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Subject: Submission of "Sorption Modeling for High-Level Waste Performance Assessment: A Literature Review".

Dear Ms. Mearse:

This letter transmits the subject report, in accordance with Change 1 (may, 1991) of the Project Plan for the Sorption Modeling for High-Level Waste Performance Assessment Research Project. This report represents Intermediate Milestone No. 20-3704-071-102.

Please contact me or David Turner if you have any questions regarding this report.

Very truly yours,

John L. Russell

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SORPTION MODELING FOR HIGH-LEVEL WASTE PERFORMANCE ASSESSMENT: A LITERATURE REVIEW

Prepared for

Nuclear Regulatory Commission
Contract NRC-02-88-005

Prepared by

Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

August 1991

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ABSTRACT

The Sorption Modeling for High-Level Waste Performance Assessment Research Project is intended to provide an experimental and theoretical basis for evaluating the role of sorption in meeting stated performance objectives for the proposed high level waste repository at Yucca Mountain. Subtask 1.1 of the project, "Literature Review and Development of Approach Sorption Modeling" has been completed, and the results are presented in this report. The regulatory bases in 10 CFR Part 60 and 40 CFR Part 191 for considering sorption in performance assessment of the proposed repository are reviewed. Current levels of understanding of sorption mechanisms are discussed, and the physicochemical conditions of solutions, adsorbent and adsorbate phases, and geologic media that govern these processes are examined. Particular emphasis is placed on the attenuation of radionuclide migration. Sorption models, both empirical and mechanistic, are presented, and the advantages and disadvantages of each approach are discussed. The level of uncertainty in the available data is considered, and the data requirements for rigorous application of the models are also addressed. Processes other than sorption which contribute to the retardation of contaminant transport, such as precipitation/dissolution, diffusion, and radionuclide decay are also considered.

Laboratory experimental methods are reviewed, and several controlled field experiments and natural analog studies are presented and discussed. Limitations to the application of field studies in evaluating radionuclide migration are considered. The basic convection-dispersion equations governing reactive solute transport are presented, and a variety of numerical solution strategies are reviewed. Approaches to coupled hydrogeochemical modeling are outlined, and a list of evaluation criteria is presented. Currently available hydrogeochemical codes are presented, and the characteristics of each are reviewed. The CTM code, currently in development for the NRC at Pacific Northwest Laboratory, is considered to offer a good compromise between flexibility, efficiency, accuracy, and availability, as well as the most promise for future modification to address more complex problems. The current levels of understanding of the geology, mineralogy, hydrology, and geochemistry of Yucca Mountain are introduced, and the sorption chemistry of several important radioelements (U, Pu, Np, Am, and Tc) are reviewed. In the final section, the findings of the literature review are summarized, and initial recommendations are made for addressing the role of sorption in repository performance.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

TABLE OF CONTENTS (Cont'd)

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENTS

This report was prepared at the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U. S. Nuclear Regulatory Commission under contract No. NRC-02-88-005. The report presents the results of a Literature Review conducted as part of Task 1 of the Sorption Modeling for High-Level Waste Performance Assessment Research Project. The report is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC.

This report has benefitted greatly from the thoughtful comments of a number of reviewers: Bret Leslie, Michael MacNaughton, William Murphy, Roberto Pabalan, English Pearcy, and Gordon Wittmeyer. The author gratefully acknowledges their contributions. Special appreciation is due to Deanna Bump and especially Pamela Smith who prepared the final text of this document. The author also acknowledges the assistance of Curtis Gray, who provided graphics support.

EXECUTIVE SUMMARY

The purpose of this report is to provide a survey of the recent [illegible] processes on radionuclide transport. Development of sorption [illegible] studies, experimental and field studies, availability and quality of necessary data, and coupling of sorption with other processes to model reactive solute transport are considered and discussed.

Tertiary ash-flow tuffs at Yucca Mountain, Nevada are currently being evaluated as a location for a high-level radioactive waste (HLW) geologic repository. [illegible] health and safety, the ability of this repository to isolate the waste from the accessible environment is of critical importance. Therefore, the possibility of radionuclide transport from the repository to the accessible environment as dissolved constituents in moving groundwater following permanent closure is a fundamental concern. Because a multiple barrier design has been proposed, one key measure of repository performance is the degree of retardation of radionuclide migration provided by water rock interaction should the engineered barrier system fail. One of the important interaction processes is the removal of radionuclides from solution through sorption onto the geologic medium.

For a given element, sorption is influenced by a number of factors, including physical and chemical properties of the rock and the groundwater, and the physicochemical conditions of the geologic environment (e.g., temperature, surface charge, pH, Eh). In a likewise manner, for a given system, different elements exhibit a wide range of sorptive behavior in response to the defined physical and chemical conditions of the system. This response will vary as [illegible] of a number of parameters, including the chemistry of the element (e.g., [illegible] valency, oxidation state, speciation, hydration energy), the electron configuration [illegible] bond energies), and the degree of complexation attained in the solution. [illegible] The interplay between these characteristics can be quite complex, especially in the case of many of the radionuclides of interest, such as the actinides, where the atomic weight is high, and the electronic structure can be very complicated. A number of processes in addition to sorption contribute to the retardation (or acceleration) of radionuclide migration. In order to account for the relative importance of each of these mechanisms, it is necessary to use a model that can distinguish between them.

Sorption is clearly a critical process that must be considered in any performance evaluation of a potential repository site. Models that vary greatly in terms of the degree of flexibility and theoretical basis have been developed to address sorption, each offering its own advantages and disadvantages.[illegible] Empirical models are simple, but cannot discriminate between retardation mechanisms, and extrapolation to conditions beyond the experimental conditions used to determine the necessary parameters is frequently unjustified. Mechanistic models offer more flexibility, but the number of parameters is large, the available data are frequently inadequate, and coupling with flow transport requires a sophisticated geochemical model to monitor changes in fluid and mineral chemistry along flow paths.

Empirically derived models tend to present [illegible] properties. They can be efficiently incorporated into the [illegible] codes [illegible] a minimum of additional computational effort [illegible] the need for sophisticated [illegible] necessary parameters are relatively [illegible] and a great deal of effort has recently been devoted to developing and maintaining a database for a variety of radionuclides and different media of interest to the Yucca Mountain [illegible] of physicochemical properties [illegible] paths to the accessible environment [illegible] computational simplicity offered by empirical [illegible] a variety of physical and chemical conditions.

A more desirable approach, perhaps, is the development [illegible] mechanistic models, such as surface complexation and ion exchange. [illegible] well-defined sorption relationships, and a database containing the necessary equations of state for pressure-temperature variations, these models can readily extrapolate to a variety of conditions and include the effects of a variety of properties. In practice, however, the number of adjustable parameters increases with model sophistication [illegible] necessary data such as protonation deprotonation equilibrium constants [illegible] radioelements. In addition, many sorption experiments have been conducted without providing the degree of characterization necessary [illegible] models. Faced with this lack of data, the application of mechanistic models reduces to a [illegible] fitting exercise, losing the advantage of a theoretical basis, and increasing the [illegible] non [illegible]

Experimental sorption studies [illegible] dynamic column experiments. Batch sorption [illegible] in contact with a constant solution volume, have generally been more [illegible] relative simplicity. Column experiments are more difficult to perform, [illegible] have been modified to investigate saturated unsaturated flow, one pass flow, recycled flow, crushed rock, rock wafers, and rock columns. Sample preparation and laboratory procedures are generally well-established for both types of experiments, although special precautions may be necessary, depending on the element of interest or the adsorbent considered [illegible] Experimental design, characterization of the materials involved, and the interpretation of the resulting data will also depend, in part, on the data needs of the [illegible] model [illegible]

Carefully controlled field experiments can provide a crucial step between laboratory and [illegible] repository-scale conditions. A different kind of field approach [illegible] well-characterized natural analogs to reconstruct the [illegible] system and study the operation of transport mechanisms on geologic time scales. Field experiments and analog studies also provide a valuable method for the validation of reactive transport modeling codes and [illegible] performance assessment codes designed to predict the postclosure effectiveness of the proposed repository. A difficulty encountered in using field studies for evaluation [illegible] is the uncertainty inherent in characterizing a [illegible] system. Although it may be difficult, if not impossible, to provide the same degree of assurance that is available in the laboratory, field studies can still provide valuable information. Indeed, in many cases, the lack of analytical solutions to reactive solute transport problems requires that a field situation be used for validation of long term models.

Due to the relatively straightforward nature of the processes involved, much work has been done to model the transport of nonreactive solutes in homogeneous porous media. Of particular concern to the performance assessment of a HLW repository, however, is how the solution interacts with the geologic medium to retard radionuclide migration. In order to model the attenuation of contaminant transport by water/rock interaction processes, it is necessary to couple the geochemical processes governing retardation with the physical processes of fluid and mass transport. This has been done in a number of ways using a variety of simplifying assumptions and governing equations. The advent of computers has made the numerical simulation of the coupling of these two processes feasible. An iterative, two-step coupling approach is generally more efficient than direct coupling between geochemistry and transport equations, and offers the most promise for addressing increasingly complex and realistic problems. A code should also offer a variety of sorption options in order to evaluate the suitability of different approaches to modeling sorption. User-friendliness will simplify the application of the model to a variety of environments, and enhance the interpretation of the results. A number of codes currently available or in development can perform the necessary calculations to a limited extent, with varying degrees of efficiency, accuracy, and user-friendliness.

The overall performance objectives defined by 10 CFR Part 60 and 40 CFR Part 191 are concerned with the transport of radionuclides from the proposed repository to the accessible environment. In order to evaluate the role of retardation mechanisms in attenuating this migration, it is necessary to have a good understanding of the physical and chemical properties of both the environment through which the fluids will pass and the groundwater that is expected to transport the radionuclides in solution. Modeling of groundwater flow in the Yucca Mountain environment can establish limits on groundwater travel times, and can provide information on likely fluid flow paths. If groundwater travel time under physical conditions anticipated in the postclosure environment is sufficiently long, than the role of sorption may be minimized in meeting NRC and EPA performance objectives for different radioelements. Evaluation of sorption at Yucca Mountain must be considered in the context of these activities in order to limit the amount of experimental effort required to provide the necessary data for modeling radionuclide migration.

1. INTRODUCTION

The purpose of this report is to provide a survey of the recent literature on the effect of sorption processes on radionuclide transport. Development of sorption theory, sorption models, experimental and field studies, availability and quality of necessary data, and coupling with other processes to model reactive solute transport are considered and discussed.

Tertiary ash-flow tuffs at Yucca Mountain, Nevada are currently being considered as a location for a high-level radioactive waste (HLW) geologic repository. In order to maintain the public health and safety, the ability of this repository to isolate the waste from the accessible environment is of critical importance. Following permanent closure, the possibility of radionuclide transport from the repository to the accessible environment as dissolved constituents in groundwaters is a fundamental concern. Because a multiple barrier design has been proposed, one key measure of repository performance is the degree of attenuation of radionuclide migration provided by water/rock interaction should the engineered barrier system fail.

1.1. REGULATORY BASIS

The Nuclear Waste Policy Act of 1982 (as amended 1987) charges the Department of Energy (DOE), the Nuclear Regulatory Commission (NRC), and the Environmental Protection Agency (EPA) with particular responsibilities in the siting, licensing, construction, operation, and permanent closure of a high-level radioactive waste (HLW) geologic repository. The NRC regulations governing repository performance are given in 10 CFR Part 60, [illegible] accessible environment are established by the EPA in 40 CFR Part 191.

The license application of the DOE (10 CFR 60.21) is required to provide general information on the ability of the proposed geologic repository to meet overall performance objectives (10 CFR 60.112). The application must also include a Safety Analysis Report (SAR)[10 CFR 60.21(c)] containing both specific information on the geochemical properties of the system, and an assessment of the effectiveness of natural barriers. The analysis contained in the SAR is required [10 CFR 60.21(c)(1)(ii)(B)] to "determine the degree to which each of the favorable and potentially adverse conditions, if present, has been characterized" and the extent to which waste isolation is enhanced or reduced by the geologic environment.

Under the siting criteria listed in 10 CFR 60.122, sorption is specifically referred to as a favorable geochemical condition in 10 CFR 60.122(b) that will tend to inhibit radionuclide migration and "favorably affect the ability of the geologic repository to isolate the waste." Conversely, geochemical processes that "would reduce sorption of radionuclides" are listed as a potentially adverse condition [10 CFR 60.122(c)(8)] that would reduce the effectiveness of the natural barrier system. In addition, 10 CFR 60.122(a)(2) requires the adequate investigation and evaluation of the effects of potentially adverse conditions at the site, and the extent to which compensation by a combination of favorable conditions (including sorption) will allow performance objectives to be met. Clearly, any license application for construction and operation of a HLW geologic repository will necessarily address the role of sorption in performance assessment.

1.2. SORPTION IN PERFORMANCE ASSESSMENT

As discussed above, performance assessment of the proposed site is required by 10 CFR Part 60.21 and 60.122 to address the role of sorption in radionuclide migration from the repository to the accessible environment. Because of geologic heterogeneities and scaling difficulties, attempts to extrapolate laboratory data to the scale of the geologic setting have required increasingly complex numerical models to simulate water and solute transport. However, the complexity inherent in natural systems precludes numerical treatment of all aspects of the contaminant migration. Simplification of the processes involved in the attenuation of reactive solute transport is necessary in order to make the problem tractable.

Traditional approaches to modeling repository performance have tended to use a single retardation factor (R_f) to represent attenuation of solute transport. In turn, this factor is generally based on a discrete sorption coefficient (K_d) which is assumed to represent sorption/desorption processes alone. However, in addition to sorption, several other physical and chemical processes contribute to retardation of radionuclide migration, including diffusion, dispersion and precipitation/dissolution reactions. While the retardation factor approach has the advantage of simple computation, it is empirical in nature and has no basis for extrapolation beyond experimental conditions. In addition, it is unable to [illegible] of the various processes [illegible] attenuation [illegible] provide the needed theoretical underpinning.

Therefore, in order to adapt and apply experimental sorption data to modeling reactive transport at Yucca Mountain, it is necessary to understand both the theory of the processes involved in radionuclide retardation, and the conditions that will be encountered in the geologic environment.

2. SORPTION THEORY AND MODELS

2.1. DEFINITIONS

Travis and Etnier (1981) define *sorption* as those processes involving the selective uptake and storage by a solid substrate of dissolved species in solution. *Adsorption* refers to those processes representing the exchange of mass from dissolved species to the surface of a substrate (adsorbent). *Desorption* processes represent the reverse of adsorption reactions and refer to the release of species from the substrate to the solution. *Chemisorption* generally refers to sorption processes that occur through a true chemical reaction. Also included as a sorptive process, *ion exchange* is the process by which solution species substitute for readily exchangeable ions at the solid surface or in the structure of the substrate. *Precipitation* and *dissolution* are excluded from sorptive processes, but may be included in evaluating the *retardation* of radionuclide migration. These definitions are consistent with the NRC Technical Position on Determination of Radionuclide Sorption for High-Level Nuclear Waste Repositories (NRC, 1987).

Equilibrium adsorption/desorption is assumed in many situations where solute residence time is long in comparison to the rate of reaction for the sorptive process. If a closed system is assumed, then equilibrium may be appropriate. In the case of an open system, [illegible] groundwater circulation through the environment is likely. Solute residence time is likely to be shorter, and the validity of an assumption of equilibrium becomes problematic. *Kinetic* sorption [illegible]able for those systems where solute residence time is short relative to the sorption reaction. For the purposes of evaluating the degree of adsorption [illegible] reactive solute transport, residence time is assumed to be [illegible] concentration due to mechanisms other than sorption. These processes [illegible] and water/rock interaction processes other than sorption (precipitation, dissolution, [illegible] etc.).

2.2. CONTROLS ON SORPTION MECHANISMS

For a given element, sorption is influenced by a number of factors including physical and chemical properties of the rock and the groundwater and the physical/chemical conditions of the geologic environment. In a likewise manner, for a given system, different elements exhibit a wide range of sorptive behavior in response to the defined physical and chemical conditions of the environment. This response will vary as a function of a number of parameters including the chemistry of the element (e.g., redox sensitivity, oxidation state, [illegible] hydration energy), the electron configuration (ionic radius, valence, bond energy), and the degree of complexation attained in the solution of interest. The interplay between these characteristics can be quite complex, especially in the case of many of the radionuclides of interest, such as the actinides, where the atomic weight is high, and the electronic structure can be very complicated (Cotton and Wilkinson, 1976). The following is intended as a brief summary of some of the system properties that will influence the chemistry of the element of interest, and in turn its sorptive behavior.

2.2.1. Substrate Properties Influencing Sorption

For a given solute, a number of properties have been identified as affecting the adsorptive capacity of the substrate. These include the following:

Specific Surface Area (SA). The specific surface area (m²/g) of the substrate has been identified by a number of studies as a key characteristic affecting the adsorptive capacity of a given substrate (Ames et al., 1982, 1983a; Hsi and Langmuir, 1985; Fuller and Davis, 1987; Kent et al., 1988). In fact, the relation between adsorption and specific surface area has been exploited in the development of several adsorption techniques for surface area analysis (Hochella, 1990). In general, there is a positive correlation between specific surface area and sorptive capacity (Fuller and Davis, 1987). This is likely to be due to an increase in the total number of sorption sites available (Allison et al., 1990). Experiments with marine sediments (Balistrieri and Murray, 1986) indicate reduced sorption of trace metals at higher particle concentrations. As a possible explanation, the authors suggested particle aggregation at these higher concentrations, resulting in reduced effective specific surface area for adsorption. Ames et al. (1982) also identified a positive correlation between specific surface area and the cation exchange capacity of the substrate (CEC). Kent et al. (1988) list several analytical methods for determining specific surface area, including BET (gas adsorption), and differential capacitance models. James and Parks (1982) present an evaluation of the suitability of the various approaches.

Surface Site Density (N_s). As the number of available sorption sites increases, [illegible] sorptive capacity of the adsorbent is also expected to increase. For this reason, [illegible] binding model of Davis et al. (1978) specifically requires an estimate of N_s (number of sites/m²) in order to calculate total site "concentration" [i.e., total sites (moles sites/l) = SA(m²/g) x N_s(number sites/m²) x C_s(grams adsorbent/l) / N_A(number sites/mole), see below]. Again, Kent et al. (1988) list a number of approaches to analytical determination of N_s and James and Parks (1982) discuss the methods as applied to triple layer modeling (see below). For oxide surfaces, surface site density will vary as a function of pH due to the hydrolysis reactions occurring at the solid/liquid interface (Means et al., 1978b; Kent et al., 1988).

Cation Exchange Capacity (CEC). The cation exchange capacity (meq/g) is a measure of the affinity of a substrate for cations, and reflects the ability of solutes to substitute for exchangeable cations either at the surface or in the structure of the substrate. Rhue and Mansell (1988) describe a method of determining Na- and Ca-exchange capacity of soils using an acetate buffer and Cl-solutions. Von Breymann et al. (1990) have noted a correlation between minima in dissolved Mg^{2+} and maxima in sediment CEC, and suggest that those sediments with the maximum CEC have the highest amount of surface adsorbed magnesium.

Cation exchange capacity is a function of the sorbing cation (Rhue and Mansell, 1988). The relative sizes (and charges) of the exchanging cations influences exchange process. Comans and Middleburg (1987) have noted that similar ionic radii between the exchangeable and sorbing cations may lead to increased CEC. The CEC has also been observed as being positively correlated with specific surface area (Ames et al., 1982). Rhue and Mansell (1988) investigated the effect of pH on cation exchange capacity of Cecil sandy loam and observed a two- to threefold increase in CEC between pH 4 and 8. This is a result of a large pH-dependent surface charge in the soils, which Rhue and Mansell believe to be due to organic matter. An additional possibility is increased competition with H^+ for sites, resulting in lower CEC values at low pH. Balistrieri and Murray (1986) have normalized K_d values to sediment CEC as a means of comparing the sorptive characteristics of different trace metals relative to Mn content of the sorbing substrate. Ames et al. (1983c) have identified the related property anion exchange capacity (AEC), and observed that micas with low measured CEC values have the highest AEC for uranyl carbonate complexes. A similar mechanism has been proposed by Rundberg et al. (1987) to explain the observed retention of pertechnetate anion (TcO_4^-) in column experiments with crushed Yucca Mountain tuffs. Cation exchange is thought to increase with decreasing particle size (increased specific surface area). Interpretation of the results, however, will depend on how CEC values are determined (M. MacNaughton, personal communication), and Meyer et al. (1986) report evidence for a lack of correlation.

Surface Charge and Potential. The attractive forces arising from electrostatic surface charge are critical in surface adsorption. For free ions, surface charge is identified as an important sorbent property for oxides, and it is a function of pH according to surface complexation theory (Hsi and Langmuir, 1985; Kent et al., 1988). It is likely to depend on the species being sorbed. Shielded by a solvation sheath of water molecules, more readily hydrolyzable metals (i.e., lower charged hydrolysis complexes) are expected to be less affected [illegible] in these aspects than free ions (MacNaughton, 1973). The zero point of charge (pH_{zpc}) of the substrate is also important (Means et al., 1978b; Middelburg and Comans, 1991), and represents the pH at which surface charge vanishes. For a given surface, the value of pH_{zpc} is established through the uptake or release of potential determining ions (e.g., OH^- and H^+ for oxides). McCarthy and Zachara (1989) point out that ionic species may adsorb onto heterogeneous surfaces where domains of opposite surface charge can provide an attractive electrostatic force in excess of repulsion due to an overall like net charge. Stumm and Morgan (1981) report that CEC is relatively insensitive with respect to values below the pH_{zpc} and generally increases at higher pH values.

Changing surface charge affects the amount of energy transferred during the migration of an element through the electrostatic layer separating the substrate from the bulk solution. In turn, changing charge density and electrostatic potential affect the activity of a given element through the Boltzmann relationship (see below). Kent et al. (1988) also indicate that charge distribution influences the sorptive capacity of the substrate, and they identify four basic categories of sorbents based on this observation: (1) oxides, (2) multiple site, (3) fixed charge, and (4) salt-type minerals.

Crystallographic Orientation. Hiemstra et al. (1989a) have developed a surface complexation model for metal hydroxides to estimate proton affinity constants based on crystallographic considerations. For goethite, site type is found to vary with crystallographic orientation. For example, no triply coordinated surface groups were found associated with the

(100) plane. Hsi and Langmuir (1985) used crystallographic considerations based on site diameter on ferric oxyhydroxides to argue against monodentate surface complexation for $(UO_2)_3(OH)_5^+$, although crystallographic arguments alone were insufficient to distinguish between bi- and tridentate models. In studies of Cs sorption by illite, Comans et al. (1991) also note that the presence of easily dehydrated ions such as K^+ can collapse the clay structure, limiting access of the solute to favorable interlayer exchange sites. In contrast, larger, hydrated ions such as Ca^{2+} tend to "prop open" the crystal structure, enhancing solute diffusion to the favorable sites. This leads to a reduction in the degree of desorption (i.e., more pronounced irreversible adsorption) through ion exchange. Sorption of Cs and strontium by the zeolites clinoptilolite and mordenite is observed to depend on crystallographic orientation (Burns et al., 1989). Ion exchange in clinoptilolite is retarded perpendicular to (010) faces, apparently due to the absence of channels. Given crystallographic constraints, large diameter ions, asymmetric polynuclear species, and complexes of radioelements such as plutonium or uranium may be excluded from favorable binding sites, resulting in reduced sorption and/or retardation.

Grain Size. Di Toro et al. (1986) and Kent et al. (1988) stress the importance of grain size in characterizing an adsorbent. Finer grain size tends to result in increased specific surface area and site density, and therefore increased sorption, although Daniels et al. (1982) did not observe any correlation for batch experiments with Yucca Mountain tuffs. In addition, the finer grain sizes tend to concentrate the more adsorptive clay fraction. Particle size effects on sorption are likely to be less pronounced for more readily hydrolyzed metals relative to free ions (MacNaughton, 1973). Kent et al. (1988) point out that finer particles may dissolve more readily in solution, changing solution composition, leading to ambiguous results from sorption experiments. For these reasons, Kent et al. (1988) argue against using grinding methods in sample preparation. Meijer (1990) indicates that size fraction does not significantly affect sorption coefficients at sizes > 75 μm, and Beckman et al. (1988) report a threshold value of 106 μm. For smaller size fractions below these cutoff values, sorption increases, presumably due to the reasons discussed above. In contrast, Meijer et al. (1984) report that grinding did not greatly affect Cs, Ba, and Sr sorption on zeolites for any size fraction, probably due to the intracrystalline nature of favorable exchange sites.

2.2.2. Solution Properties Influencing Sorption

Solution chemistry can greatly affect the sorption of a given element. The interrelationships between these properties is discussed in depth elsewhere (Garrels and Christ, 1965; Hem, 1985; Stumm and Morgan, 1981 and references therein). Critical solution properties include the following.

Species Concentration. Sorption has generally been observed to decrease with increasing concentration (e.g., Σ m) of the species of interest. This is a basic feature of sorption experiments and field studies, and a number of modeling approaches have been developed to investigate the sorption concentration relationship (Travis and Etnier, 1981; Serne et al., 1990; Allison et al., 1990).

Solution pH. Adsorption is strongly dependent on solution pH. For many species and substrates, adsorption is generally low at low pH, increasing sharply at a pH "sorption edge" (MacNaughton, 1973; Ames et al., 1983a,b,c; Hsi and Langmuir, 1985; Sanchez et al., 1985; Davis et al., 1987; Rhue and Mansell, 1988; Kent et al., 1988; Erikson et al., 1990). As might be expected, the location of this sorption edge is dependent both on the element sorbed [e.g., ranging from pH ≈ 4-5 for Cr(II) to pH ≈ 10 for Na(I) adsorption on SiO2]), and on the adsorbent phase [e.g., from pH ≈ 4-6 to pH ≈ 7-8 for Co(II) adsorption on TiO_2 and MnO_2, respectively] (MacNaughton, 1973). Element speciation and complexation are pH-dependent. Di Toro et al. (1986) notes a decrease in the desorption of Co- and Ni-adsorbed onto clays with increasing pH. According to surface complexation theory, a number of sorbent properties (pH_{zpc}, charge and site densities, surface potential, etc.) are also pH-dependent due to surface protonation/deprotonation reactions (Kent et al., 1988; see below). Murali and Aylmore (1983c) report that during competitive sorption, selectivity coefficients (a measure of relative preference in binary systems) change as a function of pH, depending on both the sorbing species and the substrate. Finally, the solubility of many potential sorbents, particularly iron- and manganese-oxyhydroxides, is a function of pH. For example, at 25 °C and 1 atmosphere, most Fe-oxyhydroxides are unstable at low pH ($pH < 6$), except under very oxidizing conditions (Garrels and Christ, 1965). Not only does this affect the sorbing capacity of a given medium, but it can also influence the production of colloidal particles and oxide coatings (McCarthy and Zachara, 1989). Solution pH is subject to a variety of controls including $P(CO_2)$, Eh, and alkalinity, among others.

Inorganic Complexing Ligands/Speciation. The presence in solution of [illegible] complexing ligands (Cl^-, HCO_3^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, etc.) is important due to changes in the activity of the remaining uncomplexed species, and to the tendency of some elements to form complexes with different sorptive properties (Ames et al., 1983a,c; Tripathi, 1984; Hsi and Langmuir, 1985; Serne et al., 1990). Several studies (Ames et al., 1983a,c; Tripathi, 1984; Hsi and Langmuir, 1985; Siegel et al., 1990) have observed that uranium in carbonate and hydroxy-carbonate complexes is much more mobile than free uranium. Carbonate reduces uranium sorption, and carbonate complexes are poorly, if at all, adsorbed. This is probably due to reduction in charge and the associated electrostatic attraction (Serne et al., 1990), and changes in ionic radii and adsorption mechanisms. Similar decreases in sorption with increasing carbonate alkalinity are observed for thorium (LaFlamme and Murray, 1987) and plutonium (Sanchez et al., 1985) sorption on synthetic goethite. Carbonate complexation of radium, however, was found to have minimal effect on adsorption systematics (Ames et al., 1983b). Phosphate complexation of uranium was found to have minimal effect on sorption (Tripathi, 1984). The most common and best studied complexing inorganic ligands in natural waters (and at Yucca Mountain) are carbonate species. Because of the importance of carbon in at least some systems, $P(CO_2)$, pH, and ionic strength are also important in determining the effect of inorganic complexing on sorption processes.

Organic Complexing Ligands/Speciation. Organic complexing ligands have been examined in detail (Serne et al., 1990 and references therein). In general, the organo-metallic complexes are either neutral or anionic molecules, resulting in reduced sorption and enhanced radionuclide migration because of reduced electrostatic attraction. Organic compounds can also serve as reductants for redox sensitive elements. In addition, the solubility of many radionuclides is increased by the presence of organic ligands. Conversely, the presence of net positive charged sites on some insoluble organics may serve to attract anionic species such as $^{129}I^-$. Schindler and Stumm (1987) report that increasing concentrations of the organic compound 2,2'-bipyridine shift the sorption edge of Cu(II) on amorphous silica to lower pH (from pH = 4-6 to pH = 2-4). Means et al. (1978a,b) suggest that the organic compound EDTA has served to enhance ^{60}Co migration at Oak Ridge, and it may be even more effective in mobilizing actinides (Am, Cm, Pu, Th, and U) in a variety of oxidation states. Lieser and Bauscher (1988) note that with decreasing redox potential, Tc-sorption coefficients increase sharply at pH = 6.5-7.5 as Tc(VII) reduces to Tc(IV). However, because Tc(IV) tends to form various humic acid complexes, Tc-migration may be enhanced by organics, even under reducing conditions where less mobile Tc(IV) is the dominant species. The most common organic ligands are natural ligands such as humic and fulvic acids, and man-made chelates such as EDTA used in the decontamination process. Organic solubility is dependent on both the type of organic compound and pH (Serne et al., 1990). Toste et al. (1984) suggest that the presence of a strong organic chelator in solution may be more important than the oxidation state for the migration of some radionuclides.

Redox Conditions Speciation. As discussed above, the sorptive properties of many ions depend on the speciation of the element. Because of the electrostatic effects and complexation associated with species charge, speciation in turn depends on the oxidation state in solution, especially those elements which hydrolyze readily (Sanchez et al., 1985; Hsi and [illegible] 1989a;b; Serne et al., 1990). Many radionuclides exhibit markedly different characteristics in solution depending on oxidation state. Alemi et al. (1991) note that selenate adsorption was greater under reducing conditions. Choppin (1988) reports that the complexation strength of plutonium decreases from Pu(IV) > Pu(VI) > Pu(III) > Pu(V). Hydrolysis tends to remove Pu(IV) from solution at pH > 2-3 due to the creation of readily adsorbed species, or relatively insoluble species such as $Pu(OH)_4$. Solubility is also controlled by redox conditions (Langmuir, 1978a,b), and radiocolloid formation has also been shown to depend on oxidation state (McCarthy and Zachara, 1989; Orlandini et al., 1990). Serne et al. (1990) suggest that some sorption mechanisms may only be important for a particular oxidation state. Due to a net negative charge of most porous media, some elements are mobile when in an anionic or neutral form, but strongly retarded when present as cations. Oxidation state has also been observed to affect the formation of more mobile anionic complexes (Toste et al., 1984), and Bock et al. (1989) identify the reduction of Tc^{7+} (readily transported as TcO_4^-) to Tc^{4+} as an important prerequisite to sorption.

The oxidation potential of the fluid can also affect the sorptive characteristics of the substrate. This is especially important in the case of ferric hydrous oxides and organic chelators, where redox potential affects site density and pH_{zpc}.

Competitively Sorbing Species. The presence of other species in solution may indicate competition for a finite number of sorption sites. Although there is evidence to suggest that cumulative sorption of all species will exceed that of any individual element, competitive sorption will act to reduce the sorption of a given species (Griffin and Au, 1977; Harter and Baker, 1977; Murali and Aylmore, 1983a,b,c). If enough time is available, the system will reach sorption/desorption equilibrium, but total sorption total concentration relationships may be nonuniquely defined (Murali and Aylmore, 1983b). In addition, some sites may only be available to one type of competing ion (Murali and Aylmore, 1983c).

Colloids, Particulates. Colloids have been suggested as a potentially critical factor in enhancing radionuclide migration (McCarthy and Zachara, 1989). By binding to colloidal particles (< 450 nm in diameter) suspended in solution, a contaminant may be carried by a mobile fluid phase. Because species charge is decreased through binding, solute retardation due to interaction with the solid matrix tends to be reduced. The formation of radiocolloids (either organic or inorganic) has been suggested to accelerate the migration of actinides in Mortandad Canyon, New Mexico (Penrose et al., 1990), although there is some question about the influence of surface effluent in the system. Studies also indicate that radionuclides tend to be more closely associated with a specific particle size fraction, depending on the element. Penrose et al. (1990) found that 85 percent of the transported plutonium was associated with colloidal particles between 25-450 nm, while 43 percent of the americium was associated with particles < 2 nm in diameter. Association with larger particles may enhance retardation due to filtration of the colloids from solution by pores in the matrix (McCarthy, 1990) or through flocculation and settling (Shainberg, 1990). Orlandini et al. (1990) report that the affinity of actinides for colloidal particles is also pH-dependent. Plutonium and americium also tend to be [illegible] particles while thorium is irreversibly bound (Orlandini et al., 1990). Colloidal stability and activity depend on a number of physicochemical properties of the solution [Eh, pH, $P(CO_2)$, etc.]. For example, gradients in these properties can lead to the precipitation of solid phases that may act as mobile colloids (e.g., iron oxides)(McCarthy and Zachara, 1989). In order to identify and characterize the role of colloids in sorption processes, care must be taken to avoid the introduction of artifacts during drilling, sampling, and filtration, including the creation or removal of colloids, changing the chemical or physical properties of the solution, or the breaking up of colloidal aggregates (McCarthy and Zachara, 1989).

Temperature. The intensive property temperature is critical in many aspects of adsorption. Ames et al. (1982; 1983a,b,c) indicate that uranium sorption coefficients change in a complex fashion at temperatures ranging from 5° to 65° C, although for a given substrate, U-sorption tends to decrease with increasing temperature. A lack of pH and $P(CO_2)$ control in these experiments, however, complicates the interpretation of these results. Meier (1990) reports that measured sorption coefficients generally increase with temperature, although early high-temperature studies are plagued by poorly-constrained recrystallization of the substrate. Solubility, complexation, redox, pH, and electrostatic potential are all temperature dependent. Many empirical models, however, are only determined at a single temperature (hence the term "isotherm"; see below), and are of limited application. Retardation through precipitation/dissolution, and the kinetics of the various attenuation mechanisms are also a complex function of temperature. It is clear that any attempt to model reactive solute transport at the field scale must include constraints on existing and anticipated temperature conditions (Kent et al., 1988).

Ionic Strength. Solution ionic strength has a very pronounced effect on activity/concentration relationships, and in turn affects sorption processes. Ionic strength is explicitly included in models used to correct for nonideality effects (e.g., Debye-Hückel, Davies, etc.) in mass-action calculations, and in the Gouy-Chapman relationship between surface charge and potential gradients used in surface complexation models of adsorption/desorption (see below). As ionic strength increases at constant pH, the diffuse layer is compressed, electrostatic potential gradients increase, and the solvation energy of the surface becomes more critical (Kent et al., 1988).

Changes in ionic strength may reflect different concentrations of complexing ligands in solution, resulting in changes in adsorption characteristics as discussed above. Di Toro et al. (1986) observed a decrease in Co and Ni sorption by montmorillonite with increasing ionic strength. Liu et al. (1991) observed a similar effect for Cs, Sr, and Co sorption by clay, carbonate, and andesite. Liu et al. (1991) ascribed the decrease either to increased complexing with ligands in solution or competition for sorption sites from large cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+}. In addition, in noncompetitive Ra and U sorption studies (Ames et al., 1982, 1983a,b,c) temperature effects on measured sorption coefficients tend to become more pronounced at higher solute concentrations. [illegible] and Sanchez et al. (1985), however, observed no apparent effect of ionic strength on thorium and plutonium adsorption. Finally, as ionic strength decreases, charged colloidal particles [illegible] generally disaggregated and stabilized in suspension where they can act to enhance solute mobility (McCarthy and Zachara, 1989).

2.2.3. System Properties Influencing Sorption and Retardation

In using sorption characteristics to model solute transport through porous media, the physical and chemical characteristics of the medium must be considered.

Degree of Hydrologic Saturation. The degree of hydrologic saturation of the medium affects the chemical properties of the fluid phase. Ionic strength, pH, redox potential and other fluid properties may all be affected to varying degrees (Yang et al., 1988; Meijer, 1990), which in turn has an effect on sorption properties as outlined above in Section 2.2.2. The degree of saturation is also related to bulk density (and water/rock ratio) and is explicitly incorporated in a K_d-retardation factor approach to sorption modeling (see below). In addition, the presence of a gas phase and the related two-phase flow may also affect sorption in ways that are poorly understood at present (Bradbury et al., 1988; Russo, 1989a). Russo (1989a) notes that as the water content of a soil increases, the differences between a reactive and nonreactive solute profile decrease.

Composite Mineralogy. Because of the highly variable sorptive properties of different minerals, it is necessary to have some idea of the composite mineralogy of a sorptive medium along the fluid flow path. Several authors (Serne and Relyea, 1982, Meyer, 1990; Serne et al., 1990) have discussed the use of weighting techniques based on the sorption coefficients of pure minerals and the modal composition of primary and secondary minerals in the rock. The data of Honeyman (1984) and Altmann (1984), however, indicate that predictions made in this fashion are often unreliable, and can both underpredict and overpredict sorption.

Water Rock Ratio. Honeyman (1984) reported that differences in sorption are apparent depending on the concentration of solids in solution for single adsorbents. Other studies have observed similar behavior (Higgo and Rees, 1986, Balistrieri and Murray, 1986, Fuller and Davis, 1987). Generally, sorption is observed to increase with adsorbent concentration at low particle concentrations. Studies of Mg adsorption by Balistrieri and Murray (1986) indicate that above concentrations of about 400 mg/L, sorption becomes relatively insensitive to adsorbent. Theoretical considerations (Murali and Aylmore, 1983b) and experimental data (Griffin and Au, 1977; Harter and Baker, 1977) suggest one possible mechanism underlying the water rock relationship. Upon desorption from the solid, one (or more) "native" species are then free to compete for available sorption sites with the spike element in solution. Therefore, higher solid concentrations (i.e., lower W/R ratio) may result in an increase in competing cations in solution. If the system is modeled as a single species system, when in fact multiple species are present through desorption from the solid phase, the apparent sorption of the species of interest will appear anomalously low.

Fluid Flux and Fluid Mixing. The importance of kinetics in sorption reaction depends on the time the solute is in contact with the sorbing substrate. Equilibrium sorption [illegible] for those systems where the sorption rate is fast relative to the residence time of the solute. Where either slow sorption or short residence time prevents the system from reaching equilibrium, kinetic sorption is appropriate. This will be a function of the type of adsorbent (e.g., oxide vs. clay). Residence time will also be affected by other factors, including the rate at which water is flowing through the system (fluid flux), changes in solution composition due to dilution (or concentration) through mechanical fluid mixing, or other chemical reactions.

Atmospheric Composition. The influence of atmosphere has been observed in a number of studies, particularly with respect to the influence of $P(CO_2)$ on carbonate complexing (Hsi and Langmuir, 1985; Payne et al., 1990a; Carroll and Bruno, 1991). Solution properties such as alkalinity, pH, and Eh will be affected by the atmosphere in contact with the fluid, and many experiments on redox-sensitive elements are performed in an inert atmosphere to minimize these effects. McCarthy and Zachara (1989) also note the effect of oxidation and $P(CO_2)$ on colloid formation. Introduction of an oxidizing atmosphere may precipitate Fe-oxyhydroxides which can act as sorbents or colloidal particles, and changes in $P(CO_2)$ may result in the precipitation of a colloidal suspension.

2.3. SORPTION MODELS

Much of the literature dealing with sorption processes has been generated in the fields of soil science and chemical engineering to study the interplay between water, organic and inorganic solutes, and soil particles. A number of approaches have been used to develop an experimental database and to construct models that reproduce the observed results. These range from simple empirical equations fit to a particular data set, to more detailed theoretical treatments that address the microscale processes operating during solute uptake and removal from solution. Travis and Etnier (1981), Morrey (1988), Serne et al. (1990), and [illegible] et al. ([illegible]) provide excellent summaries of the various modeling approaches that have been applied to sorption processes. The following treatment is largely based on, and provides an extension of, these previous reports.

2.3.1. Empirical Sorption Isotherms

Equations relating solute concentrations in coexisting solid and liquid phases can be generated for individual data sets through fitting curves and empirical coefficients to the data (Ames et al., 1982, 1983a,b,c). Because experimental sorption data are generally obtained at a single, constant temperature, these empirical equations are known as "sorption isotherms." Empirical models have been developed to describe [illegible] equations [illegible] (Travis and Etnier, 1981).

As mentioned above, a drawback common to all empirically-derived sorption models is the inability of the method to discriminate between different processes that contribute to the removal of the solute from solution (Reardon, 1981; Coles and Ramspott, [illegible]; Miller and Benson, 1983; Kelmers et al., 1987; Kent et al., 1988). Consideration of [illegible] decay-series disequilibria (e.g., [illegible]) can provide information on rates of water-rock interaction and the relative importance of different retardation mechanisms (Ku et al., [illegible]). Applications of this type may, to some extent, circumvent the limitations of empirical sorption models related to the lumping of retardation processes. Also, extrapolation of isotherms beyond the experimental conditions used to derive the necessary empirical coefficients is generally not based on any theoretical justification. Empirical models are largely unsuited to rapidly changing systems, and the method is necessarily limited to restricted ranges in conditions (Miller and Benson, 1983; Parker and Jardine, 1986; Kent et al., 1988; Park and [illegible], [illegible]). Therefore, in order to evaluate the adequacy of an empirical approach, it is critical to have an understanding of the magnitude of changes anticipated in the system of interest. In addition, empirical techniques are largely developed for, and limited to, single species transport. Because aqueous speciation cannot be addressed by empirical approaches, these methods may be inadequate to model the interactions that occur during multi-species transport ([illegible] and Rees, [illegible]).

2.3.1.1. *Linear Equilibrium Adsorption*

The simplest type of sorption isotherm is a linear equilibrium adsorption isotherm of the general form

$$S = K_d C \qquad (2\text{-}1)$$

where **S** (g/g) is the concentration of solute adsorbed onto the solid phase, **C** (g/ml) is the concentration of the solute in solution, and $\mathbf{K_d}$ (in ml/g) is an empirically determined "distribution coefficient", a measure of concentration of a given ion in the solid phase relative to its concentration in the liquid phase. A number of different notations have been used to represent linear sorption coefficients values, including **D**, $\mathbf{R_d}$, **and** $\mathbf{R_s}$. In this report, $\mathbf{K_d}$ will be used for consistency. A linear isotherm (or $\mathbf{K_d}$) approach generally assumes that $\mathbf{K_d}$ is constant and develops the general retardation factor ($\mathbf{R_f}$) through the relationship

$$R_f = 1 + \frac{\rho_b}{\theta} K_d \qquad (2\text{-}2)$$

where ρ = bulk density, and θ = porosity. This retardation factor can be derived from with the convection-dispersion equation (see Section 4) and has been used to describe reactive solute transport in a number of systems and (Selim and Mansell, 1976; Selim, 1978; Grove and Wood, 1979; Krishnaswami et al., 1982; Ebinger et al., 1990). A particularly limiting characteristic of the K_d approach is the inability to recognize a maximum sorption limit. In actuality, because there is a finite number of sorption sites, sorption reaches a practical upper limit (Travis and Etnier, 1981). In addition, Honeyman (1984) has observed that sorption frequently depends on the solid concentration of the system, which could be a consequence of the influence of the maximum sorption limit. Balistrieri and Murray (1986) noted a similar effect. In experiments using natural seafloor sediments, K_d initially increased with increasing particle concentrations, becoming relatively insensitive at concentrations greater than 400 mg/l.

Valocchi (1984) has proposed an "effective K_d" approach to sorption modeling which is based on mass balance considerations for a finite step across a sharp migration front (i.e. negligible dispersion). The method assumes local equilibrium, and requires knowledge of the aqueous and sorbed phase compositions both upstream and downstream from the reaction front. Changes in aqueous and sorbed phase concentrations across the reaction front (ΔC and ΔS, respectively) are related to an "effective K_d" (i.e. $K_d = \Delta S/\Delta C$) which in turn can be related to an effective retardation factor through an equation of the same form as Eqn (2-2). The advantage of this approach relative to the constant K_d approach is that the "effective K_d" considers **S** and **C** upstream and downstream of the reaction front, and K_d is no longer treated simply as a unique property of the medium. Valocchi (1984) applies the method to non-linear sorption for homovalent binary exchange. Competitive sorption can only be modeled by approaching each species individually, and the technique does not allow for interaction between solutes. On comparison to a finite-element simulation (CHEMTRN - Miller and Benson, 1983), the effective K_d approach of Valocchi (1984) was able to match computed positions for the solute front very well. Application to a field problem at the Palo Alto Baylands indicates that the approach can predict the position of the solute front reasonably well. The author notes, however, that if hydrodynamic dispersion is significant, more detailed numerical models are required.

2.3.1.2. *Freundlich Equilibrium Adsorption*

The Freundlich isotherm (Freundlich, 1926) is nonlinear and defined by the relationship:

$$S = K_{Fr} C^{n} \qquad (2\text{-}3)$$

where S and C are as in Eqn. (2-1), and K_{Fr} and **n** are empirical coefficients. For the special case where **n** = 1, Eqns. (2-1) and (2-3) are identical. However, recent work (Serne and Muller, 1987; Serne et al., 1990) indicates that **n** may vary significantly from 1 for elements present only in trace amounts. If the sorption/concentration data can be represented by a Freundlich isotherm, a plot of log S vs. log C should result in a straight line with a slope equal to **n**, and an intercept of log K_{Fr}. The Freundlich isotherm has been widely used to model heavy metal and radionuclide sorption (Street et al., 1977; Sidle et al., 1977; Ames et al., 1983a,b,c; Alemi et al., 1991). As is the case for a linear sorption isotherm, no maximum is placed on uptake through sorption.

[illegible] (1978) have modified the Freundlich [illegible] account for a shift to linear sorption at high phosphate concentrations. Below a critical concentration C_c, sorption/concentration relations are described by the equation

$$S = aC + K_{Fr} C^{n} \qquad (2\text{-}4)$$

For concentrations above C_c, the linear relationship:

$$S = aC + X_o \qquad (2\text{-}5)$$

describes the correlation between sorption and concentration. In both cases, K_{Fr}, and **n** are empirical coefficients, **a** and X_o are the slope and intercept of the linear portion of the isotherm, and $C_r = (X_o/K_{Fr})^{1/n}$. This modification has only been applied to phosphate adsorption.

Murali and Aylmore (1983a,b) have considered competitive sorption where all species follow Freundlich isotherms:

$$S_i = \frac{K_{Fr,i} C_i^{n_i+1}}{[\Sigma_j \alpha_{ij} C_j]} \qquad (2\text{-}6)$$

where the K_{Fr}, S, C, and n are the same as in Eqn. (2-3), and $\alpha_{ij} = K_{Fr,i}/K_{Fr,j}$ is an empirical competition parameter. A number of studies (Murali and Aylmore, 1983c and references therein) have shown sorption characteristics similar to those predicted using the isotherm presented in Eqn. (2-6) (Murali and Aylmore, 1983b). Murali and Aylmore (1983c) point out, however, that their comparison was limited to only a qualitative evaluation because adsorption data were incomplete for all participating species.

2.3.1.3. *Langmuir Equilibrium Adsorption*

The Langmuir isotherm was initially developed to describe gas adsorption (Langmuir, 1918). Adapted to solution chemistry, the approach introduces the idea of an upper limit to surface adsorption, avoiding this particular drawback of the linear and Freundlich isotherms. Its general form is:

$$S = \frac{K_{La} b C}{(1 + K_{La} C)} \qquad (2\text{-}7)$$

where b is the maximum adsorption capacity of the substrate (grams solute/gram adsorbent), and K_{La} is a constant representing the strength with which the solute is bound to the substrate (l/meq). From Eqn. (2-7), the fraction of occupied sites is related to the product of K_{La} and C. For example, if $K_{La}C$ is unity, then half of the sites (b/2) are occupied. Values for b can be determined for a given data set by plotting C/S versus C. From Eqn. (2-7), this should yield a straight line with a slope of 1/b and an intercept of $1/K_{La}b$. Travis and Etnier (1981) point out that the Langmuir theory is based on monolayer adsorption which may not be appropriate for variable heat of adsorption [i.e., the difference between the activation energies for adsorption and desorption (Yingjajaval, 1979)]. If this property varies as a logarithmic function of surface coverage, however, the standard Langmuir isotherm can be shown to be equivalent to the Freundlich equation (Travis and Etnier, 1981).

The Langmuir isotherm assumes that all sorption sites are homogeneous. Because of this assumption, it has met with limited success in geologic applications where the media under consideration are typically heterogeneous (Ames et al., 1982; Serne et al., 1990). The approach is most successful for those applications where variations in pH and sorbed ion concentration are limited (Ames et al., 1982). Despite these limitations, Langmuir sorption has been widely used (Frost and Griffin, 1977; Reeves and Kirkner, 1988; von Breymann et al., 1990), and in several studies, (McLaughlin et al., 1977; Ryden et a

1977; Middleburg and Comans, 1991), non-linear sorption has been described by combining several different Langmuir isotherms to fit the data.

The Langmuir isotherm has been modified to provide a better fit for individual data sets. A two-surface Langmuir model has been proposed by a number of authors (Travis and Etnier, 1981 and references therein; Reeves and Kirkner, 1988). Each site exhibits its own values for **b** and **K_{La}**, and each is treated independently of the other as shown by the equation:

$$S = \frac{K_{La1} b_1 C}{(1 + K_{La1} C)} + \frac{K_{La2} b_2 C}{(1 + K_{La2} C)} \qquad \textbf{(2-8)}$$

Another modification of the Langmuir isotherm has been proposed to accommodate competitive sorption between two homovalent cationic species (Boyd et al., 1947). The isotherm has the form:

$$\frac{(C_1/C_2)}{S} = \left(\frac{b_2}{K_{La1} b_1}\right) + \left(\frac{C_1}{b_2 C_2}\right) \qquad \textbf{(2-9)}$$

where the subscripts 1 and 2 refer to the sorbing ion and the ion being replaced at the substrate surface, respectively. This approach has been used to model sorption by montmorillo[illegible] (Griffin and Au, 1977) and Zn-sorption by soils (Harter and Baker, 1977). Murali and Aylmore (1983a,b,c) have also developed Langmuir-type isotherms for competitive sorption and have also extended the application into simple kinetic models (see below).

Murphy and Helgeson (1987, 1989) have used the Langmuir isotherm for hydrogen and aluminum adsorption on pyroxene and feldspar, respectively, to rationalize data for the pH-dependence of the pyroxene dissolution rate and the dependence of the feldspar dissolution rate on dissolved aluminum. Polzer and Fuentes (1988, 1991) have also modified the Langmuir isotherm to fit radionuclide sorption concentration data for tuffs from Yucca Mountain. Their modification, designed to consider heterogeneous sorption, is expressed as:

$$S = \frac{b K_{La}^{\beta} C^{\beta}}{(1 + K_{La}^{\beta} C^{\beta})} \qquad \textbf{(2-10)}$$

where the additional adjustable parameter β represents site heterogeneities and **K_{La}^{β}** is an average distribution coefficient of the same units as **K_{La}** in Eqn. (2-7).

