be used to determine the relative importance of each mechanism, assuming chemical equilibrium. Coprecipitation removes solute as an impurity in precipitating mineral phases, rather than as a stoichiometric compound of the solute. Although MINTEQA2 is not currently able to model solid solution effects, it may be possible to develop a subroutine that uses simplifying assumptions such as ideal ionic mixing to model the effects of coprecipitation.

## **3.3 HYDROGEOCHEMICAL MODELING**

### **3.3.1 Modeling Laboratory Studies**

Dynamic column experiments are essentially small-scale, one-dimensional models of solute transport. Experimental design is discussed in Turner (1991). The solute breakthrough curve is a function of the retardation of the solute relative to water velocities, and as such it is appropriate to use hydrogeochemical modeling for these types of experiments.

Dynamic U-sorption experiments will be performed at CNWRA (Pabalan, 1991c). Uranium breakthrough will be modeled using the CTM code, which should provide insights into the abilities of simplified models to simulate radioelement transport using different approaches to retardation. Sensitivity analyses will be performed to identify critical parameters, important boundary conditions, and potential weaknesses in the approach (and codes) used. Studies conducted with natural waters [e.g., the Alligator Rivers Project (ARAP), Payne et al., 1990] will be modeled to evaluate the effects of ionic strength, and competing cations on radionuclide adsorption. Transport modeling will also provide insight into the roles of dispersion and diffusion into dead-end pore space as potential retardation mechanisms. Other studies with potential as test-cases are listed in Turner (1991).

### **3.3.2 Modeling Controlled Field Studies**

Carefully controlled field studies have been undertaken to monitor solute transport. These include studies such as the INTRAVAL Las Cruces Trench Experiment, the DRIGG Site, and others listed in Turner (1991). Although largely restricted to non-radiogenic elements, these types of studies offer insight into transport processes at scales larger than are practicable in the laboratory.

Once confidence has been gained in the ability of the CTM code to model transport at the laboratory-scale, the approach will be used to monitor reactive solute transport in selected study areas. Application will depend on the determination of the flow paths, and the mineralogies of the geologic media. Sensitivity analyses will be performed to help identify the relative importance of various boundary conditions (mineralogy, temperature, permeability). Because of the complexities inherent in any natural system, one important goal of this will be to develop simplified models for application to field problems. Initial models will be one-dimensional. Two-dimensional conceptual models will be developed where possible, and simulated as additional data become available and the as the code is adapted to more powerful computer systems.

### **3.3.3 Modeling Natural Analogs**

Where possible, natural analogs will be used at a variety of scales to test and validate the results of long-time model predictions. In terms of radioelement transport, uranium is the most likely analog, in systems such as uranium mill tailings (UMT) (Erikson et al., 1990), and uranium deposits (Percy and Murphy, 1991a). Because they are designed to specifically address radionuclide migration, the natural analog studies at Peña Blanca (Percy and Murphy, 1991b) and Alligator Rivers (Payne et al., 1990) are expected to provide valuable corroborative information. Experience gained in modeling laboratory and controlled field studies will allow the development and application of simplified models in those analog systems that are perhaps less well characterized. As is the case with controlled field studies, initial models will

be one-dimensional, with the goal of two- and three-dimensional simulations as the systems are better understood and the software is configured for more powerful systems.

### **3.4 HYDROGEOCHEMICAL MODELING-YUCCA MOUNTAIN**

It is anticipated that developing conceptual models of the Yucca Mountain system will be an ongoing activity, and will be conditioned by the experience gained in the activities outlined above. As data become available from site characterization activities, and likely fluid flow paths are identified, boundary and initial conditions appropriate to hydrogeochemical modeling of the Yucca Mountain system will be established. To a large extent, boundary and initial conditions will depend on scenario development accomplished as part of site characterization and performance assessment. Hydrogeochemical modeling will start with intentionally simplified hydrological and mineralogical conditions. Possible hydrologic conditions that could cause relatively rapid transport will be investigated. The mineral phases that are most important to retarding radionuclide transport will be modeled as they would interact with radionuclides. More detailed conceptual models will be developed based upon information from the ongoing site characterization program as it evolves.

### **3.5 QUALITY ASSURANCE**

The work outlined above will be conducted in accordance with the Center Quality Assurance Manual. Baseline versions of the MINTEQA2 and CTM codes will be maintained at the Center, and documentation and records of all modifications will be maintained in accordance with code configuration control as outlined in CNWRA Technical Operating Procedure (TOP)-018. Scientific notebooks will document modifications to the databases and list data sources.

## **4.0 SCHEDULING, PERSONNEL REQUIREMENTS, AND DELIVERABLES**

### **4.1 SCHEDULING**

The following is intended as a brief summary of the activities proposed for Task 2 of the Sorption Modeling Research Project. Specific deliverables and milestones are listed below in Section 4.4. Identification of key radionuclides and development of thermodynamic and sorption databases appropriate to these elements are activities that will be initiated at an early stage in the program. Attention will initially be focused on uranium data to take timely advantage of experiments conducted as part of Task 3. As new data become available, the databases may be further modified throughout the proposed program. Validation of geochemical modeling results and comparison of sorption models will begin only when the databases have been sufficiently developed, and will be a continuing activity as processes and conditions are better understood. In a similar sense, initiation of hydrogeochemical modeling will begin when geochemical modeling activities have provided sufficient information on valid approaches to

simplified geochemistry. Development of conceptual models of Yucca Mountain will begin early in the program, and will continue to be refined as site characterization and scenario development proceed. Clearly this is an idealized program; any or all of these steps will be dependent on, and conditioned by, the others. In addition, the goals and approaches outlined above are subject to change as our understanding of sorption processes develops and additional data become available. For this reason, activities will be conducted in tandem; the schedule as presented, is tentative and necessarily subject to change as work progresses.

**4.2 PERSONNEL REQUIREMENTS**

As needed, personnel for this study will include CNWRA scientists D. R. Turner, R. T. Pabalan, W. M. Murphy, B. Leslie, G. W. Wittmeyer, and R. T. Martin. Additional work may require the hiring of consultants or summer interns, who will be qualified and contracted on a case-by-case basis in accordance with Center procedures.

**4.3 COMPUTER REQUIREMENTS**

Current versions of MINTEQA2 and CTM are configured for IBM PS/2 Model 70 computers available at the Center. As more complex systems are considered (natural waters, two- and three-dimensions), it is expected that mini- and/or mainframe computer time will be required. Configuration to these systems will be accomplished as necessary. In addition, the Center Silicon Graphics IRIS workstation may be used for advanced graphics data display. As required, computer accounts will be arranged on Center or Institute computing facilities.

**4.4 DELIVERABLES AND MILESTONES**

Pending approval, results of research activities conducted under this work plan will be reported in the CNWRA Quarterly and Annual Research Reports as discussed under Task 4 of the Project Plan for Sorption Modeling for High-Level Waste Performance Assessment. Specific deliverables and milestone dates include:

- Intermediate Milestone: Preliminary report on development of thermodynamic and sorption databases for key radioelements - CNWRA Quarterly Report, May 14, 1992
- Major Milestone: Compilation of formatted thermodynamic databases for key radioelements - September 30, 1992
- Major Milestone: Compilation of empirical and surface complexation databases for key radioelements - CNWRA Annual Report, February 12, 1993

- Intermediate Milestone: Report on initial geochemical modeling studies and comparison of sorption models - CNWRA Quarterly Report, May 14, 1993
- Major Milestone: Report on initial hydrogeochemical modeling of simple laboratory-scale systems - CNWRA Quarterly Report, November 11, 1993
- Major Milestone: Report on initial hydrogeochemical modeling of intermediate-scale controlled field experiments - CNWRA Annual Report, February 11, 1994
- Intermediate Milestone: Report on the development of simplified conceptual models for hydrogeochemical transport at Yucca Mountain - CNWRA Quarterly Report, May 13, 1994
- Major Milestone: Report on preliminary hydrogeochemical modeling results for simplified systems at Yucca Mountain - September 30, 1994

It is also anticipated that, following NRC review and approval, research results will be disseminated at national and international meetings and published in peer-reviewed journals.

**5.0 COST ESTIMATE**

While the work proposed under this work plan is more specific than the activities outlined in the approved project plan (Pabalan, 1991a), it is considered to be within the scope of the Sorption Modeling for Performance Assessment Research Project. Most of the cost of the initial work will be related to labor; computer time will be an additional cost as mainframe capabilities are required for more complex simulations. It is anticipated that this work will be conducted in accordance with the spending plans provided in the approved project plan.

**6.0 REFERENCES**

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