2.3.1.4. Dubinin-Radushkevich Equilibrium Adsorption

The Dubinin Radushkevich (D-R) isotherm (Dubinin and Radushkevich, 1947) takes the general form:

$$S = b[\exp(K_{DR}[RT\ln(1 + \frac{1}{C})]^2)] \tag{2-11}$$

S, K_{DR} and b are similar in form to Eqn. (2-9), but are more general in nature than the values in the Langmuir isotherm, allowing for representation of heterogeneous types of sorption sites. The gas constant (R) and absolute temperature (T, in K) are included in the equation, and C is the steady-state aqueous concentration of the solute of interest. Because of the exponential form of the equation, a plot of ln S vs $[RT(\ln(1+1/C)]^2$ results in a straight line with a slope equal to K_{DR} and an intercept of ln b.

Unlike the Langmuir isotherm, the D-R isotherm does not require the assumption of a single, homogeneous type of sorption site. The parameters represent to some extent the net effect of a variety of different sorption sites. Because the parameters are determined empirically, however, the relative contributions of the various sites is not distinguished by the model, and no conclusions can be drawn about their relative importance in the sorption process. Ames et al. (1982, 1983a) have fit Cs- and U-sorption data using the D-R isotherm. By assuming small, homogeneous regions where the Langmuir isotherm is valid, a sorption energy E is determined from the relationship:

$$E = \frac{[(-K_{DR})^{-0.5}]}{\sqrt{2}} \tag{2-12}$$

The magnitude of E can be used to estimate the sorption mechanism operating in the heterogeneous system (i.e. chemisorption, ion exchange, etc.). Ames et al. (1982) report that removal of Fe-oxides from the system caused the sorption data to revert to a simple Freundlich isotherm. Dalal (1979) has also used the D-R isotherm to model phosphorous sorption in soils.

2.3.2. Kinetic Sorption Models

Kinetic sorption models have been used to simulate conditions where sorption processes are believed to operate relatively slowly in relationship to solute residence time (Selim, 1978; Nyffeler et al., 1984; Comans and Middleburg, 1987; Comans et al., 1991; Middleburg and Comans, 1991). Under these conditions, the degree of sorption continues to change with time, and frequently does not reach equilibrium, at least within the time constraints of the experiment. Kinetic sorption is also revealed by a hysteretic relationship between adsorption and desorption experimental data (Jannasch et al., 1988; Comans et al., 1991). Because time is a factor in kinetic models, sorption is dealt with as a separate process and the term "isotherm" is not strictly applicable. Under equilibrium conditions, however, simple kinetic models reduce to the commonly used equilibrium isotherms described above (Murali and Aylmore, 1983a). While in theory kinetic models are mechanistic, in practice, experimentally determined rate constants are often unavailable for a given system, and the constants are commonly used as fitting parameters in a manner similar to sorption isotherms.

2.3.2.1. *Linear Kinetic Sorption*

First-order kinetics have found the most application in modeling nonequilibrium sorption (Selim, 1978; Griffin and Jurinak, 1974; Murali and Aylmore, 1983a,b; Nyffeler et al., 1984; Valocchi, 1989; Cvetkovic and Shapiro, 1990). As applied to soil systems, this equation has the general form:

$$\frac{dS}{dt} \quad k_1 C \quad k_2 S \qquad (2\text{-}13)$$

where S and C are the same as previously defined, and k_1 and k_2 are rate constants for adsorption and desorption, respectively. Although k_1 and k_2 can be determined experimentally, the data are frequently unavailable and an empirical approach is used to fit Eq. (2-13) to sorption data (Selim, 1978). At equilibrium (i.e., $dS\ dt = 0$), Eqn. (2-13) reduces to the linear sorption isotherm with $K_d = k_1/k_2$.

2.3.2.2. *Nonlinear Kinetic Sorption*

Nonlinear reaction kinetics have also been applied to [illegible] processes (Mansell et al., 1977; Middleburg and Comans, 1991). The sorption/concentration relationship for soils is similar to Eqn. (2-13):

$$\frac{dS}{dt} \quad k_1 C^n \quad k_2 S \qquad (2\text{-}14)$$

where k_1 is the adsorption (forward) rate coefficient, k_2 is the desorption (backward) rate coefficient, C, and S are the same as Eqn. (2-13), and n is an empirical coefficient. Adsorption is described as a nonlinear process in Eqn. (2-14), while the desorption process is linear. When $n = 1$, Eqn. (2-14) is identical to linear kinetic sorption described by Eqn. (2-13), and under equilibrium conditions, Eqn. (2-14) reduces to the Freundlich sorption isotherm with $K_F = k_1/k_2$. Equation (2-14) has been used to describe pesticide, herbicide, and phosphorous migration with $n < 1$ (Enfield and Bledsoe, 1975; Fiskell et al., 1979). Mansell et al. (1977) have proposed using a combination of Eqns. (2-13) and (2-14) to describe phosphorous migration through soils. Nyffeler et al. (1984) have modified Eqn. (2-14) to model sorption concentration data from trace element sorption in natural aquatic systems. By defining a distribution ratio (K_d) at equilibrium such that $K_d(t = \infty) = (k_1\ C)\ k_2$, the authors obtain values for the rate constants k_1 and k_2 through fitting a curve to $K_d(t)$ sorption concentration data.

2.3.2.3. *Kinetic Product Sorption*

Enfield (1974) has described an empirical kinetic model of the form:

$$\frac{dS}{dt} = aC^{b}S^{d} \tag{2-15}$$

where **a**, **b**, and **d** are empirical constants. Travis and Etnier (1981) point out that this model provides no upper limit on adsorption, a limitation shared with the Linear and Freundlich equilibrium isotherms. Enfield (1974) and Enfield and Bledsoe (1975) were able to obtain a better fit to data on phosphorous migration in a variety of soils using Eqn. (2-15) rather than Eqn. (2-14). This is perhaps to be expected, however, since an empirical model such as Eqn. (2-15) is expressly designed to fit observed data. In addition, the relatively unconstrained nature of the coefficients may lead to a non-unique fitting of the data.

2.3.2.4. *Kinetic Langmuir Sorption*

Several studies (Travis and Etnier, 1981; Murali and Aylmore, 1983a; Jennings and Kirkner, 1984) describe a modification of the Langmuir isotherm [Eqn. (2-7)] to address kinetic sorption, such that:

$$\frac{dS}{dt} = k_1C(b - S) - k_2S \tag{2-16}$$

where k_1 and k_2 are adsorption and desorption rate constants, respectively, and all other variables are as in Eqn. (2-7). In a manner similar to linear and nonlinear first order rate equations, Eqn. (2-16) reduces to the Langmuir adsorption isotherm at equilibrium, with $K_L = k_1/k_2$. Travis and Etnier (1981) point out that any coupling of this model with the convection-dispersion equation will require numerical solution as there is no analytic solution. Murali and Aylmore (1983a,b) have proposed a general kinetic Langmuir equation to address competitive sorption by substituting the summation of total sorbed concentrations (i.e., $b-\Sigma S$) for all species (j) of interest in the first term on the right side of Eqn. (2-16).

2.3.2.5. *Kinetic Mass Transfer*

In the kinetic mass transfer sorption model as described by Travis and Etnier (1981), sorption and concentration are related through the equation:

$$\frac{dS}{dt} = k(C - C^{*}) \tag{2-17}$$

where **k** is an empirical parameter which addresses the diffusion of the solute of interest through a liquid layer around the sorbing substrate, and C^{*} is the concentration of the solute at the substrate/liquid interface. C^{*} can take on a variety of forms, depending on the equilibrium between the solid and the liquid phases across the diffusive layer. If this can be described by a linear isotherm, then Eqn. (2-17) reduces to the reversible linear model [Eqn. (2-13)]. If this relationship can be predicted by a Langmuir isotherm, then Eqn. (2-17) is equivalent to the Kinetic Langmuir isotherm (Eqn. 2-16).

2.3.2.6. Two-Site Kinetic Models

Many sorption experiments have revealed evidence for more than one type of sorption process (Parker and Jardine, 1986; Comans and Middleburg, 1987; Davis et al., 1987; Jannasch et al., 1988; Middleburg and Comans, 1991; Comans et al., 1991). An initial stage of rapid, adsorption accompanied by ready desorption is commonly followed by slow, continued uptake without desorption. Solute uptake continues during the slower stage of adsorption, and sorption equilibrium is frequently not reached for the duration of the experiment. A two-site model has been developed to explain these results, by proposing one site that achieves sorption equilibrium rapidly, while sorption at the second site is slow, and requires the use of a kinetic model. Several models have been used for the equilibrium site, including linear (Cameron and Klute, 1977), Freundlich (Selim et al., 1976), and Langmuir (Middleburg and Comans, 1991) isotherms. First-order reversible models have generally been applied to the kinetic site. In experiments on zinc and tin sorption onto natural particulates, Jannasch et al. (1988) have proposed modeling the earlier, rapid stages of sorption as a sequence of three linear, first-order kinetic steps, each with a different time scale.

An example (Selim et al., 1976) of a governing equation resulting from this type of approach

$$\frac{\partial S}{\partial t} = \left[\frac{k_1}{k_2}\frac{\theta}{\rho}MC^{M-1}\frac{\partial C}{\partial t}\right] + k_3\frac{\theta}{\rho}C^{N} - k_4(1-f)C \qquad (2\text{-}18)$$

where **f** is the fraction of sorption sites occupied (i.e., $0 \leq f \leq 1$), **M** is the empirical exponent of the Freundlich isotherm [i.e. n in Eqn. (2-3)], and **N** is the exponent for a first order reversible kinetic model [Eqn. (2-14)], and k_1, k_2, k_3, and k_4 are constants.

Several studies (Comans and Middleburg, 1987; Davis et al., 1987; Jannasch et al., 1988; Comans et al., 1991; Middleburg and Comans, 1991) have examined the processes responsible for the observed differences in rates of sorption. The rapid sorption on the equilibrium site is generally ascribed to surface processes, perhaps due to surface charge (see below). The second site is controlled by either slower sorption processes such as ion exchange, or uptake through precipitation/dissolution. The rates of these latter processes are in turn controlled by solute diffusion across a surface layer of finite thickness, mass transport by advection/dispersion, diffusion through the crystal lattice, or the kinetics of precipitation. Selim et al. (1976) suggest that two-site sorption characteristics may depend on the residence time (i.e. solution velocities) of the solute. Equilibrium sorption sites are expected to predominate for short residence times because of the shorter time scale of these sorption processes. As solute between the solid and the liquid phases across the diffusive layer. If this can be described by a linear isotherm, then Eqn. (2-17) reduces to the reversible linear model [Eqn. (2-13)]. If this relationship can be predicted by a Langmuir isotherm, then Eqn. (2-17) is equivalent to the Kinetic Langmuir isotherm (Eqn. 2-16).

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2.3.2.7. *Additional Kinetic Models*

Travis and Etnier (1981) describe several other models that have seen limited application in describing kinetic sorption. These include the Elovich model (Roginsky and Zeldovich, 1934), which assumes an exponential relationship, with empirically derived coefficients, between total sorption and the fraction of occupied sites. This approach has been used to describe pesticide and phosphate adsorption during transport through soils (van Genuchten et al., 1974; Kyle et al., 1975). Fava and Eyring (1956) developed a model using empirical constants, and a dimensionless measure of the initial distance from sorption equilibrium. This requires a knowledge of the initial sorption conditions, and the equilibrium sorption for the system under consideration. This method, originally developed to describe the reaction between detergents and fabrics, has been applied to the sorption of pesticides by soils and organic matter (Lindstrom and Boersma, 1970).

2.3.3. Simple Mass-Action Ion Exchange Models

Ion exchange is based on the concept of interaction at the solid-liquid interface, resulting in the uptake of a reactive solute from solution, and sequestering it in the solid phase. Rather than simply "sticking" to the surface of a substrate, the solute is assumed to exchange with an ion that initially occupies a given site at the surface (Serne et al., 1990, Allison et al., [illegible] of this approach over the empirical models discussed above [illegible] thermodynamically determined parameters. The surface can be described in terms of the general chemical reaction:

$$SOH{\cdot}M_1 + M_2 \rightleftharpoons SOH{\cdot}M_2 + M_1 \qquad (2\text{-}19)$$

where M_1 and M_2 are the initial exchangeable ion, and the exchanging solute, respectively, and $SOH{\cdot}M_i$ represents the surface site occupied by a given ion. Using mass-action relations, a selectivity coefficient (K_{ex}) can be devised such that

$$K_{ex} = \left[\frac{[M_1^{+}][SOH{\cdot}M_2]}{[M_2^{+}][SOH{\cdot}M_1]} \right] \qquad (2\text{-}20)$$

where the bracketed quantities represent thermodynamic activities.

As in other geochemical equilibria, the thermodynamic activity of each component is considered in the mass-action expression. Component activity coefficients (i.e. $\gamma_i = a_i/m_i$), if not available from experimental data, can be derived using one of several approaches (Debye-Huckel, Davies equations, etc.). Frequently, however, activity coefficients are assumed unity and the bracketed terms in the mass-action expression in Eqn. (2-20) reduce to concentrations (e.g. molality). A number of different approaches have been used to address the effects of non-ideal mineral solid solution on ion exchange characteristics (Pabalan, 1991). Although as developed here the treatment considers only homovalent, singly charged cations, the mass-action theory is equally valid for heterovalent exchange in multivalent systems, and for anion exchange.

Serne et al. (1990) indicate that for simple systems, the mass action expression can be further simplified by using mass balance relationships. From mass balance considerations, expressions can be derived of the form:

$$CEC = m_{SOH\,M_1} + m_{SOH\,M_2} \tag{2-21}$$

$$m_{Total} = m_{M_1^+} + m_{M_2^+} \tag{2-22}$$

where **CEC** is the cation exchange capacity (meq/kg$_s$), which is a measure of the total concentration of exchangeable sites for the solid, and $\mathbf{m_{Total}}$ is the total concentration of the solute in the system (meq/kg$_{aq}$). By further assuming constant values for **CEC** and $\mathbf{m_{Total}}$, and substituting these constants into Eqn. (2-20) a simplified expression is derived for $\mathbf{K_{ex}}$ such that:

$$K_{ex} = \frac{(m_{SOH\,M_1})(m_{Total} - m_{M_1^+})}{(CEC - m_{SOH\,M_1})(m_{M_1^+})} \tag{2-23}$$

Serne et al. (1990) point out that these simplifying assumptions are only valid for systems of two cations, with only trace concentrations of the sorbing solute. For more complex systems, the general expression given in Eqn. (2-20) must be used.

In an effort to simplify ion exchange models for more efficient computer solutions, Krupka et al. (1988) have developed a single ion adsorbate model for hydrous iron oxide that neglects electrostatic effects. Binary ion exchange at the surface is treated as the sum of two half-reactions:

$$A^{m+}_{aq} + mX_s \rightleftharpoons AX_{m(s)} \tag{2-24a}$$

$$B_{aq}^{n+} + nX_s \quad BX_{n,s} \tag{2-24b}$$

with a selectivity coefficient $K_{ex} = K_B/K_A$ where K_A and K_B are the equilibrium constants of Eqns. (2-24a) and (2-24b), respectively. If one of the half reactions is chosen as a reference [e.g., Eqn. (2-24a)], then for reactions involving a reference cation (A^{m+}), K_{ex} can be expressed as:

$$(K_i)^m \quad K_{ex}(K_r)^n \tag{2-25}$$

where K_i is the adsorption constant for cation **i**, and K_r is the dissociation constant for the reference cation [e.g., **r=A** assuming Eqn. (2-24a) as a reference]. The half reaction

$$HX_s \quad H_{aq}^{+} + X_s \tag{2-26}$$

is assigned an equilibrium constant of unity by Krupka et al. (1988) and used as a reference half reaction. Based on this simplifying assumption, exchange constants are computed for a limited number of cations.

2.3.4. Electrostatic Sorption Models

During sorption reactions, the substrate and the solution interact in a complex manner. Sorption properties of the substrate are affected by solution chemistry (especially pH), and in turn, the process of sorption by the solid affects the solution chemistry. Many potential adsorbents exhibit variably charged surfaces. If the polarity of the adsorbent is the same as that of the solute, then charged surfaces will tend to repel ions in solution. If the polarity is reversed, aqueous species will be attracted to the substrate. Electrical work done in moving ions across this "zone of charge influence" will in turn affect the activity of aqueous species near the charged surface relative to the bulk solution. This change in activity is governed by the exponential Boltzmann relation

$$a_{i,s} \quad a_i[e^{\frac{\phi F}{RT}}]^z \tag{2-27}$$

where $a_{i,s}$ is the activity of a given ion **i** in the aqueous solution near the charged surface, a_i is the activity in the bulk solution, $e^{\phi F/RT}$ is the Boltzmann factor, **z** is the valence charge of the ion of interest, **F** and **R** are the Faraday (coulombs eq^{-1}) and ideal gas (J K^{-1} mol^{-1}) constants, respectively, and **T** is absolute temperature (K).

Electrostatic sorption models differ from simple mass action models in that additional terms are introduced to account for energy transfer during these electrostatic interactions. Developed largely for iron oxide minerals, several surface complexation models address the effect of electrostatic potential on surface sorption processes: diffuse layer, constant capacitance, and triple layer (Davis et al., 1978; Davis and Leckie, 1978, 1980; Hayes et al., 1989; Serne et al., 1990; Allison et al., 1990). For oxides, these models assume a surface comprised of amphoteric hydroxyl groups (OH_2^+, OH^0, O^-, etc.), treating surface adsorption as a combination of protonation deprotonation and complexation reactions of the form:

$$SOH + H^+ = SOH_2^+ \quad \text{(Protonation, } K_+) \qquad (2\text{-}28a)$$

$$SOH = SO^- + H^+ \quad \text{(Deprotonation, } K_-) \qquad (2\text{-}28b)$$

$$SOH + M^{2+} = SOM^+ + H^+ \quad \text{(Complexation, } K_{M^{2+}}) \qquad (2\text{-}28c)$$

where **SOH** represents a neutral surface site. Intrinsic surface acidity constants (**K_+, K_-**) and equilibrium constants $\left(K_{M^{2+}}\right)$, can be defined for these reactions using mass action considerations analogous to Eqn. (2-20). In turn, activities modified by electrostatic effects (Eqn. 2-27) are inserted into these expressions, resulting in the mass action expression.

$$K_{M^{2+}} = \left(\frac{[SOM^+][H^+]e^{-\psi F/RT}}{[SOH][M^{2+}](e^{-\psi F/RT})^2} \right) \qquad (2\text{-}29)$$

Although the reactions written above are for divalent cation adsorption in Eqn. (2-28c), the complexation approach is valid for mono- and multivalent cation and anion exchange, limited only by data availability.

Because of the protonation/deprotonation reactions occurring at the surface, adsorption can be presented as a function of pH for surface complexation models. In additio given the relationships outlined in Eqn. (2-27), finite changes in the ionic strength of the bulk solution affect the protonation/deprotonation reactions, thereby affecting adsorption/desorption. The ability to account for variable physical-chemical conditions give surface complexation models a flexibility of application based on theoretical considerations. This is an advantage compared to the restricted applicability of empirically-derived isotherms. The various electrostatic modeling approaches differ in how the electrostatic potential (Ψ) is extended from the charged surface into the bulk solution, and how changes in solution electrolyte concentration affect reactions at the particle surface.

Adsorption reactions are modeled through simultaneously solving equations for equations for conservation of surface sites, charge balance, and mass-action. Mass balance for the surface sites is based on the total number of available sorption sites (T_{SOH}) such that:

$$T_{SOH} = (N_S) \times (SA) \times (C_S) \qquad (2\text{-}30)$$

where **N_s** represents surface site density (sites/m²), **SA** is specific surface area (m²/g), and **C_s** is the concentration of the adsorbent in solution (mg/l). Eqn. (2-30) is then combined with charge-potential relationships specific to a given model (see below), and activity and mass-action relationships analogous to Eqn. (2-29) that describe concentration distributions of surface species and aqueous speciation as a function of pH and electrostatic potential.

A simplified complexation model was used by Davis et al. (1987) to model Cd^{2+} adsorption onto calcite. In this model, a simple binding coefficient (**K**) was used in the complex formation reaction:

$$Cd^{2+} + S = S\text{-}Cd^{2+} \qquad (2\text{-}31)$$

where **S** is a calcite surface site. An adequate fit to the data was obtained for an empirical constant value of **log K = 4.8**, neglecting the effect of pH on **log K** which is typically observed for hydrous oxides.

2.3.4.1. *Diffuse Layer Surface Complexation*

In surface complexation models, the particle surface carries a charge (σ_s), and is separated from the solution by a diffuse layer of nonspecifically bound counterions. The surface charge is balanced by the charge on the diffuse layer (σ_d) such that:

$$\sigma_s + \sigma_d = 0 \qquad (2\text{-}32)$$

[illegible] conceptual model of the Diffuse Layer Model (DLM) proposes that protonation/deprotonation and adsorption only occur in one plane at the surface solution interface, and that only those ions specifically adsorbed in this inner "o-plane" contribute to the total surface charge ($\sigma_s = \sigma_o$)(Figure 2-1). In the diffuse layer, the Stern Grahame extension of the Gouy-Chapman relationship for symmetrical electrolytes is used to describe the interdependence between electrolyte concentration (ionic strength), charge ($\sigma_d = -\sigma_o = -\sigma_s$ at the boundary between the o-plane and the diffuse layer), and electrostatic potential ($\Psi_d = \Psi_o$) such that:

$$\sigma_o = -\sigma_d = (\sqrt{\varepsilon\varepsilon_o IRT})\sinh\left[\frac{(z\psi_d F)}{2RT}\right] \qquad (2\text{-}33)$$

where **z**, **F**, **R**, and **T** are as defined in Eqn. (2-27), ε is the dielectric constant, ε_o is the permittivity in free space (8.85 x 10^{-12} coulombs^2/J m), and **I** is solution ionic strength.

2.3.4.2. *Constant Capacitance Surface Complexation*

The constant capacitance model (CCM) (Schindler et al., 1976) is similar in concept to the diffuse layer model. For a single-layer model at high ionic strength and/or low surface potential, it is a special case of the DLM (Allison et al., 1990). As in the diffuse layer model, total surface charge is determined by the charge of a single plane of

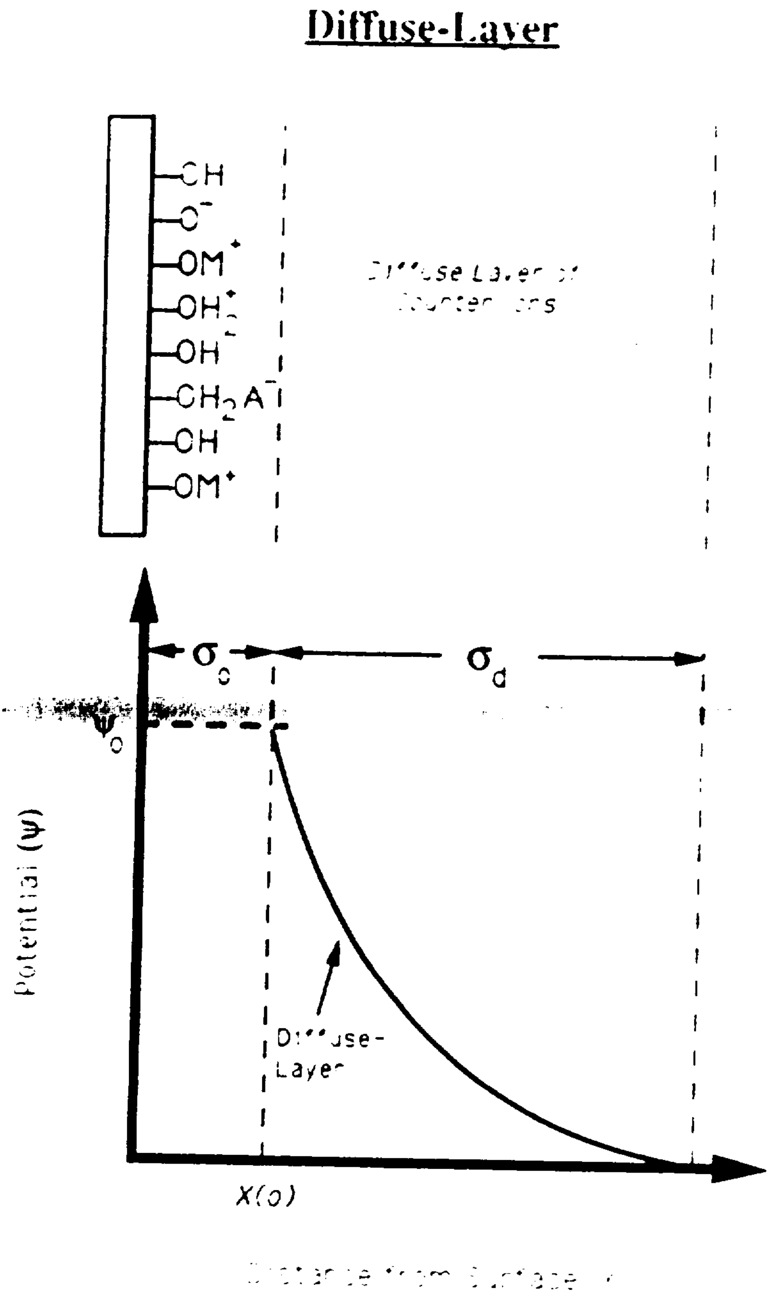

Figure 2-1. Schematic diagram of the Diffuse-Layer surface complexation model. See text for an explanation of symbols.

specifically adsorbed ions attached to available surface sites. Mass action and mass and charge balance equations are identical between the two models.

In contrast to the DLM, however, the CCM assumes that the charged surface is isolated from the bulk solution by a plane of constant capacitance (Figure 2.2). Based on this assumption, the total charge of the surface ($\sigma_d = -\sigma = -\sigma_o$) is related to surface potential ($\Psi_o = \Psi_d$) through the simple equation

$$-\sigma_o = \sigma_d = C_1 \Psi_o \qquad (2\text{-}34)$$

where C_1 (Farads/m²) is a constant capacitance term. This relationship results in a linear potential gradient from the charged substrate to the bulk solution (Figure 2.2). The constant capacitance approach is limited to a specific ionic strength, however, as changes in ionic strength require recalculation of C_1. Allison et al. (1990) indicate that the constant capacitance term is frequently not provided as a characteristic property of a given system, but applied instead as an empirical parameter fit to the data. This has the advantage of providing a better fit to a given data set, but at the expense of the theoretical basis of the resulting equation.

2.3.4.3. *Triple Layer Surface Complexation*

The triple layer surface complexation (TLM) model (Davis et al., 1978; Davis and Leckie, 1978; 1980) is similar to the diffuse layer and constant capacitance models in assuming that the charged surface is comprised of amphoteric hydroxyl groups. Mass balance and mass-action expressions for protonation/deprotonation reactions and surface complexation reactions are also treated in the same fashion. In contrast to the two previously discussed models, however, charge potential relationships are described by a conceptual model that divides the zone influenced by surface charge into three layers (Figure 2.3). In the TLM, the outer, diffuse layer of counterions (d-plane) is separated from the charged surface by two layers of constant capacitance, designated (from the surface outward) the o- and β-planes. Protonation/deprotonation reactions at surface sites are restricted to the inner o-plane, while the specifically adsorbed ions are assigned to the β-plane (Figure 2.3). As a direct result of its construction, the TLM allows surface complexation reactions of ion pairs of the general form

$$SOH + C^+ = SO^-C^+ + H^+ \qquad \text{(for cations)} \qquad (2\text{-}35a)$$

$$SOH + A^- + H^+ = SOH_2^+A^- \qquad \text{(for anions)} \qquad (2\text{-}35b)$$

with equilibrium constants K_{ca} and K_{an} similar in form to Eqn. (2-30) (Kent et al., [illegible]; Serne et al., 1990).

Surface charges in the TLM are designated σ_o and σ_β for the o- and β-layers, respectively. At the boundary between the β-layer and the diffuse layer, the diffuse layer charge (σ_d) is defined such that:

Constant Capacitance

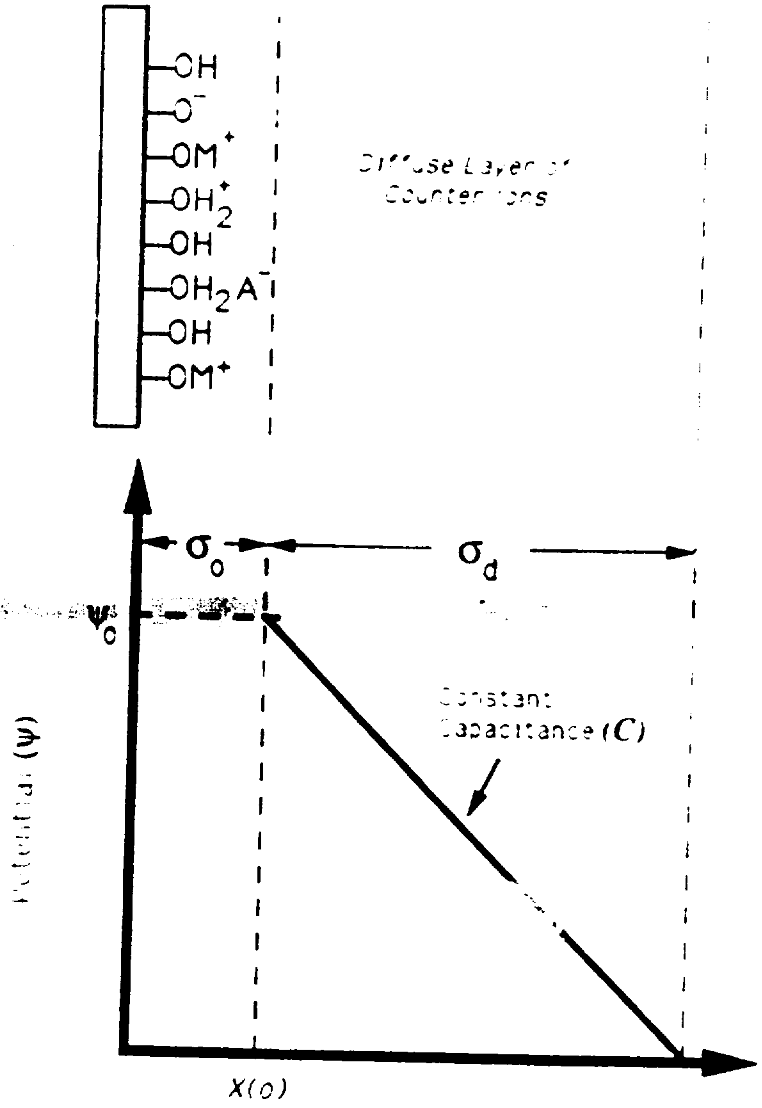

Figure 2-2. Schematic diagram of the constant capacitance surface complexation model. See text for an explanation of symbols.

Triple-Layer

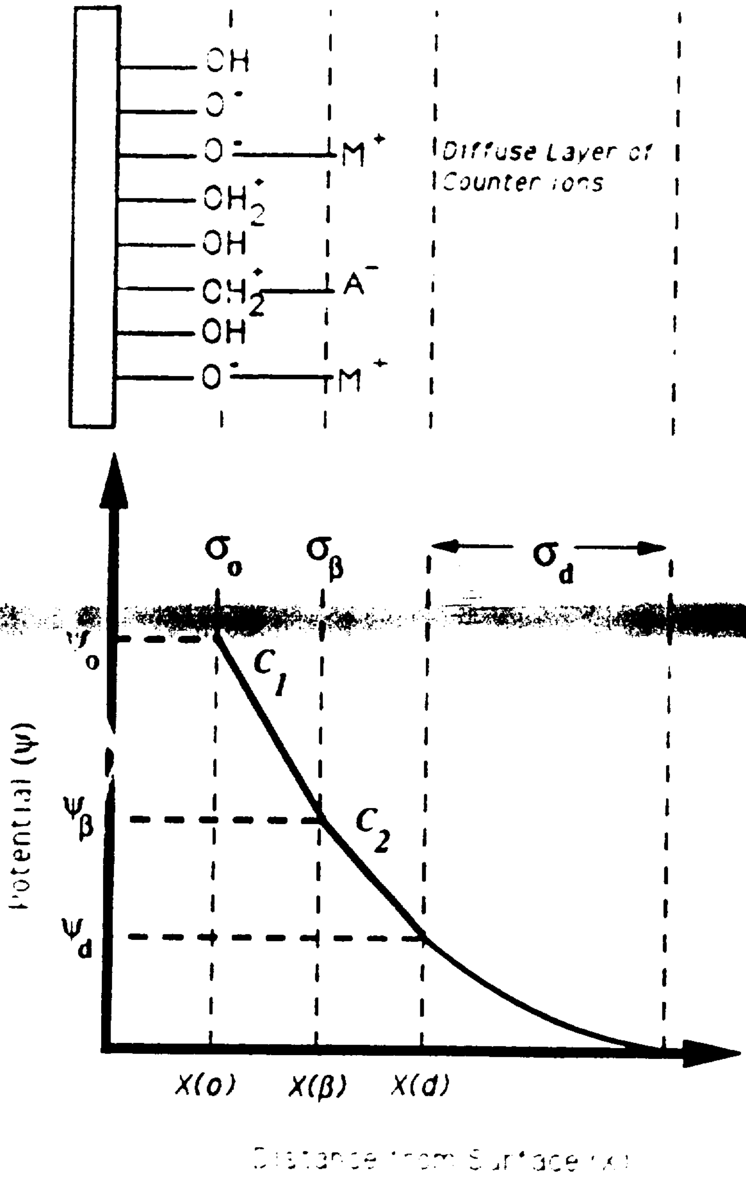

Figure 2-3. Schematic diagram of the triple-layer surface complexation model. See text for an explanation of symbols.

$$\sigma_o+\sigma_\beta+\sigma_d=0. \qquad (2\text{-}36)$$

Electrostatic potentials are described for the different layers in the following fashion:

$$\sigma_d=-(\sqrt{\varepsilon\varepsilon_o IRT})\left[\sinh\frac{(z\psi_d F)}{2RT}\right] \qquad (2\text{-}37a)$$

$$\sigma_o=(\psi_o+\psi_\beta)C_1 \qquad (2\text{-}37b)$$

$$\sigma_o+\sigma_\beta=(\psi_\beta+\psi_d)C_2=-\sigma_d \qquad (2\text{-}37c)$$

where C_1, and C_2 (Farads/m^2) are capacitances associated with the areas between the o- and β-planes and β- and d-planes, respectively (Figure 2-3). In most applications, the outer layer capacitance C_2 is fixed at 0.2 Farads/m^2, and the inner layer capacitance C_1 is used as a fitting factor (Kent et al., 1988). Mass balance, and mass-action are identical to diffuse layer and constant capacitance models, but the three layer model requires modification in the charge balance (Eqn. 2-36).

The triple layer model has been used to model sorption in a number [illegible] 1984; Hsi and Langmuir, 1985; Sanchez et al., 1985; Dzombak and Morel [illegible] applications have largely been restricted to hydrous oxide systems. Kent et al. (1988) describe the approaches that will be necessary to characterize silicates, carbonates, aluminosilicates, and whole rocks in order to apply electrostatic models to these substrates. Benjamin and Leckie (1981) and Hiemstra et al. (1989a) have proposed further elaboration of the model to incorporate several chemically distinct types of surface sorption sites. Each of these sites would interact with the sorbing ions in a distinct fashion. Hiemstra et al. (1989b) have used titration adsorption studies to identify at least three types of surface sites for goethite that are associated with specific crystallographic planes.

Krupka et al. (1988) have offered a simplified one-layer surface complexation model for hydrous iron oxides. For a limited number of ionic species, a number of simplifying assumptions were made. Electrostatic terms were neglected in the model, and activities were assumed unaffected by coulombic surface charge effects. Only one type of binding site (HFO$^-$) was assumed at the surface, and all sorbing cations compete equally for available sites, forming only one type of complex. Constant values were chosen for site density (N_s = 0.2 moles of sites/mole iron). Laboratory data for acid/base titrations were used to determine surface reaction coefficients (K_+, K_-, and $K_{M^{2+}}$ from Eqn. 2-28) for the solutes of interest.

2.3.5. Necessary Parameters for Sorption Model Application

Each of the sorption models presented above requires a certain minimum amount of data for its application in radionuclide migration from a geologic repository. These requirements will depend not only on the conceptual model on which the approach is based, but also on the availability of specific parameters. All of the models require sorption concentration relationships. In some cases, necessary input parameters (such as activity coefficients) will not be available explicitly from experimental data, but simplifying assumptions or theoretical treatment (such as the Davies equation) will allow approximations of these values.

2.3.5.1. Parameters for Empirical Sorption Models

Empirical sorption isotherm models each rely on a number of empirically determined parameters. These range from the simple K_d values for the linear adsorption isotherm (Eqn. 2-1) to the multiple constants necessary for a two-site kinetic adsorption model (Eqn. 2-18). Empirical coefficients appropriate to different models can be obtained for a given data set by recasting the data using the sorption concentration expressions of the new model. This can be done by curve fitting, or by plotting variables against one another on linear or logarithmic scales to determine slope and intercept values. Based on the goodness-of-fit, the more appropriate model is chosen. It is possible, however, that for systems with a large number of empirical coefficients, non-unique values might serve to reproduce the data.

Due to its simplicity, the K_d model has been applied most frequently, and a large amount of data is available for a number of substrates, elements and water compositions. Examples of these types of databases include the Sandia Sorption Data Management System (SSDMS) described by Siegel et al. (1989), the NEA sorption database (Ticknor and Rüegger, 1989), and the summaries of sorption measurements available at Yucca Mountain (Thomas, 1987; Beckman et al., 1988). The Freundlich isotherm requires a value for the constant K_{Fr}, and in addition, some estimate is necessary for the empirical exponent **n**. As discussed above, these can be obtained from plotting ln **S** vs. ln **C**. Rather than simple empirical constants, the more mechanistic Langmuir and Dubinin-Radushkevich isotherms require constants (K_{La} and K_{DR}, respectively) which represent energies of sorption. In addition, these isotherms require some estimate of the adsorption capacity of the substrate. In practice, however, experimental values for the constants neglect aqueous speciation of the solute, resulting in a more empirical application of these isotherms.

2.3.5.2. Parameters for Kinetic Sorption Models

Like equilibrium sorption isotherms, the required number of parameters varies depending on the model considered. Adsorption and desorption rate constants are required for most of the models. The kinetic product model (Eqn. 2-15) requires three separate adjustable parameters, and the kinetic Langmuir model, like the Langmuir equilibrium isotherm, requires a value for maximum adsorption capacity of the surface. The kinetic class

transfer model (Eqn. 2-17) utilizes an empirical parameter **k** and some measure of the **concentration** of the solute at the substrate/liquid interface. The two-site model requires four **constants** (two first-order rate constants, two Freundlich coefficients), two empirical exponents, **and** a value for the fraction of sites occupied (**f**). As is the case with equilibrium sorption **isotherms**, experimental kinetic data are generally only available for a limited number of ions **and** substrates, and the constants are applied as curve fitting parameters. In addition, kinetic rate **constants** are frequently acquired under site-specific conditions, and may not be suitable when **extrapolated** to a new environment (Meier, 1990).

2.3.5.3. *Parameters for Simple Mass-Action Ion Exchange Models*

Simple mass-action ion exchange models require some value for the **selectivity** coefficient ($\mathbf{K_{ex}}$). For a simple, two cation system, the simplifying assumptions used **to develop** Eqn. (2-23) require values for the cation exchange capacity (**CEC**) and the total **concentration** of ions in solution ($\mathbf{m_T}$). Serne et al. (1990) indicate that in developing Eqn. (2-**23), CEC** and $\mathbf{m_T}$ are considered constant, assumptions that may not be appropriate for an open **system**, or for variations in cation speciation. Stumm and Morgan (1981) point out that **CEC is dependent** on charge, which in turn is dependent on pH according to Gouy theory. **Experimental** data indicates that **CEC** remains relatively constant at lower pH values, but **increases** with **pH** above the pH at the zero-point of charge ($\mathbf{pH_{zpc}}$). This suggests that the **assumption** of constant **CEC** may be appropriate for pH < $\mathbf{pH_{zpc}}$.

Allison et al. (1990) point out that total ion exchange will vary as a [illegible] of soil composition, and the amount of exchangeable cations [illegible] available. For a truly rigorous application of the ion exchange model, some knowledge of activity-concentration **relationships** (i.e. activity coefficients) and mineral compositions are necessary. In addition, **Allison** et al. mention that selectivity coefficients are generally only available for common ions **such as** Na^+, K^+, Ca^{2+}, etc., and a few well-characterized substrates.

2.3.5.4. *Parameters for Electrostatic Sorption Models*

Electrostatic sorption models are more robust in application than **empirical models** by adopting a more mechanistic approach to sorption. This flexibility is gained **at the expense** of simplicity by incorporating an increasing number of adjustable parameters to **accommodate** increasing model complexity (Table 2-1). For the diffuse layer model, these **parameters** include intrinsic acidity (hydrolysis) constants for surface protonation/deprotonation **reactions** ($\mathbf{K_+}$ and $\mathbf{K_-}$) and sorption site density ($\mathbf{N_s}$). Surface characteristics such as specific **surface area** (**SA**) and solid concentration ($\mathbf{C_s}$) are also necessary (Eqn. 2-30). Adjustable **parameters** for the constant capacitance model are identical to those identified for the DLM ($\mathbf{K_+}$, $\mathbf{K_-}$, and $\mathbf{N_s}$) plus the capacitance $\mathbf{C_1}$. The increasingly mechanistic approach employed in the **triple layer model** results in a larger number (7) of adjustable parameters than either the diffuse **layer**, or constant capacitance models. These including intrinsic acidity constants for surface **hydroxyl groups** ($\mathbf{K_+}$ and $\mathbf{K_-}$), ion-pair complex association constants ($\mathbf{K_{an}}$ and $\mathbf{K_{cat}}$), surface site

Table 2-1. SURFACE COMPLEXATION REACTION AND MODEL PARAMETERS (FROM SERNE ET AL., 1990)

DLM Reactions	CCM Reactions	TLM Reactions
Protolysis Reactions:		
$SOH_2^+ = H^+ + SOH \quad K_+$	Same as DLM	Same as DLM
$SOH = SO^- + H^+ \quad K_-$	Same as DLM	Same as DLM
Surface Complexation Reaction:		
Coordination Complexes:		
$SOH + Me^+ = SOMe + H^+ \quad K_{Me}$	Same as DLM	Same as DLM
$SOH + L^- = SL + OH^- \quad K_L$	Same as DLM	Same as DLM
Ion-Pair Complexes:		
[illegible]	Not Allowed	$SOH + C^+ = SO^- - C^+ + H^+ \quad K_{C}$ $SOH + A^- + H^+ = SOH_2^+ - A^- \quad K_{An}$
Charge/Potential Relationships:		
$\sigma_o = \sigma_d = -0.1174\sqrt{I}\,\sinh(zF\Psi_d/2RT)$	$\sigma_o = -\sigma_d$	$\sigma_d = -0.1174\sqrt{I}\,\sinh(zF\Psi_d/2RT)$
$\Psi_o = \Psi_d$	$\sigma_o = C_1\Psi_o$	$\sigma_o = (\Psi_o - \Psi_b)C_1$
	$\Psi_o = \Psi_d$	$\sigma_o + \sigma_b = (\Psi_b - \Psi_d)C_2 = -\sigma_d$
Adjustable Model Parameters for Titration Data:		
K^+, K^-, N_s	K^+, K^-, N_s, C_1	$K^+, K^-, K_{Cat}, K_{An}, N_s, C_1, C_2$ (a)

(a) C_2 usually assumed fixed at 0.2 F/m^2.

site density (N_s) and two capacitance values (C_1 and C_2). Smith and Jenne (1988, 1991) present a tabulation of TLM parameters for a variety of elements and oxides.

Because of these parameter requirements, surface complexation models have largely been limited in application to experimental systems (Tripathi, 1984; Hsi and Langmuir, 1985; LaFlamme and Murray, 1987). Kent et al. (1988) list characteristics of a variety of oxide substrates, conditions for application of various data sets, and the primary references for much of the data. Kent at al. (1988) also describe various approaches that may be used to extend surface complexation approaches to more complex systems. Smith and Jenne (1988, 1991) report TLM parameters for Mn- and Fe-oxides for a number of elements, and present a strategy for estimating missing acidity constants data based on effective charge, ion size, and hydrolysis behavior of the ionic species of interest. In addition, Smith and Jenne point out instances where a triple-layer model may not be an appropriate conceptual model for sorption (e.g. Cd^{2+}-sorption onto α-FeOOH).

2.3.6. Discussion - Model Advantages and Disadvantages

Many of the advantages and disadvantages of the various models have been presented above. Empirical models are generally simpler in mathematical construction. Due to the relatively straightforward application of these models, abundant experimental data have been generated to determine the necessary empirical coefficients for a variety of elements and substrates (Siegel et al., 1989; Beckman et al., 1988; Meijer, 1990). However, this simplicity comes at the expense of flexibility. Because the empirical nature of these models tend [illegible] processes together (Siegel et al., 1990), it is difficult, if not impossible, to discriminate between the various factors influencing solute uptake. Empirical models cannot adequately account for the effects of various physical-chemical parameters which may compete and interact in a complex manner to control contaminant retardation. In addition, the importance of various physical-chemical conditions cannot be determined using empirical models without running a large number of carefully controlled experiments (e.g., controlling all other variables, while varying pH through a range of values). Without a mechanistic understanding of sorption processes, extrapolation of an empirical model beyond the experimental conditions used to generate the data fitted by the model is unjustified in many instances. Further complicating the application of empirical models is the frequent lack of good experimental control (Siegel et al., 1989) such as temperature, grain size, pH, sample preparation, etc.

As the theoretical basis for the model increases, the flexibility and applicability of the model generally increases as well. Mass-action and surface complexation models utilize theoretical relationships governing interaction between an electrolyte solution and a charged substrate of a particular structure and composition. By explicitly defining the relationships between a number of system parameters, these models are much more robust, and can be extended beyond experimental conditions to a wide range of environments. As sophistication increases, however, the data requirements and the number of adjustable parameters increases as well. The incorporation of a mechanistic sorption approach such as ion exchange or surface complexation in a reactive solute transport model requires a more complex geochemical equilibrium code in order to keep track of the required solution/solid properties. Coupling of these approaches with transport codes may lead to excessive amounts of computational time and memory requirements (see Section 4). In addition, much of the data necessary for rigorous application of these models are frequently either unavailable or poorly constrained at present (Kent et al., 1988; Siegel et al., 1989; Hayes et al., 1989; Serne et al., 1990; Meijer, 1990). Much of the data are only available for pure or synthetic minerals, and extrapolation to natural solid solutions and composite materials is problematic (Kent et al., 1988; Meijer, 1990).

Several studies (Serne and Muller, 1987; Serne et al., 1990; Meijer, 1990) suggest using a K_d approach to place conservative limits on radionuclide sorption and transport. This is desirable in part due to the computational simplicity of the approach, and in part due to the straightforward approach to data generation. If experiments are designed to approach the conditions in the environment of interest, and the natural conditions remain relatively constant, an empirical model may be suitable (Pietrzak et al., 1981). If the environment is anticipated to vary between known (or estimated) conditions, the extremes can be used to establish bounding limits on sorption. System parameters may also be approximated by incremental changes in experimental conditions to achieve an approximation of changing conditions in the geological environment.

Meijer (1990) suggests that a conservative limit on overall sorption may be obtained by choosing the K_d value representative of the least sorptive unit for the radionuclide [illegible]. If solute transport modeled using this value [in Eqn. [illegible]] meets the performance objectives established in 10 CFR Part 60 and 40 CFR Part 191, then this can be taken to provide some level of assurance as a defensible lower limit on radionuclide migration. This approach can also be used to identify those radionuclides that may be of concern and require a more mechanistic approach. Serne and Muller (1987) support this use of the K_d approach as a bounding method, suggesting that if modeling indicates performance objectives can be met with a low K_d value, and experiments indicate that expected K_d values are much larger, then the need for more sophisticated modeling is reduced.

2.4. OTHER SOLUTE TRANSPORT RETARDATION PROCESSES

Other processes can act to remove radionuclides from solution and otherwise retard the transport of radionuclides in solution. Rubin (1983) defines six broad classes of chemical reactions based on reversible/irreversible and homogeneous/heterogeneous criteria, and surface (adsorption/desorption, ion exchange) versus classical (precipitation/dissolution, redox) reactions. Physical retardation of transport can include mechanical dispersion and diffusion into dead-end pores (Neretnieks and Rasmuson, 1984; van Genuchten et al., 1984; van Genuchten and [illegible], 1987).

2.4.1. Precipitation/Dissolution Processes

Many studies have identified precipitation/dissolution as a mechanism that may operate concurrently with sorption processes to control the uptake of contaminant species in solution (Comans and Middleburg, 1987; Davis et al., 1987; Kirkner and Reeves, 1988; Erikson et al., 1990, and many others). Although interaction between these two processes is complex, involving permeability changes, changes in solution chemistry [pH, Eh, P(CO), etc.], and the creation of new sorbing substrates and colloids, under most conditions they will operate in tandem to retard contaminant migration. Extensive treatment of precipitation dissolution is beyond the scope of this report, however, and it will be discussed briefly as it relates to sorption.

Several studies have observed multiple-step solute uptake (Davis et al., 1987; Fuller and Davis, 1987; Jannasch et al., 1988; Comans et al., 1991; Middleburg and Comans, 1991). Initially rapid uptake is governed by reversible, equilibrium processes, followed by slow, increasingly irreversible uptake that is controlled by reaction kinetics. One interpretation attributes these features to a continuum between surface sorption and precipitation. For example, Davis et al. (1987) and Fuller and Davis (1987) have proposed a three step model to explain Cd-uptake by calcite: Step IA involves reversible equilibrium adsorption of Cd to the hydrated $CaCO_3$ surface; Step IB entails the kinetic diffusion of Cd into the hydrated layer to form a Cd-Ca solid solution; and, Step II involves the recrystallization of the solid solution layer governed by surface precipitation kinetics. This model proceeds at a faster rate at lower pH, and as the precipitate ages, the surface free energy (and sorptive capacity) of the layer will decrease. A similar model has been proposed for Cd-uptake by hydroxyapatite (Middleburg and Comans, 1991).

Empirical approaches not involving short-lived radioisotopes are unable [illegible] discriminate between retardation due to precipitation/dissolution processes and that due to adsorption/desorption mechanisms. In order to evaluate sorption, much effort has been devoted to designing experiments that minimize the effects of precipitation dissolution (Davis et al., 1987; Meijer, 1990). To this end, it is important that the feed solution in sorption experiments does not become oversaturated with respect to stoichiometric compounds of the spiked element over the anticipated range of experimental conditions. In practice, this may be difficult to maintain for multispecies, ligand-bearing systems where the number of potential compounds is quite large. In addition, the use of dilute solutions may not be appropriate for the extrapolation of sorption experimental results, since empirical methods are probably only valid for experimental conditions similar to those expected in the field (see above). Kent et al. (1988) also point out that crushing of substrate materials for experiments may result in fine grained material that is readily dissolved to change solution concentrations, especially at higher temperatures. While this dissolution may not affect the overall concentration of the radioelement in solution, it is likely to produce changes in solution properties such as pH, and ionic strength that can affect sorptive behavior. In addition, dissolution of the adsorbent will compete with the radioelements for sorption sites. Mineral and solution composition will affect the precipitation/dissolution characteristics of the solid phase, and must be accounted for

Geochemical modeling (e.g. Murphy, 1991) provides some predictive capability for evaluating precipitation/dissolution of radioelements. With the onset of precipitation, geochemistry, hydrology, and transport become coupled, resulting in a highly nonlinear system

(Kirkner and Reeves, 1988), and simple empirical techniques cannot be used to interpret the progressively more complex systematics of solute uptake. Several hydrogeochemical codes have been developed that specifically address coupled sorption and precipitation/dissolution (Miller and Benson, 1983; Noorishad et al., 1987; Erikson et al., 1990; see Section 4). Computer simulations using the CTM code (Erikson et al., 1990) indicate that retardation involving both precipitation/dissolution and adsorption/desorption results in the greatest attenuation of uranium transport in mill tailings. The authors also point out that once concentration is reduced below the solubility limit, precipitation cannot remove more solute from solution unless physical/chemical conditions change. Adsorption continues to remove solute as new sorption sites are encountered along the fluid pathline, but even this process is limited to a finite number of adsorption sites.

2.4.2. Anion Exclusion

Anion exclusion has been proposed as a mechanism operating counter to sorption processes to accelerate solute migration (Barnes, 1986; Rundberg et al., 1987; Bond and Phillips, 1990b; Mansell et al., 1991). The basic premise of the process is that anionic species are repelled by the net negative surface charge found in the matrix of most groundwater systems. This repulsion results in a reduction in the effective volume available for transport of the anions. Because of momentum conservation requirements, the smaller volume must be compensated by a faster flow rate in order to maintain total flux at a constant value, and the breakthrough curve of the anionic species will precede that of a nonreactive solute. Hoffmann et al. (1983) [illegible] suggested anion exclusion as an explanation for the early arrival of bomb ^{36}Cl relative to tritium in pump tests surrounding nuclear detonation sites at the Nevada Test Site. Similar early arrival relative to tritium has been observed for Br in the Las Cruces Trench Experiment (W. [illegible]eyer, personal communication). Rundberg et al. (1987) report the results of column experiments on Cl^-, F^-, NO_3^-, SO_4^{2-}, TcO_4^-, and I^- with crushed Yucca Mountain tuff samples containing smectite clays and/or zeolites. Of these anionic species, all but F^- displayed early breakthrough relative to tritiated water. The excluded volume was shown to be comparable to the volume of the intracrystalline channels in negatively-charged zeolites, suggesting that the effective diameter (due to electrostatic repulsion) of the anions exceeded the size of the channels. Bond and Phillips (1990b) investigated the effects of various interactions at the water/rock interface, and determined that the anion content of the infiltrating solution was the only characteristic affecting anion exclusion. In Cl^- transport, for example, if mass balance was preserved, the excluded volume for a given soil was only a function of the Cl^- content of the infiltrating fluid; the observed breakthrough was independent of both the solution composition and the cation valence. Barnes (1986), noting that excluded volume decreases with solute concentration (Bond et al., 1984), has simulated exclusion using a negative sorption isotherm. This indicates that the solute pulse arrives earlier at higher solution concentrations.

2.4.3. Diffusion/Dispersion

Mechanical dispersion and diffusion into dead end pores and fractures have been proposed as additional retardation mechanisms (Bear and Verruijt, 1987). Dispersion due to mechanical forces is enhanced by the presence of heterogeneities in the medium resulting in a complex fluid velocity field. Molecular diffusion along chemical gradients can also serve to attenuate solute migration. Unlike mechanical dispersion, molecular diffusion can continue to operate in the absence of fluid movement, provided a chemical gradient is maintained, and it will become relatively more important as velocity decreases (Bear and Verruijt, 1987). These two mechanisms are generally combined in the hydrodynamic dispersion coefficient (**D**) in the transport equation (See below, Eqn. 4-3). In fracture flow, diffusion along chemical gradients between the fracture and the rock matrix has been proposed as a mechanical process for the retardation of solute transport (Neretnieks, 1980; Neretnieks and Rasmuson, 1984). This has the added effect of providing a larger surface area for sorption than would be possible if solute migration was confined to fracture flow alone (Freeze and Cherry, 1979). In addition, diffusion between permeable and impermeable layers in a stratified medium can provide for the temporary removal of solute from solution in the permeable layer and sequestering in the less permeable unit (Gillham et al., 1984).

2.4.4. Radioactive Decay

The amount of a given radioelement in solution will change as the element [illegible] This process is well-understood, and represented by the half-lives of each radionuclide and its subsequent daughter products. In many cases, the daughter elements of a complex radionuclide decay chain are also radioactive, and must be considered in performance assessment. Because of the variability in the radioactive decay rates of the elements along the chain, radioelements increase and decrease as a relative proportion of the total inventory at different rates in a highly nonlinear fashion. With time, however, all of the radionuclides in a decay chain tend towards a "secular" equilibrium in which each has the same activity. Kerrisk (1985) and Oversby (1987) have addressed differential decay to determine the important radionuclides in the waste as a function of time after emplacement, relative to NRC and EPA standards. This is an important consideration in modeling radionuclide transport for a HLW repository, because the initial makeup of radionuclides released from the engineered barriers (i.e. the source term) will vary, depending on the time at which containment is lost. The processes of radioactive decay may also serve to decrease radionuclide retardation, either through radiolysis of the groundwater or alpha recoil that promotes desorption of the radionuclide into the liquid phase (Krishnaswami et al., 1982). If precipitation is included in total retardation, then the attenuation of radionuclide migration becomes half-life dependent. Neglecting precipitation/dissolution, Krishnaswami et al. (1982) introduce a model which suggests that for a given radioelement, the isotopes with a shorter half-life tend to display smaller values for K_d and R_f. McKinley and Alexander (1990) point out that this is inconsistent with the conventional definition of K_d, however, and question the validity of many of the assumptions by Krishnaswami et al. (1982) in developing the model.

3. EXPERIMENTAL AND FIELD STUDIES

3.1. EXPERIMENTAL SORPTION STUDIES

Experimental sorption studies have generally been of two types: batch sorption studies and dynamic column experiments. Batch sorption studies, which place a known amount of a solid in contact with a constant solution volume, have generally seen more application due to their simplicity. Column experiments are more difficult to perform, but they have been modified to investigate saturated/unsaturated flow, one pass flow, recycled flow, crushed rock, rock wafers, and rock columns. Both types of experiments will be described in the next section. Sample preparation and laboratory procedures are carefully described in a number of studies for both batch sorption (Thomas, 1987; Higgo et al., 1990; Triay et al., 1991; Lu et al., 1991; and many others) and column-type experiments (Bond, 1986; Rundberg et al., 1987; Bond and Wierenga, 1990, and many others). The discussion presented below is intended as an outline of the methods in general use at the present time. The results of specific studies are discussed in Section 5 and in Appendix A.

3.1.1. Batch Sorption Experiments

Batch sorption experiments generally involve adding a known mass of solid to a fluid which is spiked with a known concentration of the element of interest. The solution is commonly agitated during the experiment, and the duration of the experiment is usually chosen [illegible] equilibrium is reached. Kinetic experiments are also used to investigate sorption reaction rates. The adsorbent is separated from the solution phase, and the concentrations of the element associated with the solid and liquid phases are measured. In this way, the uptake of the solute by the solid is monitored.

Solids are prepared in a variety of ways for batch sorption experiments. Disaggregated samples are commonly used to allow suspension of the solid in solution. If the sample is not naturally disaggregated (i.e. rock vs. soils and sediments), the sample is crushed and sieved. Size fractions are generally chosen between 75μm-500μm in order to minimize particle size effects on sorption (see Section 2.2.1). Grinding has been cautioned against due to the possibility of creating nonrepresentative reactive grain surfaces (Kent et al., 1988). Analysis of the Yucca Mountain sorption data base by Beckman et al. (1988) established a cutoff minimum particle size of 106μm to minimize these effects, while Meijer (1990) indicates that particle size is poorly correlated to sorption except for the finest fraction (< 75μm). For experiments using pure minerals, physical mineral separation and ultrasonic cleaning are used to produce a pure mineral separate. Crushed rock experiments are also useful to measure the properties of bulk rock samples. The composition of the solid in batch experiments is characterized by a number of analytical techniques including scanning electron microscope, electron microprobe and X-ray diffraction. Samples are then carefully rinsed in ultrapure deionized water and dried to remove any contamination introduced during sample preparation. For those experiments with redox-sensitive elements, samples are kept in a controlled atmosphere (Hakenen and Lindberg, 1991). Thin wafers on the order of 1-2 mm thick can be

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Waters used in batch sorption experiments can include natural waters or synthetic groundwaters prepared to approximate conditions in the field. Samples are commonly equilibrated with the unspiked water prior to the sorption experiment (Thomas, 1987; Triay et al., 1991). In order to minimize colloidal effects, solution experiment waters are commonly ultrafiltered to screen particles < 0.03μm in diameter prior to spiking. Complexation effects can be investigated by adding the appropriate ligand (e.g., CO_3, SO_4, EDTA, etc.) to the solution in varying concentrations. Low concentrations of the spike ([illegible] M) are used to remain below saturation levels of stoichiometric compounds of the spiked element in order to avoid the complicating factors of precipitation (Meijer, 1990). At the same time, however, concentrations must not be so undersaturated as to promote dissolution of the solid [illegible] studies indicate, any correlation between sorption coefficients, adsorbent concentration, and solute concentration must be recorded. Solution pH and Eh must be controlled for many redox-sensitive elements in order to characterize oxidation states and speciation. For species where carbonate complexation is important (U, Pu, Np, etc.), experiments are usually performed in an inert atmosphere (usually N_2) to minimize the effect of atmospheric CO_2 on solution alkalinity, or in an atmosphere where $P(CO_2)$ can be externally controlled.

Temperature is held constant in a given run for batch sorption experiments. Thermal effects on sorption can be studied, however, by examining sorption systems at a variety of temperatures (Ames et al., 1982, 1983a,b,c). Water rock ratios must also be recorded, in order to evaluate potential sorption effects related to the proportion of solid to liquid have been observed (Honeyman, 1984; Balistrieri and Murray, 1986). Experiment containers are generally made of inert synthetic materials such as polyethylene or teflon in order to minimize scavenging of the spiked element by the vessel walls. In some cases, however, vessel [illegible] interaction can be significant. In spite of using teflon vessels, Triay et al. (1991) observed up to 84 percent loss of Am to container walls during sorption experiments lasting 70 days. Similar losses were recorded for the containers used to store the feed solution prior to the solution experiments. Losses of this type must be accounted for in mass balance considerations of the sorption data. Centrifugation is generally used to separate the fluid from the solid phase(s) for chemical analysis, although many experiments are designed to draw sample aliquots from the solution as the experiment progresses with time. Ultrafiltration can be used to remove any remaining colloidal material from the supernatant (Patera et al., 1990). Frequently, the solid is resuspended in a deionized solution to investigate the effects of desorption. Nakayama and Sakamoto (1991) describe a method used to evaluate Np adsorption-desorption which involves adjustments in solution pH to new values after sorption equilibrium has been attained, allowing the system to reequilibrate, and then readjusting the pH to the initial values. These experiments combined with time-series results (Meijer, 1990) can be used to gain insight into the degree of equilibrium attained in the batch experiments and the reversibility of the sorption reactions.

3.1.2. Column Experiments

For column experiments, fluids and crushed solids are prepared in a manner similar to that for batch experiments. In contrast to the batch sorption experiments, however, column experiments are able to simulate dynamic reactive solute transport at the laboratory scale (Meijer, 1990; Alemi et al., 1991). Crushed material (or soil) is packed into the column (commonly acrylic) which is usually on the scale of tens of millimeters to several meters in length. Although these types of experiments are generally conducted in a vertical column, the column can be oriented at any angle. Bond and Wierenga (1990) indicate that column orientation does not affect fitting an analytical curve to breakthrough data for [illegible]. In saturated experiments, deaired water is applied at a constant head at the top of the column until all of the pore space has been filled (Bond, 1986). Flow rates are controlled until steady state has been achieved. The hydrodynamic dispersion in such column experiments should also be carefully determined as a function of water velocity in order to separate out the effects of mechanical processes on solute migration.

After flow has reached a steady state, the [illegible] the top. Generally, the input is in the form of a pulse, [illegible] applied. A nonreactive solute such as tritium is first eluted through the column to determine the free column volume and to establish a baseline against which to measure the retardation of the breakthrough curve for a reactive solute (Rundberg et al., 1987). Early arrival of the tritiated water can also be used to detect zones of preferential flow along the walls of the column apparatus. Water can either be gathered and recirculated through the column to approximate a closed system, or a fresh feed solution can be continuously introduced at the top of the column to simulate an open, one-pass system. Eluted water is measured for the concentration of the element of interest, and mass balance constraints allow determination of the concentration remaining associated with the solid phase. The column may be disassembled to evaluate the substrate and the pore water concentrations. Phillips and Bond (1989) have described a nondestructive method involving centrifugation of the column using a high-density, water-immiscible organic liquid to displace pore fluids in the column materials.

The effects of variable saturation can also be investigated using unsaturated column experiments similar to those described by Gaudet et al. (1977) and Bond and Wierenga (1990). In these experiments, steady unsaturated flow is obtained by applying a controlled suction at the base of the column for a constant flux of solution. Resistance probes can be used to determine *in situ* solute concentrations of ionic species (Gaudet et al., 1977) and [illegible] the location of the solution front. These probes must, however, be calibrated individually as a function of water content and ion concentration. Gamma ray densitometers are used to determine the saturation profiles in the column as a function of depth. Several studies (Bond, 1986; Bond and Wierenga, 1990) describe unsteady, unsaturated flow experiments using variable flow rates.

In addition to crushed rock, soils, and mineral separates, column experiments can also be performed, in the optimal case, using a solid rock column. These experiments are difficult to conduct, and can only be used currently under high pressure gradients for either highly permeable rock or elements with only limited sorption in order to achieve breakthrough in laboratory time scales. Conca (1990) has demonstrated the capabilities of his Unsaturated Flow Apparatus (UFA) in determining transport parameters in unsaturated materials. This apparatus achieves a desired water content by using an ultracentrifuge with an ultralow constant-rate flow pump to apply solution.

3.1.3. Experimental Methods - Comparison

Both batch sorption and column experiments have characteristics which provide valuable insight into sorption processes. Batch sorption experiments have the advantage of being relatively simple, resulting in comparatively straightforward interpretation of the data. The simplicity of the experiment readily allows numerous runs so that sensitivity analyses of the effects of various parameters such as temperature, water/rock ratio, solution composition, pH, [illegible] and particle size may be performed. Time-series experiments can be performed to determine the time needed to reach equilibrium sorption. Batch sorption has the disadvantage of being performed in a static system. Field studies indicate that application of batch results frequently underestimates field-scale retardation by as much as several orders of magnitude (Gillham et al., 1984; Waldrop et al., 1985; Naymik, 1987; Jannasch et al., 1988). Kinetic and perhaps physical heterogeneities may contribute to this discrepancy; these are processes which are largely beyond the ability of the batch technique to evaluate. Water/rock ratios in batch equilibrium experiments are typically much higher than those encountered in the subsurface (Bond and Phillips, 1990c), leading to concerns about the applicability of the results to rock-dominated natural systems. Additionally, techniques used in batch experiments, such as agitation, may lead to the breakup and dissolution of the substrate, or the formation of colloidal materials which complicates data interpretation. Through careful consideration of experimental conditions, however, it is possible to isolate sorption processes for evaluation using batch sorption techniques.

In contrast to batch experiments, column-type experiments represent a flow transport system, and more accurately reflect the situation encountered in the subsurface. By adjusting flow rates, it is possible to evaluate the degree of sorption equilibrium obtained in a dynamic system, and to evaluate the possible effects of geochemical processes (e.g., anion exclusion and slow sorption kinetics) on solute breakthrough. Column experiments also offer a dynamic model against which to validate hydrogeochemical transport codes (see section 4). In contrast to relatively simple batch techniques, however, the complexity of column experiments makes application to sensitivity analyses more difficult. Because no two columns will be identical with respect to interconnected porosity and other physical characteristics, replication of results tends to be poor, and isolation of a single process for evaluation is difficult, if not impossible. Also, the complex interplay between factors contributing to physical retardation (porosity, dispersion, and diffusion) and chemical retardation processes in a flow, makes the interpretation of the data more difficult for column experiments (Meier, 1990)

3.2. FIELD EXPERIMENTS

Carefully controlled field experiments can provide a crucial step between laboratory scale and repository-scale conditions (Waldrop et al., 1985). A different kind of field approach involves the use of well-characterized natural analogues to reconstruct the hydrogeologic system and study the operation of transport mechanisms on geologic time scales (Pearcy and Murphy, 1991a). Field experiments also provide a valuable method for the validation of reactive transport modeling codes.

3.2.1. *In Situ* Field Migration Experiments

Waldrop et al. (1985) and Ababou (1991) provide an extensive listing of *in situ* migration experiments conducted to determine lateral and longitudinal dispersivity in the saturated and unsaturated zones at scales varying from one or two meters to many kilometers. The Borden Landfill site in Ontario (Sudicky et al., 1983) and the Bonnaud site in France were [illegible] Waldrop et al. (1985) as two of the more reliable experiments for transport in the saturated zone. The Commission of the European Communities (CEC) Mirage project has also initiated several *in situ* experiments for radionuclide migration under saturated conditions in the Boom Clay at the Mol site in Belgium, and the DRIGG site in Cumbria, Great Britain (Avogadro, 1990; Williams et al., 1991). The INTRAVAL Las Cruces Trench site (Wierenga et al., 1986), designed to study flow and transport in the unsaturated zone, is currently planning tests with chromium as a reactive tracer, but the data are not currently available (G. Wittmeyer, personal communication). Field studies of reactive solute transport have also been conducted at the Nevada Test Site in rocks similar to those at Yucca Mountain (Cole and Ramspott, 1982). The following is a brief discussion of general characteristics of *in situ* migration experiments. The reader is referred to Waldrop et al. (1985), Avogadro (1990), and Ababou (1991) and references therein for discussions of specific sites.

Figure 3-1 shows the general structure specific to the DRIGG site experiment in cross-section, but it is also suitable to show some of the basic features of other controlled field experiments (e.g., Fuentes et al., 1989). It is critical to have some understanding of the geologic medium under consideration (porosity, permeability, hydraulic conductivity, etc.). A dense sampling through drill holes or trenching will allow a relatively fine discretization of the physical properties of the medium. The fluid chemistry should be well characterized, and injection and withdrawal of fluids from the aquifer should be monitored to determine the extent to which a steady-state has been achieved. Packing off the injection and withdrawal wells can be used to a certain extent to isolate specific horizons (i.e. a confined aquifer) of interest.

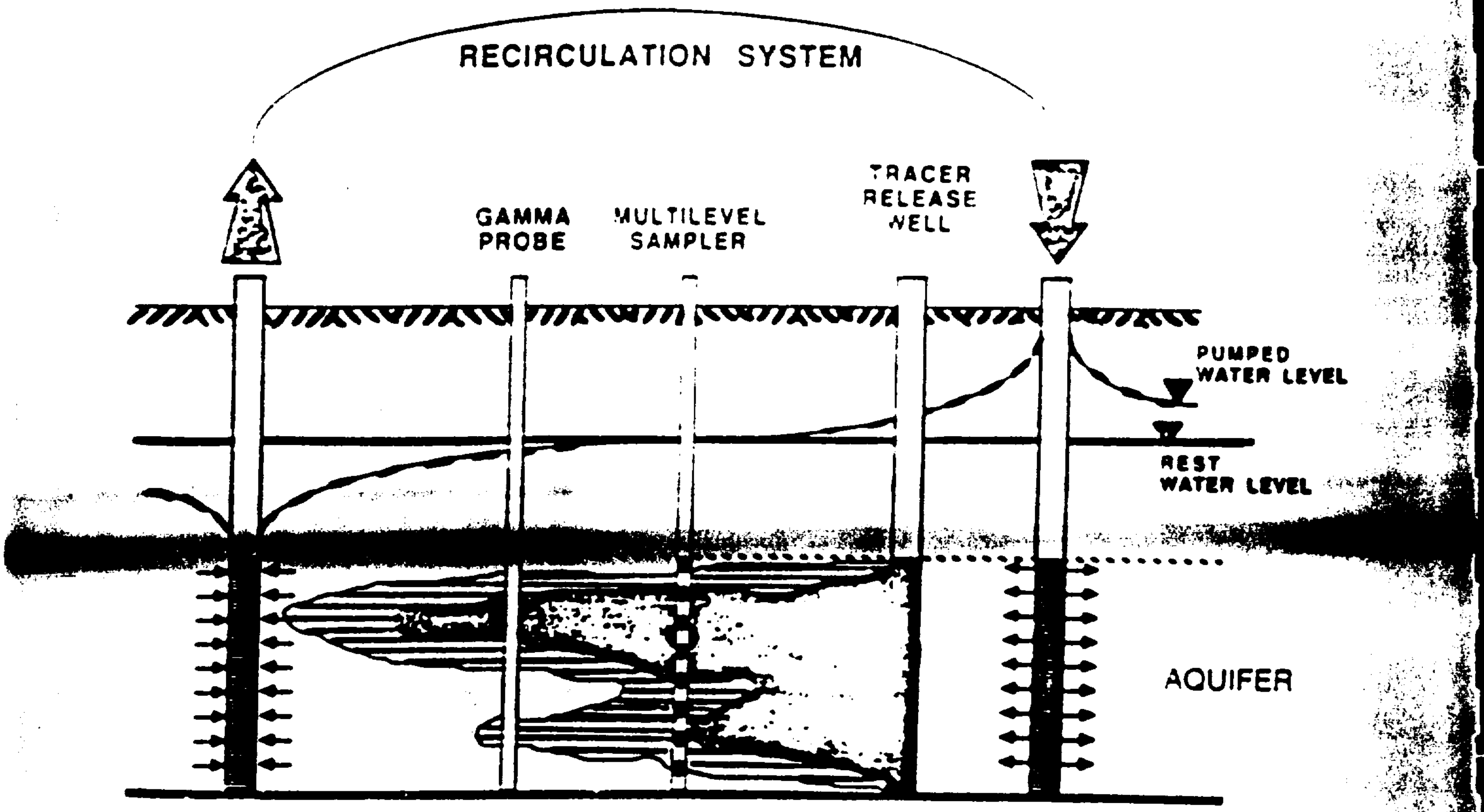

Figure 3-1. A schematic diagram of the tracer tests conducted at the DRIGG site in Cumbria, Great Britain (from Avogadro, 1990).

although the influence of a pumped well will be felt in layers outside of the packed-off interval. If transient phenomena are being studied, then a number of monitoring wells using multilevel sampling are necessary to monitor the progress of the solute through the medium. Gamma probes can be used to measure the moisture content of the medium, and suction lysimeters and tensiometers can measure capillary pressures.

Once steady flow has been achieved, then a spiked feed solution is introduced to the aquifer and its progress through the medium is monitored. Tritium, chlorine, iodine, and bromine are commonly used as nonreactive tracers to establish baseline solute transport. Waldrop et al. (1985) recommend using tracers with different molecular diffusion coefficients to evaluate the effect of molecular diffusion on solute transport. Simple feed solutions are generally preferred in order to minimize the uncertainty that may result from complexation, speciation, and competition between different elements. Sampling and analysis should be performed carefully in order to measure fluid properties (Eh, pH, $P(CO_2)$, etc.) under conditions as close to those in the field as possible. Slow withdrawal rates on the order of 1 liter/min or less using a peristaltic pump are generally recommended (Gschwend, 1990) in order to minimize the introduction of well material into the water samples. Fluid characteristics (e.g., pH, Eh, TDS) will reach equilibrium values with pumping, but at different rates. Open-air storage of samples prior to analysis should be minimized (Gschwend, 1990). Ultrafiltration of the fluids (Avogadro, 1990) can be used to remove colloids for analysis. Colloids, if present, should be characterized and evaluated.

Similar in design to laboratory column experiments, but at a much larger scale (commonly up to 10 m), caisson experiments offer a bridge between laboratory and field systems ([illegible] Polzer, 1987). The caisson is generally constructed from vertical steel cylinders on the order of 1-2 m in diameter and 5-10 m in height (Fuentes and Polzer, 1987). A number of caissons are commonly arranged around a central, empty caisson that is used to provide access to the instrumentation of the different experiments. The cylinder is packed with the material of interest, usually crushed rock, above a base of sand and gravel. A drain is placed at the bottom of the system. Drip infiltration is usually applied at the upper surface of the caisson to establish the fluid flow regime of the system. This is followed by the pulsed introduction of a spiked feed solution. Instrumentation (e.g., tensiometers, suction lysimeters, neutron moisture probes), placed at a number of levels in the caisson, is used to sample the solution and monitors the passage of water and solute through the system.

Trench experiments of the type conducted by INTRAVAL (Wierenga et al., 1986) at Las Cruces, NM, are slightly different in construction (Figure 3-2) from the aquifer experiments described above. In these experiments, a trench is dug into the soil. The soil is extensively sampled and characterized at the trench face and through cores taken during the drilling of monitoring wells. During the experiment, water is applied to the surface through drip irrigation networks of varying geometry until a quasi-steady state is achieved. A tracer is applied to the surface, and through the instrumentation installed in the trench face and in a series of wells, water movement and solute transport are monitored.

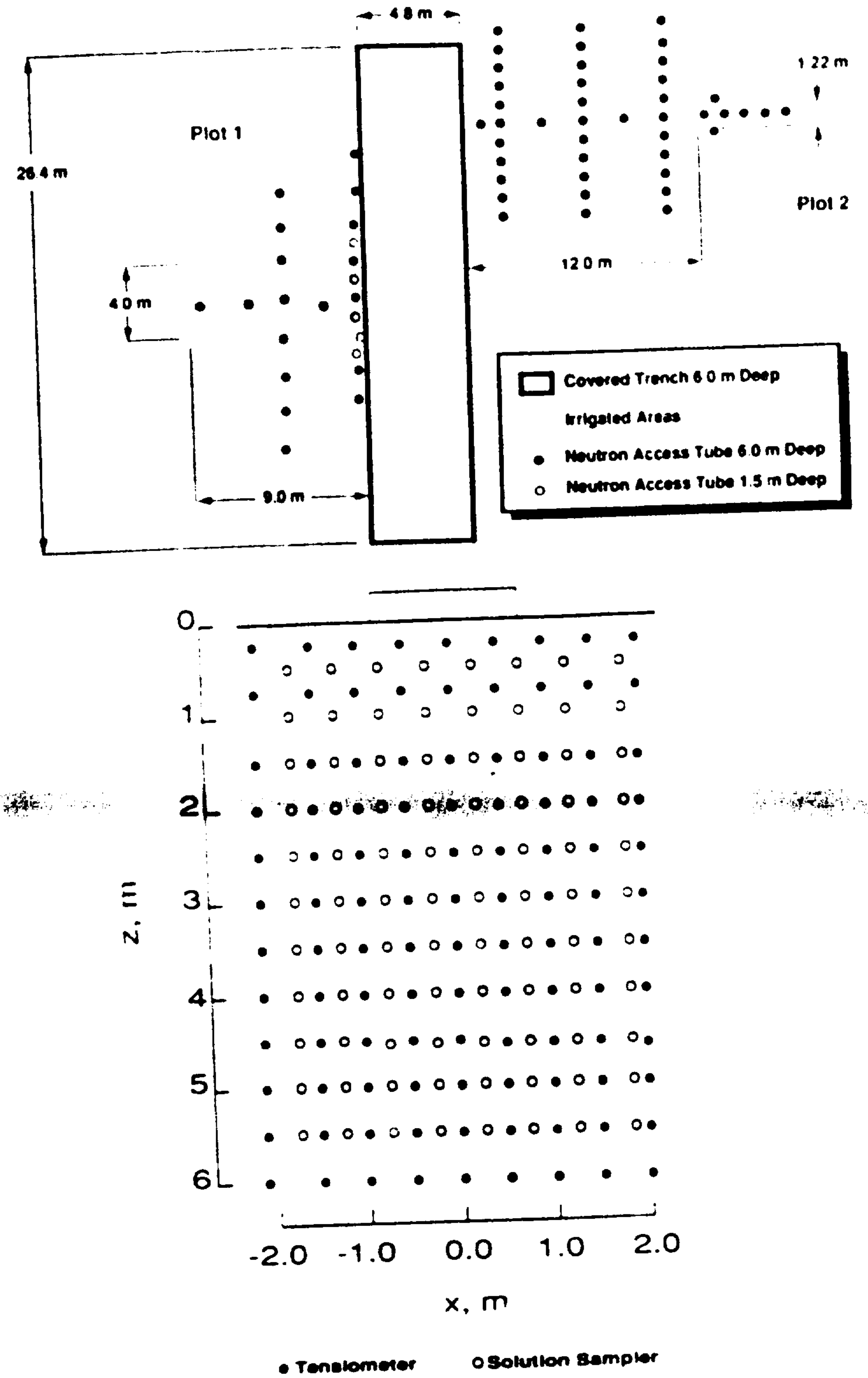

Figure 3-2. (a) Plan view of the INTRAVAL Las Cruces Trench Site. (b) Cross section of the trench face showing the soil sample locations and material zones used in numerical simulations (from Hills and Wierenga, 1991).

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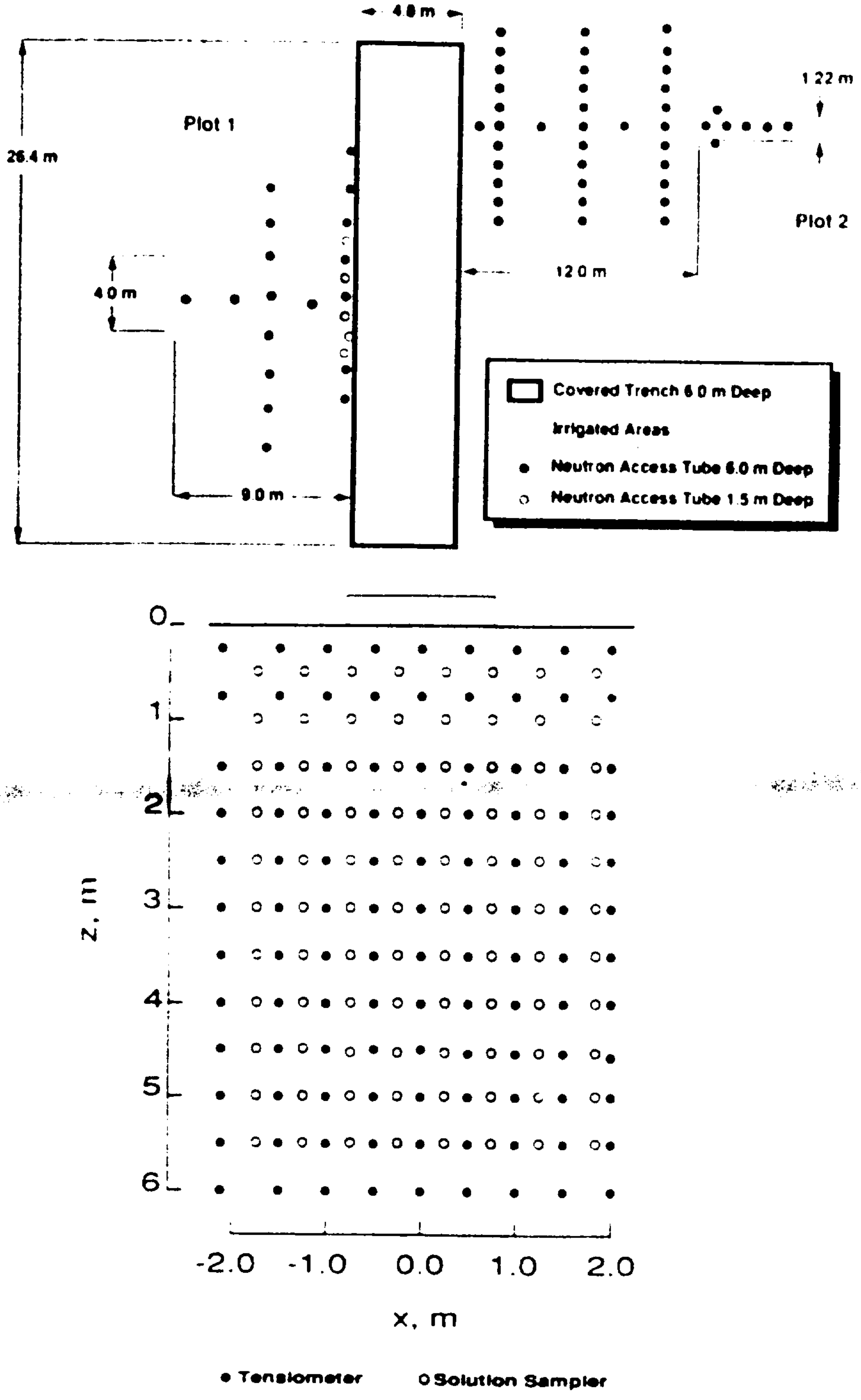

Figure 3-2. (a) Plan view of the INTRAVAL Las Cruces Trench Site, (b) Cross section of the trench face showing the soil sample locations and material zones used in numerical simulations (from Hills and Wierenga, 1991).

3.2.2. Analog Migration Studies

Natural analog studies provide a method for evaluating solute migration at geologic scales in time and space. The examination of carefully chosen and well characterized analog sites can provide information not readily obtained from relatively short term, controlled field studies. Unfortunately, the spatial and temporal scales and the necessarily complex chemistries involved are a drawback inherent to analog studies. Overprinting and scale-induced heterogeneity both serve to limit the degree of certainty with which the system can be defined after-the-fact. Boundary and initial conditions, as well as the source terms and physical chemical properties of the system all contribute to the general uncertainty of reconstructing the problem. In addition, finding a natural analog which unambiguously represents the area and processes of interest may be difficult, if not impossible (Pearcy and Murphy, 1991a). Despite these limitations, these studies may be the only way to evaluate contaminant migration in natural systems over geologic time scales. Uranium-series disequilibria can be used to obtain some quantitative information on the roles of various retardation processes in radionuclide migration (Finnegan and Bryant, 1987; Ku et al., 1991).

Analogs can vary in size from centimeter scale processes such as the migration of depleted uranium from expended artillery shells (Ebinger et al., 1990) to the kilometer scale of ore deposits and mining districts such as the Alligator Rivers project in Australia (Short et al., 1988; Payne et al., 1990a,b) or the Pena Blanca site in Mexico (Pearcy and Murphy, 1991a,b,c). The Koongarra system in the Alligator Rivers region has received particular [illegible]rd to the mobilization, transport, and adsorption of uranium under saturated conditions during the weathering of the ore body. Carbonate and phosphate complexation is believed to have played an important role in uranium migration, and iron oxyhydroxides are believed to have been the principal sorbing phases controlling the distribution of uranium in the dispersion fan (Payne et al., 1990b; Payne and Waite, 1991).

As discussed above, unlike a controlled field experiment, a natural analog provides, in essence, a "snapshot" of the net effects of transport processes. Interpreting the processes involved requires careful research in order to reconstruct the system and the roles played by the various transport processes responsible for the current distribution of a given solute. The reader is referred to Pearcy and Murphy (1991a) and references therein for a detailed discussion of geochemical analogs pertinent to radionuclide transport.

4. FLOW, TRANSPORT, AND HYDROGEOCHEMICAL MODELS

4.1. SOLUTE TRANSPORT

Due to the relatively straightforward nature of the processes involved, much work has been done to model the transport of nonreactive solutes. Of particular concern to the performance assessment of a HLW repository, however, is how the solution interacts with the geologic medium to retard radionuclide migration. In order to model the attenuation of contaminant transport by water/rock interaction processes, it is necessary to couple the geochemical processes governing retardation with the physical processes of fluid and mass transport. This has been done in a number of ways using a variety of simplifying assumptions and governing equations. The advent of computers has made the numerical simulation of the coupling of these two processes feasible, while the advances made in computer speed and memory, and in the efficiency of numerical schemes has allowed for the handling of increasingly complex and realistic problems. Several excellent summaries of modeling schemes, numerical methods, coupling mechanisms, geochemical equilibria, computer requirements, etc., are currently available (Kincaid et al., 1984a,b; Waldrop et al., 1985; N[illegible], 1986; van Genuchten and Jury, 1987; Morrey et al., 1986; Nav[illegible], 1987; Barr[illegible]; Se[illegible]; Mangold and Tsang, 1991).

4.1.1. Deterministic Transport-Homogeneous Media

In a classical, deterministic approach, mass transport is governed by the convection-dispersion (or advection-dispersion) equation (Freeze and Cherry, 1979). The transient, one-dimensional transport of a non reactive solute [illegible] general form of the equation is

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial x}\left[(\theta D)\frac{\partial C}{\partial x} - qC\right] \qquad (4\text{-}1)$$

where **C** is the solute concentration (g/ml) in the liquid, θ (ml/ml) is the porosity of the medium (equal to water content in a saturated medium), **D** is the hydrodynamic dispersion coefficient (m^2/s), and **q** is the water flux (m/s). For reactive solute transport, Eqn. (4-1) is modified to account for water/rock interaction such that

$$\frac{\partial}{\partial t}(\theta C + \rho_b S) = \frac{\partial}{\partial x}\left[\theta D\frac{\partial C}{\partial x} - qC\right] \qquad (4\text{-}2)$$

where **S** is the solute concentration (g/g) adsorbed on the solid phase and ρ_b (g/ml) is the bulk density of the medium (Selim et al., 1990). By assuming that the medium is homogeneous with respect to material properties, and that fluid flow is at a uniform, steady state, θ, ρ_b, **q** and **D** can be treated as constants. By further assuming local equilibrium is attained with respect to adsorption, Eqn. (4-2) is greatly simplified to

$$R_f \frac{\partial C}{\partial t} = \left(D \frac{\partial^2 C}{\partial x^2} - \frac{q}{\theta} \frac{\partial C}{\partial x} \right) \qquad (4\text{-}3)$$

The retardation factor (R_f) is a measure of the attenuation of solute transport relative to water velocity (or to the transport of a non-reactive solute) that is defined by the relationship:

$$R_f = \left(1 + \frac{\rho_b}{\theta} \frac{\partial S}{\partial C} \right). \qquad (4\text{-}4)$$

If sorption processes are assumed to be the only attenuation mechanisms, $\partial S/\partial C$ is defined based on the sorption model used (see section 2), and the specific form taken by R_f will vary. For the simplest case of a linear sorption isotherm, Eqn. (4-4) is the appropriate form for R_f.

As discussed in section 2.3.1, Valocchi (1984) has proposed an "effective K_d" approach by using the approximation $\Delta S/\Delta C \approx \Delta S/\Delta C = K_d$ to represent changes across the migrating solute front. Selim et al. (1990) use a similar approach to develop a transport equation for the retardation of monovalent cations with aqueous concentrations of C_1 and C_2, and sorbed concentrations of S_1 and S_2. Retardation is governed by binary ion exchange, which in turn can be expressed in terms of a selectivity coefficient $K_{12} = K_{ex}$ such that:

$$K_{12} = K_{ex} = \left[\frac{(S_1)(C_2)}{(S_2)(C_1)} \right]. \qquad (4\text{-}5)$$

By assuming that total solution concentration $C_T = C_1 + C_2$ and adsorption capacity $S_T = S_1 + S_2$ are constant, a nonlinear ion exchange sorption isotherm for ion 1 is derived

$$S_1 = \left(\frac{K_{12} C_1}{[1 + (K_{12} - 1) C_1]} \right) \qquad (4\text{-}6)$$

Substituting this relationship for the transport of ion 1 in Eqn. (4-3) results in a retardation factor expressed by the equation:

$$R_f = 1 + \left(\frac{\rho_b S_T K_{12}}{\theta C_T [1 + (K_{12} - 1) C_1]^2} \right). \qquad (4\text{-}7)$$

A similar approach can be taken to derive transport equations for ion 2

Because the bulk density term in the advection/dispersion equation depends in part on the density of the fluid, the solute concentration and temperature of the fluid can affect transport (Herbert et al., 1988). If the solution is a dilute electrolyte solution, or the concentration does not change markedly over the time and area of interest, the effect can be neglected, and the assumptions made to derive Eqn. (4-3) remain valid If sharp concentration fronts, high salinities and variable temperatures are anticipated, however, realistic models of solute transport needs to account for systematic density gradients as a function of time and space.

Treatments similar to those developed in Eqns. (4-3) through (4-7) are appropriate if a single sorption process is assumed dominant in governing solute retardation. In practice, however, several mechanisms can contribute to the apparent retardation of solute transport including precipitation/dissolution, diffusion, fluid mixing, etc. Under these conditions retardation will behave in a much more complex manner than described using the simple R approach in Eqns. (4-3) or (4-7). Numerical solutions coupling geochemical equilibrium relations with transport equations will then be required to account for the [illegible] controlling contaminant transport (see below).

In solving for advective-dispersive solute transport, two [illegible] are available: Eulerian and Lagrangian. The more common Eulerian viewpoint is that of solute transport past fixed points in space. This requires solution of the coupled advective and dispersive parts of the transport equation [Eqn. (4-3)] using numerical methods such as finite-difference or finite-element schemes. This approach is computationally easier than the Lagrangian method due to the rigidly defined computational matrix, but as a result of the wave-like nature of the advection term, it is subject to a variety of numerical [illegible] and dispersion), particularly at discontinuities in the system. In contrast, the Lagrangian viewpoint monitors the progress of "particles" (i.e., mass of solute) moving along with the transport medium (fluid, gas). By decoupling the advective and dispersive parts of the transport equation, the Lagrangian approach avoids the numerical instabilities of the Eulerian approach. For numerical simulation using a Lagrangian approach, particle distribution due to advective transport is calculated based on the flow velocities determined for the system. At each time step, the dispersive part of the transport equation is then solved for each particle to modify the local particle distribution that resulted from advective transport. [illegible] is perhaps more elegant than Eulerian-based methods, but it is inherently more complex as particles disperse and the number of particles to be tracked increases. Yeh and Gwo ([illegible]) have proposed a hybrid Lagrangian-Eulerian approach which uses a Lagrangian viewpoint when addressing advection terms, and an Eulerian grid while considering other terms of the transport equations.

4.1.2. Transport in Heterogeneous Media

For application to two- and three-dimensional transport, the general form of the advection-dispersion equation (Eqn. 4-2) modifies to

$$\frac{\partial}{\partial t}(\theta C + \rho_b S) = \nabla\cdot(\theta D\nabla C - qC) \qquad (4\text{-}8)$$

The treatment presented in Eqns. (4-3 through 4-7) can be extended to two- and three-dimensional transport, provided that the medium is homogeneous, and that mass transport is by piston displacement (i.e., no preferential zones of flow) (Clothier [illegible]). The general form of the advection-dispersion equation. In practice, however, most geological media are heterogeneous, and transport through permeable layers, fractures and zones of preferential flow all serve to complicate the application of a simplified model. Meyer (1990) proposes addressing heterogeneities by using a one-, two-, or three-dimensional matrix of predetermined constant K_d values for radionuclides of interest at points throughout the system. This approach is limited by the discretization capabilities of the model and the available data. In addition, while this strategy will address spatial variability, it is only valid for a limited range in physicochemical conditions throughout the environment. Major changes in the system will require that the matrix be redefined for the affected regions.

Gillham et al. (1984) have proposed an advection-diffusion model to address spreading of a nonreactive solute plume during transport in a heterogeneous layered medium. Advective transport is the principle mode of solute transport within permeable layers, relying on complex velocity distributions to account for spreading of the solute plume by mechanical dispersion. In contrast, the diffusion approach invokes molecular diffusion along chemical gradients between layers of contrasting hydraulic conductivities. As a result of this diffusion, the less permeable layers tend to act as temporary storage cells, concentrating solutes at the expense of the more permeable layers, resulting in a general attenuation of contaminant transport. This molecular interpretation requires knowledge of the contrast in unit hydraulic conductivities, unit thickness, and the molecular diffusion coefficient for the solute. Unfortunately, these parameters are not always known with any degree of certainty, and empirical techniques for estimating their value must be used (Gillham et al., 1984).

Approaches to fracture transport have generally been along two lines (Huyakorn et al., 1983). The first technique invokes dual porosity. In a dual porosity approach, the fracture network is treated as an effective porous medium. Effective values for hydraulic, transport, and sorptive properties are assigned to fracture flow based on this assumption, and solute transport is described by a series of equations similar to Eqns. (4.1) through (4.5). A coupling term is introduced to account for cross-flow and transport between the fracture and the rock matrix. Wilson and Dudley (1986) and Dykhuizen (1987) have used this approach to describe one-dimensional transport in the unsaturated zone at Yucca Mountain. Wilson and Dudley (1986) point out that if coupling time scales are short relative to transport time scales, then fracture and matrix concentrations are closely coupled. As time progresses, concentration gradients tend to diminish through dispersion and diffusion, and the cross flow term between the fractures and the matrix becomes less important, finally disappearing as the concentrations become equal. Neretnieks and Rasmuson (1984) have modified the approach to include radioactive decay during radionuclide transport in a fractured medium with varying velocity and block-size.

A second approach to modeling fracture flow is to use pipe or parallel plane flow to model transport in individual fractures separately from the rock matrix. This strategy is only practical if fracture flow is controlled by a relatively small number of dominant fractures. Huyakorn et al. (1983) have proposed that this is perhaps a more computationally efficient approach than dual porosity, and have modified the governing equations to incorporate radionuclide decay and diffusion into the matrix. The authors also note, however, that extension into three dimensions may prove problematic.

4.1.3. Stochastic Modeling

Stochastic modeling relies on a statistical treatment of probability distributions of hydraulic and transport properties [e.g., hydraulic conductivity (K), water flux (q), solute concentration (C)] to simulate heterogeneities at any scale. Means, variance, and covariance are assumed to be known. Stochastic modeling has seen increasing use in recent years as a method for addressing flow and transport in heterogeneous, fractured media. A detailed discussion of probabilistic modeling techniques is beyond the scope of this report, however, and the reader is referred elsewhere for a more extensive treatment (van Genuchten and Jury, 1987; Barry, 1990; Cvetkovic and Shapiro, 1990; Ababou, 1991). Barry (1990) indicates that the starting point for all stochastic models of solute transport is decoupling water flow and solute transport equations. The author also indicates that most stochastic applications have been restricted to nonreactive solute transport. Cvetkovic and Shapiro (1990) have used statistical treatments to examine a number of processes including equilibrium adsorption desorption, solute degradation (i.e., no desorption), and nonequilibrium kinetic sorption. Russo (1989a,b) has employed stochastic modeling approaches to evaluate reactive transport of Ca, Na, and K in the unsaturated zone. Van Genuchten and Jury (1987) have divided stochastic schemes into scaling theories, Monte Carlo methods, and stochastic continuum models.

Scaling theory [illegible] the use of a scaling factor (λ) to relate the properties of the field case to those of some hypothetical reference medium. It involves the extrapolation of microscopic relationships up to field-scale according to a set of predetermined relationships. In this fashion, Dagan (1986) identified three fundamental length scales as the laboratory, local, and regional scale. Scaling factors are assumed to be distributed according to a specific probability density function (pdf). Bresler and Dagan (1981) have applied a scaling theory approach to simulate the movement of a non-reactive solute in the unsaturated zone, and determined that the uncertainty in extrapolating to field-scale using a laboratory determined value for λ is minor relative to the uncertainty induced by the field-scale heterogeneities themselves. Van der Zee (1990) has reported similar findings based on stochastic modeling and a sensitivity analysis of the parameters of a Langmuir isotherm, and has developed set of length-scale criteria for determining when spatial variability controls the position of a field averaged front.

Monte Carlo techniques involve selecting a joint **pdf** to assign values to randomly distributed material properties of the system (e.g., **ln(K)**, K_d, θ, etc.). Once the statistical parameters of the joint **pdf** are selected, realizations of the material properties are generated using a random number generator; the flow transport problem is solved using the resulting property values. The output from the model calculations [hydraulic head (h), solute concentration (C)] is then collected and stored. This process is repeated a number of times using different coefficients in order to generate a sufficient number of possible outcomes for statistical analysis of the distribution of the model output. Based on the results of this statistical analysis, it is possible to extract information about the key parameters controlling solute transport. Van

Genuchten and Jury (1987) report the results of several studies that have used this approach, and suggest that pore water velocity is the most critical factor controlling field scale solute transport, while dispersion retardation processes are of secondary importance

In one type of stochastic continuum model, the mean values of randomly distributed hydraulic/transport properties are substituted into a deterministic transport equation of the form of Eqn. (4-3), resulting in a mean transport model. Random fluctuations from the mean values are also incorporated in the analysis, and require additional terms in the mean transport model to represent the uncertainty underlying the property values. To evaluate modified transport model, first-order approximations for the inherent uncertainty are developed the model is solved in turn using Fourier transforms. This approach allows for scaling between micro- and macro-scale dispersion by providing a dispersion coefficient that is applied asymptotically as time/distance increases. The transfer function model of Jury et al. (1986) has modified this approach by neglecting dispersion and characterizing a "lifetime probability density function" which represents the net effect of all reactive solute processes and solute input during the residence time of a solute in a unit volume of soil. This requires no knowledge about the shape of the probability density functions underlying the processes. Because of the lumping of processes, however, additional information on mass transfer within the control volume is necessary to discriminate between soil processes. Van Ommen et al. (1989) have combined the transfer function model with scaling theory to model travel time of a nonreactive solute. By describing travel time as a function of flow velocity, and velocity as function of a scaling factor (see above) distribution, travel time distribution will be dependent on the probability density [illegible] scaling factor. Sensitivity analyses indicate that the solute breakthrough is more dependent on the distribution of hydraulic conductivity

Parker and van Genuchten (1984) describe a continuum formulation that represents the field of interest as a series of one-dimensional columns, each with its own flow and transport properties that can be modelled using the deterministic transport Eqn. (4-3). Pore water velocity at a given depth and time among the columns is assumed to vary lognormally, but lateral interaction between the columns is neglected. This type of conceptual model may be appropriate for extending coupled hydrogeochemical codes such as CHMTRNS and CTM that are currently restricted to one-dimensional flow tubes (see below) to two and three dimensions.

4.1.4. Non-equilibrium Transport

The transport equations presented above are based on the "local equilibrium assumption" (LEA), where sorption processes are rapid relative to solute residence time. Time moment analysis, originally developed to estimate dispersive rate parameters for packed bed reactors, has been adapted by Valocchi (1985) to investigate the validity of a local equilibrium assumption. As applied to concentration breakthrough curves, the first three moments of the curve describe mean time to breakthrough, spreading of the solute plume, and asymmetry of the breakthrough curve, respectively. Using this approach, Valocchi (1985) has developed a set of dimensionless parameters and defined criteria to discriminate nonequilibrium and equilibrium conditions as a means of establishing the validity of this assumption for one-dimensional steady flow in a sorbing homogeneous medium. The study concludes that many basic parameters of the system, including boundary conditions, sorption rates, and the dispersion coefficient have an effect on the degree of equilibrium achieved. Valocchi (1985) also presents two modeling approaches used to simulate nonequilibrium solute transport in a porous medium. These include the physical two-region model (mobile/immobile water) of van Genuchten et al. (1984), and the chemical nonequilibrium model (Jennings and Kirkner, 1984; Nkedi-Kizza et al., 1984).

4.1.4.1. Two-Region Kinetic Transport

The two-region (or two-component) approach to modeling kinetics uses the dead-end pore space model of Coats and Smith (1964) and modified by van Genuchten and Wierenga (1976). The basic concept behind the model is the existence of two regions in a porous medium. In one region, water is mobile and free to transport ions in solution. In the second region, water is considered immobile (or stagnant in some terminologies) in dead-end pore spaces. Mass transfer between the two regions is by diffusion alone. In one dimension, the two-region convection-dispersion transport equation becomes

$$\theta_m \frac{\partial C_m}{\partial t} + f\rho_b \frac{\partial S_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} + (1 - f)\rho_b \frac{\partial S_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \qquad (4\text{-}9)$$

where the subscripts m and im stand for the mobile and the immobile regions, θ is the water content, f represents the mass fraction of the solid phase that is in contact with the mobile fluid, D is the hydrodynamic dispersion coefficient, and ρ_b is the bulk density. Diffusion between the mobile and immobile regions is controlled by the relationship

$$\theta_{im} \frac{\partial C_{im}}{\partial t} + (1 - f)\rho_b \frac{\partial S_{im}}{\partial t} = \alpha(C_m - C_{im}) \qquad (4\text{-}10)$$

where α is an empirical mass transfer coefficient between the stagnant and mobile waters. The degree of nonequilibrium represented in the system decreases as the rate of mixing between the two regions (α) increases relative to the rate of solute advection. It is important to note that the two-region model uses a local equilibrium assumption to govern relationships in the mobile and immobile regions of the system. It is therefore not a model limited by reaction kinetics, but rather permits disequilibrium due to concentration gradients at points along the direction of flow (W. Murphy, personal communication). To evaluate the degree to which overall local equilibrium is approached in a two-region model, Valocchi (1985) has expressed Eqn. (4-10) in a dimensionless form:

$$(1 - \beta)R \frac{\partial C_{im}}{\partial T} = \omega(C - C_{im}) \qquad (4\text{-}11)$$

where $\omega = \alpha L/(q)$ is a dimensionless mass transfer parameter, T is a dimensionless time equivalent to the number of pore volumes leached through a column of length L, and R is a retardation factor based on the assumption of linear sorption (i.e., $\mathbf{R} = \mathbf{R}_{m}\rho_{m} + \mathbf{R}_{im}\rho_{im} =$ $\rho_b K_d/\theta$). As ω increases, the two-region model approaches local equilibrium.

The two-region approach has been used in a number of studi Eijkeren and Loch, 1984; Mansell et al., 1988; Selim et al., 1990). Immobile water inferred from column experiments that exhibit early breakthrough and asymmetric breakthr curves (Bond and Wierenga, 1990). De Smedt and Wierenga (1979) suggest that imm water is present if fitting unsaturated transport data requires the use of a dispersion coeff much larger than that predicted for saturated fluid flow. Bond and Wierenga (1990) cond nonreactive solute transport experiments under both steady and unsteady unsaturated con to evaluate the two-site model. Under steady flow, early breakthrough and asymm breakthrough curves indicated the presence of small amounts of immobile water. unsteady flow conditions, however, the data was adequately described without inv regions. Bond and Wierenga (1990) attribute this to the differences in wetting patte case of steady flow, water flow is already established and biased towards preferential resulting in dead-end pore space. In contrast, wetting of the soil during the un experiments carried the tracer into the wetted pore space by advection alone, with little o contribution from diffusive mass transfer between mobile and immobile water. Mansell (1990) have incorporated a mobile/immobile two-region approach to nonequilibrium tr into the direct-coupled model of Valocchi et al. (1981a,b). Selectivity coefficients are to vary in space and time as a function of changes in solution normality and compositi authors report that the model was successful in predicting Na

4.1.4.2. *Two-Site Kinetic Transport*

As discussed above (section 2.3.2.6), many studies (Selim 1976; Cameron and Klute, 1977; Jennings and Kirkner, 1984; Parker and Jardine, 198 proposed a two-site approach to modeling early breakthrough curves. One site is assu be governed by equilibrium sorption, and the second site assumes kinetic sorption reactio discussed by Nkedi-Kizza et al. (1984), adsorption on the equilibrium site (site 1) is gove by a linear sorption isotherm, while sorption at the nonequilibrium site (site 2) is governed first-order, linear kinetics. Expressed in terms of adsorption at the nonequilibrium sites overall governing transport equation is:

$$\left[1 + \frac{f\rho_b K_d}{\theta}\right]\frac{\partial C}{\partial t} + \frac{\rho_b \alpha_2}{\theta}\left[(1 - f)K_d - S_2\right] = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \qquad (4\text{-}1$$

where f is the fraction of sites that are governed by equilibrium sorption, K_d is the sorption coefficient that is valid for both sites, α_2 is a first-order kinetic rate constant fo nonequilibrium sorption sites, v is the mean fluid velocity ($v = q/\theta$), and other variables (S ρ_b, D) are as defined previously.

$$K = \frac{a_D^d a_E^e}{a_B^b a_C^c} \qquad (4\text{-}14)$$

where K is the thermodynamic equilibrium constant at a given set of pressure-temperature conditions, and a_I^i is the thermodynamic activity of species I raised to the power of its reaction coefficient, i. As described above, activity/concentration relationships are generally of the form $a_I = \gamma_I m_I$, with activity coefficients (γ) either determined experimentally, or defined by one of several approximations such as the Debye-Huckel and Davies equations (Stumm and Morgan, 1981), which have been developed assuming relatively dilute solutions. Recent studies (Pitzer, 1973, 1979; Harvie et al., 1984; Plummer et al., 1988; Pabalan and Pitzer, 1990) have developed a set of virial equations (Pitzer equations) to calculate solution properties for concentrations ranging from dilute electrolyte solutions to highly concentrated brines. All activity/composition relations require additional thermodynamic data, however, and frequently an activity coefficient of one is assumed, and simple concentrations are substituted for activities in Eqn. (4-13).

The standard Gibbs free energy of reaction (ΔG_r°) can also be used (Mangold and Tsang, 1991) to describe chemical equilibrium through the relationship:

$$\Delta G_r^\circ = -RT(\ln K) \qquad (4\text{-}15)$$

From Eqn. (4-15), it is possible to calculate equilibrium constants as a function of pressure and temperature using thermodynamic relations such as the Maxwell and van't Hoff equations (Garrels and Christ, 1965), and standard state thermodynamic properties (e.g., heat capacity, enthalpy, and entropy) for the reactant and product phases. These values are tabulated in a number of thermodynamic databases for a wide variety of liquids, gases, solids, and aqueous species.

Acid-base and redox reactions can also be written in a form analogous to Eqn. (4-13), involving either the transfer of a proton (acid-base), or an electron (redox) (Mangold and Tsang, 1991). A mathematical construction similar to Eqns. (4-14) and (4-15) can then be used to express these types of reactions as functions of pH and Eh [or $pE = (F/2.303RT)Eh$, where F is the Faraday constant]. To incorporate reaction kinetics in modeling heterogeneous mineral dissolution in redox-controlled chemical transport, Liu and Narasimhan (1989a,b) have assumed a surface-controlled, first-order, empirical relationship.

4.3. COUPLED HYDROGEOCHEMICAL MODELING

Numerical codes that couple geochemical and transport models (hydrogeochemical models) have seen increasing use as tools for gaining insight into retardation processes and predicting the nature and extent of contaminant transport. Development of such comprehensive codes is being actively pursued by a number of research groups (LANL, LBL, PNL, SNL, EPRI, Stanford) using a variety of approaches. An evaluation of existing codes should consider accuracy, efficiency, flexibility, and computational requirements among other characteristics in an attempt to find the best balance between model completeness and applicability.

4.3.1. Selection Criteria

The criteria used to select a code for investigating sorption processes are similar to those used for selecting any computer program for a desired purpose. These include program flexibility, computational efficiency and accuracy, ease of input and output, computational requirements and run costs, and database requirements and availability. These are discussed in turn below.

In order to evaluate sorption processes involved in the retardation of contaminant transport, a code needs to be flexible in terms of the sorption models (K_d, empirical isotherms, ion exchange, surface complexation, etc.) available to the modeler. Solute transport codes (TRACR3D, NEFTRAN II) frequently lump sorption processes, and deal with sorption using only a retardation factor (R_f). Coupled hydrogeochemical codes ideally offer a more explicit treatment, and will be able to incorporate a wide variety of data types as they become available. In addition, in order to use numerical modeling as a evaluative tool, a code should include sorption models valid for a given approach to solute transport (e.g., the conservative K_d approach of Meijer, 1990).

Because the system of interest is necessarily poorly understood in some regards, the hydrogeochemical model should not be designed with only one system in mind. Ideally, a variety of boundary and initial conditions should be available, and the model should be able to describe a variety of physical systems (homogeneous/heterogeneous, steady-state/transient, isotropic/anisotropic, isothermal/ nonisothermal, etc.) as more complete information becomes available. Flexibility is also important in order to perform sensitivity analyses of the system to various parameters (Siegel et al., 1989).

The efficiency of a given hydrogeochemical model is not only important for investigating the problem at hand, but it will also determine the ability of the program to be adapted to more complete (and complex) conceptual models. This efficiency in turn depends on both the approach taken toward coupling and the primary dependent variables (PDV's) that are chosen to represent the problem of interest (Kirkner and Reeves, 1988; Reeves and Kirkner, 1988; Yeh and Tripathi, 1989). 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. This results in a set of nonlinear partial differential equations (PDE) that are solved simultaneously for geochemistry and transport for a given set of PDV's. For the second method, geochemistry and mass transport equations are posed independently of one another, and solved sequentially rather than simultaneously. This two-step approach has been used successfully in several studies (Cederberg et al., 1985; Walsh et al., 1982)

While one-step coupling yields a more exact solution to the problem, 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 requires the solution of only one set of equations in sequence, and uses computer resources much more effectively. Calculations (Cederberg, 1985; Yeh and Tripathi, 1989) indicate that a two-step coupling approach is more than 30 percent faster than direct coupling for a given problem. In addition, Yeh and Tripathi (1989) show 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. Numerical techniques employed in matrix formulation and solution, and iteration will also have an effect on run time, and therefore, run costs. Several studies (Yeh, 1985; Reeves and Kirkner, 1988; Yeh and Tripathi, 1989; Siegel et al., 1989) have evaluated a variety of solution strategies (e.g., successive overrelaxation, Gauss-Seidel) and iterative techniques (e.g., Picard, Newton-Raphson), and identified convergence problems. On a mainframe computer, 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. 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. This disadvantage will become increasingly apparent in [illegible] a large number of calculations to develop adequate statistics. An elaborate, computationally slow code will become the limiting step in performing these calculations, making a stochastic modeling approach untenable without invoking significant (and perhaps unrealistic) improvements in computer technology.

Thermodynamic data are of critical importance in modeling any geochemical system. A given hydrogeochemical code should use an established, current database that has been tested for accuracy and internal consistency, and is 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., 1984a,b; Krupka et al., 1988). In addition, the necessary data for modeling important processes (sorption, precipitation/dissolution, ion exchange, activity, etc.) should be available. 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 will have additional advantages of being tested through application to a wide variety of problems applications, and will also benefit from a general interest on the part of the research community in keeping the database consistent, accurate, and current. Finally, the complete database should be readily accessible to the program in order to adapt the model to a variety of systems.

Although the degree of "user-friendliness" must not be developed at the expense of the accuracy or efficiency of a program, it should be considered in code selection (Siegel et al., 1989). The program should be accessible to a variety of users with varying levels of computer skills. Complicated or awkward formatting of input can make application of the model difficult, and limit its usefulness as a tool to study a wide variety of systems or perform sensitivity analyses. Rigid input can also inhibit modification or correction of the input, perhaps leading to false starts and inaccurate data entry. Because these codes deal with potentially large numbers of chemical species and long time-intervals and distances, post-processing of the data is also important as an aid in interpreting the output from the hydrogeochemical model.

4.3.2. Codes Considered

This section is not intended to be an exhaustive analysis of reactive transport codes. In order to focus the evaluation, unnamed codes developed for a particular problem (Rubin and James, 1973; Valocchi et al., 1981a,b; Walsh et al., 1982), and more elaborate codes requiring extensive supercomputer time (e.g., DYNAMIX, Liu and Narasimhan, 1989a,b; Barry, 1990), were only given preliminary consideration and are not discussed further. In addition, future modeling will likely include stochastic methods and parallel processing (Barry, 1990), developments which are not considered here. Table 4-1 is a list of models considered to date. Information about the code characteristics and the techniques was largely collected from user's manuals and key references listed in the table; additional information is available in Morrey et al. (1986), Siegel et al. (1989) and Mangold and Tsang (1991). Two of the codes (NEFTRAN II and TRACR3D) are solute transport codes that do not explicitly account for the geochemistry of the water/rock system. The remainder of the codes are hydrogeochemical [illegible] written in FORTRAN. With the exception of CHMTRNS, all of the codes are isothermal, equilibrium models, and do not currently incorporate reaction kinetics. It is also important to note that hydrogeochemical modeling is a dynamic area of research, and future developments may result in new, more powerful codes, or extensive modification to the existing models.

The TRANQL code was developed at Stanford University, and has been used to model multicomponent transport of Cd, Co, Br, and Cl (Cederberg, 1985; Cederberg et al., 1985). The code is based on the transport code ISOQUAD (Pinder, 1976) and MICROQL (Westall, 1979), a scaled-down version of the MINEQL code. TRANQL has been evaluated by Siegel et al. (1989). The model is currently designed for one-dimensional simulation employing a mainframe computer system. The current system is able to model ion exchange and surface complexation sorption processes, but cannot handle precipitation/dissolution reactions. Pre- and post-processing routines have been developed to facilitate data entry and interpretation (Grover and Freyberg, 1987). The code is currently limited to a maximum of two mobile components and one sorbing substrate. Siegel et al. (1989) concluded that code flexibility is limited by its database, and to simulate the transport of a single solute a distance of 5 km over 10,000 years would amount to $10,000 to $40,000 in run time costs.

The FASTCHEM system (Hostetler and Erikson, 1989; Hostetler et al., 1989) was developed by Pacific Northwest Laboratory (PNL) for the Electric Power Research Institute (EPRI), and is based on the SATURN transport code and the MINTEQ geochemical code (Morrey et al., 1986). The program is modular in design, and incorporates a networked PC

Table 4-1. HYDROGEOCHEMICAL [illegible]D SOLUTE TRANSPORT COMPUTER MODELS

	TRANQL	FASTCHEM	CT[illegible]	CHEMTRN	CHMTRNS	NEFTRAN II	TRACR3D
Reference	Cederberg (1985)	Hostetler et al. (1989)	Eriks[illegible] al. (19[illegible])	Miller (1983)	Noorishad et al. (1987)	Olague et al. (1991)	Travis (1984)
Affiliation	Stanford	EPRI	PN[illegible]	LBL	LBL	SNL	LANL
Proprietary	No	Yes	N[illegible]	No	No	No	No
Speciation	Yes	Yes	Y[illegible]	Yes	Yes	No	n.a.
Complexation	Yes	Yes	Y[illegible]	Yes	Yes	n.a.	n.a.
Precipitation/ Dissolution	No	Yes	Y[illegible]	Yes	Yes	No	No
Sorption Options	SC, IE	SC, IE, Constant K_d, Isotherm	SC, IE, Constant K_d, Isotherm	SC (TLM), IE	SC, IE	R.	R,
Number sorbing species/run	2	40 Max.	>1	>1	>1	Limited by CPU Memory	Limited by CPU Memory
Sorption Options/run	1	>1	>1	1	1	1	2
Isothermal/ Nonisothermal	Isothermal	Isothermal	Isothermal	Isothermal	Isothermal/ Nonisothermal	Isothermal	Isothermal
Activity Coefficients	No	Yes Davies Extended D-H	Yes Davies Extended D-H	Yes Davies	Yes-Davies	n.a	n.a
Kinetics	No	No	No	No	Yes	No	n.a
Current Geochemical Database	MICROQL [Simplified MINEQL]	ECHEM-EICM Krupka et al.(1988)	Mod. MINTEQ (Krupka et al., 1988); Tripathi([illegible]984)	WATEQ2, Benson and Teague (1980)	WATEQ2, PHREEQE, Rimstidt and Barnes (1980) Benson and Teague(1980)	n.a	n.a

Table 4-1. (CONTINUED)

	TRANQL	FASTCHEM	CTM	CHEMTRN	CHMTRNS	NEFTRAN II	TRACR3D
Dimensions	1,2	Parallel 1-D stream-tubes	Parallel 1-D Stream tubes	Parallel 1-D Stream-tubes	Parallel 1-D stream tubes	Pseudo 3-D	1,2,3
Velocity	Constant	Variable	Variable	Can vary systematically	Can vary systematically	Distributed Velocity	Variable
Dispersion	T,L	T	T	T	L	L	T,L
Homogeneous Heterogeneous	Homgeneous	Heterogeneous	Heterogeneous	Homogeneous	Homogeneous	Heterogeneous	Heterogenous
Coupling Steps	Two Step	Two Step	Two Step	One Step	One Step	n.a.	Two Step (pseudo)
Numerical Procedure	Galerkin FEM Determ. ADE	FEM-Determ. ADE	FEM-Determ. ADE	Backward-Diff FDM Determ. ADE	Backward-Diff FDM Determ. ADE	Analytical, Distributed Velocity Method	Implicit FDM
Efficient For Multiple Runs	No	Yes	Yes	No	No	Yes	No
Current Computer Requirements	VAX Mainframe IBM 3081	IBM PC Input to IBM Mainframe	IBM PC (Model 70)	7600 CDC	7600 CDC CRAY	VAX Mainframe	CRAY at LANL
Graphics Postprocess	No	Yes	Yes	No	No	No	Yes
Preprocessor	Yes	Yes	Yes	Formatted batch	Formatted batch	No	No

Abbreviations: n.a. - not applicable, **EPRI** - Electric Power Research Institute, **PNL** - Pacific Northwest Laboratories, **LBL** - Lawrence Berkeley Laboratory, **SNL** - Sandia National Laboratory, **LANL** - Los Alamos National Laboratory, **SC** - Surface Complexation, **II** - Ion Exchange, **R** - retardation factor, **Davies** - Davies equation, **D-H** - Debye-Huckel, **T** - transverse dispersion, **L** - longitudinal dispersion, **FEM** - finite element method, **FDM** - finite difference method, **ADE** - advection dispersion equation workstation for constructing input files to an online mainframe computer for transport and geochemical calculations. Post processing of the output is performed on the mainframe for subsequent downloading and graphic display at the workstation. The code uses a modified version of the MINTEQ data base and is valid for the temperature range 25° to 100° C (Krupka et al., 1988; Criscenti et al., 1989). A Markov hydrological model is used to simulate solute movement through advection, diffusion, and hydrodynamic dispersion (Kincaid, 1988). This method involves discretizing a streamtube into a number of arbitrarily shaped bins. The total concentration of each solute in each bin is then expressed as an entry in a state vector, and the Markov transition matrix is used to predict the evolution of the state vector through time. Two-step coupling of geochemistry and transport is used for efficient computation. Only longitudinal dispersion is modeled, and a series of parallel, one-dimensional, non interacting streamtubes is used to model two-dimensional (and in theory three-dimensional) systems. Because of the streamtube construction, FASTCHEM is somewhat limited in its ability to model transient conditions. The two-dimensional flow code EFLOW is run until steady state is achieved. The steady-state flow field generated in this fashion is then processed into the necessary streamtubes by the code ETUBE. In order to simulate transient changes in hydraulic properties of the medium, it is necessary to redefine the boundary conditions at the appropriate timestep, and then run the EFLOW code again to achieve a steady-state flow field. ETUBE is executed again, and a new set of streamtubes is defined. Equilibrium geochemical processes include speciation, complexation, oxidation reduction, and several different adsorption models (K_d, empirical isotherms, ion exchange, surface complexation). Activity relationships are modeled using the Davies or the extended Debye-Huckel equations. The code is proprietary, and the licensing fee is currently set at $50,000.

The CTM (Chemical Transport Model) code (Morrey and Hostetler, 1985, Erikson et al., 1990) is currently in development at PNL for the Low Level Waste Management Division of the NRC, and incorporates many of the same methods and approaches as the proprietary FASTCHEM code. The database is the same as the FASTCHEM code, with further modifications to include the compilations of Wagman et al. (1982) and the uranium data of Tripathi (1984). The current version of the code has only been set up for one dimensional, isothermal simulations assuming equilibrium. While the CTM code is currently designed to run on an IBM PS/2 Model 70, future developments for modeling 2- and 3 dimensional systems may require mainframe capabilities. Pre- and post-processing are available for data input and output through an interactive system. Output is designed to take advantage of several commercial graphics software packages currently available for the PS/2 system (SURFER GRAPHER).

The CHEMTRN code was developed at Lawrence Berkeley Laboratory (LBL), and has been applied to nuclear waste isolation and contaminant transport (Miller, 1983; Miller and Benson, 1983). The code uses the one-step direct coupling method, and is therefore more cumbersome than the two-step codes discussed above. CHEMTRN is an equilibrium code, and is similar to FASTCHEM/CTM in that it employs a one-dimensional streamtube to model fluid flow. Due to the one-step coupling, however, storage limitations will become a problem in extending the model to multiple dimensions. The code is able to model ion exchange, surface complexation (triple-layer model only), and precipitation dissolution reactions as retardation mechanisms. No K_d or sorption isotherms are available for the code as it is currently configured. The model is limited to saturated flow through a homogeneous porous medium at constant temperature. In applications to date, the model has not employed an extensive, established thermodynamic database. The user is required to provide all of the reaction stoichiometries, equilibrium coefficients, CEC, sorption parameters, and other variables for each run using a formatted batch input. It does appear that data can be included from a variety of sources, but a database would have to be developed and modified for extensive use of this code.

The CHMTRNS code was also developed at LBL (Noorishad et al., 1987), and represents a version of CHEMTRN that has been modified to include reaction kinetics, carbon isotope fractionation, and nonisothermal behavior. Multiple sorption models can be used in a given run. Formatted batch input is used for defining the problem and inputting the initial and boundary conditions. Each input deck consists of a minimum of twenty "cards," each card consisting of from one to seven parameters. Although the elaborate input makes the code flexible enough for application to a variety of systems and situations, many of the parameters must be defined by the user, leading to complex data input. In addition, all of the thermodynamic, kinetic and sorption data must be entered each time the model is run, limiting the ability of the code to perform multiple runs for sensitivity analyses. No pre- or post-processing of the data is currently available to help in data entry or interpretation. It is assumed that data entry is similar to that for CHEMTRN.

NEFTRAN II (Olague et al., 1991) and TRACR3D (Travis, 1984) are solute transport codes and do not explicitly consider the geochemical equilibria involved in contamin[illegible] migration. As such, they are not suitable for examining specific sorption processes. However, because the bulk of the calculation time involved in modeling reactive solute transport [illegible] calculating the geochemistry, solute transport codes are much quicker. They can [illegible] adapted to model three-dimensional transport, radionuclide decay and [illegible] without overextending computer resources. In addition, they can be [illegible] and the physical aspect of solute transport can be examined in more detail.

4.3.3. Code Selection

Based on the above discussion, the CTM code has been chosen for further investigation. It offers a combination of many of the advantages while [illegible] a number of drawbacks inherent in the other codes. Although it is perhaps not as powerful as other available codes (e.g. CHMTRNS, DYNAMIX), it offers a number of features which make it a more attractive alternative. It is similar to FASTCHEM in its construction, while avoiding the licensing costs of FASTCHEM ($50,000). The two step coupling approach is employed by the CTM model, allowing the code to solve for reactive solute transport more efficiently than the one-step coupling approach used in CHEMTRN and CHMTRNS. Computer costs are minimal because the code has been adapted to the IBM PS/2 Model 70 personal computer system, although it will certainly require more powerful computer capabilities for extension into two- and three-dimensions. Also, since the Markov hydrological approach 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 models in the future. The thermodynamic database is based on the widely available MINTEQ geochemical code, which has been modified (Krupka et al., 1988) and extended to include the uranium data of Tripathi (1984). In addition, several sorption mechanisms are available for evaluating sorption processes involved in a variety of systems. The thermodynamic database is readily accessed by the program, and does not require either the extensive formatting of input or the development of a run-specific database like the CHEMTRN and CHMTRNS codes. The interactive pre-processing system will simplify modification of the conceptual model and allow for flexible application of the model. Post-processing has been used to adapt the code to SURFER and GRAPHER graphics software (C. Hostetler, personal communication), permitting a variety of data display methods. Although the code has been developed only for equilibrium geochemistry, kinetic data are currently limited or nonexistent for many of the species that are of interest in radionuclide migration; under certain conditions (e.g., long solute residence time), an equilibrium treatment may be adequate to model sorption and retardation processes for performance assessment (Valocchi, 1985).

The CTM code is being developed for the NRC Division of Low Level Waste Management (Erikson et al., 1990) and a preliminary version has been made available to CNWRA for initial adaptation and modeling studies. Because the code is in development, documentation is currently limited, although a release to the International Groundwater Modeling Center is anticipated in the fall of 1991 (C. Hostetler, personal communication).

5. YUCCA MOUNTAIN GEOLOGY AND GEOCHEMISTRY

In order to evaluate radionuclide migration at the proposed Yucca Mountain site, it is critical to have a good understanding of the physical and chemical properties of both the geologic medium that will be encountered along likely flow paths, and the water that is expected to transport the radionuclides in solution. Chapters 1, 3, 4, and 5 of the Department of Energy Site Characterization Plan (DOE, 1988, and references therein) provide a great deal of information obtained from drilling programs, laboratory experiments, and chemical analysis of the various components of the Yucca Mountain environment. The following discussion is intended as a brief summary of these findings.

5.1. YUCCA MOUNTAIN GEOLOGY

The Yucca Mountain exploratory block lies in the southern part of the Great Basin geographic province (Carr and Yount, 1988), about eighty miles northwest of Las Vegas, Nevada (Figure 5-1). The surface exposure is largely Tertiary (< 16 m.y.) ashflow and ashfall tuffs, dipping to the east at a shallow angle (5 to 30 degrees). The general sense of structural displacement in the exploratory block is down-drop to the west along a number of north trending, high-angle normal faults that dip to the west (Figure 5-2). The central part of the exploratory block itself is bounded by several major faults, but it is relatively intact and is only crossed by a few normal faults (Montazer and Wilson, 1984). The total thickness of tuffaceous units at Yucca Mountain (Table 5-1) ranges from 1.2 km to greater than 1.8 km (based on drill hole data (Carr et al., 1984). Paleozoic sediments are thought to underly the exploratory block, although Paleozoic (Silurian) carbonates have only been encountered in drillhole UE-25 p#1.

The current design approach proposes to locate the repository in the unsaturated Topopah Spring Member of the lower Paintbrush Tuff, about 300 m below the surface and 250 m above the current water table (Figure 5-2). The Topopah Spring tuff consists of a sequence of nonwelded to densely welded rhyolite tuffs and is bounded by vitrophyres at the top and base of the unit. The low-permeability welded tuffs are believed to be more densely fractured than the nonwelded units (Peters and Klavetter, 1988). The climate of the site is arid, and current rainfall is about 150 mm/yr with a net annual infiltration on the order of 0.1 to 1.0 mm/yr, although infiltration values as high as 4.5 mm/yr have been proposed (Ababou, 1991).

5.2. MINERALOGY

The distribution of diagenetic alteration of tuffaceous units at Yucca Mountain is principally controlled by the more permeable nonwelded tuffs. Broxton et al. (1987) have divided the alteration into four basic diagenetic zones (Figure 5-3) with four characteristic mineral assemblages (Table 5-2). These secondary minerals, particularly the zeolite clinoptilolite and the clay smectite, are expected to provide a sorptive barrier to retard radionuclide migration should the engineered barriers fail. Representative mineral chemistries are provided in Broxton et al. (1986).

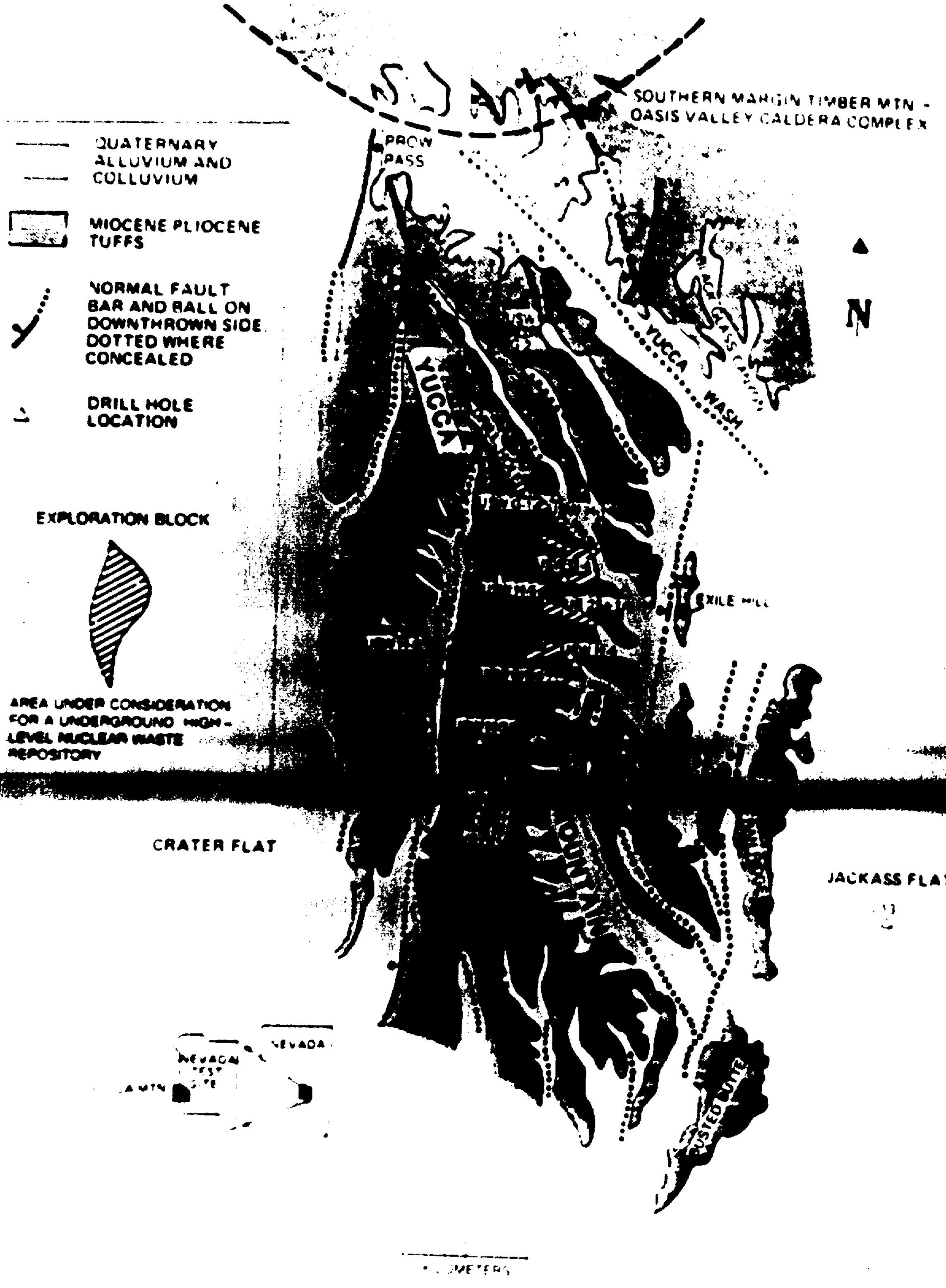

Figure 5-1. Location map for Yucca Mountain, Nye County, Nevada. The cross-hatched area is the current exploration block. Well J-13 (see text) is located in Jackass Flat to the east. (from Broxton et al., 1987)

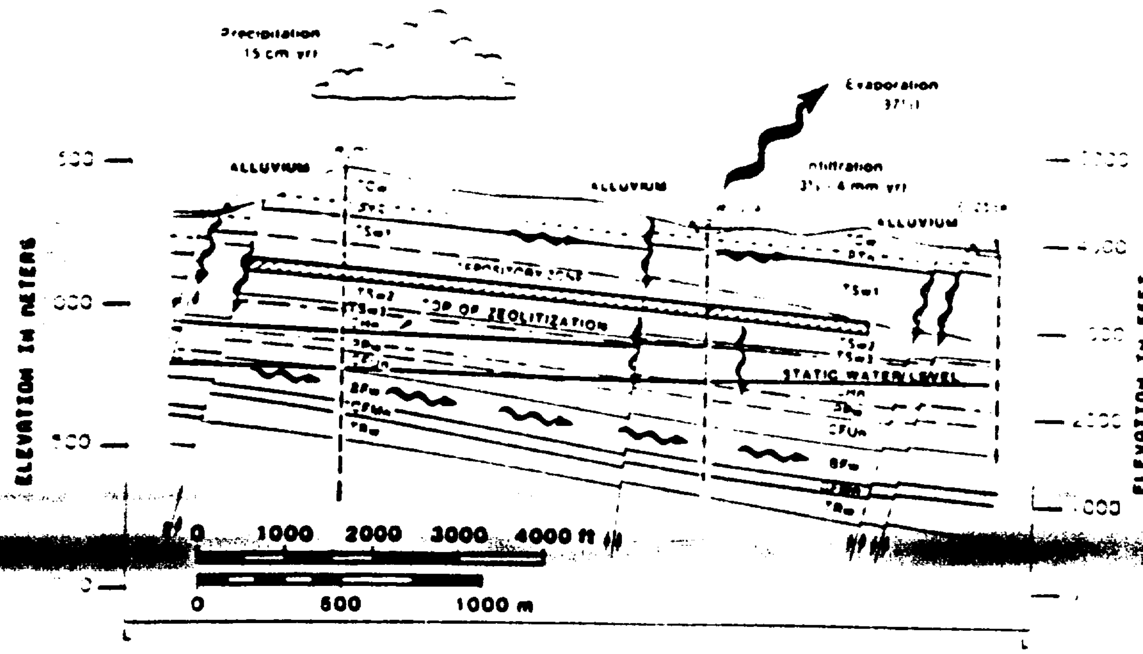

Figure 5-2. **A conceptual model for groundwater flow at Yucca Mountain. The current water table and the top of the extensive zeolitization are shown for reference (from Peters and Klavetter, 1988).**

Matrix mineralogy in the Topopah Spring tuff varies with the degree of devitrification (Figure 5-4). The texture of the tuffs is commonly porphyritic. The most common primary minerals in the groundmass (DOE, 1988) are: potassium feldspar which makes up from 60 to 80 percent of the matrix; silica minerals such as quartz, tridymite, and cristobalite comprising from 20 to 40 percent of the unit; and, biotite. Phenocrysts make up varying proportions of the unit, and consist of biotite, quartz, plagioclase, with accessory Fe-Ti oxides, hornblende, augite,

Table 5-1. STRATIGRAPHY OF VOLCANIC UNITS AT YUCCA MOUNTAIN, NEVADA (FROM BROXTON ET AL., 1987)

Stratigraphic unit	Thickness (m)	Lithology
Paintbrush Tuff		
Tiva Canyon Member	45-150	Ash-flow tuff; compound cooling unit; nonwelded vitric base; moderately to densely welded, devitrified interior with some vapor-phase crystallization
Yucca Mountain Member	0-30	Ash-flow tuff; nonwelded vitric top and base; partially welded devitrified interior with some vapor-phase crystallization; present under northern half of Yucca Mountain.
Pah Canyon Member	0-80	Ash-flow tuff; nonwelded and vitric throughout; present under northern half of Yucca Mountain.
Topopah Spring Member	240-365	Ash-flow tuff; compositionally zoned, compound cooling unit; nonwelded zones at top and base and moderately to densely welded, devitrified interior with zones of vapor-phase crystallization; vitrophyres at top and base of unit, zeolites occur both on top of basal vitrophyre and in nonwelded base of unit.
Tuff of Calico Hills	35-290	Ash-flow tuff; nonwelded to partially welded; thoroughly zeolitized at north end of exploration block; becomes vitric southward.
Crater Flat Tuff		
Prow Pass Member	85-190	Ash-flow tuff; nonwelded zones at top and base; moderately welded, devitrified interior with minor vapor-phase crystallization; nonwelded base is zeolitic; nonwelded top is zeolitic in the northern part of Yucca Mountain, but vitric to the south.
Bullfrog Member	90-190	Ash-flow tuff; compound cooling unit, nonwelded top and base, nonwelded to densely welded interior with thickness and occurrence of welded zones highly variable, zeolitic in nonwelded zones
Tram Member	155-385	Ash-flow tuff, compound cooling unit; zones of partial to dense welding vary from drill hole to drill hole; zeolitic in its nonwelded to partially welded parts; otherwise devitrified
Dacite Flow Breccia	0-120	Flow breccia, lava, and tuffs; occurrence restricted to drill hole USW G-1; zeolites irregularly distributed throughout the unit.
Lithic Ridge Tuff	185-305	Ash flow tuff, nonwelded to moderately welded, devitrified, contains few zeolite horizons
Unnamed older tuffs and lavas	365+	Ash flow tuffs, lavas, reworked volcanic sediments, dacitic to rhyolitic compositions, contains few zeolite horizons.

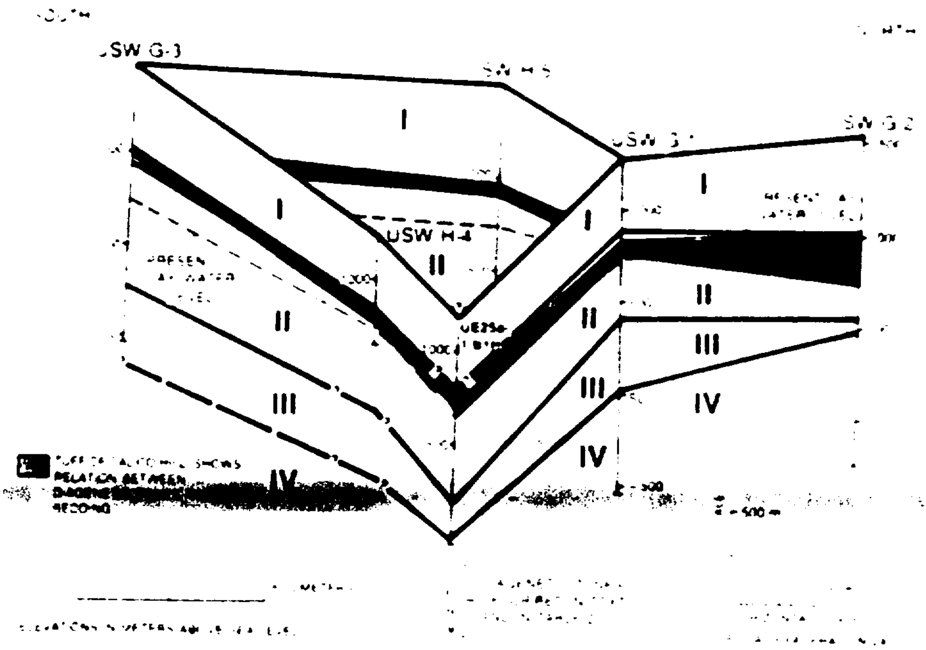

Figure 5-3. A fence diagram showing the diagenetic zones of alteration at Yucca Mountain. Drillhole locations are given in Figure 5-1 (from Broxton et al., 1987).

sphene, and zircon. Where devitrification is less prevalent, the bulk of the matrix is composed of glass shards.

Secondary minerals are dominantly zeolites (clinoptilolite, mordenite, analcime), calcite, authigenic feldspar, kaolinite, and smectite. These minerals are locally abundant and may make up as much as 70-90 percent of the rock by volume. The major zone of zeolitization spans, and extends as much as 225 m above, the current water table (Broxton et al., 1987). With depth,

Table 5-2. PROGRESSIVE MINERAL CHANGES WITH DEPTH IN TUFFS FROM YUCCA MOUNTAIN, NEVADA (FROM BROXTON ET AL., 1987).

Diagenetic Zone	Thickness (m)	Characteristic diagenetic mineral assemblages	Remarks
I	170-584	Fresh Volcanic glass, smectite, opal, cristobalite	Preservation of glass in vitric tuffs, smectite and opal are the primary alteration minerals. Ca-clinoptilolite and/or heulandite are confined to local zones of alteration. Zone I occurs above the water table.
II	480-700	Clinoptilolite, mordenite, opal, cristobalite, quartz, authigenic K-feldspar, smectite	Original volcanic glass is replaced by clinoptilolite, mordenite and silica phases. Smectite and authigenic feldspar are minor diagenetic minerals.
III	98-400	Analcime, authigenic K feldspar, quartz, smectite, calcite	Analcime, quartz, and authigenic K feldspar replace clinoptilolite, mordenite, opal and cristobalite. Heulandite is present locally at top of Zone III on the east side of Yucca Mountain. The cores of some plagioclase phenocrysts are replaced by calcite.
IV	>750	Authigenic albite, authigenic K-feldspar, quartz, smectite, calcite	Authigenic albite replaces analcime. Feldspar phenocrysts are locally altered to calcite, authigenic albite and K feldspar. Mafic phenocrysts are altered to chlorite, epidote, and iron oxides. Barite, fluorite, and sulfides occur in trace amounts. Diagenetic processes may affect devitrified rocks as well as those rocks that were formerly vitric.

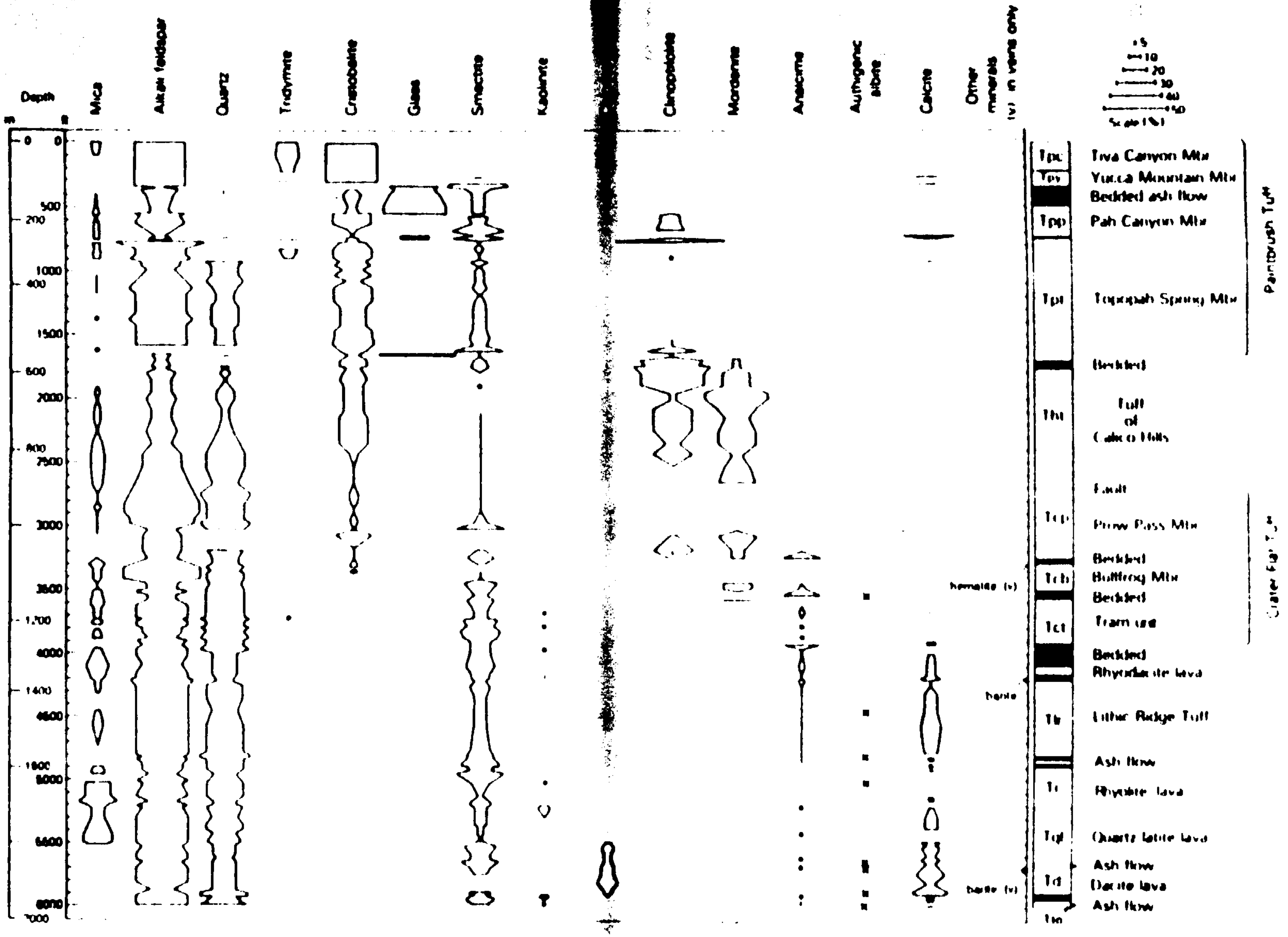

Figure 5-4. Alteration and primary mineral assemblages with depth in drillhole USW G-2 (see Figure 5-1). Determined by X-ray diffraction (from DOE, 1988).

there is a general transition from clinoptilolite to analcime to albite (Bish et al., 1981). Alteration to clinoptilolite is believed to be due to downward migration of meteoric water through the unsaturated vitric tuffs. Percolating fluids [illegible] increasingly alkaline and enriched in dissolved solids with depth, altering the vitric tuffs [illegible] the water table where groundwater compositions were appropriate for zeolitic replacement (Broxton et al., 1987). Clay alteration records a transition from smectite to illite to chlorite with depth (Bish, 1989). This transition occurs at increasingly shallow depths from south to north, and Bish (1989) suggests that this reflects hydrothermal activity associated with the Timber Mountain Caldera at about 11 m.y.

Fractures in the tuffaceous units are lined with a variety of minerals. Primary fractures associated with contraction during cooling are lined, and frequently sealed, with silica and feldspar. Later fractures are lined with secondary minerals such as zeolite (mordenite + heulandite), kaolinite, smectite, calcite, and iron oxides (hematite) and manganese oxides (cryptomelane). Zeolite fracture coatings tend to be discontinuous, and smectite is generally only present in late overgrowths. If fracture flow is dominant in the system, the sorptive properties of these minerals will control radionuclide migration through the geological environment.

5.3. GROUNDWATER CHEMISTRY

Chemical analysis of waters collected from the saturated zone in drill holes at the Yucca Mountain site have been compiled in the Site Characterization Plan (DOE, 1988), Ogard and Kerrisk (1984), Benson and McKinley (1985), Raker and Jacobson (1987), and Kerrisk (19[illegible]). Representative ionic concentrations are listed in Tables 5-3 and 5-4. Saturated zone groundwaters are predominantly oxidizing, dilute (TDS about 4[illegible] mg/l; Raker and Jacobson, 1987) sodium bicarbonate solutions. The solutions are slightly basic (pH [illegible]) [illegible] tables. In addition to sodium bicarbonate, K^+, Ca^{++}, Mg^{++}, F^-, Cl^-, SO_4^{--} and NO_3^- are present in significant amounts. Solutions are relatively dilute, and concentrated brines have not been encountered in the area. From ultrafiltration, the total concentration of colloidal particles < 0.4 μm in diameter was about 2.7×10^{-5} g/l for J-13 well water (DOE, 1988). Chemical analysis indicates that the particles are predominantly silica, iron, calcium, aluminum, and sodium, which suggests that the particles are perhaps made up of clay and iron oxide. Total organic carbon (Means et al., 1983) is about 0.14 mg/l in J-13 well water. Oxygen and hydrogen stable isotope evidence indicates a relatively unexchanged meteoric origin for most waters, and radiometric (^{14}C) age-dating indicates that the residence time of the water is typically on the order of thousands of years (Benson and McKinley, 1985).

There is no readily accessible source of flowing groundwater at the Yucca Mountain site. Instead, water from the saturated Topopah Spring tuff in the J-13 well in Jackass Flats southeast of Yucca Mountain (Figure 5-1) has commonly been used as a reference groundwater in site characterization activities (DOE, 1988; Ch. 4). However, because the repository is planned for construction above the water table, the chemistry of the waters in the unsaturated zone is expected to be an important control on radionuclide transport. Experiments to extract waters from the fractured, unsaturated rocks at Rainier Mesa to the north of Yucca Mountain indicate

Table 5-3. ELEMENT CONCENTRATIONS IN GROUND WATER FROM THE VICINITY OF YUCCA MOUNTAIN (FROM DOE, 1988)

Well[b]	Field pH	Concentrations[a] (mg/L)								
		Ca	Mg	Na	K	Li	Fe	Mn	Al	Si
USW VH-1[c]	7.5	10	1.5	80	1.9	[illegible]				23
USW H-6	7.4	5.5	0.22	74	2.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
USW H-3	9.4	0.8	0.01	124	1.5	0.22	0.13	0.01	0.81	16.9
USW H-5	7.1	1.1	0.03	54	2.3	0.04	[illegible]		0.17	17.4
USW G-4	7.1	9.2	0.15	56	2.5	0.08	[illegible]	[illegible]	[illegible]	19.6
USW H-1[c]	7.5	6.2	<0.1	51	1.6	0.04				19
USW H-4	7.4	10.8	0.19	84	2.6	0.16	[illegible]	[illegible]	[illegible]	25.9
UE-25b#1	7.7	19.7	0.68	56	3.3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
UE-25b#1[e]	7.2	18.4	0.68	46	2.5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
UE-25b#1[f]	7.3	17.7	0.66	37	3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
J-13	6.9	11.5	1.76	45	5.3	[illegible]	[illegible]	[illegible]	[illegible]	30.0
UE-29a#2	7.0	11.1	0.34	51	1.2	0.10	0.05	0.01	0.04	25.8
J-12[c]	7.1	14	[illegible]	38	[illegible]					[illegible]
UE-25p#1[g]	6.7	[illegible]	[illegible]	[illegible]	13.4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[a] Concentrations from Ogard and Kerrisk (1984) unless otherwise noted

All samples are integral water samples unless otherwise noted

[b] See Figure 4-11 for locations

[c] Data from Benson et al. (1983)

[d] -- indicates the element was not detected

[e] Bullfrog zone, 4th day of pumping

[f] Bullfrog zone, 28th day of pumping

[g] From carbonate aquifer

Table 5-4. ANION CONCENTRATIONS AND OTHER MEASUREMENTS FOR GROUND WATER FROM THE VICINITY OF YUCCA MOUNTAIN (FROM DOE, 1988)

Well[b]	Concentrations[a] (mg/L)								
	F	Cl	SO_4^{2-}	HCO_3^-	NO_2^-	NO_3^-	O_2	Detergent	Eh[c]
USW VH-1[d]	2.7	11	44	167	--	-	--		--
USW H-6	4.1	7.7	27.5	--	--[e]	5.3	5.6	--	395
USW H-3	5.4	8.3	31.2	245	<0.10	0.2	<0.1	<0.02	123
USW H-5	1.3	5.7	14.6		--	8.6	6.3	<0.005	353
USW G-4	2.4	5.5	15.7	--	-	5.5	6.4		402
USW H-1[d]	1.0	5.8	19	122	-		-	-	--
USW H-4	4.5	6.2	23.9	-	-	4.7	5.8	[illegible]	216
UE-25b#1	1.2	7.1	20.6	-	--	0.6	1.8	-	220
UE-25b#1[f]	1.5	9.8	21.0	-	[illegible]	2.2	[illegible]	[illegible]	18
UE-25b#1[g]	1.2	6.6	20.3	--	--	4.5	[illegible]	[illegible]	160
J-13	2.1	6.4	18.1	143	[illegible]	10.1	5.7	[illegible]	[illegible]
UE-29a#2	0.56	8.3	22.7	-	--	18.7	5.7		[illegible]
J-12[d]	2.1	7.3	22	[illegible]					
UE-25p#1[h]	3.5	37	129	698		<0.1		[illegible]	[illegible]

[a] Concentrations from Ogard and Kerrisk (1984) unless otherwise noted.
All samples are integrated samples unless otherwise noted.

[b] See Figure 4-11 for location.

[c] mV versus H_2 electrode.

[d] Data from Benson et al. (1983).

[e] -- indicates the element was not detected.

[f] Bullfrog zone, 4th day of pumping.

[g] Bullfrog zone, 28th day of pumping.

[h] From carbonate aquifer.

that unsaturated water compositions vary significantly, and many analyses fall outside the range observed for saturated waters (White et al., 1980). Tri-axial compression and centrifugation of core obtained from tuff units at Yucca Mountain using dry-drilling techniques, has provided chemical and isotopic analysis of unsaturated zone fluids (Yang et al., 1988; Yang, 1991). Total concentration of dissolved solids is generally greater for these fluids than that for saturated zone waters. Oxygen and hydrogen stable isotopes indicate a fairly unexchanged meteoric source, and groundwater residence time is on the order of 1000 to 4,900 years based on limited ^{14}C age dating (Yang, 1991).

5.4. CONCEPTUAL MODEL OF HYDROLOGIC FLOW AT YUCCA MOUNTAIN

The performance of the proposed repository depends on its ability to isolate high level waste from the accessible environment. Ababou (1991) identifies the principle paths of transported radionuclides to the accessible environment as vertical migration downward through the unsaturated zone to the regional water table, near-horizontal migration to the lateral compliance boundaries of the controlled area, and upward migration to the ground surface.

Montazer and Wilson (1984) and Peters and Klavetter (1988) have developed a conceptual model of the hydrogeology at Yucca Mountain, and have provided a tabulation of the hydrologic properties of the key units in the vicinity. The volcanic pile is divided into three hydrogeologic rock types: (1) Densely to moderately welded tuffs that are highly fractured but have low saturated matrix conductivities (10^{-11} m/s); (2) Nonwelded, vitric tuffs that have few fractures and relatively high saturated matrix conductivities (10[illegible] to 10[illegible] m/s); and (3) Nonwelded, zeolitized tuffs with few fractures with low saturated matrix conductivities (10[illegible] m/s). The geologic media are both heterogeneous and anisotropic on a number of scales ranging from centimeters to kilometers. Fractures are frequently filled and sealed with secondary minerals, and lithostatic pressures typically result in a decrease in fracture conductivity with depth (Rush et al., 1984).

At present, vertical migration of the infiltrating fluids through the unsaturated zone is believed to be controlled by fractures related to the high-angle normal faults that are the dominant structural feature of the exploratory block (Montazer and Wilson, 1984; Peters and Klavetter, 1988). Due to a combination of the contrasting permeabilities of the different hydrogeologic units, dipping stratigraphy, and capillary barrier effects, there is a significant component of lateral flow in the nonwelded units (Figure 5-2). This lateral flow intersects the structural features controlling vertical flow, and contributes to the overall vertical fluid flux. Some matrix-matrix flow occurs, but capillary barriers tend to retard exchange between the matrix and the fractures. Although there is debate over the total amount of infiltration at Yucca Mountain, total infiltration into the Topopah Spring tuff proposed as a host for the repository is anticipated to be very small (~ 1mm/yr, Montazer and Wilson, 1984).

Hysteresis affects hydrologic properties as the media are periodically wetted and dried. Fracture flow are perturbed by these conditions. When the matrix of the medium is partially saturated, the fractures remain relatively dry due to capillary suction, although partial fracture saturation may be reached at points of contact between the matrix blocks. As matrix saturation increases, fracture saturation also increases in a nonlinear fashion (Peters and Klavetter, 1988). In the case of partially saturated vertical flow, the fractures begin to carry water at the point at which the flux in the medium exceeds the saturated conductivity of the matrix. Experimental data indicates that small-scale fractures may need to be saturated before larger fractures conduct water (Conca, 1990). In addition, experiments involving flow under nonisothermal, unsaturated conditions (Green and Dodge, 1991) suggest that, under certain conditions, fractures may act as barriers to fluid flow rather than serve as flow conduits. Sporadic occurrences of high-intensity rainfall that are typical of the arid climate at Yucca Mountain also lead to short term perturbations of the flow regime, such as the development of transient perched water. Although the time scale of these events is much shorter than the overall time of interest for waste isolation (1000 to 10,000 years), it may be inappropriate to neglect their effect (Abanou, 1991).

5.5. CRITICAL RADIONUCLIDES AND SORPTION STUDIES

Recent studies (Kerrisk, 1985; Oversby, 1987) have attempted to determine the radionuclides that will be of critical importance following the closure of the HLW repository. Based on anticipated waste inventories, and rates of radioactive decay, those radioelements have been identified that will require some sort of attenuation mechanism to meet NRC (10 CFR Part 60) and EPA limits (40 CFR Part 191) following the 300-1,000 year period prescribed for maintaining engineered containment. These elements are the most critical for focussing studies of sorption mechanisms and retardation processes.

5.5.1. Critical Radionuclides in HLW

For high-level waste, the absolute amount of a given radionuclide is determined by the type of waste (spent fuel vs. defense high-level wastes), the burnup history, and the age of the material. Because of variable half-lives among the radionuclides, different elements will be important at different times during the 10,000 year postclosure period (Kerrisk, 1985). In addition, EPA release limits will vary depending on the type of decay. Alpha emitters and those radionuclides that exhibit enhanced biological activity (^{14}C and ^{99}Tc) are considered more hazardous, and are assigned lower cumulative release limits [~100 Ci/1000 metric tons of heavy metal (MTHM)], while those elements that do not emit alpha particles have a slightly higher limit of 1000 Ci/MTHM. In general, however, the list of radioelements is fairly short. The actinides and their decay products include isotopes of Np, U, Pu, Am, Cm, Th, Ra, and Pa. Fission products include ^{137}Cs, ^{90}Sr, ^{99}Tc, ^{126}Sn, ^{135}Cs, ^{151}Sm, ^{79}Se, ^{129}I, and their short-lived daughter elements. ^{93}Zr, ^{63}Ni, and ^{59}Ni are cladding activation products, and ^{14}C results from the activation of ^{14}N in the fuel and cladding (Kerrisk, 1985).

Solubility limits of the elements may also play an important role in restricting the release of a given radioelement to the accessible environment. Those elements which are not readily dissolved in the groundwaters that may circulate through the repository are of less concern than those that enter solution readily (Table 5-5). Based on these considerations, Kerrisk (1985) has identified those elements where the ability of the geologic medium to retard

Table 5-5. WASTE ELEMENT SOLUBILITIES IN WATER FROM YUCCA MOUNTAIN (FROM KERRISK, 1985).

Element	Solubility (moles/liter)		
	Pressurized Water Reactor Spent Fuel	Pressurized Water Reactor High-Level Waste	Defense High-Level Waste
Np	1×10^{-3}	1×10^{-3}	1 x 10[illegible]
U	4×10^{-3}	4×10^{-3}	4 x 10[illegible]
Pu	1×10^{-5}	1×10^{-5}	1 x 10[illegible]
Am	1×10^{-6}	1×10^{-6}	1 x 10[illegible]
Cm	1×10^{-6}	1×10^{-6}	1 x 10[illegible]
Th	1×10^{-8}	1×10^{-8}	[illegible]
Ra	3×10^{-7}	3 x 10[illegible]	3 x 10[illegible]
Cs	large	large	large
S[illegible]	8×10^{-4}	8×10^{-4}	8×10^{-4}
Tc	large	large	large
C	large	4 x 10[illegible]	not present
I	large	2 x 10[illegible]	large
Sn	1×10^{-9}	1 x 10[illegible]	1 x 10[illegible]
Ni	1×10^{-2}	1 x 10[illegible]	1 x 10[illegible]
Zr	1×10^{-11}	1 x 10[illegible]	1 x 10[illegible]
Sm	2×10^{-4}	2 x 10[illegible]	2 x 10[illegible]

Table 5-6. RADIONUCLIDES NOT MEETING THE NRC TECHNICAL CRITERION ON RELEASE IF ONLY DISSOLUTION LIMITS RELEASE* (FROM KERRISK, 1985)

	Radionuclide Identity at Various Decay Times		
	10^3 year	10^4 year	10^5 year
Spent fuel	^{14}C	^{14}C	^{237}Np
	^{237}Np	^{237}Np	^{59}Ni
	^{59}Ni	^{59}Ni	^{99}Tc
	^{99}Tc	^{99}Tc	^{135}Cs
	^{135}Cs	^{135}Cs	^{226}Ra
	^{129}I	^{129}I	^{129}I
High-level waste	^{14}C	^{237}Np	^{237}Np
	^{237}Np	^{59}Ni	^{59}Ni
	^{59}Ni	^{99}Tc	^{99}Tc
	^{99}Tc	**^{135}Cs**	**^{135}Cs**
	^{135}Cs	[illegible]Pu	[illegible]Pu
	^{240}Pu	[illegible]Pu	
	^{239}Pu		
Defense high-level waste	^{59}Ni	^{59}Ni	^{59}Ni
	^{63}Ni	^{99}Tc	---
	^{99}Tc	^{234}U	^{234}U
	^{234}U	^{239}Pu	^{226}Ra
	^{241}Am	^{240}Pu	
	^{239}Pu		
	^{240}Pu		
	[illegible]Pu		

* Dissolution rates greater than one part in 10^5 per year of the 1000-year inventory of that radionuclide and dissolution rates greater than 1.7×10^{-5} Ci/MTHM year.

radionuclide transport will be most critical in meeting the performance objectives of the repository (Table 5-6). During the postclosure period from 100 to 10,000 years, Kerrisk (1985) has indicated that isotopes of Am, Pu, Np, and U will be the most important, due not only to their behavior, but also the quantities in which they are present in the waste. Isotopes of C, Ni, Zr, Tc, Ra, and Sn will also be present, but the amounts are anticipated to be less.

5.5.2. Radionuclide Sorption Studies

There have been a number of recent studies on the sorption properties of the important radionuclides in HLW. Several studies (Thomas, 1987; Beckman et al., 1988; Meijer, 1990) provide an extensive compilation and evaluation of the data generated by the DOE, particularly with respect to the characterization of Yucca Mountain. Unfortunately, a large amount of data was gathered prior to establishing consistent laboratory techniques, and frequently information crucial to the unambiguous interpretation of sorption results is missing. The following is a brief summary of the sorption experiments performed on important radionuclides. The reader is referred to the DOE studies mentioned above and the annotated bibliography in the appendix for more detailed information. In addition, the proceedings of the *Second International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Nov 6-10, 1989* contains a great deal of information on a number of the key radionuclides in HLW.

5.5.2.1. Uranium

Uranium is one of the best characterized of the important radionuclides. A large body of thermodynamic data is available on aqueous uranium species and uranium minerals (Langmuir, 1978a,b; Hsi, 1981; Wagman et al., 1982; Tripathi, 1984). In addition, uranium chemistry is believed to be analogous (Cotton and Wilkinson, 1976; Pabalan and Turner, 1991) to other actinides deemed important in HLW (Pu, Am, Np).

Uranium solubility is a function of both pH and Eh. It is generally considered insoluble in the reduced U(IV) state, and is dominantly transported in the oxidized U(VI) state, although Giblin and Appleyard (1987) note that concentrated polycationic (Na, K, Ca) brines are capable of transporting reduced uranium in measurable amounts. Aguilar et al. (1991) report that uranium dissolution is greatly enhanced by the presence of chloride in solution. At low pH values (< 6 at 25° C; Langmuir, 1978a), UO_2^{2+} is the dominant aqueous species. In the absence of complexing ligands, uranyl hydroxy complexes form and dominate uranium speciation at higher pH values. In the presence of atmospheric CO_2, however, uranium complexes with a variety of ligands, especially at higher pH in bicarbonate solutions such as those encountered at Yucca Mountain (Maya, 1982). Complexation is also significant with phosphate and fluoride in solution, although less than the degree observed for bicarbonate solutions. Phosphate complexation is considered an important factor in the mobilization and transport of uranium at the Koongarra uranium system, Australia (Payne et al., 1990b). Means et al. (1978b) suggest that the organic compound EDTA may also complex with uranium (and other actinides) in solution to reduce adsorption and enhance radionuclide mobility.

Sorption studies have been carried out for a variety of substrates by a number of authors (Ames et al., 1982, 1983a,c; Tripathi, 1984; Hsi and Langmuir, 1985). The studies by Ames et al. were batch sorption studies and revealed a temperature dependence, although the exact effect was dependent on the solid of interest. Ames et al. (1983a) also noted that removal of the iron hydroxides from solution decreased sorption, and resulted in a fit to a Freundlich isotherm rather than the more elaborate Dubinin-Radushkevich isotherm. Uranium sorption by iron hydroxides exhibits a sharp increase as a function of pH at a pronounced sorption "edge". This edge varies with solution composition, total uranium, and the substrate, but generally falls within the pH range of 2 to 6 (Figure 5.5). Means et al. (1978b) credit this effect to an increase in surface charge with pH. For iron oxyhydroxides, Tripathi (1984) and Hsi and Langmuir (1985) have attributed this to the predominance and adsorption of uranyl hydroxy complexes, and have simulated the effects of pH using a surface complexation model (TLM). Means et al. (1978b) suggest that Mn oxides are a better scavenger than iron oxyhydroxides, with higher negative surface charge and CEC over the pH range of natural waters. The exact nature of the dominant adsorbed uranyl complex is uncertain, but $UO_2(OH)^+$, and $(UO_2)_3(OH)_5^+$ have been proposed by Hsi and Langmuir (1985). The recent work of Choppin and Mathur (1991) suggests that, for neutral solutions, simple hydrolytic species such as $UO_2(OH)^+$ and $(UO_2)_2(OH)_2^{2+}$ are dominant in most solutions, and $(UO_2)_3(OH)_5^+$ is only important at high uranium concentrations. Tripathi (1984) suggests that $UO_2(OH)_2$ is the dominant hydrolytic uranyl species. At high pH values, sorption then decreases rather sharply, especially in the presence of carbonate ligands.

Carbonate complexation is observed to decrease uranium sorption (Ames et al., 1983a,c; Hsi and Langmuir, 1985), although this also depends on the substrate. Ames et al. (1983c) observed an increase in uranium sorption in $NaHCO_3$ solutions for muscovite. Because the stability of uranyl carbonate complexes is a function of pH as controlled by $P(CO_2)$, the presence of $CO_2(g)$ will influence the degree of complexation and therefore, the sorption behavior of uranium in solution. In batch equilibrium experiments investigating uranium sorption onto ferrihydrite [i.e., $Fe(OH)_3$] (Payne et al., 1990b), the presence of phosphate in solution (9.5 mg/l) shifts the uranium sorption edge to lower pH values (i.e., from pH ≈ 4-5 to pH ≈ 3-4). Varying ΣPO_4 at constant pH = 4.0 verified this effect. Because the total amount of phosphate in solution is small at pH = 4.0, Payne et al. (1990b) attribute this shift to surface effects rather than to the formation of uranyl phosphate complexes.

The relative importance of different uranyl species will vary with total uranium in solution (ΣU). Because uranium sorption is controlled by uranium speciation, ΣU will also influence sorption behavior. Although Ames et al. (1982, 1983a,c) noted a general decrease in sorption coefficients with increasing ΣU, this varies with the sorbent phase. In addition, pH, Eh, and $P(CO_2)$ were not controlled externally, and the interpretation of the data may be somewhat ambiguous. Over a range of pH values, Tripathi (1984) determined a general shift of the sorption edge to higher pH with increasing ΣU. Choppin and Mathur (1991) observed a general increase in polymerization of U(VI) through hydrolysis as ΣU increased.

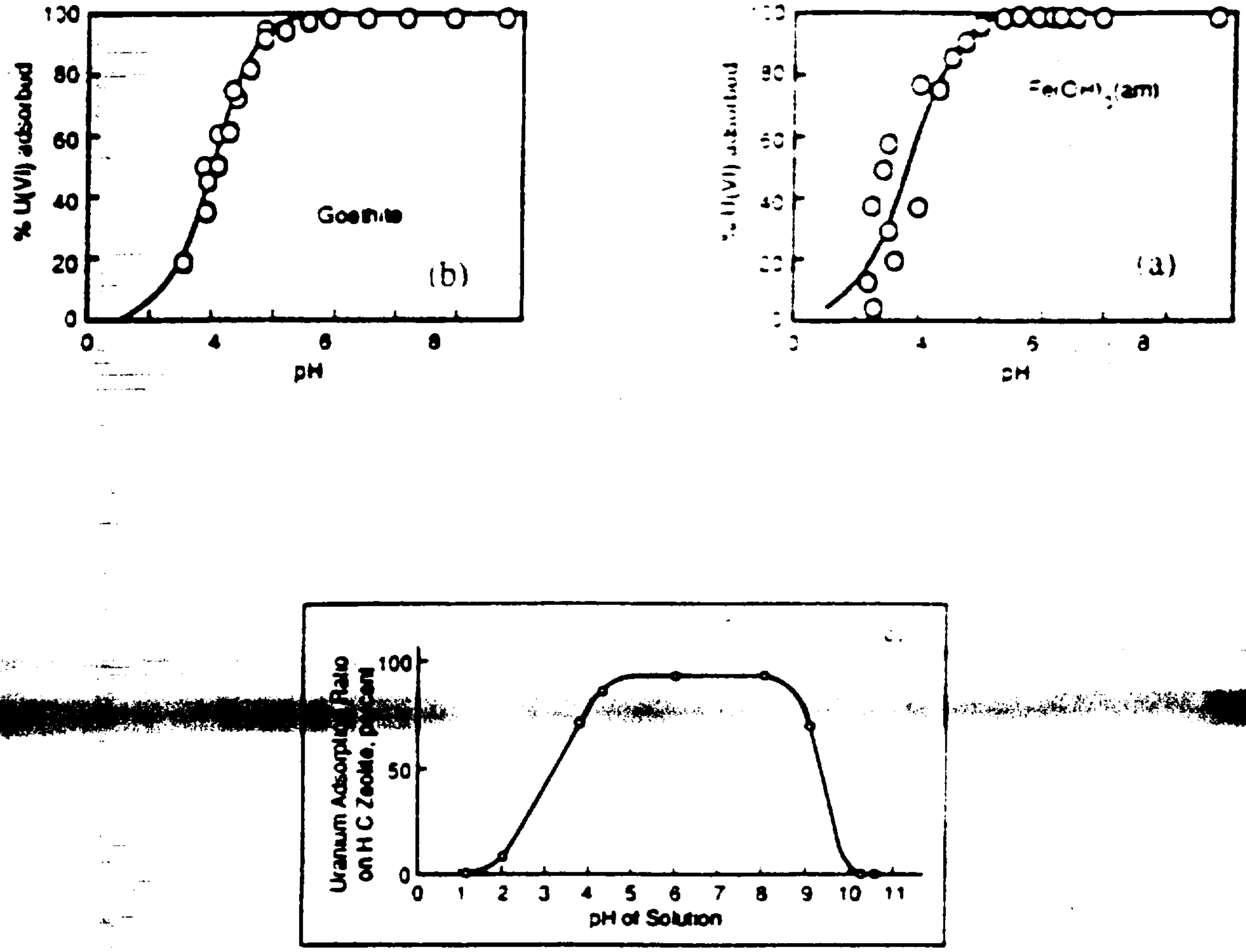

Figure 5-5. Uranium sorption vs. pH at 25°C and $\Sigma U = 10^{-5}$M in 0.1 M $NaNO_3$. Experimental results are shown by symbols, solid curves are calculated using a triple-layer surface complexation model for (a) amorphous $Fe(OH)_3$, and (b) Natural goethite (from Hsi and Langmuir, 1985); (c) The effect of pH on uranium sorption by heulandite-clinoptilolite (from Doi et al., 1975).

Little work has been done on the effect of competing cations on uranium sorption. Hsi and Langmuir (1985) determined that uranium sorption by iron hydroxides is not significantly affected by the presence of Ca^{2+} or Mg^{2+} in solution. In minerals such as clays and zeolites where ion exchange is expected to be the dominant sorption mechanism, however, sorption depends on the exchangeable cation. Uranium tends to b selected preferentially relative to monovalent cations, while divalent cations significantly redu uranium sorption (Tsunashima et al., 1981; Vochten et al., 1990). Based on field an experimental evidence, the presence of cations in solution, particularly Ca^{2+} and K^{+} in chloride brines, enhances the dissolution and transport of uranium in reducing environments (Giblin an Appleyard, 1987).

5.5.2.2. *Plutonium*

Plutonium is a redox-sensitive element, and although it shares ma characteristics with uranium, its chemistry is more complex due to the larger number of valen states and the ease with which it is hydrolyzed in water. Plutonium has four common oxidatio states, (III), (IV), (V), and (VI). For the +6 oxidation state, hydrolysis increases as a function of increases in both pH and total plutonium concentration (Choppin and Mathur, 1991). $pH=7$, hydrolysis becomes dominant at concentrations greater than 10[illegible] M, and spectrosco indicates that polynuclear species of Pu(VI) may be the predominant species at pH < (Okajima et al., 1991). In neutral solutions, Pu(IV)-hydroxide controls plutonium solub while in oxidizing solutions, Pu(V) and Pu(VI) are the dominant aqueous species [illegible] [illegible] readily forms carbonate complexes, and its speciation is therefore a function of p $P(CO_2)$ and Eh in a manner similar to uranium

In batch experiments with synthetic goethite, Sanchez et al. (1985 observed a sorption edge for Pu(IV) and Pu(V) similar to that for uranium. For Pu(IV), th edge occurs at pH 3-5, while it is pH 5-7 for Pu(V) (Figure 5-6). Pu(V) did not achie equilibrium adsorption during the experiment (20 days), and the sorption edge gradually shif to lower pH values as Pu(V) was reduced to the +4 state. Sanchez et al. (1985) used a trip layer model to simulate the adsorption of Pu(IV). The model predicted that in pure water, fo hydrolytic species, $Pu(OH)^{3+}$, $Pu(OH)_2^{2+}$, $Pu(OH)_3^{+}$, and $Pu(OH)_4^{0}$ are adsorbed by goethi Exchange studies using cation and anion resins on groundwaters at the Maxey Flats, Kentuck LLW site (Toste et al., 1984) indicate that Pu(III) and Pu(IV) may form soluble anionic species which are more mobile in groundwaters. Under oxic conditions, the authors report tha plutonium speciation is approximately 1/2 cationic, 1/4 anionic, and 1/4 neutral.

Carbonate complexation diminishes sorption, and at 20°C, alkalini greater than 1000 meq/l totally inhibited the adsorption of Pu(IV) by synthetic goethite (Sanche et al. 1985). As expected, carbonate complexation increases with increasing pH and P(CO Calculations by Murphy (1991) using the composite EQ3 database (Wolery et al., 1990) indic that for slightly basic solutions ($pH=8.6$) at 25° C, the dominant carbonate species $PuO_2(CO)_3^{2-}$. Changes in ionic strength were not observed to affect adsorption, and orga

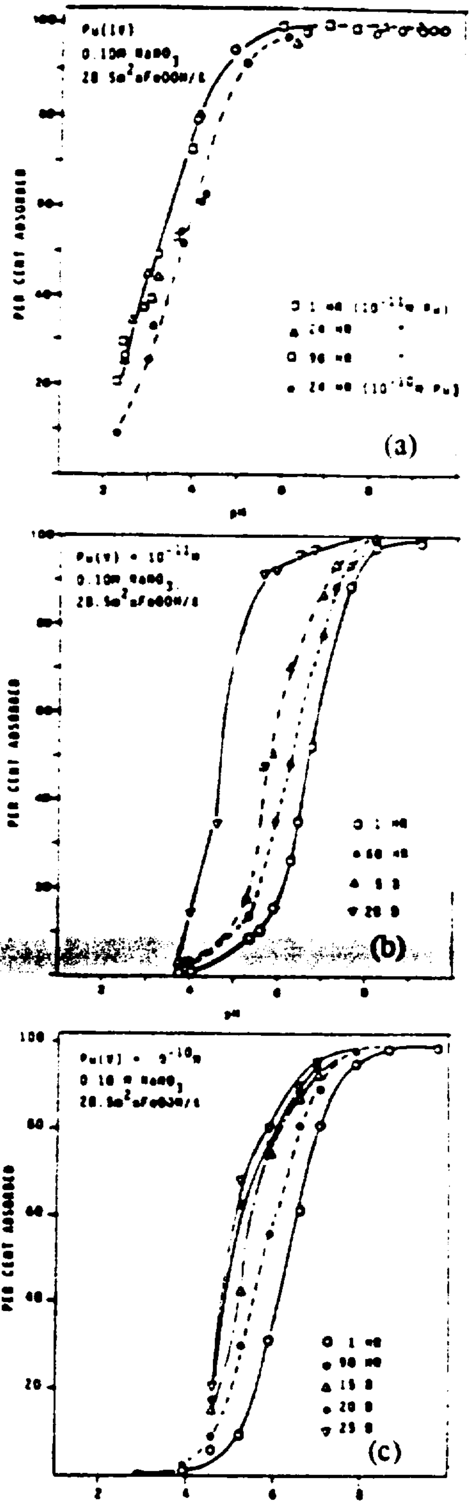

Figure 5-6. (a) Sorption of Pu(IV) onto goethite as a function of pH in 0.1 M NaNO, solution at $\Sigma Pu(IV) = 10^{-11}$ and 10^{-10} M, (b) Sorption of Pu(V) onto goethite as a function of pH in 0.1 M $NaNO_3$ solution at $\Sigma Pu(V) = 10^{-11}$ M, (c) Sorption of Pu(V) onto goethite as a function of pH in 0.1 M $NaNO_3$ solution at $\Sigma Pu(V) = 10^{-10}$ M (from Sanchez et al., 1985).

ligands were thought to modify adsorption through the reduction of Pu(V) to the more readily adsorbed +4 state (Sanchez et al., 1985).

The redox sensitivity and easy hydrolysis of plutonium leads to the ready formation of Pu-colloids in solution, and a subsequent decrease in sorption (McCarthy and Zachara, 1989). In the +4 state, Pu(IV)-colloid is stable relative to dissolved Pu^{4+} (Hobart et al., 1989). Berry et al. (1991) invoke the presence of microparticulates as a means of resolving an apparent increase in Pu(VI) sorption coefficients with increasing water rock ratios. Orlandini et al. (1990) report that in an oligotrophic lake in Wales, Pu(IV) is reversibly bound to organic colloidal particles in, while Pu(V) is non particle-reactive and readily passes through all particle filters. Over 80 percent of the plutonium is associated with particles from 5nm to > 450 nm, and in oxic waters, Pu, Am, and Th are distributed in a similar manner with respect to particle size. Penrose et al. (1990) determined that in the Bandelier Tuff at Los Alamos, NM, approximately 85 percent of the plutonium in solution was irreversibly bound to organic colloidal particles between 25-450 nm in diameter. Toste et al. (1984) report that Pu(III) and Pu(IV) colloidal particles enhanced migration from the Maxey Flats LLW site.

5.5.2.3. *Neptunium*

Neptunium is also a redox sensitive element, and can be present in oxidation states from +3 to +6 (Cotton and Wilkinson, 1976). Like uranium, Np(IV) is relatively insoluble under most conditions. Speciation calculations by Murphy (1991) using the EQ3 code and the composite database indicate that Np(V) is the dominant oxidation sta[illegible] solution in oxidizing solutions; at neutral pH, NpO_2^+ is the dominant species, while in the presence of CO_2, NpO_2CO_3 becomes increasingly significant at higher pH. Solubility decreases at higher pH values due to the formation of more insoluble Np carbonates. Calculations using available data indicate that neptunium exhibits a relatively high solubility in J-13 reference water (up to 10^{-4} M at 25° C; Murphy, 1991). Like plutonium, neptunium is readily hydrolyzed. At pH=7, polynuclear Np(VI) species will be dominant at concentrations greater than ~ 10[illegible] M (Choppin and Mathur, 1991), and in the absence of carbonate, NpO_2OH has been proposed as the dominant species at pH > 9 (Nakayama and Sakamoto, 1991).

Sorption experiments on neptunium exhibit some of the same characteristics observed for plutonium and uranium. Batch equilibrium experiments using whole rock wafers of crystalline granite indicate only partial sorption of Np(V) that is independent of rock mineralogy (Hakenen and Lindberg, 1991). In other batch experiments with iron oxyhydroxides and synthetic aluminum hydroxide, Np sorption exhibited a sorption edge pH ~ 6 to 8 (Meijer et al., 1989; Nakayama and Sakamoto, 1991) (Figure 5.7). For other natural minerals, sorption was only pronounced at pH > 9. Sorption coefficients for neptunium are relatively low (K_d=1-5 ml/g; Meijer, 1990), although they tend to be higher for carbonate bearing samples. Np-sorption reaches equilibrium rapidly, and experiments by Nakayama and Sakamoto (1991) indicate that the adsorption reactions are reversible. For experiments using distilled water, Meijer et al. (1989) report that while Np-sorption by Fe- and Mn-oxyhydroxides is relatively high, sorption by smectite and clinoptilolite remains relatively low. Kent et al.

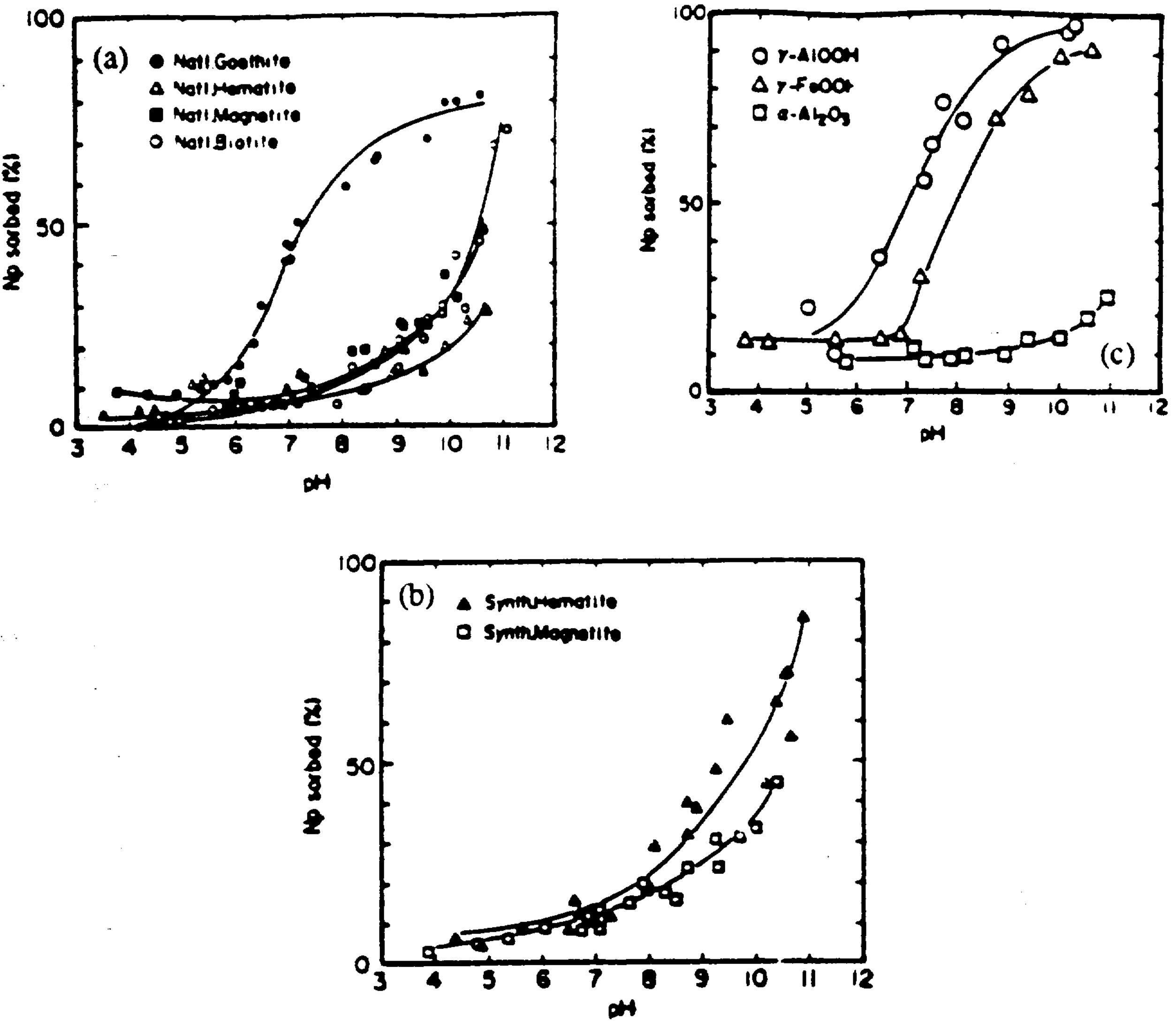

Figure 5-7. Sorption of neptunium at 30°C as a function of pH in 0.1 M $NaNO_3$ solutions. $\Sigma Np(V)=6x10^{-4}M$, and mass/volume ratio is 1 g/l. Substrates are: (a) naturally-occurring goethite, hematite, magnetite, and biotite, (b) synthetic hematite and magnetite, and (c) synthetic lepiodocrocite, boehmite, and alumina (from Nakayama and Sakamoto, 1991).

(1988) report the results of modeling Np(V) sorption by iron hydroxide at 25°C using a triple-layer surface complexation approach. Special attention is paid to the effect of hydrolysis and carbonate complexation, and activity coefficients are calculated using the Davies equation. The necessary TLM parameters are also reported. The sorption edge is observed between $pH = 5$ to 7, and in addition to pH and $P(CO_2)$, sorption was also observed to decrease slightly with decreasing Σ Fe.

5.5.2.4. *Americium*

Americium has been the focus of a large amount of work at the DOE. Its behavior is also similar to plutonium and uranium. The chemistry of americium is somewhat simpler than the other actinides because it is only stable in the +3 oxidation state observed under natural groundwater conditions (Cotton and Wilkinson, 1976; DOE, 1988, pg. 4-96). At 25°C and atmospheric $P(CO_2) = 10^{-3.5}$ atm, the carbonate complexes $Am(CO_3)^+$ and $Am(CO_3)_2^-$ are the most common species in solution at $pH > 7$. For $pH < 7$, Am^{3+} and $Am(OH)^{2+}$ are the dominant species (Meinrath and Kim, 1991), and in the absence of carbonate, at $pH < 6$, americium is present principally as free Am^{3+}, with negligible hydrolysis. At 25°C, americium is sparingly soluble in J-13 reference water (Meijer et al., 1989; Murphy, 1991). Solubility is controlled in bicarbonate solutions by the solid phase $AmOHCO_3$ in a range in pH common to natural waters (Nitsche, 1991; Murphy, 1991; Triay et al., 1991).

Sorption studies indicate that americium is strongly adsorbed in the pH range 7-8. Triay et al. (1991) performed batch sorption experiments using J-13 reference water with clinoptilolite, romanechite (a Mn-oxyhydroxide), and whole rock tuffs from Yucca Mountain. Calculated Am-sorption coefficients were high for the conditions of the experiment, ranging from 4900 for clinoptilolite to 330,000 for romanechite. The authors propose that Am-sorption occurs primarily by ion exchange for clinoptilolite, while surface complexation and subsequent chemisorption control sorption for the Mn-oxyhydroxide. The relatively large size of the Am-carbonate complexes could inhibit the ability of the clinoptilolite zeolite structure to accept Am. This mismatch may reduce the effectiveness of clinoptilolite as an Am-sorbent medium.

Like plutonium, americium is readily incorporated in colloidal particles. Penrose et al. (1990) observed that americium is predominantly associated with the colloidal fraction < 2nm in diameter, although the exact nature of the colloid is unknown. Migration was enhanced by colloid formation. Orlandini et al. (1990) determined that in oxic lake waters, > 80 percent of the americium was reversibly bound to particles > 450 nm in diameter. Estimated K_d values for binding to the colloidal particles were very high (470,000 for particles >450 nm), indicating that americium was preferentially associated with colloids relative to dissolved species in solution (Orlandini et al., 1990). Kim (1991) investigated the generation and migration of Am-colloids, and noted that Am(III) was readily adsorbed by alumina colloidal particles in the pH range 4-6, the range in which it is readily hydrolyzed (Figure 5-8).

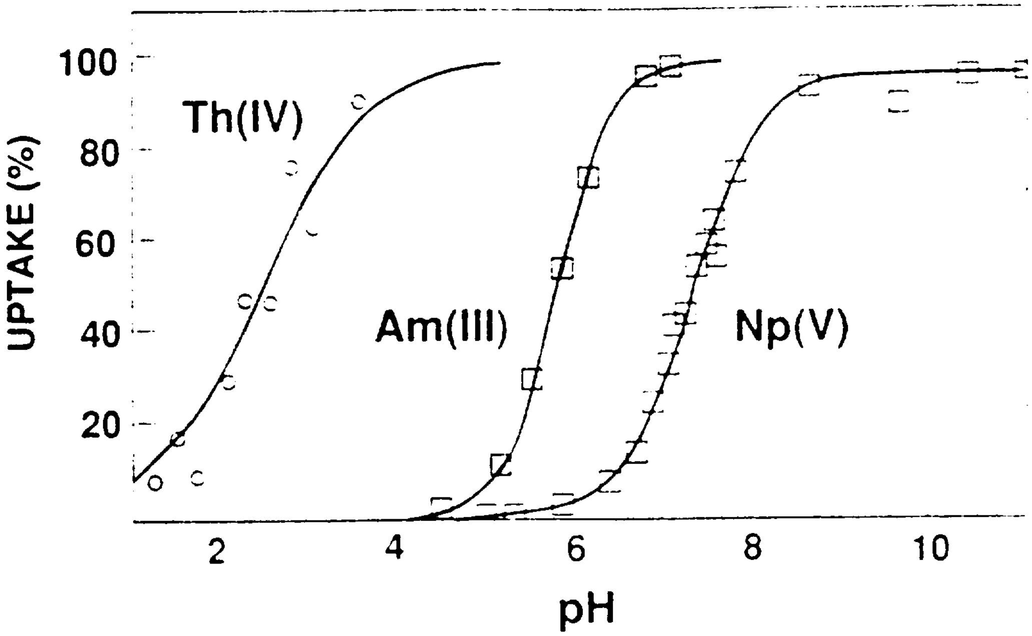

Figure 5-8. Sorption of Th(IV), Am(III), and Np(V) onto alumina colloids as a function of pH. Alumina concentrations are 10 ppm for Th(IV) and Am(III), and 200 ppm for Np(V) in 0.1 M $NaClO_4$ (from Kim, 1991).

5.5.2.5. Technetium

Technetium occurs in nature principally in the +4 and +7 oxidation states. In the +7 oxidation state, technetium tends to form the anionic complex TcO_4. Because the negative charge greatly reduces retardation in a negatively charged medium and enhances mobility, Tc is of concern in the meeting the performance objectives of the proposed repository (Kerrisk, 1985). Due to this effect, Tc-sorption is sensitive to the redox conditions of the solution (Figure 5-9). At neutral pH values, under aerobic conditions, Tc is primarily present in the +7 state, and sorption coefficients are correspondingly low (K_d = 0.1 to 0.3 ml/g; Lieser and Bauscher, 1988). Under reducing conditions, however, Tc(VII) is reduced to Tc(IV) and sorption coefficients rise markedly to K_d=1000 ml/g. At lower pH values of ~4, Tc(VII) is reduced to the +4 state at higher values for Eh, and Tc-sorption can be maintained over a greater range in Eh.

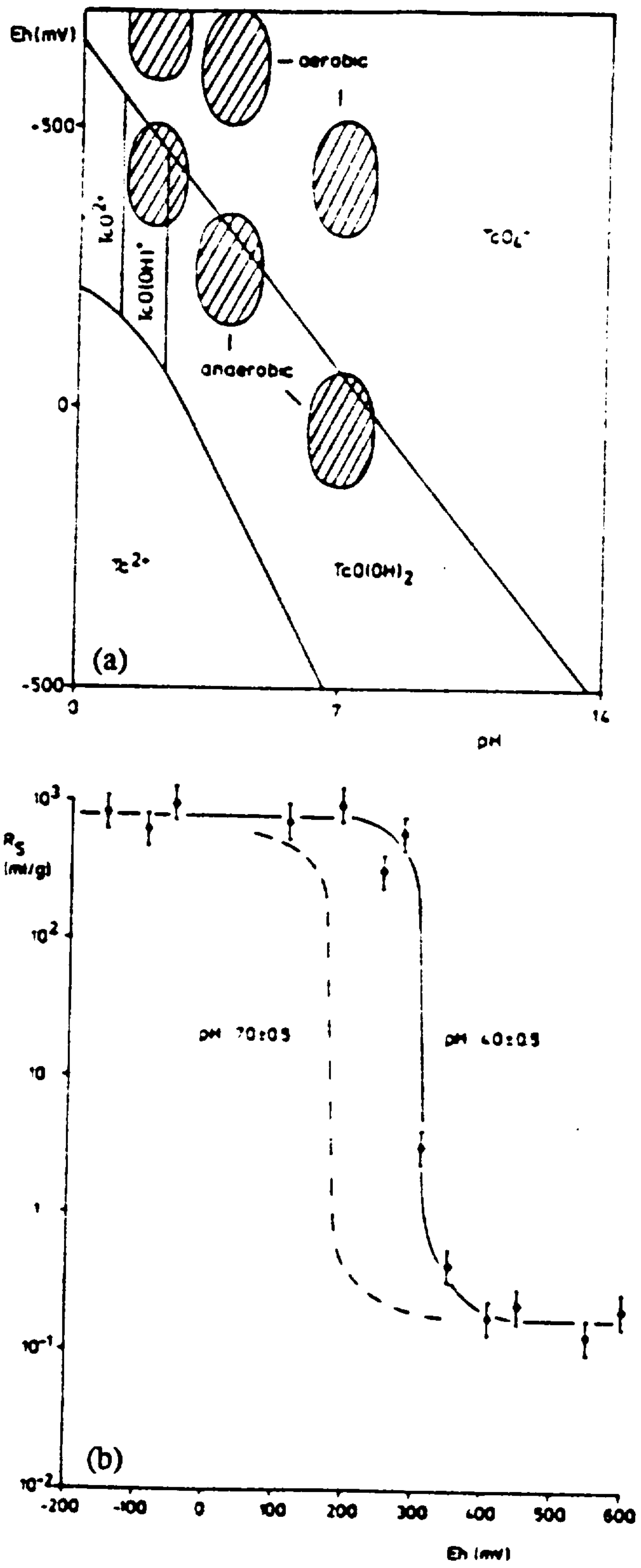

Figure 5-9. (a) Thermodynamic stability fields of Tc species as a function of Eh and pH. (b) Sorption ratios ($R_s = K_d$) for Tc as a function of Eh at pH = 4.0 and 7.0 (from Lieser and Bauscher, 1988).

Organic compounds (e.g., EDTA) do not significantly affect Tc sorption under aerobic conditions. Under anaerobic conditions, however, organics serve as reductants of TcO_4^-, and result in increased adsorption. In addition, Tc(V), which is readily adsorbed, is stabilized by complexation with EDTA (Lieser and Bauscher, 1988). Bock et al. (1988) and Lieser and Bauscher (1988) have studied the sorption of Tc by natural sulfide minerals. In general, the sorption ratios for pyrrhotite are larger than those for pyrite, galena, or sphalerite. This is probably due to the formation of Tc_2S_7, which is relatively insoluble, removing Tc from solution through precipitation. In addition, hydrolysis of pyrrhotite forms H_2S which will decrease pH during oxidation to H_2SO_4, which also increases sorption under constant redox conditions (Lieser and Bauscher, 1988). Bock et al. (1988) suggest that the key role of sulfides may be in the reduction of Tc^{7+} to Tc^{4+}. Lieser and Bauscher (1988) only detected Tc^{7+} in solution, and did not report any colloid formation.

6. SUMMARY AND CONCLUSIONS

6.1. SORPTION MODELS

Sorption is clearly a critical process that must be considered in any performance evaluation of a potential repository site. Models that vary greatly in terms of the degree of flexibility and theoretical basis have been developed to address sorption, each offering its own advantages and disadvantages. Empirical models are simple, but cannot discriminate between retardation mechanisms, and extrapolation to conditions beyond the experimental conditions used to determine the necessary parameters is frequently unjustified. Mechanistic models offer more flexibility, but the number of parameters is large, the necessary data are frequently inadequate, and coupling with flow transport requires a sophisticated geochemical model to monitor changes in fluid and mineral chemistry along flow paths.

Empirically-derived models tend to present simple relationships with discrete values for sorptive properties. They can be efficiently incorporated into transport codes; solution requires a minimum of additional computational effort, while the empirical nature of the models eliminates the need for sophisticated geochemical equilibrium codes. The experiments to determine the necessary parameters are relatively straightforward, and a great deal of effort has already been devoted to developing and maintaining a data base for a variety of radionuclides and sorbent media of interest to the Yucca Mountain project. Sorption, however, is a function of a number of physicochemical properties of both the solution and the solid media along likely fluid flow paths to the accessible environment. If sorption modeling is to take advantage of the computational simplicity offered by empirical strategies, empirical models must be adapted to a variety of physical and chemical conditions.

One approach is to develop a deterministic computational mesh discretized to include variations in sorption properties on a scale representing observed geologic heterogeneity (Meijer, 1990). With this strategy, it may be possible to use bounding conditions to establish conservative limits on sorption for the purposes of performance assessment. However, because the bounding conditions for sorption by a given medium will vary with the radionuclide of interest, an exact simulation would require the construction of a similar computational mesh for each element under consideration. In addition, because the physicochemical conditions will change as a function of time as well as space, each matrix that contains the necessary properties for each element must be reconfigured at each point in time and space where changes in the system are considered significant enough to affect sorption processes. Because a number of conditions interact in a complex manner to affect sorption, it will be difficult to create a relatively static mesh that adequately considers transient effects. In order to achieve the desired level of confidence, this type of methodical approach may demand a large database of empirical coefficients determined for a large range of conditions. This in turn will require a large number of experiments to determine the necessary parameters, and may also lead to excessive computational and computer memory requirements, severely reducing the desirability of the model.

A number of simplifying assumptions can be made in an effort to minimize some of the complications inherent in a methodical application of empirical models. One is to limit the number of radionuclides being monitored. This can be done either through focusing on those elements that are anticipated to be most important in terms of the makeup of the high-level waste and/or constitute the greatest biological hazard (e.g., U, Pu, Np, Am; Kerrisk, 1985), or by combining those elements that exhibit similar sorption characteristics (e.g., Am and Nd). A further simplification can be made by considering the least sorptive phase of the least sorptive unit for a given radioelement along likely flowpaths to the accessible environment. If the performance objectives (10 CFR 60.112 and 40 CFR Part 191) can be met assuming these characteristics, then the degree to which other units are able to sorb the radionuclide of interest may only need to be considered in as much as it provides additional assurance of a margin for error. This also introduces the additional possibility that more elaborate sorption models may not be necessary if a minimal amount of sorption is adequate to meet the defined performance objectives (Serne et al., 1990).

If solubility controls under anticipated conditions limit a given radioelement to very small concentrations in solution (e.g., Am), then sorption may not be as critical in meeting performance objectives as compared to those radionuclides that are readily dissolved. Finally, sensitivity analyses may identify the most critical variables in determining the sorptive behavior of a given radionuclide. Once these parameters are determined, it may be justifiable to disregard or discount other parameters of lesser importance. In the example of oxides, pH and complexation are observed to determine sorption to a large degree, and any consideration of sorption by these minerals should clearly include these effects.

A more desirable approach, perhaps, is the development and use of robust and flexible mechanistic models, such as surface complexation and ion exchange. Many of the simplifications discussed above for empirical models are also appropriate in the application of these more sophisticated approaches. In theory, using well-defined sorption relationships, and a database containing the necessary equations of state for pressure-temperature variations, these models can readily extrapolate to a variety of conditions and include the effects of a variety of properties. In practice, however, the number of adjustable parameters increases with model sophistication, and many of the necessary data (such as protonation/deprotonation equilibrium constants, site density, etc.), are missing, particularly for radioelements. In addition, many sorption experiments have been conducted without providing the degree of characterization necessary to justify their use in more sophisticated models. Faced with this lack of data, the application of mechanistic models reduces to a curve fitting exercise, losing the advantage of a theoretical basis, and increasing the likelihood of non-unique solutions.

In addition to gaps in the existing database, the feasibility of coupling sophisticated sorption models to transport codes must also be considered. The computational effort involved in performing the sorption calculations, and the geochemical calculations to provide the necessary information on solution chemistry, are extensive. Barring the development of more efficient computer technologies and algorithms, the use of a sophisticated sorption model may preclude the incorporation of reaction kinetics, colloidal transport, microbial activity, competitive sorption, radioactive decay, and more complex fluid chemistries.

In summary, a mechanistic approach to sorption can provide the flexibility necessary to consider a wide variety of physicochemical conditions that is lacking in empirical models. Because of the additional characterization of both the fluid and the medium required for the application of sophisticated sorption models, however, whole rock experiments on materials of complex mineralogies may not be appropriate for developing a suitable database. Experiments need to be designed and conducted in relatively simple, well-characterized systems with the goal of providing the necessary data, before complexation and ion exchange models can be rigorously applied to radioelement sorption.

6.2. HYDROGEOCHEMICAL TRANSPORT MODELS

As discussed in section 2, a number of processes in addition to sorption contribute to the retardation (or acceleration) of radionuclide migration. In order to account for the relative importance of each of these mechanisms, it is necessary to use a model that can distinguish between them. A code should also offer a variety of sorption options in order to evaluate the suitability of different approaches to modeling sorption. User-friendliness will simplify the application of the model to a variety of environments, and enhance the interpretation of the results. A number of codes currently available or in development can perform the necessary calculations to a limited extent, with varying degrees of efficiency, accuracy, and user friendliness.

Coupling of chemical equilibria and mass transport may be accomplished using either a direct coupling approach or a two-step iterative approach (Yeh and Tripathi, 1989). Although a direct approach is more exact, a two-step approach is more efficient and offers the best hope for extending coupled reactive solute transport into two- and three-dimensional simulations. This efficiency also offers the most promise for the incorporation of more detailed and complex geochemical processes such as kinetics, colloidal transport, and microbial activity as data become available, without overtaxing available computer resources. An additional consideration is the use of stochastic models in probabilistic assessment of the role of unsaturated flow and geologic heterogeneities in solute transport. These models frequently rely on performing large numbers of calculations (e.g., Monte Carlo approach) to develop the necessary population statistics. Computer intensive geochemistry calculations may be inappropriate for this type of approach, and severely limit the application of currently available hydrogeochemical codes in stochastic modeling.

The accuracy of geochemical simulations will largely depend on the database employed in the equilibria calculations (Kincaid et al., 1984a,b). Thermodynamic data on many important radionuclides are highly uncertain, particularly for redox sensitive elements such as plutonium and neptunium that are susceptible to hydrolysis. Also, the current data are too sketchy and poorly constrained to address colloidal transport and microbial activity quantitatively. The importance of these processes at Yucca Mountain should be determined, however, before a great deal of effort is expended in developing an organic chemistry data base.

Because empirical models are independent of solution chemistry and speciation, the additional effort in coupling a sophisticated geochemical code with an empirical approach that does not use the calculated chemistries may be unnecessary. Computational capability that would otherwise be necessary to perform equilibrium calculations may be freed up by a simplified geochemical approach, and used to address problems (such as radioactive decay) that are currently intractable with more elaborate, computer-intensive geochemical models. Where the coupling of empirical sorption strategies with geochemical codes will be justified, however, is in performing sensitivity analyses in simple, well-defined systems to evaluate the importance of a given sorption model.

In the initial stages, a coupled hydrogeochemical model should be applied to a well-constrained system such as a laboratory column experiment. This may validate the code, at least on a small scale, and support the selection of the strategy used to address sorption and other retardation mechanisms. With increasing scale and scale-induced heterogeneity, the validation of the code will be more tenuous as interactions become increasingly complex. It is therefore important to judiciously apply the code to well-characterized, controlled field experiments (such as the Las Cruces Trench) in order to eliminate as many extraneous variables as possible. Intermediate-scale caisson experiments (Fuentes and Polzer, 1987) may provide a valuable bridge between the laboratory and the field.

A number of natural and anthropogenic analogs may be appropriate for modeling sorption on geologic scales of space and time. Uranium mining operations and mill tailings offer the opportunity to examine the migration of a relatively well characterized radioelement that is a large component of the anticipated high level waste inventory. Autoradiography may provide information on the critical sorbing phases in the system. It is difficult (Erikson et al., 1990) to unambiguously define boundary and initial conditions in these environments, however, and the data needed for the evaluation and application of reactive transport codes may be subject to a great deal of subjective interpretation and uncertainty. It is also important to remember that most large scale geologic analogs present a time-integrated picture of the net effect of a number of complexly interrelated processes that have operated in the past. Given the relatively large uncertainties in most age-dating techniques, it may be impossible to uniquely separate out the roles played by the various mechanisms for the purposes of model validation.

6.3. RECOMMENDATIONS

The overall performance objectives defined by 10 CFR Part 60 and 40 CFR Part 191 are concerned with the transport of radionuclides from the proposed repository to the accessible environment. In order to evaluate the role of retardation mechanisms in attenuating this migration, it is necessary to have a detailed understanding of the environment through which the fluids will pass. Planned site characterization activities are described in detail elsewhere (DOE, 1988), and include evaluation of mineralogies, heterogeneities, porosity, permeability, the presence of colloids, fractures, and fluid chemistries. Evaluation of sorption at Yucca Mountain must be considered in the context of these activities in order to limit the amount of experimental effort required to provide the necessary data for modeling radionuclide migration.

Because sorption is highly dependent on the mineralogy of the sorbing medium, an initial step in applying sorption modeling to the Yucca Mountain site will involve characterizing the most likely flow paths from the repository to the accessible environment. This will require, in part, some understanding of the systematics of fracture versus matrix flow in the unsaturated zone, and the effect of geologic heterogeneities. If flow is predominantly through the fractures, then it may be more appropriate to model sorption using the secondary minerals found lining the fractures. If matrix flow is more likely, then the primary tuff minerals (and matrix secondary alteration minerals) will be more suitable. Also, matrix flow may be slow enough that the importance of sorption in meeting performance objectives is reduced. A groundwater travel time analysis [10 CFR 60.113(a)(2)] linked to the regulatory framework of the repository may provide some insight into the importance of sorption processes in meeting EPA and NRC release limits. Indeed, if groundwater travel time is shown to be slow enough that these limits can be achieved in most cases without retardation, then the need for sophisticated sorption models is mitigated. If, however, some degree of retardation is required to meet performance objectives, then additional investigation of sorption becomes necessary.

Once the principal sorbing minerals along flow paths have been identified, it may be possible to make some simplifying assumptions based on an understanding of how these minerals interact with the radioelements in solution that are of principal concern. Secondary minerals such as zeolites and clays may be successfully modeled assuming ion exchange as a principal sorption mechanism, while surface complexation would be more suitable for modeling Fe- and Mn-oxyhydroxides. Based on this strategy, it should be possible to identify gaps in the existing database and either generate the needed experimental data, or estimate the necessary parameters using an approach similar to that outlined by Dzombak (1986) for the diffuse-layer model, and Smith and Jenne (1988, 1991) for the triple-layer model. Complicating factors such as colloidal transport and microbial activity may be important, but the current levels of understanding of these processes at Yucca Mountain are inadequate for quantitative evaluation. Future site characterization should be conducted to evaluate the importance of these factors.

At the same time that the geologic media are characterized, the fluid chemistries and physical (temperature, pressure) conditions likely to be involved in transporting radionuclides from the repository should also be identified. Ideally, compositional and physical extremes would be used to establish bounding limits on retardation for comparison to regulatory requirements. In practice, however, the various radionuclides interact with fluids and solids in a complex, nonlinear fashion, and bounding limits cannot easily be determined for the system. A more realistic goal may be modeling of fluid chemistries along critical flow paths, given a reasonable starting composition. If radioelement concentrations in solution are extremely dilute (10^{-7} M or less), then radionuclide transport may have minimal effect on the gross attributes of the solution, and fluid composition will be controlled by mineralogy and solubilities along the flow path. Fluid evolution can be simulated through the use of geochemical codes.

As outlined above, further simplification may be possible in dealing with the various radioelements. Focusing on a particular, well-characterized radioelement such as uranium may provide an opportunity to use more mechanistic approaches to modeling sorption. Investigation and evaluation of various retardation mechanims for this system may lead to simplifications in the approach taken with less well understood analogous elements, such as the actinides. Additionally, the wide variety of natural occurrences of uranium provides a number of opportunities for the development and application of natural analogs in evaluating sorption models and validating hydrogeochemical transport codes. Once these assumptions are made, a coupled hydrogeochemical model can be applied to simple, laboratory scale systems designed to approximate conditions anticipated along the fluid flow path (mineralogy, saturation, fluid chemistry, etc.). The principal objective of this application should be code validation, and sensitivity analyses to determine the most important factors governing radionuclide transport through the medium. Once the most critical factors influencing retardation have been identified, it may be possible to make further simplifications, and apply the model judiciously to more complex systems such as controlled field experiments, or well characterized natural analogs.

The strategy outlined above is highly idealized, and a great deal of the applicability of this approach will depend on the degree to which the repository system can be characterized, gaps in the geochemical database identified and filled, and predictive models developed. The additional constraints of computer technology, analytical capability, data availability, and the timeframe in which the work must be accomplished (NWPAA, 1987) will undoubtedly require compromises that are difficult to predict given the present level of understanding. It is important to recognize, however, that the aim of modeling sorption in high level waste disposal is not the exact solution of the problem, but rather, evaluating compliance with defined performance criteria using scientifically defensible predictive methods. Given this goal, it may be possible to provide the necessary degree of predictive certainty, despite the limitations of currently available understanding of a number of very complex and interactive processes.

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APPENDIX A:

ANNOTATED REFERENCES

Abeliuk, R., and H. W. Wheater. 1990. Parameter identification of solute transport models for unsaturated soils. *Jour. Hydrol.* *117*: 199-224

The authors propose using parameter estimation techniques to solve inverse problems using a full numerical model. Parameter relationships are defined a priori and estimated by optimization techniques. This approach can lead to nonunique solutions, and can also lead to problems in extrapolating beyond the range of the calibration data set. The authors selected a central-differencing model that has been validated against simple analytical solutions. The inverse problem derived 1-, 2-, and 3-parameter models of hydrodynamic dispersion. The 2-parameter model was found to be both flexible and adequate. The 3-parameter model was redundant, and while the 1-parameter model does eliminate the problem of nonunique solutions, it is less flexible than the 2-parameter model. The result of the exercise is that for the soils considered, several parameterizations of the coefficient of hydrodynamic dispersion produce identical performance in simulating non-reactive solute transfer. The authors identify potential parameters such as moisture content, molecular diffusion, and specific discharge. Only 1-parameter forms were uniquely identifiable, and the authors warn that the techniques are of possibly of dubious value beyond the range of the observed system states.

Alemi, M. H., D. A. Goldhamer, and D. R. Nielsen. 1991. Modeling selenium transport in steady-state, unsaturated soil columns. *Jour. Environ. Qual.* 2[illegible]

The authors have performed batch adsorption studies, selenium transformation studies, and unsaturated column experiments to examine selenium transport. Because linear regressions of sorption/concentration data was poor, the batch data was fit to Freundlich sorption isotherms. Rates of transformation of selenium to a volatile state were also examined. Reduction to more immobile forms was believed to be the more dominant transformation process. Saturated flow was obtained in the column experiments. K_d values from the batch experiments did not adequately fit the column data. The data was adequately fitted using the convection dispersion equation with a retardation factor and an adjusted K_d. Selenate sorption was observed to be greater under reducing conditions.

Allison, J. D., D. S. Brown, and K. J. Novo-Gradac. 1990. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual.* Environmental Research Laboratory, Office of Research and Development, Environmental Protection Agency, Athens, GA.

MINTEQA2 is an established geochemical equilibrium code developed by the EPA to calculate chemical interactions between solid, gas, and aqueous phases. These calculate speciation, precipitation/dissolution, and adsorption/desorption. PRODEFA2 is an interactive code developed to aid the user in building input files for the MINTEQA2 code. Input is described and sample input/output files are provided. Mathematical and chemical approaches used by the code are described. MINTEQA2 offers seven sorption models, and can accommodate up to five different surfaces in a single run, with up to two kinds of sites for each surface. The program treats the sorption site as a new type of component. The user specifies the surface "concentration" and other surface specific parameters. The seven models are divided into two categories: non-electrostatic and electrostatic. The non-electrostatic models include: (1) Activity K_d. This provides an unlimited number of sites, and is unable to incorporate competitive sorption; (2) Langmuir adsorption. Establishes an upper limit on the number of surface sites; (3) Freundlich adsorption. An exponential rather than a linear equation. Like the activity K_d model, this model has no upper limit on the number of sorption sites; (4) Ion exchange. This approach assumes that the site is initially occupied by some exchangeable species. The user specifies reaction stoichiometries, selectivity coefficients, and the initial ion occupying the exchange sites. Electrostatic models include: (1) Constant capacitance. Only one diffusion layer. Specifically adsorbed ions define the surface charge (sigma) and influences the diffuse layer charge (sigmad), and net charge is zero. The user inputs the number of sites, the specific surface area of the solid, and the concentration of the solid in solution; (2) Diffuse layer. These models differ from the constant capacitance models in the function used to relate total surface charge to surface potential. The constant capacitance model is a special case of the diffuse-layer model for solutions of high ionic strength and surfaces of low potential; (3) Triple Layer Model. This model invokes an inner (o-plane) layer that hosts protonation deprotonation reactions. Specifically adsorbed ions are assigned to the second (beta) layer. Non-specifically adsorbed ions reside in the outer, or d-layer The author is required to enter two capacitance terms and three electrostatic components for each run

Ames, L. L., J. E. McGarrah, B. A. Walker, and P. F. Salter. 1982. Sorption of uranium and cesium by Hanford basalts and associated secondary smectite. *Chem. Geol.* 35: 205-225.

Batch equilibrium experiments were conducted to examine Cs and U sorption by crushed basalts from Hanford, WA and associated secondary smectite. Synthetic groundwaters typical to the area were used in experiments run at 23 and 60 degrees C for 60 days. A positive correlation was found between surface area and cation exchange capacity (CEC). After considering several isotherms, the data were fitted using a Dubinin-Radushkevich (D-R). Cs distribution coefficients are generally higher than those for U, especially for a smectite substrate. Temperature effects for Cs are also more pronounced than those for uranium, with a decreasing sorption maxima with increasing temperature. In contrast, uranium sorption increases with increasing temperature due to the thermal instability of uranyl carbonate. After removal of hydrous ferroxides (HFO) from the system, uranium sorption decreased and the D-R isotherm reverted to a simple Freundlich isotherm.

Ames, L. L., J. E. McGarrah, and B. A. Walker. 1983a. Sorption of trace constituents from aqueous solutions onto secondary minerals. I. Uranium. *Clays Clay Mineral.* 31: 321-334.

Batch equilibrium experiments were performed at 5, 25, and 65 degrees C to examine the effects of solute concentration, temperature, solution compositions, on the sorption of uranium onto secondary minerals. These minerals include kaolinite, montmorillonite, silica gel, opal, nontronite, glauconite and clinoptilolite. The study begins with a literature review of uranium sorption studies. Natural minerals were used, and all had a degree of solid solution. $NaHCO_3$ and NaCl solutions were used to introduce uranium to the sorbent phases. Redox, pH and $P(CO_2)$ were not controlled externally. The sorption data is reported in tables, and was fitted to a Freundlich isotherm. The calculated distribution coefficients (D) indicate that sorption generally decreases with increasing temperature in NaCl solutions. In $NaHCO_3$ solutions, U-sorption is generally lower than that in NaCl solutions, but sorption increases with temperature, probably due to the thermal instability of uranyl carbonate complexes. Sorption generally increases with decreasing uranium concentration. Addition of ferric oxyhydroxide increased sorption by secondary minerals by as much as two orders of magnitude, and the data was observed to fit a Dubinin-Radushkevich sorption isotherm rather than a Freundlich isotherm.

Ames, L. L., J. E. McGarrah, and B. A. Walker. 1983b. Sorption of trace constituents from aqueous solutions onto secondary minerals. II. Radium. *Clays Clay Mineral.* 31: 335-342.

Batch equilibrium experiments were used to investigate radium sorption onto clinoptilolite, montmorillonite, nontronite, opal, silica gel, illite, kaolinite, and glauconite. Experiments were run using both NaCl and $NaHCO_3$ solutions, but since $NaHCO_3$ had little effect (i.e., no Ra-carbonate complexing), more effort was concentrated on NaCl experiments. There was no external control on redox or pH of the solution, and experiments were run for 30 days at 5, 25, and 65 degrees C. A modified Freundlich isotherm was fit to the data. In this relative sense, Ra-sorption decreased in order from clinoptilolite, nontronite, glauconite, montmorillonite, kaolinite, opal, and silica gel (K_d ~ 30,000 ml/g). The best sorbent phases are those secondary minerals with the highest exchange capacities (except montmorillonite). In general, Ra is more strongly sorbed than uranium, and except for glauconite and nontronite, sorption decreases with increasing temperature. Sorption increases with solute concentration, and for clinoptilolite, Ra-sorption also increases with NaCl. Precipitation is proposed as a radium removal mechanism.

Ames, L. L., J. E. McGarrah, and B. A. Walker. 1983c. Sorption of uranium and radium by biotite, muscovite, and phlogopite. *Clays Clay Mineral.* 31: 343-351.

Uranium and radium sorption by natural biotite (Bt), muscovite (Mu), and phlogopite (Ph) can be described by a Freundlich isotherm. The authors stress that K_d isotherms are only useful for the temperature (T), pH, solution composition, and uranium concentration of the experiments. Surface area, cation exchange capacities (CEC), and anion exchange capacity (AEC) for uranyl carbonate were determined for the micas used as the sorbent phase. Micas with low CEC showed the highest AEC for uranyl carbonate, although AEC is a function of the measured ion. In batch equilibrium experiments, U was introduced in both NaCl and $NaHCO_3$ solutions (for carbonate complexation), while Ra was studied using only NaCl solutions. Experiments were conducted for 30 days at 5, 35, and 65 degrees C, and solution pH and Eh were not externally controlled. For low-U NaCl-solutions, U-sorption on both Mu and Bt decreased markedly with T. Temperature-dependence decreased for with increasing U concentration. For a $NaHCO_3$ solution, U-sorption behaved similarly to that for an NaCl solution, but total sorption was greatly enhanced, for Mu and reduced significantly for biotite. This is likely due to carbonate complexation in the bicarbonate solution. The author presents tables of calculated Freundlich constants. With increasing T, Ra-sorption increased for Mu, while decreasing for Bt. At higher T, Ra-precipitation occurred. For phlogopite, U sorption increased with increasing T for both NaCl and $NaHCO_3$ solutions, although sorption for $NaHCO_3$ is very low (K [illegible] 2 ml/g). The authors conclude that Ra appears to compete with alkaline earths, while U travels mainly as carbonate and hydroxide complexes.

Balistrieri, L. S., and J. W. Murray. 1986. The surface chemistry of sediments from the Panama Basin: The influence of Mn oxides on metal adsorption. *Geochim. Cosmochim. Acta 50*: 2235-2243.

Trace metals in marine sediments are released as Mn and Fe oxides are reduced. K values are used in a comparative sense only, because this approach is only of limited value in discriminating between processes. Marine sediments from the Panama Basin and synthetic goethite and buserite (Mn-oxide) are used in 45 to 50 day batch experiments at constant pH (~7.6), T (25° C). A W R ratio effect is observed on K, with an initial increase in K with increasing particle concentrations. For concentrations greater than 400 mg/l, most K_d's are independent of particle concentration. Two mechanisms are proposed to explain this effect: (1) colloid formation controls solute uptake at lower concentrations, while adsorption becomes proportionately more critical at higher concentrations, (2) particle aggregation occurs at higher particle concentrations to reduce effective adsorption surface area. K [illegible] comparison. For a given surface non normalized K_d varies by 4 to 5 orders of magnitude for different metals sorbing to the same substrate, and 1/2 to 2 1/2 orders of magnitude for the same metal adsorbing to different solids. Three trends are observed: (1) Sc, Be, Cs are associated with aluminosilicates; (2) Fe, Sn, U, Pb, and Pu are associated with Fe oxides; (3) Mn, Cd, Ba, Co, Ni, Zn are associated with Mn-oxides. Increasing solid Mn content increases the loading of Zn, Co, Cd, Ba, and Pb. Cs, Be, Sc, Sn, Pu, and Fe are not affected.

Barnes, C. J. 1986. Equivalent formulations for solute and water movement in soils. *Water Resourc. Res.* 22: 913-918.

The author notes the mathematical similarity between solute movement through saturated soils, and water movement in unsaturated soils. Using this similarity, the mathematical equivalence is developed for the test case one dimensional, steady flow at uniform moisture content in an isotropic, homogeneous medium. The author points out that the application need not be restricted to this case. Small time and large time solutions are developed, and the nonlinearity of adsorption isotherms is considered. Anion exclusion (i.e. a negative isotherm) is discussed, and it is noted that excluded volume decreases with solute concentration. Multi dimensional and flux-concentration relations are discussed, and a mathematical formulation for solute-flux concentration is developed.

Barnes, C. J. 1989. Solute and water movement in unsaturated soils. *Water Resourc. Res. 25*: 38-42.

The author points out that for unsaturated conditions where convective velocity and water content are varying, one cannot simply relate solute and water transport. Formal similarity only holds for constant velocity of solutes in soils with uniform water contents. The author then develops a theory of coupled solute/water movement, with special attention paid to the case where hydraulic conductivity (K,) is dependent on concentration of the solute. A one-dimensional, nonswelling soil, with nonhysteretic water characteristics and an unspecified, nonlinear sorption isotherm are used in the model. The modified method of characteristics (Lagrangian concept) is used in defining the problem. Both coupling and decoupling of K, and solute concentration were modeled. For fully coupled transport (K, depends on concentration, and saturation (S) depends on moisture content), the solute and water fronts will separate at a more rapid rate than in the uncoupled case. The model tracks N+1 subfronts for a solution containing N solutes, and the ordering of the individual subfronts will depend on solute velocities, which in turn are dependent on the interaction terms (K, and competitive adsorption terms).

Barry, D. A. 1990. Supercomputers and their use in modeling subsurface solute transport. *Rev. Geophys. 28*: 277-295.

A review of the use of supercomputers to model solute transport. The governing equations are developed, followed by numerical solution techniques (direct methods, iteration, preconditioned conjugate gradient method). A variety of data analysis (Bootstrapping, jackknifing, cross validation) and data display techniques are also discussed. The author points out that the problem of nonisothermal, multiphase, multispecies, density-dependent solute transport in a variably saturated heterogeneous porous media is beyond the limits of current computing technology. Assumptions to simplify the problem include an isothermal system (i.e. thermal density effects are negligible), non-deformable media, and system closed to the production or removal of the solute of interest. The author addresses stochastic modeling, and includes a theoretical treatment of the derivation of the governing equations for the ensemble mean concentration by averaging over the velocity field. Particle tracking is also mentioned as a numerical technique for reactive and nonreactive solute transport. The DYNAMIX code, which solves for reactive transport by assuming complete mixing of aqueous species, is mentioned. The paper states that this code can be modified to handle more complex adsorption/desorption models than are currently used.

Beckman, R., K. Thomas, and B. Crowe. 1988. *Preliminary Report on the Statistical Evaluation of Sorption Data: Sorption as a Function of Mineralogy, Temperature, Time, and Particle Size*. Los Alamos National Laboratory, LA-11246-MS, Los Alamos, NM

The study reports the results of sorption experiments conducted at Los Alamos on tuffs from Yucca Mountain. The authors use the sorption ratio (R_d) instead of the distribution coefficient (K_d) since K_d implies equilibrium which is often not reached in the laboratory. At equilibrium, $R_d = K_d$ and can be used to define a retardation factor (R_f). The authors discuss the sorption database of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. The database includes particle size, T, pH, atmosphere of the experiment, concentration, experiment length, batch sorption ratio, desorption time, batch desorption ratios, and references. The information is classified according to tuff type. Regression techniques are used to identify key factors affecting sorption. These include a check of covariance between variables and the statistical significance of the data. The key factors controlling sorption appear to be sorption time, particle size, and mineralogy. The authors present a preliminary analysis of drill set data. Sorption ratios are generally highest for zeolitized and clay-altered tuffs. Sample mineralogy was estimated, and weighted sorption ratios determined for composite rocks. The authors conclude that predicted sorption values should be used with care. Frequently the data are too few, and the parameters are too highly correlated to make a generalized interpretation.

Bock, W.-D., H. Bruhl, C. Trapp and A. Winkler. Sorption properties of natural sulfides with respect to technetium, *Scientific Basis for Nuclear Waste Management XII*, Eds. W. Lutze and R. C. Ewing, Materials Research Society, Pittsburgh, PA, p. 973-977.

The article addresses the sorption of (TcO_4) by natural sulfides such as pyrite, pyrrhotite, stibnite, galena, and loellingite ($FeAs_2$). Batch, flow through column, and recirculation column experiments were performed on natural mono-mineralic fillings, mineral mixtures, and natural sediments. There is increasing fixation of technetium with increasing amounts of sulfides, decreasing volume/mass ratios, and decreasing Tc concentration. There appears to be a decrease in pH for pyrite due to oxidation and hydrolysis, and sorption increases with decreasing pH. In general, for times longer than 70 days, sorption decreases such that Pyrrhotite ~ Stibnite > Galena > Loellingite > Pyrite > Chalcocite > Sphalerite. Reduction of Tc^{7+} to Tc^{4+} may be most important requisite to sorption. The results indicate that near equilibrium requires long-term experiments, and constant monitoring of fluctuations in Eh and pH which lead to an "aging" of the precipitates, and the release of coprecipitated or adsorbed radionuclides. Materials Research Society Symposium Proceedings

Bond, W. J. 1986. Velocity dependent hydrodynamic dispersion during unsteady, unsaturated soil water flow: Experiments. *Water Resour. Res.* 22: 1881-1889.

The author examines the effect of the velocity dependence of hydrodynamic dispersion on solute transport under unsteady, unsaturated flow conditions. The velocity dependence is particularly important at short times or high inflow rates. The study develops an approximate analytical solution to evaluate the problem using a moving coordinate Q. One dimensional column experiments were designed such that unsteady, unsaturated flow was reached through wetting fine sand. From experimental results, an empirical relationship between the hydrodynamic dispersion coefficient (D) and the Peclet number (Pe) is developed for tritium transport. The relationship predicts normalized tritium activity well, and does not require the invocation of a large immobile water component, as has been the case in other experiments. The author suggests that part of the reason may be due to the fact that rather than relying on wetting the medium, these experiments were performed such that variable saturation was reached by draining a saturated soil column. This has resulted in a greater likelihood of isolated porosity (and immobile water).

Bond, W. J., and I. R. Phillips. 1990a. Approximate solutions for cation transport during unsteady, unsaturated soil water flow. *Water Resour. Res.* 26: 2195-2205.

This article provides 1-dimensional approximate analytical solutions for the transport of a single reactive solute in unsaturated porous media. No particular form of exchange equation or adsorption is assumed, and the method is suitable for any non linear adsorption isotherm, although the exact approach taken depends on the shape of the adsorption isotherm. Adsorption is assumed a function of solute concentration alone. Other assumptions include: local equilibrium, equilibrium adsorption, constant total charge concentration in solution and solid, dispersion and the shape of the adsorption isotherms are viewed as noninteracting and can be effectively uncoupled and then recombined, water content and pore water velocity are treated as constant in the region of dispersion, no preferential flow, no production or decay of solute, and the soil is infinite in both the positive and negative direction of transport. Using a moving coordinate system (LaGrangian method of characteristics), the authors derive analytical solutions for both linear and non-linear adsorption isotherms. The derivation is applied to the three isotherm types of Lai and Jurinak (1972): (1) a "favorable" isotherm that is convex upward for adsorbed concentration(q) vs. solute concentration in solution(c) (i.e., $d^2q/dc^2 < 0$); (2) an "unfavorable" isotherm that is concave upwards ($d^2q/dc^2 > 0$), and: (3) a multisite isotherm that is both concave and convex. Non-linear adsorption causes spreading of the solute front, even in the absence of dispersion. In addition, for nonlinear adsorption the position of the solution phase front and the sorption front are not the same. Under unsteady flow conditions, uncoupling the concentration profiles due to dispersion and to nonlinear adsorption introduces some error which becomes less at longer times. For favorable isotherms, all concentrations must advance at the same rate in the absence of dispersion, and an exact analytical solution is possible. The concentration profile defined is not constant for all times. For the multisite isotherm, the favorable and unfavorable segments of the isotherm are treated separately. The isotherm results of batch Ca-Na-K studies, with diffusion coefficients derived from the values for the individual ionic species, are compared to the predicted values with good agreement.

Bond, W. J., and I. R. Phillips. 1990b. Ion transport during unsteady water flow in an unsaturated clay soil. *Soil Sci. Soc. Amer. Jour.* 54: 636-645.

A Lagrangian approach is used to model solute transport for a series of unsteady, unsaturated Na-Ca-K column exchange experiments on initially Ca-saturated soils. Anion exclusion is determined to accelerate anion transport. Magnitude of the effect, modeled as reduced permeability, depends on surface area and charge density, ambient concentration of soil solution, and valences of the anions and cations in the soil. When expressed in terms of activity ratios, exchange isotherms for Na-Ca and K-Ca fall on a single curve for each system over a range of solution concentrations. Provided that there are no zones of preferential flow, the front of non-reactive solute approximates the water front. The position of the reactive solute front is a function of x, t, and alpha, where alpha depends on the nature of reactions between the solute and the solid phase. For excluded anions, alpha is a function of water content, concentration, and bulk density. For exchangeable cations, alpha is a function of density and K_d (either linear or non-linear K_d). Alpha is then used to predict reactive solute front location. Since the non-reactive (tritium) and the water front is essentially the same, it is assumed that no immobile water was present. Anion content of the infiltrating solution is the only characteristic affecting transport by anion exclusion. For Cl, if mass balance is preserved, excluded water content is not a unique function of solution composition and ion valence for a given soil. Assuming linear exchange, a favorable exchangeable cation profile (ECP) is predicted to move ahead of solution-cation profiles, and are sharp and steep. For unfavorable ECP's, the profile still moves ahead in a diffuse fashion. The model calculates the center of mass of the profiles of total cation concentration per unit soil volume. Since K-Ca is more favorable than Na-Ca exchange, it is expected to be less retarded. Experiments, however, show that they are the same. This is assumed to be due to the fact that the infiltrating solution is homoionic and the initial concentrations of Na and K in solution are small. The effective K_d approach of Valocchi (1984) is completely general, and can be applied regardless of the reactive solute

Bond, W. J., and I. R. Phillips. 1990c. Cation exchange isotherms obtained with batch and miscible-displacement techniques. *Soil Sci. Soc. Amer. Jour.* 54: 722-728.

The authors compare results from standard batch equilibrium experiments with those from unsteady, unsaturated, miscible displacement destructive sampling techniques (Phillips and Bond, 1989). The authors point out some of the drawbacks to batch equilibrium including: breakdown of soil aggregates and solubilization of soil components due to agitation, soil/solution ratios that are much smaller than those in natural soil systems, and changes in solution concentration and composition during the equilibration period. Miscible-displacement does not suffer from these problems. Two types are described, those that rely on destructive sampling, and those used to analyze breakthrough curves (BTC). The method of Phillips and Bond (1989) is of the first type. The results for Na, Ca, Mg, are essentially the same for the two methods, suggesting that the miscible displacement technique is a feasible alternative to batch equilibrium studies. The microscopic Peclet number (Pe) is used to determine how well equilibrium was approached. A

Pe less than one indicates a time scale for diffusion less than that for advection, and sufficient time was available for diffusion of Na and K into soil aggregates.

Bond, W. J., and P. J. Wierenga. 1990. Immobile water during solute transport in unsaturated sand column. *Water Resourc. Res. 26*: 2475-2481.

Column experiments are treated as one-dimensional vertical/horizontal transport of a non-reactive solute through a nonaggregated, loamy fine sand to confirm the presence or absence of immobile water in unsaturated media for steady and unsteady flow. The first test for the presence of immobile water is tailing in the breakthrough curve (BTC). Approximate analytical solutions for both steady and unsteady flow, with and without immobile water are developed and fitted to the data. Immobile water is required to match the observed BTC for steady flow. There is only a small amount of deviation, so only a small amount of immobile water is inferred. For unsteady flow, however, the equation without immobile water described the data from all but one experiment very well, and no immobile water is inferred. Column orientation does not affect the fit. The authors explain the differences in terms of wetting patterns. For the unsteady case, tracers are carried into wetted pore spaces by advection, with little diffusion. In the steady case, water flow is already established, and is biased towards larger pores, resulting in the formation of immobile zones, although this is slow relative to the time-scale of the experiment.

Bradbury, J. W., D. J. Brooks, and T. Mo. 1988. Effects of evaporation in unsaturated fractured rock on radionuclide transport. *EOS 69*: 1209.

ABSTRACT - Mechanisms in unsaturated fractured rock affecting contaminant transport have recently taken on particular importance since the Department of Energy was directed to characterize the Yucca Mountain site repository. For example, evaporation, or drying of the rock, has commonly been viewed as a mechanism that would reduce radionuclide migration to the accessible environment, because water is considered the dominant transporter of most radionuclides. However, significant gas flow in boreholes in unsaturated fractured tuff has been observed in both Yucca Mountain (Weeks, 1987) and Apache Leap (Rasmussen, 1988) fractures. At large negative pressures, fractures in unsaturated media have generally been viewed as barriers to ground water flow with most of the flux occurring in the porous matrix (Preuss and Wang, 1987). By coupling radionuclide-bearing matrix flow toward the fracture surfaces with evaporation at those surfaces, aided by significant gas flow, fractures can be viewed as features where radionuclides are concentrated. This paper presents analyses of the information supporting evaporation on or near fracture surfaces which could lead to enhanced radionuclide migration under transient fracture-flow conditions.

Bresler, E. 1973. Simultaneous transport of solutes and water under transient unsaturated flow conditions. *Water Resourc. Res.* 9: 975-986.

This is an early paper in unsaturated solute transport. The author develops the governing convection-dispersion equation for one-dimensional vertical transport of a nonreactive solute. The model ignores sink/source and adsorption effects. The underlying assumptions include the validity of Darcy's law in the unsaturated zone. An implicit finite difference solution to the transient one-dimensional case is developed, with mass balance checks for convergence. The agreement with a steady-state analytical solution is excellent. The numerical solution is also compared to field infiltration data. Agreement is generally good. Based on these comparisons, the author concludes that the diffusion of solute under the conditions of the field experiment are negligible. Mechanical dispersion is only important during the infiltration period in regions close to the welling front. Soil diffusivity becomes more important as velocity decreases.

Bresler, E., and G. Dagan. 1981. Convective and pore scale dispersive solute transport in unsaturated heterogeneous fields. *Water Resourc. Res.* 17: 1683-1693.

The study investigates transport of non-reactive solutes in unsaturated, horizontally heterogeneous soils using a stochastic approach to hydrodynamic properties. The model neglects pore-scale dispersion, and attributes solute transport to fluid convection alone. Additional assumptions include: negligible heterogeneity and steady water flow in the vertical direction only. A model is developed where scaled hydraulic conductivity (Y), Recharge (R), and dispersivity (gamma), are variables of interest. For a given run, two of these variables were treated as random, and the third was considered as deterministic. Solute transport is governed by 3 non-linear interacting processes: (1) fluid convection where velocity profiles vary spatially, (2) unevenly distributed recharge; (3) variable dispersivity. In applying the model, the main effect of process (3) is to smear out sharp concentration fronts, with little effect on solute distribution. If larger, field-scale dispersivities are used to reflect heterogeneity, however, the effect of variable dispersivity can become significant. The effect of process (2) varies significantly over the maximum allowed range. Over a more restricted, reasonable range, the effect is not significant, but process (2) becomes more important for a more uniform soil. Fluid convection is by far the most important process controlling solute distribution. This is perhaps not surprising, given the initial assumption that solute transport is by fluid convection alone. The authors conclude that since the effect of processes (2) and (3) are relatively minor, they can be treated as constants, and only the variability in hydraulic conductivity (K_s) needs to be considered. In general, however, even average solute distribution is not well solved by the Convection-Dispersion equation using constant coefficients for all hydrodynamic properties.

Burns, R. O., T. S. Bowers, V. J. Wood, J. D. Blundy, and M. E. Morgenstein. 1989. Reactivity of Zeolites Forming in Vitric Tuffs in the Unsaturated Zone at Yucca Mountain, Nevada. *Proceedings from Nuclear Waste Isolation in the Unsaturated Zone: Focus '89* 101 - 112.

The authors give thermodynamic stability relations of clinoptilolite and other zeolites with relation to J-13 water, and the effect of Na-Ca substitution and temperature on stability. Clinoptilolite at Yucca Mountain is considered an important sorptive barrier to contaminant transport. Na-substitution is observed to decrease the clinoptilolite stability field, as is increasing temperature. K-clinoptilolite may be stabilized at higher temperatures. Clinoptilolite also exhibits high cation exchange selectivity for Cs and to a lesser extent Sr. Previous experiments did not account for crystallographic orientation, solid solutions, and mineral heterogeneities, whereas this study reports on oriented crystals. Cs exchange experiments were performed in a shaking bath at 60 degrees C. The effect of Cl- and/or HCO_3-solutions were also studied, as were the effects of competitive sorption between Cs, Sr, and Ba. Crystal orientation affects both Cs- and Sr-sorption. The experiments suggest that 010 dominated crystals are less effective at sorbing Cs, particularly in sodium bicarbonate groundwaters. Competition with Sr and Ba also lowers Cs-sorption considerably.

Butters, G. L., W. A. Jury, and F. F. Ernst. 1989a. Field scale transport of bromide in an unsaturated soil. 1. Experimental methodology and results. *Water Resourc. Res.* 25: 1575-1581.

The authors report the results of a field study of non-reactive solute (Br) migration. The field-size is 0.64 ha, and slow drip irrigation was used to maintain unsaturated steady flow conditions. Pulse input of NaBr was used as a tracer, and sampling was performed to 4.5 m depth. Average mass recovery of about 100 percent indicates efficient sampling. Breakthrough curves (BTC) varied with location. The authors attribute this to tortuosity. Spatial variation is assessed using spatial distribution of the so-called transport volume (or pore volume water content). Variability between sites is blended together through averaging to produce a field average BTC for each depth. For field-average solute concentrations: (1) Maximum field solute concentration decreases with depth; (2) Mode or mean of the average concentration increases linearly with depth; (3) Distributions are positively skewed; (4) the BTC become more symmetrical with depth. The study indicates the importance of vertical variability in addition to lateral variability. The volume of water necessary to move the center of mass of a solute pulse to a given depth is greatly in excess of the average pore volume, indicating the tortuosity of the solute transport paths.

Butters, G. L., and W. A. Jury. 1989b. Field scale transport of bromide in an unsaturated soil 2. Dispersion modeling. *Water Resourc. Res.* 25: 1583-1589.

The authors use the results from the field scale study reported in Butters and Jury (1989a) to validate; (1) a deterministic convection-dispersion (CDE) model, and, (2) stochastic-convective

lognormal model (CLT). Neither the CDE nor the CLT predicts the early breakthrough or tailing of the breakthrough curve (BTC), although the CLT does a better job. The authors suggest that assuming Fickian diffusion is therefore, not appropriate. The CDE underpredicts the maximum depth of solute penetration. The apparent decrease and then increase in field-scale dispersivity with depth is not possible in a macroscopically homogeneous soil. Possible explanations include: (1) Finer-textured soil inducing an increase in lateral mixing; (2) finer-textured soil preserving local variations in water flux, assuming no increase in lateral mixing. The authors conclude that many homogeneous soil models are calibrated from shallow experiments, where there is an observed linear growth in dispersivity. Because changes in dispersivity are apparently non-linear with greater depth, these models will not be accurate below the depth of calibration.

Carroll, S. A., and J. Bruno. 1991. Mineral-solution interactions in the U(VI)-CO2-H2O system. *Radiochim. Acta 52/53*: 187-193.

Surface area was determined for an analysis grade calcite powder. For sorption isotherm experiments, initial $P(CO_2)$ were chosen at 0.97 and 0.1 atm. Final values were [illegible] after one month of reaction. Kinetic experiments were performed using a thin film continuous flow reactor which allows changes in solution chemistry without disturbing the solid phase. A Vanselow exchange reaction is described for $(UO_2)^{2+}$ and Ca^{2+} at the mineral-solution interface, and mass action equations are developed using an exchange constant K_v. In the isotherm experiments, less than two percent of U(VI) was removed from solution, and no coprecipitation was observed. Increasing $P(CO_2)$ from 10^{3} to 10^{2} stabilizes uranyl carbonate species relative to hydroxyl species at lower pH. U-sorption increases with aqueous concentration up to surface site saturation. If physical processes control sorption, then aqueous concentrations should be controlled by U- and Ca-carbonate solubilities, assuming ideal solution, $\log\{Ca^{2+}\}/\{UO_2^{2+}\}$ should be independent of pH. However, the observed pH-dependence indicates that adsorption is a chemical surface process, not a physical one. The limited adsorption is probably due to large U(VI) - O bonds in solution relative to Ca ionic radii (up to 2.43 angstroms for U-carbonate complexes). The kinetic studies confirm the control of U adsorption by surface reactions. Weak sorption to calcite is anomalous compared to other trace elements. Other studies indicate that Am^{3+} and Nd^{3+} sorption to calcite is quite extensive.

G. A. Cederberg. 1985. *TRANQL: A Ground Water Mass-Transport and Equilibrium Chemistry Model for Multicomponent Systems*. Ph.D. Dissertation. Stanford Univ., Stanford, CA.

Several sorption models and coupling models are discussed, and their application and limitations are addressed. These include a mixing cell approach for coupling, the effective K_d approach for sorption of Valocchi (1984), and the direct coupling of mass transport and chemical equilibrium. TRANQL uses a two-step approach, resulting in a set of differential equations for solute transport coupled to a set of algebraic equations describing chemical equilibrium. A solution is reached by iteration between the two equation sets. Mass transport is solved using a Galerkin

Finite Element approach, while chemical equilibrium incorporates the Newton-Raphson iterative scheme. The TRANQL version described incorporates the MICROQL (a scaled down version of MINEQL) geochemical code, and is limited to fewer than thirteen components and thirty species by the database. Sorption is modeled using surface complexation, and the specific case of Cd migration in a Cl/Br solution is evaluated. Organic acids can also be investigated using a constant charge model for sorption. Using aquifer porosity and bulk density, sorption sites are treated as one of many components. Mass balance is used as a check. Mass transport also includes a source/sink term for a given species due to aqueous complexation. Mean dispersivity is used, and molecular diffusion is assumed negligible. Binary and ternary systems are possible, as is a two-dimensional application. The current application assumes local chemical equilibrium and unit activity, and is limited to a one-dimensional, isotropic medium. Input requires knowledge of the stability coefficient of the sorbed phase (a function of pH), surface site necessary, and fluid composition. Reactions must be established by the user for complexation/dissolution for all species of interest. The sorption equilibrium constants that result from each characterization of the sorbing substrate must be determined for each multicomponent/porous medium.

Cederberg, G. A., R. L. Street, and J. O. Leckie. 1985. A groundwater mass transport and equilibrium chemistry model for multicomponent systems. *Water Resour. Res.* 21:1095-1104.

The authors discuss the one-step approach to coupling fluid flow and solute transport by incorporating all of the interaction chemistry directly into the transport equations. This approach is more rigorous, but it is also more cumbersome. The coefficient matrix must be solved for each time step, and the sorption isotherms must be known explicitly. For this reason, TRANQL employs a two-step approach to solve the geochemical equilibria separately, and pass on the resulting algebraic relations to the transport portion of the code. This approach has the advantage of being quicker, since the coefficient matrix is not solved at each time step, and because the chemistry is reduced to a set of algebraic equations, it is not necessary to have the sorption isotherm defined explicitly. The authors present a one-dimensional version of TRANQL, stating that the code is adaptable to two-and three-dimensional problems (although the additional calculation time and code complexity are not given). Surface complexation (either constant capacitance or triple-layer) and constant charge (restricted to small changes in pH) sorption models can be used. The code can also model ion exchange. A sorption stability coefficient, equivalent to log K for sorption exchange reactions, is needed as input for the model. TRANQL combines the geochemical equilibria code MICROQL with the transport code ISOQUAD. The codes have no restrictions on boundary conditions, and use a Galerkin-finite element scheme to solve the equations. A centered approximation of the time interval is used in the implicit formulation of the transient case. Geochemistry is modeled as an equilibrium system, without considering reaction kinetics. The code has been used to model Cd transport. For this system, linear sorption isotherms were judged to be inadequate for modeling sorption processes. The code is 30 percent faster than the one-step code of Valocchi et al. (1981a,b), and is designed to run on an IBM 3081 system. The authors give no indication of a practical limit to the selected time step, or how much computational effort would be needed to model a time interval on the order of 1,000 or more years.

Charbeneau, R. J. 1984. Kinematic models for soil moisture and solute transport. [illegible] *Resourc. Res. 20*: 699-706.

The author presents one-dimensional, vertical analytical solutions of water content and downward moisture flux with depth. General non-linear, equilibrium sorption isotherms are considered, and the solutions only consider gravity flow, neglecting capillary pressure gradients. Both continuum and discontinuum models are developed for wetting front migration. A retardation factor (R) is developed, which is dependent on soil bulk density, moisture content, and the derivative of the sorption isotherm at the concentration of interest. The model [illegible] shows that the displacement of solute during some arbitrary wetting sequence is dependent on the total depth of water front infiltration, not on the transient variations in the infiltration rate.

Choppin, G. R. 1988. Chemistry of actinides in the environment. *Radiochim. Acta 43*: [illegible]

A short paper that describes the chemistry of plutonium in the environment [illegible] Plutonium can exist in four oxidation states (III,IV,V,VI) over the range in pH and Eh [illegible] in nature. Pu(III)and Pu(IV) are found as simple hydrated cations, while V and VI [illegible] dioxo-cations. Complexation strength is normally Pu(IV) > Pu(VI) > Pu(III) > Pu(V), and hydrolysis tends to remove Pu(IV) from solution above pH 2-3 due to adsorption processes. The author suggests using the data for Am(III), Th(IV), Np(V), and U(VI) to estimate plutonium stability constants. Organic matter also is observed to have an affect on plutonium transport. Finally, the author indicates that the extreme insolubility of $Pu(OH)_4^0$ should be used as a limiting factor for Pu-solubility in geochemical modeling.

Clothier, B. E. 1984. Solute travel times during trickle irrigation. *Water Resourc. Res. 20*: 1848-1852.

The author develops a three-dimensional model of non-reactive solute transport based on piston fluid displacement during trickle irrigation. The governing equations of the model are developed, and bench-top unsaturated flow experiments using Br as a tracer are described. Solute input is from a point source. Diffusion/dispersion of the solute is neglected, and solute transport is treated solely by advection.

Coles, D. G., and L. D. Ramspott. 1982. Migration of ruthenium-106 in a Nevada Test Site aquifer: Discrepancy between field and laboratory results. *Science 215*: 1235-1237.

A report on the results of field tests at the Nevada Test Site show that Ru 106 travels at approximately the same rate as tritium in Tertiary tuffaceous alluvium. The principle complex is RuO_4^{2-}, and sample contamination is considered an unlikely explanation. Even using the lowest K_d values from batch sorption experiments (K_d ~ 10 to 8,000), the Ru-106 migration cannot be modeled. A maximum K_d of 0.3 is necessary for observed migration. The authors urge caution in the use of laboratory K_d values obtained from batch sorption techniques, especially for those elements that occur naturally in more than one valence state.

Comans, R. N. J., M. Haller, and P. De Preter. 1991. Sorption of cesium on illite: Non-equilibrium behaviour and reversibility. *Geochim. Cosmochim. Acta. 55*: 433-440.

Batch equilibrium experiments are described in detail to study both Cs adsorption and desorption processes for an illite substrate. Cs-adsorption is characterized by a rapid initial phase, followed by slow, continued Cs uptake. Desorption is fast initially, followed by slow reuptake. Equilibrium is not reached for either process, even after two weeks. Calculated K_d values and adsorption/desorption isotherms indicate that sorption is generally higher and more rapid in a Ca-environment relative to a K-environment. Cs-sorption appears reversible in K-illite, but hysteresis between adsorption/desorption isotherms in the Ca/Cs system indicates irreversibility. The degree of reversibility apparently depends on both the slow sorption process and the competing cation. Rapid sorption is believed to be due to planar surface charges, while slower sorption of Cs results from diffusion to interlayer exchange sites near clay particle edges where it is not easily remobilized. Easily dehydrated ions such as K^+ tend to collapse the clay structure, making access to these energetically favorable interlayer exchange sites difficult. Larger, hydrated ions such as Ca^{2+}, however, tend to "prop open" the structure, and diffusion to favorable sites is enhanced. Selectivity coefficients for the are higher for the Cs/Ca system relative to Cs/K system. Based on the above discussion, this is believed to be due to preferred Cs-sorption at interlayer sites that are more readily accessible in the expanded hydrated Ca-clay structure relative to the dehydrated K-clay structure.

Comans, R. N. J., and J. J. Middleburg. 1987. Sorption of trace metals on calcite: Applicability of the surface precipitation model. *Geochim. Cosmochim. Acta 51*: 2587-2591.

Trace metal sorption studies of calcite have generally exhibited rapid initial adsorption, followed by continued slow uptake. The slow uptake is generally thought to represent precipitation of the cation from solution. The authors propose a precipitation model to treat trace metal sorption onto calcite. The model is largely a continuum between adsorption and precipitation, and describes the formation of a surface phase with a composition varying from the original solid (calcite) to pure precipitate of the sorbing cation. The authors develop the theory of the model. One point of interest is the release of Ca^{2+} during adsorption of Mn^{2+} to maintain charge balance.

during proton transfer. The model is applied to previous studies for Cd, Mn, Zn, and Co. Results are reproduced fairly well, despite differences in experimental procedure for the different studies. In general, sorption is observed to increase as the ionic radius of the sorbing cation approaches that of Ca^{2+}.

Conca, J. L. 1990. Experimental determination of transport parameters in unsaturated geologic media. in: *Radionuclide Adsorption Workshop*. Los Alamos National Laboratory, Los Alamos, NM: 28-83.

The author reports on the use of the Unsaturated Flow Apparatus (UFA) to determine transport parameters for a variety of geologic media, including gravel, soil, bentonite, crushed tuff, and whole rock cores (Tiva Canyon and welded Topopah Springs tuff). The apparatus uses an ultracentrifuge with an ultralow constant-rate flow pump to achieve a desired steady-state water content in the unsaturated media. The apparatus and the sample preparation are described. Diffusion coefficients, hydraulic conductivities, and retardation factors were all determined as a function of water content. Standard deviation on repeated runs was 50 percent for diffusion coefficients. Diffusion coefficients were controlled by water content to a larger extent than material type, and surface water content on gravels and soils controlled the upper limit on the overall diffusion coefficient of the material. Diffusion coefficients initially decrease gradually with water content. The dropoff becomes steep as the surface water film becomes thinner and less continuous. Overall conductivity increases with water content and gravel size. Internal porosity (within particles) also plays a minor role. In the bentonite experiments, diffusion coefficients for a variety of radionuclides decrease with decreasing water content. Experiments with silt lenses in sand indicates that diffusion is affected and that the silt will act as a sink for contaminants for which it has an affinity. In the experiments with rock cores, the author notes that smaller fractures must saturate before larger fractures will start to conduct water.

Corn, F. E., E. G. Staes, and C. T. Miller. 1989. Vapor phase mass transfer and sorption in groundwater systems. *EOS 70*: 325.

ABSTRACT - Contamination of the vapor phase of the unsaturated zone by Volatile Organic Chemicals (VOC's) has received considerable attention in the literature recently. It is now apparent that vapor-phase mass transfer is an important factor that affects contaminant movement and interphase contaminant distribution in the subsurface. Vapor-phase mass transfer leads to difficulty in source identification and may prolong aquifer remediation when purge-well methods are used alone. The presence of high concentration of VOC's in the vapor phase has lead to the development of new methods for the monitoring and the rehabilitation of aquifers, which exploit the tendency of these compounds to partition to the vapor phase. A new experimental apparatus was developed to measure vapor-phase mass transfer in a sorbing porous media. The results of the experimental studies are shown in which mass transfer is measured for the solute toluene and a variety of porous media (glass beads and aquifer material) as a function of the degree of water saturation. Steady-state results of the vapor-phase mass-transfer is analyzed to show the effects of mass transfer to the aqueous and solid phases. The degree of saturation is shown to affect profoundly sorption to the solid phase and the resultant transient mass transfer behavior. A mathematical model is formulated for solute transport in a three phase system: vapor, aqueous, and solid. The model includes a two-site sub-model that describes the rate of approach to the final nonlinear sorption/desorption equilibrium. The model is used to simulate the data collected in laboratory experiments, and the resu[illegible] ompared to a model analysis, which is used to establish criteria for assuming local equili[illegible] among the phases present.

Cvetkovic, V. D., and A. M. Shapiro. 1990. Mass arrival of sorptive solute in heterogeneous porous media. *Water Resourc. Res. 26*: 2057-2067.

The authors develop a stochastic arrival time model to address sorption-desorption reactions during solute transport. Lagrangian velocity is used to track one sorptive particle in a 3-D heterogeneous porous media, neglecting molecular diffusion. The rate coefficients of the forward/reverse sorption reactions (k_1 and k_2, respectively) vary randomly. The analysis results in a mobile/immobile two region model. The model is first applied to a nonreactive solute to establish a baseline for subsequent models. A reactive solute is then introduced instantaneously to the system. For the three cases considered, the authors made the following observations: (1) For equilibrium transport, a coefficient ($K_d=k_1/k_2$) is introduced. If K_d is finite and assumed negatively correlated with hydraulic conductivity, additional travel-time is added to the nonreactive baseline. If K_d is independent of hydraulic conductivity, the retarding effect on solute breakthrough is less. Experimental cumulative breakthrough is best modeled by the arithmetic mean of K_d; (2) For solute degradation (i.e. no desorption, k_2 independent of hydraulic conductivity), variation due to k_1 depends on the magnitude of its geometric mean. The total can be retarded by as much as a factor of four for the values considered; (3) Nonequilibrium sorption-desorption is more delayed relative to the nonreactive case with increasing distance from the solute input. Constant k_1 and k_2 generally underestimate cumulative mass arrival at a given time, while arrival time generated with harmonic mean sorption parameters most closely approximates the case of variable k_1 and k_2. The authors conclude that variability in sorption parameters generally decreases the effect of sorption-desorption on breakthrough curves relative to constant parameters. The effects of diffusion associated with immobile regions are typically indistinguishable from sorption-desorption using first order linear kinetics.

Davis, J. A., C. C. Fuller, and A. D. Cook. 1987. A model for trace metal sorption processes at the calcite surface: Adsorption of Cd^{2+} and subsequent solid solution formation. *Geochim. Cosmochim. Acta 51*: 1477-1490.

The authors have studied Cd^{2+} sorption on calcite using solutions undersaturated with respect to $CdCO_3$ to avoid precipitation/dissolution complications. Theory is presented and a model is developed for a distribution coefficient using mass balance principles and solubility products. Experimental methods are described in great detail. Sorption, desorption, calcium isotopic exchange, $CdCO_3$ solubility are investigated. Aqueous speciation was calculated using the code MINEQL. Cd-sorption generally proceeded in three steps: (1) fast initial adsorption; (2) latter stages of initial adsorption where the rate of uptake decreased significantly; (3) slow uptake at a decreased, but constant rate which continued for the eight day duration of the experiment. Sorption generally decreased with increasing pH, and after rapid initial uptake, reversibility decreased steadily with increasing time until most of the sorbed Cd(II) was no longer in a rapidly reversible state. The authors hypothesize the formation of a solid solution layer at the calcite surface. Ostwald ripening (a balance between the new precipitate and crystallization) is believed to control the thickness of this layer. Ripening proceeds at a faster rate at lower pH. As the precipitate ages, the surface free energy (and sorptive capacity) of the layer will decrease. Based on these results, the authors propose a three-step model: Step IA--Reversible Cd surface adsorption to hydrated $CaCO_3$ at the calcite surface. Step IB--Diffusion of Cd into the hydrated layer. Step II--Recrystallization of the hydrated layer to form a carbonate solid solution. Steps IA and IB are controlled by Cd diffusion rates. Step II is controlled by surface precipitation rates, although the solid solution is not ideal. The presence of Mg^{2+} in solution reduces Cd uptake because of competition for exchange with Ca^{2+} in the hydrated layer.

Dayal, R., R. F. Pietrzak, and J. H. Clinton. 1986. Source term characterization for the Maxey Flats low-level radioactive waste disposal site. *Nuclear Technol.* 72: 158-177.

The Low-Level Radioactive Waste Disposal Site at Maxey Flats, KY is characterized. The site is at least partially saturated due to perched water. Waste at the site was mostly contaminated materials and the waste itself, and included some ^{233}U, ^{235}U, and Pu. The leachate was extensively modified relative to ambient groundwater. Because of the low permeability of the trenched soil, water tends to collect in the trenches, and leads to extended leaching time. Anoxic waters develop. Alkalinity, CO_2(aq), and NH_3(aq) content of the leachate increases due to aerobic and anaerobic decomposition processes. Methane generation and sulfate depletion leads to a reducing environment, and there is some buffering by nitrogen phases, and Fe- and Mn-oxides. The leachate is enriched in CO_3^{2-} and HCO_3^-, as well as Na^+, K^+, Fe^{2+}, Mn^{2+}, and Cl^-. There are also significant waste-derived organics. Dissolved radionuclides include tritium, ^{60}Co, ^{90}Sr, $^{134,137}Cs$, $^{238,239,240}Pu$, ^{241}Am, ^{22}Na, and ^{54}Mn. The high DOC tends to keep ^{60}Co and Pu-radionuclides in solution.

De Smedt, F., and P. J. Wierenga. 1984. Solute transfer through columns of glass beads. *Water Resourc. Res.* *20*: 225-232.

Early breakthrough and tailing is observed for nonreactive solute transport in unsaturated glass bead experiments. To describe this phenomenon with the classical convection-dispersion equation requires using a hydrodynamic dispersion coefficient (D) 20 times larger than that for saturated columns. The author avoids this problem by attributing the effect to the presence of mobile and immobile water in the experimental column. Dispersion between the mobile and immobile fractions are addressed, and mass transfer is assumed proportional to the difference in concentration between the mobile and immobile water. In general, immobile water was observed to increase linearly with total water content. A linear fit between D and the mobile water velocity (v) shows that the transfer coefficient for solute transport between mobile and immobile water fractions were observed to increase proportionally with the fluid velocity. The author concludes that early breakthrough is a transient phenomenon that is associated with short distances of solute transport. Within the limits of the model as presented, early breakthrough and tailing are not expected to be observed in "long" column experiments, but larger values for D will still be needed.

Di Toro, D. M., J. D. Mahoney, P. R. Kirchgraber, A. L. O'Byrne, L. R. Pasquale, and D. C. Piccirilli. 1986. Effects of nonreversibility, particle concentration, and ionic strength on heavy metal sorption. *Environ. Sci. Technol. 20*: 55-61.

There is some evidence for irreversibility for Co and Ni sorption onto montmorillonite (Mont) and quartz (Qz). Partition coefficients (K_d) and possibly the degree of irreversibility are sensitive to particle size, nature of oxide coatings, dissolved organic carbon (DOC), zero point charge (ZPC), pH, ionic strength (I), and complexing ligands. The authors propose experimental methods to investigate these effects. Linear sorption and desorption isotherms are developed. pH did not affect irreversibility. A pronounced water-rock ratio effect was observed, and in general, K_d decreases with particle concentration, an inverse relationship possibly due to a decrease in reversible K_d. Kinetics are probably unimportant for the Co-Ni system, although reversibility is incomplete because of metastable equilibrium. Resuspension and dilution experiments were also conducted to evaluate the possibility of the inverse K_d/concentration relationship resulting from experimental artifacts. These experiments indicate that the possibility of flocculation, complexing ligands, or a dissolved third phase is unlikely. A particle-interaction model is developed to explain the inverse relationship by breaking down desorption into spontaneous and particle-interaction components. A reversible K_d was derived to fit the Co-montmorillonite and Ni-quartz data. At low particle concentrations, desorption is primarily by spontaneous desorption, while particle-interaction desorption increases with concentration. The authors suggest that particle-interaction desorption is controlled by physical, not chemical factors. Metal-clay sorption decreases with increasing I, but the adsorption/desorption is essentially constant and independent of I and the sorbate-sorbent pair.

Dykhuizen, R. C. 1987. Transport of solutes through unsaturated fractured media. *Water Research 21*: 1531-1539.

The author develops a model for solute transport in fractured porous media using a two-system report. Matrix pore flow and fracture network flow are treated as two separate flow systems superimposed over the volume of interest. The model includes a term "W" for cross-flow from the matrix pores to fractures. Sorption is treated in the model using K_d and linear isotherms. The model assumes equal hydraulic head in two regions, and gravity flow (neglecting capillary pressure). The model is only valid for these assumptions, and the author presents calculations in the appendix for determining the validity of these assumptions in the region of interest. In addition, problems are encountered for solutes that diffuse across the boundaries of control volume. As solute reaches these boundaries for longer times, the domain must be expanded to a larger region. The model is applied to a simple calculation using hydrologic properties measured at Yucca Mountain. One-dimensional, finite difference model of steady-state vertical infiltration at 1 mm/yr assuming an initial solute concentration of zero. A two-layer model is assumed. In the upper later, solute concentrations are identical in fractures and matrix pores, but differ widely in the second layer (Topopah Springs)

Ebinger, M. H., E. H. Essington, E. S. Gladney, B. D. Newman, and C. L. Reynolds. June 1990. *Long-Term Fate of Depleted Uranium at Aberdeen and Yuma Proving Grounds Final Report, Phase I: Geochemical Transport and Modeling*. Los Alamos National Laboratory, LA-11790-MS, Los Alamos, NM.

This paper reports the results from a field computer modeling study of migration and transport of depleted uranium (DU) from artillery shell fragments at the Aberdeen (APG) and Yuma (YPG) Proving Grounds. Soil samples were collected beneath the penetrator fragments, and samples were collected from soil and water in the surrounding environment in order to establish background concentration levels. Both U concentration and $^{235}U/^{238}U$ ratios were determined since the ratios are different for DU versus naturally occurring U (0.0020 vs. 0.0075). At APG, uranium concentration decreased exponentially with depth, carrying the DU ratio signature with it. At YPG, U decreased linearly with depth, and only the natural ratio signature was present at depth. Schoepite was found at the surface. In the computer study, EQ3/EQ6 was used to model geochemical equilibria. For high Eh, schoepite is the most likely secondary mineral. For low values of Eh, DU oxidized to UO_2 and less uranium in solution is predicted than for higher Eh. The solute transport model employs a constant retardation factor (R), assuming constant one-dimensional transport and a slug input. R was varied for different runs, but it was kept constant for a given run. For R > 1, solute transport is retarded relative to water velocity. The arbitrary range used in R was 1, 10, and 100. The authors suggest that R > 100 is appropriate for Fe-hydroxides. In conclusion, the authors determined that dissolution, transport, and reprecipitation operate at the wetter APG, while physical erosion and transport are the processes operating at the more arid YPG.

Erikson, R. L., C. J. Hostetler, and M. L. Kemner. 1990. *Mobilization and Transport of Uranium at Uranium Mill Tailings Disposal Sites*. Division of Low-Level Waste Management, Office of Nuclear Material Safety and Safeguards, U.S. Nuclear Regulatory Commission, NUREG/CR-5169 or PNL-7154, Washington, D.C.

A general coupled chemical transport model (CTM) has been developed and applied to uranium migration from four LLW uranium mill tailing (UMT) sites. Uranium migration is controlled by Eh and pH. More soluble U(VI) is strongly partitioned into the aqueous phase at low pH, and adsorbs to solids at higher pH. Similar behavior is reported for other heavy transition metals and radionuclides. Uranyl complexation with dissolved CO_3^{2-} and $(PO_4)^{3-}$ generally reduces adsorption. The current discussion neglects organic complexing. For surface adsorption, ferric hydroxide (HFO) is considered the most critical sorbent phase. Simple surface complexation site-binding is used to calculate uranium adsorption onto the surface of amorphous HFO. The percent adsorption is at a peak for pH in the range 4-10. For total $CO_3(aq) > 0.01$ M, the maximum percent adsorption is reached at pH 8. Uranium must compete with H^+, Ca^{2+}, and SO_4^{2-} for binding sites. The authors give a general description of reactive transport codes. Precipitation/dissolution, specific-ion adsorption, and ion exchange are the primary retardation mechanisms. The one-step and two-step coupling methods are presented and compared. CIM is currently a one-dimensional, two-step model. In the Markov hydrologic model, mobile constituents are distributed by advection, diffusion, and dispersion along a 1-D pathline that has been divided into a number of arbitrarily shaped bins. The geochemical step reacts transported solutes with the immobile components in a given bin. Hydrologic parameters are assumed constant, and adsorption capacity is used to refer to surface sites available for specific-ion adsorption. The Davies equation calculates activity coefficients, and a modified version of the MINTEQ database is used in the model. Five separate input files are generated in an interactive session with a preprocessor module. These files include main run parameters, the geochemical model, the hydrologic model, the initial conditions, and the boundary conditions. The user can specify either equilibrium speciation solubility adsorption geochemistry or constant K_d retardation. The code uses a postprocessor to display the results. The conceptual model discussed includes steady state, local equilibrium, and slug input. Four runs were made: (1) adsorption only, with no buffering by carbonate; (2) adsorption only with finite acid buffering capacity; (3) solubility reactions only with finite buffering capacity; (4) all attenuation mechanisms, with competitive effects of sorption solubility. Uranium migration after 30 years is compared to migration of a conservative solute (Cl) at 50 m/yr. In the model, the adsorbed uranium is remobilized by a low pH front. For case 1, uranium migration is retarded to 44 m/yr; case 2 - 26 m/yr; case 3 - 8 m/yr; case 4 - 8 m/yr. The distance for exceeding a baseline was least for case 4. For solubility attenuation alone, local K_d can range from several hundred in zones of mineral precipitation to 0 where precipitation is inhibited.

Fuller, C. C., and J. A. Davis. 1987. Processes and kinetics of Cd^{2+} sorption by a calcareous aquifer sand. *Geochim. Cosmochim. Acta 51*: 1491-1502.

Calcareous sands from the saturated zone of the Borden site in Ontario are used to study Cd-sorption. The authors describe the experimental methods in great detail. Batch experiments were conducted using Cd-EDTA solutions that were undersaturated with respect to $CdCO_3$. Cd uptake was observed to occur in two steps. An initial, fast adsorption step reached equilibrium in 24 hours, and was followed by slow continued uptake at a constant rate for at least seven days, the maximum experiment time. Ninety percent of the Cd was sorbed in the initial few hours. Initial sorption was reversible, but as time increased, Cd become irreversibly adsorbed to the sand substrate. The authors observed greater sorptive efficiency at lower water rock ratios, and EDTA was not adsorbed. The fine grained fraction of the sand was more sorptive (greater surface area). While amorphous iron was only of minor importance, other secondary minerals (especially calcite) were observed to be efficient sorbents. Sorption was divided into three stages: Step IA--diffusion-controlled reversible adsorption; Step IB--diffusion into micropores or into a hydrated solid-solution layer at the calcite surface; Step II--precipitation at the solid solution layer, controlled by surface precipitation rates. The authors favor the formation of a solid solution layer due to the similar ionic radii for Cd and Ca. Calcite appears to control sorption processes in the sand. Mass balance is used to describe sorption for pure minerals (Cc, Qz) and it is apparent that quartz has only a minor effect on overall sorption. The authors address solute transport modeling. In general, a local equilibrium assumption (LEA) is only suitable for Step IA. Steps IB and II are too slow, and a kinetic approach should be used. A K_d approach is also insufficient to model solute transport. The authors suggest a metal buffering approach to circumvent complications due to speciation of the sorbing solute. Binding constants for this method will depend on both pH and water/rock ratios

Gaudet, J. P., H. Jegat, G. Vachaud, and P. J. Wierenga. 1977. Solute transfer, with exchange between mobile and stagnant water, through unsaturated sand. *Soil Sci. Soc. Amer. Journal 41*: 665-671.

This is one of the first papers to use mobile/immobile water to model delayed breakthrough and asymmetrical (i.e, tailing) concentration profiles. For the classical convection dispersion equation to be valid, the authors assume a noninteracting solute, and all fluid takes part in the transport. Immobile (stagnant) water is assumed to transport solute only by diffusion along chemical gradients, while mobile water is able to transport the solute through both diffusion and convection, and interacts with immobile water through diffusion. The authors describe and develop an explicit FDM model and a lab model for comparison. Changes were monitored in salt concentrations for an unsaturated, uniform sand column using CaCl as a leaching solution. A dispersion coefficient was determined by the slope of the experimental breakthrough curve, while a mass transfer coefficient between the mobile and immobile water is determined by the slope of the tailing of the transport profile. From the numerical model, solute breakthrough was most sensitive to the fraction of mobile water. Both the amount of immobile water and the degree of tailing were found to increase with decreasing moisture content. The authors conclude by pointing out the need for direct methods to measure the diffusional mass transfer coefficient

Gaudet, J. P., and G. Vachaud. 1979. Transient transport of solute during infiltration through unsaturated soil. *EOS 60*: 823-824.

ABSTRACT - A new model is proposed to describe transient infiltration of solutes in an unsaturated material using the concept of polyphase flow with partition of fluid between a mobile and an immobile fraction. Experimental evidence of this assumption has been obtained in the laboratory for steady and transient unsaturated water flow conditions. Water content, water pressure and solute concentration ($CaCl_2$) were measured simultaneously, independently and nondestructively at different depths of a sand column submitted to different initial and boundary conditions. The results were used to characterize the hydrodynamic and dispersive parameters, i.e.: the hydraulic conductivity soil water pressure-soil water content relationships and the values of the apparent dispersion, mobile fraction and exchange coefficient (between the mobile and the stagnant fraction) with the local water content and the local water velocity. Finally, the model is solved numerically, where the unsaturated water infiltration is first determined. The solute flow is then solved, using a chromatographic model of flow with coupling between two sets of equations: a dispersive-convective equation for the mobile fraction, and a non-linear first order exchange equation between the mobile and the immobile fraction. The parameters of the exchange equation are water content and water velocity dependent. It is shown that this model can predict accurately the advance of solute, the flux of solute, and the non symmetric pattern of the solute distribution in the column during a transient infiltration with a pulse of solute imposed at the soil surface. Reversely, none of those values can be simulated with the classical one parameter dispersion equation.

Gelhar, L. W., and J. L. Wilson. 1975. Solute transport in the unsaturated zone. *EOS* 56: 979.

ABSTRACT - An approximate analytical method is described which leads to a solution of the mass transport equation for non-uniform unsteady flows characterized by streamlines fixed in space. The method is based on the solution of characteristic equations to find the 'location' of the solute, and approximate techniques to find the 'shape' of the solute distribution. The method is applied to the study of conservative, non-interacting chemicals. An even simpler approximate analytical analysis is utilized to reveal some basic features of mass transport during one-dimensional vertical infiltration. The analysis shows that the rate of propagation of a moisture pulse is two to four times the rate of propagation of a conservative solute pulse. The more complicated analytical procedure utilizing characteristics is then applied to problems involving one, two or three dimensional steady moisture absorption, one dimensional steady vertical infiltration, and one-dimensional absorption and vertical infiltration. Various properties of mass transport for one-dimensional flow problems are examined and illustrated. It is found that the choice of boundary conditions, soil properties, the amount of dead end pore space, and the behavior of dispersion coefficient influence the amount of mixing, and in the case of the first three, the location of the solute as well. The results of the analytical solutions are compared to field data and a numerical simulation.

Giblin, A. M., and E. D. Appleyard. 1987. Uranium mobility in non-oxidizing brines: field and experimental evidence. *Applied Geochem.* 2: 285-295.

The authors present evidence for transport of uranium in a non-oxidizing environment. Tradifional through is that U(IV) is much less soluble than U(VI) and is essentially insoluble. Field evidence suggests, however, that polycationic brines are able to transport uranium over short distances in reducing environments. The authors describe the Wollaston Group in Saskatchewan, Canada, presenting evidence for the involvement of Ca- and Na-fluids in an evaporitic environment. Na- and Cl-rich metasomes, extensive albitization, and scapolite in the metamorphic rocks indicate brine/rock interaction. Evidence for reducing conditions includes pyrite, graphite, and low oxidation ratios. Syngenetic uranium in the region has been remobilized and redeposited in areas related to Na-Ca-Mg-Cl metasomatism, suggesting dissolution and transport in a reduced environment by metasomatic polycationic brines. Synthetic Salton Sea brines were used in laboratory dissolution experiments with natural pitchblende and synthetic uraninite at 60 and 200°C. Uranium dissolution and transport increase with increasing m(Cl), showing no signs of slowing, even after 1000 hours. At 200°C, there is evidence for transport of U(IV). Uranium dissolution is not a strong for a pure NaCl brine, suggesting that Ca^{2+} and K^{+} in polycationic brines are more effective. This may be due to lower pH caused by Ca^{2+} hydrolysis. Alternatively, Cl activity may be greater in polycationic solutions, producing more U-chloride complexes to enhance dissolution and transport. While uranium transport is small in reducing environments, the continuous circulation of fresh fluids through large volumes of country rock may provide sufficient remobilization to form ore grade deposits.

Gillham, R. W., and J. F. Pickens. 1977. Solute transport in unsaturated porous media considering hysteretic hydraulic properties. *EOS* 58: 393.

ABSTRACT - Hysteresis in the hydraulic properties of unsaturated porous media is well documented in the literature, and there is considerable information concerning the consequences of hysteresis with respect to the flow of water under partially saturated conditions. In this paper the consequences of hysteresis with respect to the prediction of solute transport rates are demonstrated. Hysteresis will have its major effect on the velocity parameter of the transport equation. Velocity is generally determined from a solution of the flow equation in which the Darcy flux is divided by the water-filled porosity. In solutions of the pressure head form of the flow equations, substantial errors in predicted water content, and consequently in predicted velocity, can arise if a non-hysteretic solution is applied to a hysteretic flow situation. In addition to velocity, hysteresis can affect other velocity or water content dependent parameters such as the dispersion coefficient. The flow portion of a finite-element solution of the solute transport equation was tested against experimental data in the literature for hysteretic flow. Having established the validity of the model for predicting flow, it was applied to a hypothetical solute transport problem in which the flow was hysteretic. The concentration results obtained when the hydraulic parameters were considered to be hysteretic were significantly different from the results of the non-hysteretic simulations.

Gillham, R. W., E. A. Sudicky, J. A. Cherry, and E. O. Frind. 1984. An advection-diffusion concept for solute transport in heterogeneous unconsolidated geological deposits. *Water Resour. Res.* *20*: 369-378.

The authors propose an advection diffusion model for solute transport through heterogeneous, layered media, as opposed to a mechanical advection dispersion model. The authors point out the difference in longitudinal dispersivity between lab values on the order of [illegible] and field scale (1 to 100 m). Basically, this difference limits the applicability of advection/dispersion, which relies on a complex velocity distribution to disperse a solute plume. Advection/diffusion, however, uses vertical molecular diffusion between layers of contrasting hydraulic conductivities. In this treatment, less permeable units bounding an aquifer act as temporary storage for a transported, non-reactive solute, producing strongly dispersed concentration profiles. Because molecular diffusion is time-dependent, the migration of the centroid of the solute plume is retarded relative to groundwater velocity. Mathematical expressions are developed and compared to chloride migration at the Borden site in Ontario. The concentration profiles at Borden are not inconsistent with the model of vertical diffusive mixing between layers, although varying solute input could also explain the data.

Gvirtzman, H., N. Paldor, M. Magaritz, and Y. Bachmat. 1988. Mass exchange between mobile freshwater and immobile saline water in the unsaturated zone. *Water Resour. Res.* 24: 1638-1644.

The authors present an in situ field application of a mobile-immobile solute transport model incorporating terms for radioactive decay. Tritium migration in an unsaturated loess in an arid climate (Israel) is used as the study case. Using a constant exchange rate coefficient (alpha) of solute between mobile and immobile waters cannot reproduce the observed tritium profiles. The authors modify alpha to include the kinetics of dispersion of the clay minerals [illegible] function of time and location. An empirical constant beta is used to represent the [illegible] permeability "clogging" due to clay dispersion. With this modification, the mobile-immobile approach is able to adequately reproduce the observed tritium profiles.

Hakanen, M., and A. Lindberg. 1991. Sorption of neptunium under oxidizing and reducing groundwater conditions. *Radiochim. Acta* 52/53: 147-151.

Neptunium sorption was investigated under a range of redox conditions from aerobic, to anoxic, to reducing conditions. Batch experiments used about 2 ml of low salinity natural and synthetic groundwaters spiked with low concentrations of Np (10^{-14} to 10^{-5} M). The solids were in the form of thin wafers (1-2 mm) of granitic rocks. Np(IV) and Np(V) were separated from one another. Sorption was higher under anoxic conditions compared to aerobic conditions (70 percent vs. 45 percent), and sorption was comparable between the four different rock waters. Sorption appeared to be independent of initial Np concentrations in groundwater. After five days, all of the Np was in the +5 oxidation state. Under reducing conditions, sorption was about 70 percent, and almost all of the Np was in a +4 state. Np(V) did not readily dissolve in the reducing fluids. Experiments with teflon wafers indicate that the reduction of Np to a +4 state does not depend on mineral surfaces under aerobic conditions. Under reducing and anoxic conditions, however, the surface acted as a holding reductant or oxidant for sorbed neptunium, depending on the original oxidation state of the Np. Np-partitioning in the experimental system was not affected by the mineral composition of the wafer.

Hiemstra, T., W. H. van Riemsdijk, and G. H. Bolt. 1989a. Multisite proton adsorption modeling at the solid/solution interface of (hydr)oxides: A new approach. I. Model description and evaluation of intrinsic reaction constants. *Jour. Colloid Interface Sci. 133:* 91-104.

A surface complexation model is developed for more than one type of reactive surface group (proton adsorption by surface complexation). The model is developed primarily for metal hydroxides, to estimate proton affinity constants (pK) based on crystallographic and physical-chemical considerations. The local contribution to the free energy of interaction (and therefore to pK for proton adsorption) is defined explicitly. These contributions include repulsion of adsorbable protons by local cations and anions. Equilibrium constants are estimated for proton association by different surface group types. Protonation reactions are considered. Equilibrium constants for -O and -OH bonds are related to v L, where v is cation valence, and L is the charge separation distance. L is estimated in solution based on the ionic radii. The coordination number (CN) of the cation is needed to estimate charge distribution. Log K for -O ligands average 13.8 log units larger than those for -OH ligands. This suggests that only one type of these complexes can be protonated in solution, and one protonation reaction per group. In order to accurately determine pK, the case of one reactive site surface is investigated. For gibbsite, Me-H distance (L) is determined from crystallographic data. Protonation is treated as a two-step association reaction. Using this as a basis, equations are developed for multiple surface sites and site density of specific surface groups. These are related to pH. Three cases are possible with respect to the position of two consecutive log K values in titration pH ranges (1) If one log K is at or near the pH of titration, only one protonation is needed; (2) Log K is symmetric about the pH of titration (doubly coordinated groups); (3) Log K of both sites is outside the pH range of interest. These cases may be an important consideration where titration/adsorption experiments are concerned.

Hiemstra, T., J. C. M. De Wit, and W. H. van Riemsdijk. 1989b. Multisite proton adsorption modeling at the solid/solution interface of (hydr)oxides. A new approach. II. Application to various important (hydr)oxides. *Jour. Colloid Interface Sci. 133:* 105-117.

At a (hydr)oxide surface, the affinity of proton adsorption differs for several types of surface groups. Equilibrium constants (log K) for certain types of these groups depends on: (n) the number of coordinating cations, (z) valence of the cations, and (CN) the coordination number of central cations of the crystal structure. Experimental capacitance may differ for different preparations of the same mineral. The authors evaluate the relationship between surface charge density and pH from the literature, and fit the data to a Stern capacitance model. Titration experiments with gibbsite and goethite were performed to characterize surfaces. For goethite, at least three types of surface groups were found: (I) singly coordinated; (II) doubly-coordinated, and (III) triply-coordinated. The surface charge density is calculated for a given crystallographic plane. The 100 plane contains only (I) and (II) surface groups, quite different from 010 and 001 faces. The program MUSIC was developed to determine log K for the different site types. For silica colloids, proton adsorption on Si-OH and Si_2-O surface groups is considered to be negligible due to low log K values. Different surface charge density-pH relationships for other (hydr)oxides is due to differences in charge attribution

Higgo, J. J., W. E. Falck, and P. J. Hooker. 1990. *Sorption Studies of Uranium in Sediment-Groundwater Systems From the Natural Analogue Sites of Needle's Eye and Broubster.* Commission of European Communities. EUR 12891, Luxembourg.

Describes results of sorption experiments of ^{233}U from natural groundwater onto peat from Broubster and silt from Needle's Eye under atmospheric conditions and different pH values at T=10°C. Kinetics are followed for NE silt. The results analyzed are together with speciation modeling to understand sorption mechanisms. Two different sets of experiments were carried out with NE silt. In the first, pH was maintained at 6.0 by addition of HCl. In the second, pH allowed to drift from initial pH=6.7 to 7.9. Distribibution ratios at pH 6.0 were higher than at 6.7-7.9. At both pH values an initial rapid sorption was followed by slow sorption but only at pH 6.7-7.9 did the slow sorption follow first-order kinetics during the first week. Speciation modeling showed that under the experimental conditions, uranium should be present as a mixture of negatively charged and neutral carbonate complexes with the proportions of each species differing markedly at pH 6.0 and 7.0. It is postulated that $UO_2(CO_3)_2^{2-}$ and UO_2CO_3 are more readily sorbed than $UO_2(CO_3)_3^{4-}$ and that sorption of uranium carbonate complexes is by displacement of carbonate ligands in a series of surface-complexation reactions with oxide surfaces. The NE groundwater used in the experiments was very different in composition to that in the field because it had been stored in air, and iron and Mn oxyhydroxides had precipitated out. U-speciation in a groundwater, taken from the same horizon, but analyzed immediately after collection was, therefore, modeled under both reducing (Eh = 0 mV) and oxidizing (Eh=400 mV) conditions. It seems probable that in the field, even under oxic conditions, sorption and organic complexation will be higher than in the lab experiments. At zero Eh most of the U should be reduced to the IV state and strongly sorbed. If organic material is available complexation is likely to be complete. Distribution ratios for Broubster peat were greater than 10^4 ml/g at pH values of both 6.5 and 7.0. Speciation modeling indicated that carbonate complexation should dominate in the groundwater, but it is suggested that given sufficiently strong interaction with the solid substrate then, as a result of mass action, complexation sorption will be nearly complete. Most likely distribution coefficients for use in migration modeling: Silt layers at NE: 1)oxidizing, with pH 6.5-8.0: Best estimate K_d = 100 ml/g, range = 10 to 1000 ml/g; 2) oxidizing, with pH 6.5-4.0. Best estimate K_d = 1000 ml/g, range 100 to 10,000 ml/g; 3) reducing (Eh suggest values: Best estimate K_d > 10,000 ml/g, range 1000 to 10^5 ml/g.

Higgo, J. J. W., and L. V. C. Rees. 1986. Adsorption of actinides by marine sediments. Effect of the sediment/seawater ratio on the measured distribution ratio. *Environ. Sci. Technol. 20*: 483-490.

The authors develop the concept of distribution ratio (R_d) as a means of evaluating adsorption of actinides by marine sediments. K_d is shown to be dependent on the conditions in the lab

Although K_d and R_d are numerically equal, R_d implies nothing about equilibrium and reversibility. Three broad classes of particles determine R_d: ionic particles (< 1nm); Humic complexes; large particles (>10-50nm). For two solutes, if R_d of one is as high as 10^5, adsorption is very sensitive to even minute amounts of a low R_d species. Desorption experiments are described for two sea sediments from the Mid Atlantic: Am(III), Np(V), and ^{238}Pu(variable oxidation). ^{241}Am sorption-desorption is not as irreversible as previously thought, due to presence of some low-R_d Am (R_d(Am) ~ 10^5). Np is more soluble than ^{235}Np by four orders of magnitude (R_d(Np) ~ 1000), and Pu sorption-desorption is assumed irreversible to a large extent for the red clays examined, but for carbonates, Pu sorption-desorption is reversible. In summary: Low R_d species are probably simply microparticulate material that has remained with the solution after phase separation. At low solid/solution ratios, observed R_d will be close to that of the species with the highest R_d, decreasing as the solid/solution ratio increases. The authors also suggest that microparticulate particles (colloids) may lower the observed R_d.

Hobart, D. E., D. E. Morris, P. D. Palmer and T. W. Newton. 1989. Formation, characterization, and stability of plutonium(IV) colloid: A progress report. In Nuclear Waste *Isolation in the Unsaturated Zone: Focus '89*. Los Alamos National Laboratory, Los Alamos, NM: 118-124.

The article characterizes colloid formation with Pu(IV). This study have attempted to characterize Pu(IV) colloids in solution. Pu(IV) colloid has a different electronic absorption spectrum from Pu^{4+}. Crystallographic symmetry varies between PU(IV) complexes. Similarity to spectra for high-fired PuO_2 suggests structural similarities exist for colloids suspended in solution. The initial rate of colloid oxidation is quite fast when oxidation is achieved by Ce(IV). The oxidation appears to follow second order kinetic behavior, and the potentials are easily distinguished from those for dissolved Pu(IV), indicating stability of the colloid. Reduction and oxidation rates are faster for smaller colloid particles than for larger colloid particles. The authors outline the need for additional future work using Raman and X-ray spectroscopy.

Hoffmann, D. C., W. R. Daniels, K. Wolfsberg, J. L. Thompson, R. S. Rundberg, and S. L. Fraser et al. 1983. *A Review of a Field Study of Radionuclide Migration from an Underground Nuclear Explosion at the Nevada Test Site*. Los Alamos National Laboratory, LA-UR-83-[illegible] Los Alamos, NM.

The study reports the results of monitored radionuclide migration from the Cambric detonation site after 10 years. The detonation was below the water table in alluvium at the Nevada Test Site. Five satellite wells were used to monitor tritium migration, and the authors describe both the drilling program and the sampling procedure used. An effective overall retention factor (Ref) is derived. This factor is similar to K_d, and reports solute transport relative to tritium transport. The authors also report the results of bomb ^{36}Cl. Both Cl breakthrough and maximums precede that of tritium, suggesting anion exclusion. Similar behavior may occur for ^{129}I, but has not been conclusively identified. Iodine is lost in the elution process, suggesting some type of retardation mechanism, or possibly a neutral species. Most of the radioactivity at the site remains in the fused detonation core.

Hsi, C. D., and D. Langmuir. 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochim. Cosmochim. Acta 49*: 1931-1941.

Uranyl adsorption is most complete in the pH range 5 to 8.5, regardless of the sorbent phase. Critical sorbent properties include surface area, surface charge and potential, effects of adsorption on complexation, sorbate ion competition, ionic strength, all of which are a function of pH. Using batch equilibrium methods, the authors consider the effect of pH, competing cations, and carbonate complexing on uranyl adsorption by four minerals: goethite, amorphous HFO, hematite, and natural specular hematite. Two-step kinetics are observed for uranyl adsorption onto all four materials, and most of the experiments, with the exception of synthetic hematite (7 days), reached sorption equilibrium in about 4 hours. The first step was rapid adsorption, and occurred in minutes. The second step was slow diffusion and alteration, and could last for days. Competing Ca and Mg were observed to have no significant effect on uranyl adsorption at values of 0.001 M. Adding sodium bicarbonate to solutions inhibited the adsorption of uranium on all four materials. The surface complexation site-binding model of Davis et al. (1978) and the geochemical code MINEQL were used to model uranyl adsorption. Initially assuming that uranyl ion $(UO_2)^{2+}$ is the only adsorbed species provided a poor fit. For the pH range of strongest adsorption, the dominant species are $UO_2(OH)^+$ and $(UO_2)_3(OH)_5^+$. Incorporating these species into the model resulted in excellent agreement with experimental results, and contributions of $(UO_2)^{2+}$ appeared fairly small. Modeling cannot uniquely describe the experimental results. Several combinations of mono-, bi-, and tri-dentate surface sites can fit the data equally well. Crystallographic evidence suggests bi- and tri-dentate rather than mono-dentate complexing. The model fit is not as good for total dissolved U vs. pH. Probably due to goethite impurities. The model was modified to match uranyl hydroxide and uranyl carbonate adsorption data. The results suggest that the chemical component of bond energy is the same from oxide to oxide, and may use the same intrinsic complexation constants. The authors suggest that at low T, U-sorption is more important than U-mineral precipitation in retarding uranyl transport.

Huyakorn, P. S., J. W. Mercer, and D. S. Ward. 1985. Finite element matrix and mass balance computational schemes for transport in variably saturated porous media. *Water Resour. Res. 21*: 346-358.

The authors stress the importance of mass balance as a means for evaluating numerical results and determining unacceptable values. The study introduces the Slice Successive Overrelaxation (SSOR) matrix scheme. The example presented uses a linear sorption isotherm to determine the effective retardation coefficient as a function of saturation. The model (SATURN) uses an upstream weighted residual finite element approximation of the Convection-Dispersion equation. An unconditionally stable Crank-Nicholson time-stepping scheme is also used, and the model avoids the mass-lumping procedure. Field compressibility is assumed small compared to the porous medium. Upstream weighting is not used where the Peclet number (Pe) is not large enough to create numerical stability problems (i.e. dispersion-dominated systems). The numerical results are checked against three experimental examples: (1) One-dimensional transport during adsorption of water in a soil tube; (2) one-dimensional transport during infiltration in an unsaturated soil; (3) two-dimensional transport in an unsaturated soil slab. The match is not good at early times due to coarse spatial and temporal discretization. There is also some smearing of the concentration fronts. Error in mass balance are dampened with time.

Huyakorn, P. S., B. H. Lester, and J. W. Mercer. 1983. An efficient finite element technique for modeling transport in fractured porous media 2. Nuclide decay chain transport. *Water Resourc. Res. 19*: 1286-1296.

The authors present a finite-element model (FEM) for the simulation of nuclide chain transport in fractured porous media. The model employs a discrete fracture approach which the authors have determined is more efficient than a dual-porosity approach, although the approach may not be suitable for a three-dimensional problem. The model accounts for matrix diffusion, and multi-species transport. A retardation coefficient (Ri) is used to model adsorption, which is treated as an irreversible process (i.e. no desorption). The authors derive equations for one-dimensional Cartesian and radial coordinate systems. One-dimensional flow and transport is assumed along fractures. The FEM used in the fractures is an upstream weighted residual formulation which is believed by the authors to avoid the numerical oscillations inherent in the Galerkin FEM for advection-dominated systems (high Peclet number, Pe). The Galerkin FEM is used, however, to model matrix flow (low Pe). The model requires initial concentration distributions as input. The model is verified against other numerical models and analytical solutions. Results agree well with the analytical solutions for one-dimensional transport of three radionuclides and three components in fractured porous media. Compared to other numerical codes, the prediction of the early parts of the breakthrough curves (BTC) is not as good. The authors believe this is due to coarse spatial and temporal discretization

Jannasch, H. W., B. D. Honeyman, L. S. Balistrieri, and J. W. Murray. 1988. Kinetics of trace element uptake by marine particles. *Geochim. Cosmochim. Acta* 52: 567-577.

Scavenging in marine environments is believed to be a two step process. Dissolved species first adsorb to particles, which then settle out of solution. If residence time is long relative to sorption processes, then local equilibrium between the dissolved and particulate phases may be valid. The authors use kinetic data to determine important uptake processes. Uptake rates of four radiotracers by natural particulates in water from Puget Sound was measured. The experiments are described in great detail. About 87 to 93 percent of the tin (Sn) and 2 to 7 percent of the zinc (Zn) in solution is bound. All radiotracers reached equilibrium K_d's within a matter of days. More strongly sorbed (higher final K_d) are sorbed faster initially. A kinetic model using first-order rate equations and regression of experimental data is developed. Both one-step (X < = > Y) and two-step (X < = > Y < = > Z) models are discussed. A two-step approach fits the data better. In this model, strongly binding metals can be considered in apparent equilibrium. The linear free energy relationship between two metals, and proportionality of activation energy to free energy of formation, is used to distinguish between sorption/desorption processes. A slope of one indicates a common desorption process, more likely a physical process that is independent of the metals involved. Since rate constants are proportional to K_d, the rate-limiting step is inferred to be the breaking and formation of bonds. Since this is on the order of seconds, other methods are necessary for slower uptake. Early stages of uptake cannot be modeled by one- or two-step models, but can be modeled as a series of first-order reversible reactions. Three linear steps provides the best fit. The rate-controlling processes are separate, each with a different time frame, from minutes to days. A sequential kinetic model is developed, as is a parallel model. Four potential controlling processes are discussed with respect to the inferred time scales: (1) very fast direct adsorption; (2) mass transport by advection/diffusion; (3) ion exchange; (4) biological activity. The authors note that natural distribution coefficients are still approximately one order of magnitude larger than lab values, suggesting still further and slower processes are involved.

Jinzhong, Y. 1988. Experimental and Numerical Studies of Solute Transport in Two-Dimensional Saturated-Unsaturated Soil. *Jour. Hydrol.* 97: 303-322.

Two-dimensional experiments were performed for saturated-unsaturated solute transport. Early breakthrough and tailing of solute distribution is believed to be indicative of the existence of mobile and immobile water. The author uses a Lagrangian-Eulerian method of characteristics approach to solving the two-dimensional dispersion convection equation with mobile-immobile water. The solute is allowed to disperse in the mobile water, while diffusion is the dominant process in immobile water. The immobile water content is held constant. The medium is modeled as an isotropic, porous medium, and the numerical approach employed is Galerkin-finite element. The model neglects sorption. In the experiments, the soil-water characteristics were determined using tensiometers, and hydraulic conductivity (K) was determined for steady/state infiltration. The method of characteristics used avoids numerical dispersion and oscillation problems at high fluid flow velocities. The reasonable fit of the experimental data by model calculations suggests that the mobile-immobile water method is suitable in unsaturated conditions.

Jury, W. A., G. Sposito, and R. E. White. 1986. A transfer function model of solute transport through soil. 1. Fundamental concepts. *Water Resour. Res.* 22: 243-247.

A transfer function model (TFM) is developed for the special case of non-reactive solute transport through saturated/unsaturated flow with both pulse input and step change input. The development relies on selecting a control volume such that no solute reaches the boundary in the time scale of interest. In soils, this only includes the volume of fluids effective in solute transport. For chromatographic or convection-dispersion equations, this is considered equivalent to the mobile volume. The authors use a stochastic approach where random solute input time and random solute residence time are defined through normalized joint probability density functions. The authors introduce the concept of a lifetime density function which is a model representation of all soil processes (i.e. lumped processes) only concerned with the net effect. A detailed understanding of mass transfer within the control volume or across boundaries is needed if discrimination between soil processes is desired. If the net effect is more important, then the TFM only requires the solute mass loss rate from the soil. The TFM implies nothing about the shape of the underlying travel-time probability density function. It is applicable to any mechanistic model of solute transport which is consistent with mass balance considerations.

Kelly, W. R. 1987. A Modeling Study of Geochemical Interactions at the Sheffield, Illinois Low-Level Radioactive Waste Disposal Site. *Nuclear and Chem. Waste Management* 7 [illegible]

This is a modeling study of the geochemical behavior at the Sheffield, IL low-level radioactive waste site using three computer codes: PHREEQE for groundwater [illegible], WATEQF for aqueous speciation and mineral saturation, and BALANCE for mass balance prediction of probable chemical reactions. The site is saturated below 9m. Trench leachate is high in TOC, HCO_3^-, Ca^{2+}, Mg^{2+}, tritium, SO_4^{2-}, and Fe^{2+}. The conditions are not as reducing as Maxey Flats and West Valley, and is the site monitored by three wells. One of the wells is assumed equal to trench leachate, and the other two are assumed on the same flowpath from general hydrology alone. Mixing is estimated using tritium and a simple lever rule, and PHREEQE, WATEQF, and BALANCE are used to calculate the composition, speciation, saturation, and geochemical reactions of the mixed water. Fluid flow was estimated at 75 [illegible] gradient tracer tests alone, no fluid flow modeling was used. BALANCE predicts reactions but uses no thermodynamic data. The user qualitatively assess water quality data and provides phases that are both geologically reasonable and account for observed changes in chemistry. Only Na, K, Ca, and Mg ion exchange are considered. Sorption is not specifically addressed, except as a possible mechanism for observed decreases in Na, K, and Mg.

Kent, D. B., V. S. Tripathi, N. B. Ball, J. O. Leckie, and M. D. Siegel. March [illegible] *Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments.* U.S. Nuclear Regulatory Commission, NUREG/CR-4807, SAND86-7175. Washington, D.C.

Necessary variables and factors are outlined for applying triple-layer surface complexation models (TLM) to radionuclide migration, and experimental methods for determining these values are discussed. TLM does not explicitly account for several sorption phenomena, including binding-site intensities and competitive sorption. Both adsorbent and adsorbate phases must be well-characterized, including the adsorption characteristics of the adsorbent, thermodynamic data for the formation of aqueous species, and stoichiometries and intensities for the formation of surface complexes. Adsorption systematics differ as a function of total concentration. Site density can be measured by the extent of solute adsorption as a function of decreasing solid/solution ratio and exchange capacity is measured over a wide pH range. The study lists cation exchange capacities (CEC) and specific surface areas for crushed Yucca Mountain tuff. However, using crushing and grinding during sample preparation creates a bias favoring more abundant primary minerals, even though secondary minerals are often the principal minerals in contact with moving solutions. In addition, grinding leads to the production of readily dissolved fine-grained amorphous materials that will change fluid composition in ways that are difficult to predict. Linear adsorptivity models which use a weighted average of properties of the constituent components to characterize composite materials is valid only for special cases. The model is also frequently unrepresentative of the sorptive character of the medium in an inconsistent fashion (over- and underestimating sorption), and grinding has been used frequently to generate sorption coefficients.The authors outline 4 mineral classes important to sorption: (1) Oxides (2) Oxides with multiple site-types (3) fixed-charge minerals (4) salt-types. Type (1) oxides are best-characterized, and a table of oxide adsorbent properties for TLM is given. The study includes a parameter sensitivity analysis of TLM for the Cd-TiO2 system. The model is relatively insensitive to the stoichiometry of the surface species, but it is sensitive to inner layer capacitance, surface association constant, and surface area and site density. K_d may underestimate sorption if complexation of the adsorbate is extensive, and may overestimate sorption if precipitation or other reactions are neglected. It is important to correct thermodynamic data to the appropriate reference state. For TLM, this is infinite dilution. Case examples are listed that extract TLM input parameter data from titration experiments, and an example is also included that corrects Np thermodynamic data to infinite dilution reference states.

Kerrisk, J. F. 1985. *An Assessment of the Important Radionuclides in Nuclear Waste.* Los Alamos National Laboratory, LA-10414-MS, Los Alamos, NM.

This report presents a rough estimate of the importance of various radionuclides in reactor spent fuel, reactor high-level waste, and defense high-level waste. The author first develops an inventory of radionuclides for each of the three principal types of waste. Based on decay times for the various radioelements, relative amounts are reported for times ranging from 100 to 100,000 years. The EPA release limits are converted to Curies 1000 MTHM (metric tons of heavy metals), and compared to the estimated radionuclide inventory. Based on this comparison, the relative importance of the various radionuclides is given as a ratio of inventory to the EPA limits. Based on this relative importance, solubility is discussed as a limiting factor on radionuclide release. Bulk waste dissolution is proposed as a maximum upper limit on dissolution. For radionuclides with large solubilities, bulk waste dissolution will become the rate-controlling step for releasing the radioelement to the environment. NRC release rate limits must also be considered. At 10,000 years, ^{14}C, ^{99}Tc, and ^{129}I are important, since they are highly soluble and travel in anionic, poorly sorbed forms. ^{59}Ni, ^{135}Cs, ^{237}Np, [illegible]Pu, and ^{234}U are also important radionuclides which will not meet NRC regulatory limits without additional retardation. The author presents rough calculations for required retardation factors at Yucca Mountain based on NRC limits, radioactive decay (half-life) and groundwater travel time (1,000 and 20,000 years). Based on the preceding disscussions, Am, Pu, Th, Np, and U are identified as critical radioelements present in large amounts relative to EPA release limits. C, Ni, Zr, Tc, Ra, and Sn ar also important, but present in smaller concentrations. Finally, C and I may be transported in the gas phase and will require special treatment.

Kirkner, D. J., and H. Reeves. 1988. Multicomponent Mass Transport With Homogeneous and Heterogeneous Chemical Reactions: Effect of the Chemistry on the Choice of Numerical Algorithm. 1. Theory. *Water Resourc. Res. 24*: 1719-1729.

Equations governing are developed for solute transport in a homogeneous, saturated porous medium. Local equilibrium and identical dispersion for every species are assumed. Algebraic equations are developed for solution phase reactions and precipitation/dissolution. Sorption is handled as competitive surface complexation, using an equilibrium constant for surface adsorption reactions. Complex adsorption is neglected. Three types of problem formulations (A,B,C) are considered. First (A), a one-step approach is used to develop a set of nonlinear differential/algebraic equations coupling transport and geochemistry. The problem is simplified using concentration of the sorbed form of each component as an implicit function of total soluble concentration. This reduces the number of unknowns, but the implicit relation between sorption and velocity requires solving a set of nonlinear equations for each time step to evaluate sorption as well as precipitation/dissolution. The second formulation (B) is a two-step coupling approach. Total component concentration is considered as a primary unknown, and precipitates no longer appear as primary unknowns. The third formulation (C) is also two-step coupling, and differs from (B) depending on the numerical algorithm employed. Without precipitates, all three formulations are similar, but with precipitation, transport and chemistry become coupled in formulation (A), and (B) and (C) are more efficient. The authors stress that the nature of the chemistry will affect both problem formulation and algorithm selection. Numerical formulation is set up using backwards differencing and either a Picard or Newton-Raphson (N-R) iteration scheme.Picard iteration is an explicit Eulerian approach, and convergence depends on nonlinear terms arising due to sorption. For Picard iteration, one-step coupling (A) will never be as efficient as two-step coupling. Newton iteration is more bulky due to a need to couple all component equations together, but this inefficiency is frequently offset by second order convergence (relative to first order convergence for Picard iteration). Storage is more critical for Newton iteration. N-R iteration addresses this limitation by holding the Jacobian matrix constant, thereby eliminating the need to reformulate the matrix for each time step.

Kool, J. B., J. C. Parker, and M. T. van Genuchten. 1987. Parameter estimation for unsaturated flow and transport models: A review. *Jour. Hydrol 91*: 255-293.

The first part of the paper deals with the estimation of hydraulic properties and parameters. For equilibrium solute transport, the authors first treat the simple case of linear sorption. They identify five parameters that must be identified prior to the solution of the Convection-Dispersion equation: R, D, v, mu, and gamma, where R = retardation; D = the dispersion coefficient;

v = mean pore water velocity; my = first order degradation coefficient, and; gamma = zero-order production coefficient. The authors then develop a model for non-equilibrium transport. They outline a two-site model of adsorption, where one site is governed by equilibrium sorption, and the other is governed by first-order kinetics. This model requires additional knowledge of the reaction rate parameter, alpha, and a site distribution parameter, beta. They point out that this model makes no assumption about exchange, although if it is linear, it can be evaluated using an analytic solution, while numerical solutions are necessary for non-linear adsorption. The authors note further, that if diffusion is approximated by first-order exchange, an identical mathematical model is achieved by using the two-region mobile/immobile model of nonequilibrium sorption. The authors also address the process of increasing the size of the problem to field-scale. They outline a method of defining the field as a set of parallel columns, and arithmetically averaging computed column values to determine the field-scale values. Lateral flow, transverse dispersion, and vertical heterogeneities are neglected in this approach. Finally, the authors address the type of data necessary, and the error that can be expected in the data.

Krishnaswami, S., W. C. Graustein, K. K. Turekian, and J. F. Dowd. 1982. Radium, thorium and radioactive lead isotopes in groundwaters: Application to the in situ determination of adsorption-desorption rate constants and retardation factors. *Water Resour. Res.* 18: 1633-1675.

This article reports the results of in situ measurements of sorption characteristics of Uranium (U), Radium (Ra), Thorium (Th), and Lead (Pb) performed on groundwater samples from unconfined, saturated aquifers in Connecticut. The authors present a good discussion of field and laboratory techniques. The distribution of pairs of isotopes suggest that adsorption is reversible. Neglecting precipitation dissolution, a model is developed that incorporates radionuclide decay in an expression for first order reversible adsorption desorption. This expression (K) in turn is related to the sorption K_d in the derivation of a retardation factor (R_f). R_f is shown to be equal to the production activity (in solution) ratio for a given radionuclide. Because of the assumptions of the model, R_f may be equal or nearly proportional to the ratio of the isotope half-lives. For a given radionuclide, the isotope with the shorter half-life will have lower values of K and R_f. Using the expressions derived in the paper, the authors apply the model to radionuclides in the ^{238}U and ^{232}Th decay chains in the Connecticut groundwaters. Rate constants are estimated relative to the half-life of the radionuclide. In general, migration of the radionuclides is severely retarded, and the authors conclude that Ra, Th, and Pb sorption reaches rapid equilibrium. Excess ^{234}U cannot be used to age date the waters because the supply rate of ^{234}U cannot be estimated precisely. The model is not a transport geochemical equilibrium model, and the roles of specific sorption reaction processes cannot be evaluated.

LaFlamme, B. D., and J. W. Murray. 1987. Solid solution interaction: the effect of carbonate alkalinity on adsorbed thorium. *Geochim. Cosmochim. Acta* 51: 243-250.

Batch equilibrium experiments were performed using Th-spiked lakewater and a synthetic goethite substrate to evaluate the effect of pH, ionic strength, and alkalinity on Th-sorption. Sorption decreases with increasing Th in solution. There is no significant change in sorption due to increasing ionic strength, up to I = 2.0. Th-sorption is a function of pH with an adsorption edge between a pH of 2 and 5. Sorption decreases with increasing alkalinity. At pH=9.0, adsorption decreased starting at an alkalinity of 100 meq/L and disappeared all together by 300 meq/L. The authors attribute this to competition for sites and the formation of Th species, with competition the most important effect. Triple layer surface complexation is used to model Th sorption. Modeling took three steps: (1) Determination of adsorption constants for thorium hydrolysis; (2) Adsorption of carbonate species on goethite; (3) Consideration of the effect of Th-carbonate species on Th-sorption. The computer code MINEQL finds the association constant by fitting the pH/Th-adsorption edge. The result is a series of equations describing adsorption of the species on goethite. As a result of the modeling, it was determined that carbonate complexation decreased in importance as the solid/solution ratio increased. The authors conclude with a call for better thermodynamic data.

Lieser, K. H., and C. Bauscher. 1988. Technetium in the hydrosphere and in the geosphere II Influence of pH, of complexing agents and of some minerals on the sorption of technetium. *Radiochim. Acta 44/45*: 125-128.

With increasing redox potential, Technetium sorption coefficients drop sharply at pH 6.5 to 7.5. At lower pH, Tc(VII) is reduced to Tc(IV) and high sorption ratios are maintained over a greater range in Eh. Tc(IV) forms various humic acid complexes, while Tc(VII) does not. Sorption by pyrrhotite(Po), pyrite(Py), and magnetite(Mt) are investigated. Batch equilibrium experiments were conducted under both aerobic and anaerobic conditions for: (1) variable pH, (2) addition of EDTA, and (3) 30 mg of pyrrhotite, pyrite, and magnetite. Actual groundwaters were used in the experiments. After equilibration, the solution was filtered (< 450 nm) to check for colloid formation. For pH 3-9, sorption is low for aerobic, and high for anaerobic conditions. At low salinity, equilibration took over 10 days. Under aerobic conditions, EDTA had no significant effect. Under anaerobic conditions, however, sorption was greater due to stabilization of Tc(V) through EDTA-complexation. Only Po affected apparent sorption (increase) under aerobic conditions. This was assumed due to formation of Tc sulfides and hydrolysis of Po to form H_2S which was further oxidized to H2SO4, decreasing solution pH. Py and Mt had less effect due to lower solubility in an aerobic environment. No colloids were formed, and only Tc(VII) was found in solution

Liu, C. W., and T. N. Narasimhan. 1989a. Redox controlled multiple species reactive chemical transport. 1. Model development. *Water Resourc. Res.* 25: 869-882

To deal with redox-controlled equilibria conditions, the multicomponent transport model DYNAMIX draws on a redox sequence from fully-oxidized to fully-reduced waters. The sequence is: (1) oxygen; (2) iron-rich; (3) sulfide-rich; (4) methane rich. By analyzing the concentration of a given redox couple and using its equilibrium constant, the model can identify major redox couples controlling the redox potential in a given system. DYNAMIX couples the equilibrium code PHREEQE with the transport code TRUMP. A two step coupling is employed, solving first for chemical transport, and then chemical equilibrium for each grid block. Activity coefficients are calculated using the Davies equation, and the model is therefore only reliable at fairly low ionic strengths. A search routine looks for the most stable mineral assemblage based on the assumption of a minimum Gibbs free energy. Mass balance is performed as a check on the concentration of each mineral. The code can model the kinetics of dissolution, which are treated as a source term in the model, but not precipitation. Surface-controlled reactions are assumed to be the rate-limiting step. Dissolution is transport-controlled, and considered to be congruent. The porous media is assumed to be made up of uniform spherical grains. Only longitudinal dispersion is considered, and transverse diffusion is assumed negligible. Sorption/desorption is not currently considered, and retardation is only modeled by dissolution precipitation. An explicit scheme is used, and a maximum time-step is calculated based on capacitance, conductance, and advectance. The sequence of steps performed at each time-step by the model is: (1) Initial conditions and degree of equilibrium are set by the equilibrium model; (2) Transport; (3) Concentration changes for each element (and oxygen), kinetic rate equations, and speciation and mass reaction transfer are calculated by PHREEQE; (4) Final concentration of each component is calculated and precipitation/dissolution is performed. The mineral mass is updated and the sequence repeats. The authors emphasize that because complete mixing between aqueous mixing is assumed, the presence of incomplete mixing (which they acknowledge in natural systems) may result in some error.

Liu, C. W., and T. N. Narasimhan. 1989b. Redox-controlled multiple-species reactive chemical transport. 2. verification and application. *Water Resourc. Res.* 25 883-910

The authors compare results of the DYNAMIX chemical transport code to the one-dimensional codes PHASEQL/FLOW and THCC. A test case of transport of four species (A, B, C, and D) through the porous medium AB in a one-dimensional column was used. Fluid velocity was set at 1 m/yr. A, C, and D are in solution, and C and D are nonreactive solutes. Unit activity coefficients were assumed. Agreement between the three codes was very good. A uranium transport problem in the seven component system Na, Ca, Si, C, U, H, and e (electron) was also developed. Eighteen aqueous species and complexes were modeled, and run for 12 days. Modeled uranium migration was significantly retarded by precipitation reactions. If redox conditions were internally controlled by redox reactions in the system, the redox front is sharper than if there was an external source of electrons, and was a better model of natural systems. In comparison to a nonreactive uranium species, external control retarded migration by a factor of 5, while assuming internal control resulted in retardation by a factor of only two. Agreement was reasonably good with the one-dimensional codes. The model was then applied to the natural system of supergene copper enrichment at Butte, Montana. Transport in the vadose zone was modeled by assuming a reduction factor to groundwater velocity based on degree of saturation. For a model run of 2000 years, with oxygen buffered by diffusion of the atmosphere in the leached zone, a sharp redox front appeared in simulation, similar to that observed at Butte. A greater time would be necessary, however, to reproduce Cu concentrations observed in nature. DYNAMIX was also applied to arsenic and selenium migration. These were significantly retarded by redox precipitation reactions. To model the transport for 30 years for 400 nodes, the model required 3.4 hours of CPU time on a CRAY XMP 14. Since the model is limited to a maximum time step by its explicitly numerical formulation, the model may not be appropriate for longer times unless the system is extremely simplified or the grid is very coarse. The authors note that approximately 99 percent of the CPU time is involved in the geochemical equilibria calculations.

Liu, W., J. Lo, and C. Tsai. 1991. Sorption of Cs, Sr and Co on andesite and coral limestone. *Radiochim. Acta 52/53*: 169-175.

In a series of batch experiments, natural water samples filtered at 0.45 microns were spiked with radionuclides of Cs, Sr and Co at concentrations from 10[illegible] to 10[illegible] M and added to crushed andesite, coral limestone, and clays. Blank tests checked for adsorption onto vessel walls. A second set of experiments immersed polished thin sections in spiked solutions for seven days. These sections were examined using autoradiography to determine sorbing mineral phases. Three types of sorption were defined and characterized based on sorption ratios (R_d): physical adsorption at the mineral surface, ion exchange, and one directional processes such as precipitation. Carbonate sorption is controlled by physical processes, clays by ion exchange. Andesite is controlled by physical adsorption for primary minerals, and ion exchange for secondary minerals. Sorption ratios decrease with increasing solution ionic strength. The authors attribute this decrease to either increased competition for ion exchange sites, or complexation with common anions to reduce radionuclide affinity for sorption sites. Increased competition is the apparent cause of the salt effect with Cs and Sr. For Co, complexation appears to be the controlling process. Cs-sorption is unaffected by pH changes, while Sr-sorption increases markedly above pH 10 due to co-precipitation with calcite. Co sorption is affected by pH in an irregular fashion, perhaps due to the formation of a small amount of complexes during pH adjustment with NaOH and HCl. Autoradiography suggests that sorption in limestone is largely limited to detrital clays (Cs, Sr) and precipitation of $CoCO_3$.

Lowson, R. T., S. A. Short, B. G. Davey, and D. J. Gray. 1986. U-234/U-238 and Th-230/U-234 activity ratios in mineral phases of a lateritic weathered zone. *Geochim. Cosmochim. Acta 50*: 1697-1702.

Selective phase extraction methods were used to examine the association of U, Th, and Ra with adsorptive phases in soils at Alligator Rivers, Australia. Phases examined include amorphous iron, crystalline iron, $NaCO_3$ and the remaining clay quartz resistate. Concentrations of ^{238}U, ^{234}U, and ^{230}Th associated with iron-phases are 1 to 2 times greater than in the resistate. ^{226}Ra concentrations are about the same order in iron and resistate phases. For iron phases at a given depth, isotope concentrations are observed to increase down the decay chain ^{238}U to ^{234}U to

^{230}Th, and then decrease on decaying to ^{226}Ra. In the resistate, concentrations increase as ^{234}U decays to ^{226}Ra. Similarity of ^{234}U/^{238}U activity ratios in groundwater and amorphous iron suggests adsorption/desorption equilibrium between these two phases. The evidence indicates that the kinetics for chemical processes is equal to or less than the half life of ^{230}Th (75,200 years). High ^{234}U/^{238}U ratios in resistate phases indicate that these have become inaccessible to groundwater. The reverse would be expected, since ^{234}U would be preferentially released. This indicates that ^{234}U transfer is counter to groundwater gradients, suggesting that alpha recoil or some other external mechanism is controlling transfer in the resistate. Enrichment of Ra over parent ^{230}Th in the resistate may also be interpreted in terms of alpha recoil.

Magaritz, M., I. B. Brenner, and D. Ronen. 1990. Ba and Sr Distribution at the Water-Table: Implications for Monitoring Ground-Water at Nuclear Waste Repository Sites. *Applied Geochem.* 5: 555-562.

The authors note previous studies that demonstrated microscale (tens of centimeters) heterogeneities with respect to major and minor anions (Cl, NO_3, SO_4). They have studied the distribution of Ba and Sr as radionuclide analogs in the water table region. The study reports on waters from calcareous sands in Israel, an arid climate similar to Yucca Mountain, although the rate of recharge is higher (150 mm/yr vs. ~2mm/yr). Both vertical and horizontal heterogenities in Ca, Cl, Ba, Sr, and SO_4 were found on a microscale level using a new multi-later sampling system. Transition from unsaturated to saturated conditions occurred over 50 cm. Intense biological activity was observed in the water table region, and dropped off with decreasing dissolved oxygen 3-9 cm below the water table. Sr and Ba were associated with the carbonates, and Ba was also controlled by barite. Ba in solution increases and SO_4 decreases in the water table region, and the reduction of SO_4 leads to the dissolution of barite. The authors conclude that since ions may be part of the liquid or solid phase, and microscale heterogeneities occur, composite water samples obtained with a pump are not adequate to characterize ground waters, and should not be used in prediction.

Mangold, D. C., and C. Tsang. 1991. A summary of subsurface hydrological and hydrochemical models. *Reviews of Geophysics* 29: 51-79.

This article is a valuable summary of the theory and methods involved in geochemical transport, and hydrochemical (hydrogeochemical) numerical modeling. The authors begin with a summary of the theory behind fluid flow modeling and the different approaches that have been used. Chemical modeling is also discussed, summarizing mass action considerations and activity/molality relationships. General reactive transport equations are derived, and sorption schemes are discussed. Numerical formulations are developed, and model validation is discussed. The most useful part of the article is the tabulation of 56 geochemical, solute transport, (1-, 2-, and 3-dimensional saturated/unsaturated), and hydrochemical models. Extensive references are given. Code characteristics are listed in the tables, including affiliated institution, numerical approaches, sorption and kinetic models, coupling techniques, temperature limitations, availability, etc. Following the tables are short discussions of the codes including developmental history, previous applications, and extent of code verification. The article is an excellent survey of research developments through late 1990.

Mansell, R. S., S. A. Bloom, [illegible] M. Selim, and R. D. Rhue. 1988. Simulated transport of multiple cations in soil using variable selectivity coefficients. *Soil Sci. Soc. Amer. Journal 52*: 1533-1540.

The authors have modified a one-dimensional, finite-difference, equilibrium chromatographic model to incorporate mobile/immobile water and variable ion selectivity coefficient (Kij). Generalized multicomponent exchange isotherms are assumed, using simple binary-exchange Kij for all combinations of ion species. All activity coefficients are assumed unity. Short time steps are used initially, and increased by 5 percent for each iteration until a stable maximum was reached. The time step generally varied from 15 to 300s. Cumulative mass balance errors were calculated for the sum of all cation species as well as for individual species during each simulation. The authors also give requirements for experiments in order to evaluate a transport model: (1) Breakthrough curves (BTC) for cation concentration in column effluent; (2) Initial composition of ion species in both exchange phases and solution; (3) Composition of the applied solution; (4) Liquid pore velocity; (5) Hydrodynamic dispersion coefficients; (6) Soil bulk density; (7) Volumetric water content; (8) Soil cation exchange capacity (CEC), and; (9) Binary exchange isotherms for each pair of cation species considered. The model was applied to miscible displacement experiments of Na, Ca, Mg (Lai et al., 1978). Ternary and binary exchange isotherms were approximated for all pairs. Analysis showed that the model was relatively insensitive to diffusive transfer between the mobile-immobile water, and more sensitive to the fraction of immobile water. Varying Kij better models tailing, but tends to overestimate overall retardation, and leads to somewhat larger mass balance errors. Mass balance errors were unequally distributed among the three ions considered. Increasing the fraction of immobile water tends to decrease retardation of the BTC, but increases tailing. The authors identify three future considerations: (1) Ion pairing; (2) Speciation, and (3) Chemical disequilibrium.

Mansell, R. S., S. A. Bloom, and L. A. G. Aylmore. 1991. Simulating cation transport during unsteady, unsaturated water flow in sandy soil. *Soil Science*. (in press)

A preprint that presents a finite-difference model for the transport of multiple species during unsteady, unsaturated flow. The analysis begins with a review of postulated models governing transport of both conservative and reactive solutes. The model addresses both equilibrium models and non-equilibrium two-site and two-region (mobile/immobile water) models. General observations include: (1) During unsteady, unsaturated flow, the non-reactive solute front lags behind the wetting front, and hydrodynamic dispersion (D) increases with pore velocity; (2) If the soil pores are completely available for solutes, then displacement is piston-like (mobile water). Immobile water may be due to a variety of processes such as anion exclusion and can lead to incomplete displacement, and (3) A non-uniform initial distribution stretches or contracts the propagated solute pulse, and asymmetry of solute transport. The pulse becomes more symmetric as time increases. For applying the competitive ion exchange model to fluid, the ion selectivity coefficient (K) becomes important. A large selectivity coefficient favors displacement of the native cation by the transported cation, and large ratios of cation exchange capacity (CEC) to solution normality (N) provides for greater retardation of a given solute. K is not determined based on mineralogy, but is determined as a soil property in the lab, and it does not address mineral equilibria resulting from precipitation/dissolution. Sorption is addressed in a weighted retardation factor (R). For the numerical model presented, one-dimensional, non-hysteretic flow is considered. In order to model fluid transport, Richard's equations are solved for head distribution and water content. Both binary and ternary cation exchange (Na, Mg, Ca) were considered. In the modeling runs, the following observations were made: (1) An increase in K increases the completeness of displacement of the native cations by the transported cations, and the solute front is increasingly dominated by the displaced native cations. (2) The model checks mass balance during a run. For a highly competitive invading cation (high K), smaller time steps are needed to avoid unacceptable mass balance. (3) For applied soil water conditions with variable solution normality (CT) much less than 1 (i.e. a low infiltration rate), the model is numerically unstable.

Marley, N. A., J. S. Gaffney, K. A. Orlandini, and C. P. M. Dugue. 1990. An evaluation of an automated hollow-fiber ultrafiltration apparatus for the isolation of colloidal materials in natural waters. *Hydrol. Processes* (preprint)

Hollow-fiber ultrafiltration is evaluated as a means of sampling subsurface colloids for analysis. Four sizes are available, ranging from 0.45 microns to 3000 MW. Slow pumping rates on the order of 4-96 ml/min are needed to avoid sample contamination in the field. A field study was performed using radiotracers Cd, Zn, and Y from four surface waters and one groundwater in Illinois and South Carolina. Reproducibility was observed to be better than 15 percent, with 95 percent recovery. The highest organic content was found associated with the 3000 to 30000 MW (1 to 2.5 nm) range. Samples needed to be analyzed in the field in order to get accurate DOC measurements. Fe, Zn were mostly associated with small organic colloids. The results indicate that some of the larger "organic" colloids in groundwater may be clays coated with active humic materia. The authors point out that filtering assumes spherical particles, and that the actual particle shape may have an impact on particle fractionation.

Maya, L. 1982. Hydrolysis and carbonate complexation of dioxouranium(VI) in the neutral-pH range at 25 C. *Inorg. Chem. 21*: 2895-2898.

The author begins by discussing the importance of hydrolysis and carbonate complexation in modeling the migration behavior of uranium in nature. He then identifies uranyl, uranyl hydroxides, and uranyl carbonate species believed to be important in near-neutral pH range for natural waters at relatively low $P(CO_2)$ (i.e., log $P(CO_2)$ = -3.5 to -2.0). Experiments are described in detail using analytical, spectroscopic, and electrochemical means to verify the formation of a hydroxycarbonato U-species with a U/CO_3 mole ratio of about 2.0. The apparent formula of this species is $(UO_2)CO_3(OH)_3^-$. The stability constant of this uranyl hemicarbonate is developed by fitting the data to functions describing the charge balance and mass balance as related to total uranium concentration.

McCarthy, J. F., and J. M. Zachara. 1989. Subsurface transport of contaminants. *Environ. Sci. Technol. 23*: 496-502.

A good survey article of the effect of colloidal particles on contaminant transport. Several studies have shown that colloids have acted to enhance contaminant migration. Characterization of colloids in situ is difficult, however, due to artifacts introduced by sampling procedures such as drilling muds, introduction of atmosphere (changes in pH, Eh, P(CO_2), etc.), and the breakup of colloids. Colloidal matter includes clays (both detrital and authigenic), hydrous oxides, iro oxides, carbonates, silica, etc. A number of physical-chemical processes can introduce colloidal material to the mobile fluid phase, including gradients in pH, Eh, and P(CO_2) due to flu mixing or organic processes. The reduction of Fe-oxide cements, disaggregation and stabilization of colloidal particles in suspension. Decreased ionic strength expands double layers, and increases surface charge, stabilizing the colloid. Sorption may in itself act to stabiliz colloids due to charge reversal and a subsequent increase in surface charge. Geochemical processes and physical filtration act to remove colloids from suspension. Positively charged colloids will be removed from solution due to the net negative charge displayed by most porou media. Conversely, zones of preferential flow will enhance colloidal stability in suspension due to reduction in particle-particle collisions that could lead to colloid attachment or aggregation. The effects of colloids will depend on the complex interplay of surface site density, surface area, and preconditioning of surfaces. An empirical K_d approach may be altered to reflect colloidal effects, leading to a reduced retardation factor for contaminant migration. However, constant K_d approaches are inadequate. The authors conclude with suggestions for the use of colloids in remediation projects, and urge more research into characterizing the role of colloids.

Means, J. L., D. A. Crerar, and J. O. Duguid. 1978a. Migration of radioactive wastes Radionuclide mobilization by complexing agents. *Science 200*: 1477-1481.

A study of EDTA-enhanced migration of cobalt at Oak Ridge National Laboratory (ORNL). Fracturing is thought to reduce a rock's sorptive capacity because exchange sites adjacent to the fissures are saturated with exchangeable cations in the waste. EDTA is present in the wast because it is used as a decontaminating agent. EDTA forms strong complexes with radionuclides and diminishes adsorption. Evidence suggests that uranium may migrate in the same manner. In the presence of EDTA and other naturally occurring organics, ^{60}Co resists adsorption by laboratory resins. Seventy percent of uranium, and 90-95 percent of ^{60}Co associated with organics above a molecular weight of 700. The authors identify a number o other organics: palmitic acid, phthalic acids, mono- and di-carboxylic acids. These are weake complexing agents than EDTA. EDTA is thermally stable and very persistent in natural system

(12 to 15 years). Am(III), Cm(III), Pu(III), Pu(IV), Pu(VI), and Th(IV) are at least as high for complexing as Co^{2+}. The authors conclude by suggesting that decontamination agents other than EDTA be used.

Means, J. L., D. A. Crerar, M. P. Borcsik, and J. O. Duguid. 1978b. Adsorption of Co and selected actinides by Mn and Fe oxides in soils and sediments. *Geochim. Cosmochim. Acta* 42: 763-1773.

The authors investigate Fe and Mn oxides as adsorbing substrates for actinides and ^{60}Co in sediments at Oak Ridge National Laboratory. EDTA, which is used in decontamination operations at nuclear facilities may contribute to mobilization of Co and certain actinides. Fe and Mn-oxides act as sinks for U, Th, and Co. Mn-oxides are considered a better scavenger [illegible] values of both negative surface charge and cation adsorption capacity over pH ranges [illegible]. Sorption increases with pH due to increased surface charge, but Mn-oxides [illegible] adsorb even at zero surface charge. Some ion exchange is inferred, and [illegible] is predominantly Mn(IV). The authors review experimental techniques used to [illegible] sorption capacity of Fe- and Mn-oxides. K_d values were determined to give a relative [illegible] sorptive capacity. ^{60}Co content most closely correlates with Mn-oxide concentration, [illegible] no systematic correlations with Fe and organic concentration. Size fractions are used [illegible] distinguish between clays and particle coatings of Mn and Fe-oxides. Cobalt sorption on clays should be concentrated in the 0.2 to 2 micrometer size fraction, but observed in all size fractions [illegible]. The data suggests that adsorption is by particle coatings rather than clays. [illegible] Am, ^{238}Pu, and ^{244}Cm are also most strongly associated with Mn-oxides. Again [illegible] coatings rather than clays are dominant. The authors conclude that water chemistries should be maintained where Mn-oxides are least soluble (high pH and/or high Eh) to maximize sorption at nuclear waste site. They also suggest that artificially bolstering Mn-oxide levels at [illegible] should be considered.

[illegible] A. 1990. *Yucca Mountain Project Far-Field Sorption Studies and Data Needs.* Los Alamos National Laboratory, LA-11671-MS; UC-510. Los Alamos, NM. September.

[illegible] of sorption experiments related to the Yucca Mountain Project (YMP). Justification [illegible] presented for using K_d's determined from batch equilibrium experiments, and a tabulation of K_d's determined for the sorption of different radionuclides by the various volcanic units at Yucca Mountain. The effect of radionuclide speciation is thought to be minimal, since at average K_d [illegible] include these at equilibrium. In addition, if physicochemical conditions remain fairly [illegible] the constant K_d approach is suitable. Batch equilibrium experiments on pure minerals [illegible] proposed for use in estimating whole-rock sorption. Larger ranges of water composition [illegible] be easily accommodated once they are determined. The author reviews batch equilibrium [illegible] stressing the importance of using an undersaturated field solution in order to av[illegible] [illegible]/dissolution effects. Dynamic column experiments with crushed materials a[illegible] [illegible] but whole-rock experiments (intact core) are extremely difficult due to th[illegible] constraints. Future experiments should be designed to include all major rock types and all anticipated water, temperature, and waste composition conditions. Theoretical sorption models are also discussed (surface complexation, ion exchange, etc.). Colloids and kinetic sorption are considered, and the different sorption experiments in the YMP database are also considered. Possible sorption mechanisms are identified. NRC concerns are discussed, and a strategy is outlined for addressing those concerns that are considered important. The current DOE position on sorption is outlined: (1) Retardation factors (+/- isotherms) are appropriate, as long term water-rock composition does not change much; (2) the present database needs to be further developed with regard to actinides and other fission products; (3) clays and zeolites are sorptive for alkalis and alkaline earth elements, but have exhibited no special affinity for actinides and REE; (4) batch experiments are needed for actinides and REE. Additional studies are needed to evaluate the water/rock ratio effect; (5) kinetic data is needed; (6) experimental modeling of waste-form leaching is needed; and (7) there is a need for data on solution speciation, selectivity coefficients, mineral surface characteristics, surface complexes, and detailed host rock mineralogies for theoretical modeling.

Meijer, A., I. Triay, S. Knight and M. Cisneros. 1989. Sorption of radionuclides on Yucca Mountain tuffs. *Nuclear Waste Isolation in the Unsaturated Zone: Focus '89*. Los Alamos, NM: 113-117.

Evidence from sorption experiments on Yucca Mountain tuffs at Los Alamos National Laboratory suggests that the sorption coefficient (K_d) values determined by equilibrium batch experiments for most radionuclides are large (» 10 ml/g). Tc, Np, and U apparently have slightly smaller K_d values. Sorption of Cs, Ba, and Sr are dominated by ion exchange with zeolites, while the K_d increases for these elements on zeolites with increasing water/rock ratio. The authors are concerned with the effect of using crushed rock vs. natural rock in the experiments. Examination of the Cs, Ba, and Sr data suggest that the effects are minimal. It should be noted that both types of experiments were batch equilibrium experiments. The authors believe that, while batch equilibrium experiments are not identical to anticipated field conditions, they do provide conservative limits to sorption processes that can be used to assess the future performance of a repository at Yucca Mountain. The authors clearly believe that sorption coefficients for alkali and alkaline earth elements will be large in the Yucca Mountain environment.

Middleburg, J. J., and R. N. J. Comans. 1991. Sorption of cadmium on hydroxyapatite. *Chem. Geol. 90*: 45-53.

The authors present a study of Cd^{2+} adsorption on hydroxyapatite (HA). Experimental methods (batch) are described in detail. Radiotracers used to calculate aqueous and sorbed concentrations. Following solution separation, the solid particles are re-suspended to check reversibility of sorption reactions. The zero point charge ranges from 7.5 in deionized water to 11 in a solution containing 10^{-3} M Ca^{2+}. A hydroxyapatite surface will therefore have a positive charge in most natural waters, and the electrostatic potential between HA and natural solutions tends to impede rather than promote Cd-sorption. Aqueous speciation is calculated using the code WATEQF. At low cadmium concentrations, solution pH is buffered and the data is treated as a sorption isotherm. At higher concentrations, the solution becomes saturated with respect to $CdCO_3$, and precipitation controls Cd activity. Fast initial uptake of Cd can be fitted by a Langmuir isotherm, and is controlled by reversible adsorption desorption for the first several hours. At longer times, uptake continues at a slower, non-reversible rate. This is believed to reflect the increasing influence of precipitation and recrystallization processes.

Miller, C. W. 1983. Earth Sciences Division. *CHEMTRN User's Manual.* Lawrence Berkeley Laboratory, LBL-16152, Berkeley, CA.

This report is a user's manual for the equilibrium reactive transport code CHEMTRN. The author includes an introduction of the basic equations used to solve for geochemical equilibrium, ion exchange, surface complexation (TLM), and one-dimensional transport. No K_d values or sorption isotherms are available in this version of CHEMTRN. The code does not have its own data base, and the user must supply the equilibrium constants, selectivity coefficients, CEC, site density, sorption parameters, etc., for all reactions to be considered. The code uses a one-step coupling to develop a set of nonlinear algebraic differential equations that are solved using finite difference techniques. A Newton-Raphson technique is used to iteratively solve the equations. Only one sorbing substrate is available for each run. Four example problems are given, and sample input and output decks and the source code (FORTRAN) for the driver program and the subroutines are provided in the appendix.

Miller, C. W., and L. V. Benson. 1983. Simulation of solute transport in a chemically reactive heterogeneous system: Model development and application. *Water Resour. Res.* 19:381-391.

CHEMTRN is a one-dimensional hydrogeochemical model designed for solute transport in a saturated porous medium. Included are the processes of dispersion diffusion, advection, ion exchange,dissociation of water, speciation and complexation, and is able to model activity/concentration relations using the Davies equation. Local equilibrium and a finite density of exchange sites are assumed. CHEMTRN employs a one-step coupling of transport and geochemistry, resulting in a set of nonlinear PDE. The model can theoretically be expanded to 2- and 3-D problems using parallel, non-interacting 1-D streamtubes, although the authors admit that memory storage requirements may be excessive. According to the authors, CHEMTRN introduces artificial dispersion. This is minimized by choosing a time-step such that the Courant number (Cr) = 1. An adjustable time step is also possible, based on rates of convergence. The authors have used the model to examine the effects of variable K_d as opposed to "rather arbitrary" values of reasonable magnitude. Sorption decreased mobility of Sr by 90 percent, while higher NaCl concentration lowered the degree of Sr sorption. Increasing both Na and Ca in the fluid results in the enhanced transport of Sr, which the authors ascribe to increased competition for a finite number of sorption sites. The effect of pH and complexation on Sr sorption is not great, but the authors predict that these effects could be significant for actinides. The authors conclude that a constant K_d is inadequate to model sorption unless it is measured or calculated in a way that exactly duplicates the conditions of the environment, and then only if the wasteform does not significantly alter the groundwater chemistry. The authors also state that the model has been modified to consider both precipitation/dissolution and surface complexation as retardation mechanisms.

Morrey, J. R. 1988. *FASTCHEM Package. Volume 4: User's Guide to the ECHEM Equilibrium Geochemistry Code*. Electric Power Research Institute, EA-5870-CCM, Vol. 4, Palo Alto, CA.

This report is part of the five-volume set used to describe the hydrogeochemical code FASTCHEM. This volume describes the geochemical equilibrium module ECHEM. The report begins with a definition of terms used in ECHEM, and proceeds to develop the mathematical equations governing the conceptual model of the code. This is based on mass-action, mass balance, and charge balance constraints. The model is able to incorporate activity/concentration relationships using either the Davies or extended Debye-Huckel equations to calculate activity coefficients. ECHEM is based on the EPA code MINTEQ2, and is able to incorporate a number of adsorption models into simulations. These include activity K_d, Freundlich, and Langmuir isotherms, ion exchange, double and triple-layer surface complexation and specific ion models. The finite-element numerical algorithms and iteration/convergence schemes used in solving the governing equations are presented, the structure of the code is outlined. Examples in defining [illegible] (conceptual model, material and boundary chemistries) for the code are given, and a description of input and output is presented. Thirty-two test cases and the results of the model are described, and five applications are discussed.

Morrey, J. R., C. T. Kincaid, C. J. Hostetler, S. B. Yabusaki, and L. W. Vail. 1986. *Geohydrochemical Models for Solute Migration. Volume 3: Evaluation of Selected Computer Codes*. Electric Power Research Institute, EA-3417, V.3, Palo Alto, CA.

Test cases are used to evaluate three transport codes (SATURN, FEMWATER1/FEMWASTE1, and TRANS), two geochemical codes (MINTEQ and EQ3NR/EQ6), and one geohydrochemical code (FIESTA) as part of an EPRI project to develop geohydrochemical models. For the cases of variable pH, $P(CO_2)$ and constant $P(O_2)$, MINTEQ and EQ3/EQ6 agree fairly well, although there is divergence for predicted mineral saturation. MINTEQ does not model reaction kinetics, while EQ3/EQ6 does not model sorption. MINTEQ test runs compare various sorption (K_d, Langmuir, Electrical Double Layer) models with attenuation experiments (Cu and As). Langmuir and K_d approaches produced similar results in terms of speciation, and only carbonate species are affected to any extent. Speciation is similar for all sorption models, but Cu and As concentrations are significantly lower for surface complexation. Both codes demonstrated convergence problems. Inappropriate initial activities and highly pH-dependent species can cause MINTEQ to fail due to wide variations in ionic strength between iterations caused by Newton-Raphson iteration. MINTEQ does not balance charge, and input parameters are not formatted with sufficient accuracy to ensure precise electrical neutrality. The authors suggest that by breaking water movement into discrete periods, transient behavior can be modeled using steady-state approaches. MINTEQ performed consistently better than EQ3/EQ6 in the test cases considered, and is more amenable to modification for coupled transport applications. The authors recommend MINTEQ as a geochemical code because it would be easier to add reaction-path modeling to MINTEQ than to modify EQ3/EQ6 to include adsorption, constant pH, $P(CO_2)$, etc. MINTEQ will need to be scaled down for coupling to transport codes. Two-step coupling is recommended to maximize code flexibility. One-step coupling is more mathematically exact, but is much more demanding computationally. Also, a two-step approach is easier for future modification. Solid solution, microbial interaction, nonisothermal moisture movement, multiphase flow, or geochemically altered permeability may be important, but due to their complexity, they may not be included in the current (1986) development schemes. The finite-element code SATURN is recommended as the transport code for future investigation. The geohydrochemical model FIESTA is currently limited to a 1-dimensional homogeneous, saturated porous medium. Using two-step coupling, transport is accomplished through advection and dispersion, then geochemical speciation is performed. Pore water velocity and the dispersion coefficient are held constant. Boundary conditions are constant, and initial concentrations can be specified for each element. There is a maximum of 6 components, and interaction with the substrate is through adsorption using either 1 to 1 ion exchange or a Langmuir isotherm. Competitive sorption is possible, but the model cannot handle surface complexation or precipitation/dissolution. There is no mass balance or activity correction for water.

Murali, V., and L. A. G. Aylmore. 1983a. Competitive adsorption during solute transport in soils: 1. Mathematical models. *Soil Science 135*: 143-150.

The authors begin by presenting linear, Freundlich, and Langmuir empirical sorption isotherms. These isotherms are then modified in a straightforward manner to model kinetic sorption using first-order adsorption/desorption constants. At equilibrium, these reduce to the equilibrium isotherms. In considering multicomponent, competitive adsorption, general Freundlich and Langmuir isotherms are developed, and special cases (relative concentration, relative sorbed concentration, etc.) are considered for binary systems. The treatment is not, however, limited to binary systems. The Langmuir isotherm is further modified for competitive, kinetic sorption. An empirical approach is developed for multispecies transport which computes solution phase concentrations for all species. Single species equilibrium adsorption is calculated using the appropriate isotherm. Competition is characterized by an additional empirical parameter $P(j)$ such that $\Sigma[P(j)] = 1$. A normalization of equilibrium sorption coefficients is one choice for P such that $P(i) = K(i)/\Sigma_j K(j)$. The authors also develop an isotope exchange model based on a competitive model

Murali, V., and L. A. G. Aylmore. 1983b. Competitive adsorption during solute transport in soils: 2. Simulations of competitive adsorption. *Soil Science 135*: 203-213

A report of computer simulations performed using empirical competitive sorption models developed in Murali and Aylmore (1983a). Based on these simulations, several different cases of equilibrium (Freundlich and Langmuir) and kinetic (Langmuir) competitive sorption are considered. Freundlich and Langmuir isotherms are presented in general and linearized forms for single species and binary competitive sorption. Simulation (3) shows that total sorption is a non-unique function of total solute concentration for multispecies systems. Simulation (4) demonstrates the water/rock ratio effect on adsorption. Following desorption from the substrate, released ions will compete for sorption sites with species already in solution. From computer simulations of competitive adsorption, the authors demonstrate that using a single-species approach in a multispecies system will result in predicted Langmuir equation coefficients [K(La) and Q] that vary as a function of bulk density (water/rock ratio). Only a multiple linear regression approach accurately determines Langmuir coefficients. Also, coefficients are better estimated at a variety of water/rock ratios to discriminate competitive sorption effects. Simulation (5) considers dynamic Langmuir, competitive sorption. Adsorption in excess of equilibrium values may occur. The apparent sorption of a species will decrease due to competition. Simulation (6) uses competitive Freundlich isotherms to predict reduced sorption in binary systems relative to single-species sorption. The increase in K as a function of increasing competition is more than offset by an accompanying decrease in the Freundlich exponent (n).

Murali, V., and L. A. G. Aylmore. 1983c. Competitive adsorption during solute transport in soils: 3. A review of experimental evidence of competitive adsorption and an evaluation of simple competition models. *Soil Science 136*: 279-290

The authors examine the experimental literature for evidence of competitive sorption. Most experiments are of the batch equilibrium type performed at higher water/rock ratios than those found in nature. In addition, shaking is used to enhance equilibrium sorption. The authors recommend using conditions closer to those anticipated in the field. Competition is examined for phosphate, bicarbonate, selenite, sulfate, and organic anionic compounds, and also for cation sorption. Competitive sorption is not required in every case, as some sites may sorb a particular ionic species to the exclusion of others. Cumulative adsorption exceeds that of individual species, while competitive sorption reduces the adsorption of an individual ion relative to a single-species, non-competitive system. The authors comment that pH can affect the selectivity coefficient in binary systems, and site one study where this was observed for phosphate, selenite, and arsenate. The authors also suggest that desorption from a substrate, and subsequent resorption through competitive sorption may be a possible mechanism for the water/rock ratio effect observed in Ca, Zn, and Pb binary systems.

Nair, S., D. Longwell, and C. Seigneur. 1990. Simulation of chemical transport in unsaturated soil. *Jour. Environ. Eng. 116*: 214-235.

The authors present a one-dimensional, sequential iteration model of contaminant transfer in both aqueous and gas phases. They develop the governing equations separately for gaseous and aqueous transport. Sorption equilibrium is assumed at the gas/water, gas/solid, and water/solid interface since sorption processes are assumed to operate according to first-order kinetics much faster than the transport time scale. Partitioning coefficients are developed for contaminant between phases and are treated as constants. Retardation factors are then developed for aqueous and gas phases as functions of these coefficients, moisture content, porosity, and soil bulk density. The model assumes no initial contaminant gradient, and uses average mean values for infiltration initial and boundary conditions. The equations are solved using finite element numerical methods. In simulation, the model is applied to a hypothetical clayey soil, and a temperature gradient is assumed, although the temperature term is only incorporated in the molecular diffusion term. From the simulations, the bulk of the contaminant transport is observed to occur in the aqueous phase. The authors conclude that chemical kinetics, and non-linear sorption can be easily incorporated into the sequential iteration approach as outlined.

Nakayama, S., and Y. Sakamoto. 1991. Sorption of neptunium on naturally-occurring iron-containing minerals. *Radiochim. Acta 52/53*: 153-157.

An investigation of neptunium-sorption on a variety of natural Fe-bearing minerals and synthetic aluminum compounds. Np(V) (4×10^{-7} to 6×10^{-6} M) was used as a spike for 0.1 M $NaNO_3$ solutions in batch experiments performed under ambient aerobic conditions. pH was not adjusted during sorption. Based on blank runs (no solids), sorption onto polyethylene or glass vessel walls was negligible at pH < 7, and about 10 percent at pH 10-11. Time-series experiments were run to investigate sorption kinetics. For natural goethite and biotite, most sorption occurred in 30 minutes, followed by a slow approach to equilibrium. A maximum of about 2 days was required to reach equilibrium for goethite; most solids required substantially less time (2-5 hours for biotite). After reaching sorption equilibrium, pH was changed and the system allowed to reequilibrate. pH was then readjusted to the original value, and the system allowed to reequilibrate again. These experiments demonstrate that sorption was reversible for all solids. Sorption on goethite and synthetic aluminum hydroxides exhibited a sharp pH "edge" between 6-8. For other minerals, sorption increased sharply above pH 9. Surface area alone cannot account for differences in pH-dependence, suggesting additional input from mineral surface properties such as zero point charge, surface charge density, and pH-dependent Np speciation. Reduction and oxidation of Np at the mineral surfaces was not clearly observed in this research.

Naymik, T. G. 1987. Mathematical modeling of solute transport in the subsurface. *CRC Critical Rev. of Environ. Control 17*: 229-251.

This article is largely a review of articles and computer codes published 1980-1985 that deal with water/solute transport in the subsurface. The author points out that longitudinal dispersivity on the field scale is generally 4-6 orders of magnitude greater than lab values. Fickian diffusion alone is not adequate to describe solute transport. There is some suggestion that at some depth, current convective models are no longer valid. Competitive adsorption is also pointed out as an area of active research. Two-dimensional, reversible sorption was also modeled in 1982 at Idaho National Energy Labs for chlorine and tritium.

Neretnieks, I., and A. Rasmuson. 1984. An approach to modelling radionuclide migration in a medium with strongly varying velocity and block sizes along the flow path. *Water Resourc. Res. 20*: 1823-1836.

The authors present a model for radionuclide migration in a fractured medium. Sorption will vary as a function of water residence time and available surface sites. An integrated finite-difference method (IFDM) is presented to calculate the effect of increased surface area due to fracture lineaments. Transport is modelled by longitudinal dispersion and advection. Sorption is instantaneous surface sorption, and diffusion into the rock matrix and sorption onto micropore surfaces. Fractures and varying block sizes are incorporated into the model. The authors develop the theory for advection-dispersion fracture flow. Radial flow is also possible. The model includes radioactive decay. Reversible sorption is modelled using a K_d approach, while a "pseudobody" approach is used to model flow. This approach assumes that all shells at some distance from a surface behave alike. The model is then applied to sample problems of crystalline rock at Finnsjo, Sweden. Simplified analytical solutions are presented, including a case with no dispersion, and velocity as a function of distance. The effect of surface sorption and increasing Peclet number (Pe) is to increase the time to solute breakthrough. The numerical code indicates that retardation increases with decreasing block size (and therefore increasing surface area). Retardation in a lineament may be of similar magnitude to retardation in a low permeability medium.

Nielsen, D. R., M. T. Van Genuchten, and J. W. Biggar. 1986. Water flow and solute transport processes in the unsaturated zone. *Water Resourc. Res.* 22: 89S-108S

A general review of the status of water flow and solute transport in 1986. The authors point out the dependence of hydrologic properties (K_s) on solute concentration and pH. Increasing solute concentration increases the thickness of the electrical double layer, while increasing pH decreases K_s due to charge reversals from (+) to (-) in oxide minerals in the soils. Water transport must also consider capillary or matric pressure and electrochemical potential in addition to gravitational forces. They also point out some of the deficiencies of applying Richards equations to fluid flow in the unsaturated zone. Temperature and hysteretic effects are significant. The authors suggest that colloid transport is critical, and that most soils are dominated by constant-charge colloids. The convection-dispersion equation has not performed well for strongly sorbed species. Models of adsorption include: (1) a 3-step process involving diffusion from bulk solution to liquid film; diffusion at a constant rate across the film, and; surface kinetic reaction; (2) a two-site model that uses an adsorption term with two components, one governed by equilibrium and the second involving first-order kinetics. Another physical model of water transport splits the domain into mobile and immobile waters. Equilibrium transport is assumed for the mobile waters, and diffusion is used for mass transfer between the mobile and immobile waters. Even a small amount of immobile water can lead to an uneven distribution of sorption sites, and zones of preferential flow. This model is similar to the two-site model. Simplifications are possible for transport in structured soils. Studies are attempting to develop an effective dispersion coefficient that lumps all the effects of interaggregate diffusion for use in a classical Fickian diffusion model.

Nkedi-Kizza, P., J. W. Biggar, H. M. Selim, M. T. van Genuchten, P. J. Wierenga, and J. M. Davidson et al. 1984. On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol. *Water Resour. Res.* 20: 1123-1130.

The authors investigate the relationship between two types of conceptual models for nonequilibrium transport. The first model is physical, diffusion controlled nonequilibrium using a two-region (mobile/immobile) approach. The second model invokes first-order, reversible kinetics using a two-site approach. The mathematical equivalence is developed for dimensionless forms of the two models. The dimensionless equations are based on instantaneous, linear, and reversible sorption. Four independent, dimensionless parameters are developed. These include a retardation factor (R), a column Peclet number (P), a partition coefficient (beta, a measure of the maximum degree of system nonequilibrium), and a mass transfer coefficient (omega, the rate at which equilibrium is approached from an initial nonequilibrium state). Two dependent variables, dimensionless concentrations are also used, but the physical properties represented by the variables (c_1 and c_2) differ between the two models. In the two region model, for example, c_2 represents the average solute concentration of the immobile water, while in the two-site model, this variable describes the adsorbed concentration associated with the non equilibrium, type 2 sites. Experimental column studies with ^{45}Ca, ^{36}Cl, and tritiated water. Three dimensionless parameters (R, beta, omega) were shown to be sufficient for model parameter estimation. Both models were equally successful in reproducing the observed asymmetric breakthrough curves (BTC's). On a macroscale, the methods are equivalent, but because of differences in the dependent variables, microscopic measurements inside the columns are necessary to discriminate between the two models.

Noorishad, J., C. L. Carnahan, and L. V. Benson. 1987. *Development of the Non-Equilibrium Reactive Chemical Transport Code CHMTRNS*. Lawrence Berkeley Laboratory, LBL-22361, Berkeley, CA.

The CHMTRNS code is a modified version of the CHEMTRN code (Miller and Benson, 1983). The code relies on one-step coupling of geochemistry and transport, and is currently able to model one-dimensional transport in a saturated, porous medium. The modifications have included the ability to incorporate reaction kinetics, oxidation/reduction, precipitation/dissolution, stable carbon isotope fractionation, and variable temperatures. Sorption is modeled through surface complexation, precipitation/dissolution, and ion exchange. The model can be extended to two- and three-dimensions by using a series of non-interacting, parallel stream tubes. A variety of boundary and initial conditions are possible, and the report gives several test cases including kinetic dissolution of calcite/silica, stable carbon isotope fractionation, and non-isothermal oxidation and reduction. Data entry is by formatted batch input, and can be very complex. The appendix lists the source code (FORTRAN IV), and several examples of input and output.

Nyffeler, U. P., Y. Li, and P. H. Santschi. 1984. A kinetic approach to describe trace element distribution between particles and solution in natural aquatic systems. *Geochim. Cosmochim. Acta 48*: 1513-1522.

The authors present a kinetic approach for the sorption of a number of elements. Experiments (batch) using seawater and natural marine sediments are described in detail. Two groups of elements are defined based on sorption characteristics. Group 1 includes Sn, Zn, Cs, and [illegible] elements which rapidly reached constant K_d values after a few days. Group 2 (Fe, Mn, Co) elements show slowly increasing K_d values over the time of the experiment (max. 108 days). Group 1 elements rapidly reach adsorption/desorption equilibrium in a few days, suggesting reversible surface complexation processes. For Group 2 elements, K_d is much lower for desorption than adsorption, inferred by the authors to represent initial sorption by surface complexation, followed by diffusion into the crystal lattice. Curve fitting to experimentally determined adsorption/desorption K_d's as a function of time is used to derive first order rate constants at a given temperature. The model reproduces in situ data for U/Th disequilibria well, and also fits controlled field data for Mn, Fe, Co, Zn, Sn, Cs, and Hg well. The authors conclude that the limited equilibrium assumption is valid only if the solute residence time is [illegible] in comparison to sorption rates. Kinetic approaches should also be used for [illegible] changes with time.

Olague, N. E., D. E. Longsine, J. E. Campbell, and C. D. Leigh. 1991. *User's Manual for the NEFTRAN II Computer Code*. U. S. Nuclear Regulatory Commission. NUREG/CR-5618. Washington, D. C.

This report presents user's instructions for the NEFTRAN II solute transport code. The manual begins with a description of the conceptual models and the theoretical basis for flow, source, and transport incorporated in the code. The first model is the time dependent network flow model. This model uses mass conservation and finite element methods to calculate the flow net for saturated/unsaturated flow appropriate to the region of interest. NEFTRAN II offers the user the option of directly inputting pore velocities and bypassing the flow network model, and an analytical flow model is also available. Fluid density and viscosity are calculated as a function of temperature, pressure, and composition. The governing equations for the source model and the theory used to incorporate radionuclide decay chains are described. The user is also allowed to specify a release time in the simulation. Time step is determined on the basis of leach pulse, decay, residence time, and flow peak. There are several source options, including leach-limited source, a solubility limited source, and combinations of leach and solubility limits. NEFTRAN II uses a distributed velocity method (DVM) model similar to particle tracking methods to simulate solute transport. This incorporates the convective-dispersion equation with a variable retardation factor. The code is able to account for the effects of time dependent saturation on the retardation factor. The user also has the option of implementing the two region mobile/immobile water approach of van Genuchten and Wierenga (1976). The development of governing equations and descriptions of their implementation by the code is followed by a description of the structure of the code and the various subroutines used. A sample input deck is provided to aid in data entry, and sample problems are provided for verification of the approach.

Orlandini, K. A., W. R. Penrose, B. R. Harvey, M. B. Lovett, and M. W. Findlay. 1990. Colloidal behavior of actinides in an oligotrophic lake. *Environ. Sci. Technol.* 24:706-712.

The authors investigated the distribution of the actinides Pu, Am, Th, and Cm among different colloidal size fractions. Samples were collected in an oligotrophic lake in Wales, and filtered over 6 size fractions. Actinides were observed to have a strong affinity for particulates, which was dependent on pH, inorganic ions, oxidation state, and the presence of colloidal organic material (COM). COM strongly complexed with the more reduced species (Am(III), Pu(IV), Th(III)). Over 80 percent of these three actinides were associated with the > 450 nm size fraction. Pu(V) was non-particle reactive, passing through all the particle filters. Pu(IV), however, was particle reactive. Pu, Am were reversibly bound to the colloids, while Th was more irreversibly bound. The authors calculated binding coefficients (K_d) based on the distribution ratio of the actinides between colloidal particles (> 1.5 nm) and solution (< 1.5 nm). K_d is much higher by a factor of 20 when based on the 1.5 nm minimum particle size.

Park, S. W., and J. O. Leckie. 1989. Radionuclide interactions at mineral/solution interfaces in the subsurface environment. *EOS* 70: 1099.

ABSTRACT - Assessment of the long-term fate of radionuclides deposited in deep geological nuclear waste repositories requires the identification and understanding of processes involved in the release or retention of radionuclides within likely geological settings. The underlying assumption in this relation is that a better understanding of the basic chemical reactions of radionuclides at mineral/solution interfaces will contribute to both a better insight into the environmental fate of these radionuclides and better estimation of radionuclide retardation in the subsurface environment. Much of the early work was directed at determining the ratio of the concentration on solids to the dissolved concentration in water. This ratio, often referred to as a distribution coefficient, K_d, is used in transport codes to calculate the partitioning of radioelements between ground water and surrounding solids. However, the use of the K_d is limited because the K_d, rather than being a constant depends on a solution composition and solid properties. In this study, chemical reactions between the uranyl ion and corrensite are characterized under various conditions of importance in the subsurface environment. Along with information on the physical and chemical characteristics of the corrensite and solution chemistry, the partitioning of the uranyl to the solid is described by the triple layer surface complexation model.

Parker, J. C., and P. M. Jardine. 1986. Effects of heterogeneous adsorption behavior on ion transport. *Water Resourc. Res.* 22: 1334-1340.

A two-site model is used to address nonequilibrium adsorption and the effects of surface heterogeneities on ion transport. The sites differ on the basis of kinetic versus equilibrium adsorption behavior. Assuming constant and equal ionic strengths for invading and resident solutions, sorption equations are developed using dimensionless parameters and concentration-dependent Vanselow selectivity coefficients (K_v). Although K_v is independent of ionic strength, it is a function of adsorbed solute concentration, mean salt activity, and the concentration of exchangeable ions in solution. These equations are combined with a one-dimensional convection-dispersion equation to derive a set of nonlinear ion transport equations, solved using time-centered finite difference methods. The model is applied to binary, heterovalent K-Ca exchange. The soil chosen for the application has K_v's that are highly concentration-dependent. Type 1, equilibrium sites exhibit a marked preference for Ca^{2+} at low concentrations, while Type 2 (kinetic) sites have a high affinity for K^+ at low concentrations. The effects of using constant values for K_v and K_v as a function of sorbed ion concentration are compared to breakthrough predicted assuming a linear isotherm. A linear adsorption isotherm may provide a satisfactory approximation under specific conditions, but extrapolation beyond the experimental data is unjustified.

Patera, E. S., D. E. Hobart, A. Meijer, and R. S. Rundberg. 1990. Chemical and physical processes of radionuclide migration at Yucca Mountain, Nevada. *Jour. Radioanalytical and Nuclear Chemistry* 142: 331-347.

A summary of past and proposed research done by the DOE investigating radionuclide migration. Critical nuclides that will be studied for both solubility and sorption are: Np, Pu, Am. Solubility studies only will be carried out on U, Th, Ra, Zr, Sn, Ni. Cs, and Tc are not studied because it is expected that total concentration of these highly soluble elements will be a function of dissolution of the waste package and adsorption. Carbonate ions are the principal potential complexing agents for U, Pu, Np, and Am. Three types of colloid formation will be examined: (1) Radiocolloids-pure particles of radionuclide; (2) Natural colloids-natural minerals, and; (3) Pseudocolloids-natural colloids combined with ionic/solid forms of radionuclides. Pu, Am form stable colloids, and particulate size, density and bulk charge are the most important physical characteristics of colloid transport. Sorption mechanisms investigated using batch equilibrium batch studies include: ion exchange, surface complexation, and precipitation. Ion exchange sorption ratios are not very different for crushed clay and zeolite compared to those for solid samples because the exchange sites are largely intracrystalline. Am, Pu, Np are more complicated, as there are no simple correlations between sorption ratios and abundances of major ion exchange minerals, and Np and Am exhibit unretarded breakthrough. The authors believe that these elements are strongly sorbed onto Fe and Mn oxides and oxyhydroxides. Sorption of anionic species such as TcO_4 is believed to be less important in the Yucca Mountain environment. Problems with batch sorption experiments include: dissolution of the substrate, precipitation, and colloids in groundwater (which can be removed through ultrafiltration). In addition, inaccurate estimates of radionuclide solubility lead to unsatisfactory concentrations in the experimental solutions. Batch equilibria experiments in series are proposed to estimate kinetics, and comparing the results to column experiments with variable flow rates. While acknowledging drawbacks, the DOE clearly prefers the batch technique for its simplicity. They believe that batch equilibrium can be used to establish the bounding cases (ie g. identify where the sorption coefficient is so high that additional experiments are redundant). Sorption kinetics can be determined by observing the dispersion of breakthrough curves as a function of mean pore water velocity in column experiments. The authors propose to perform column experiments, first using crushed tuff, then intact tuff, and finally fractured tuff. They comment that using simple advection dispersion equation (ADE) to predict solute distribution generally underestimates initial breakthrough, and the results improve when a time dependent equivalent dispersion coefficient is used.

Payne, T. E., J. A. Davis, and T. D. Waite. [illegible] Modeling of Uranium Sorption to Substrates From the Weathered Zone in the Vicinity of the Koongarra Ore Body. in P. Duerden (ed.), *Alligator Rivers Analogue Project First Annual Report 1988-1989*. Austral. Nucl. Sci. Technol. Organization. 39-46.

A surface complexation model is applied to laboratory batch column data for uranium sorption. The authors indicate that a major difficulty in the application is in identifying major sorbing phases and characterizing them relative to necessary model parameters such as surface site density, acid-base, and complexation. In this application, the authors assume that Fe-oxides are the major sorbing phases. Lab results before and after removal of amorphous Fe oxides are compared to natural systems. Uranium sorption characteristics of single substrates are compared to those for well characterized weathered zone substrates. In the absence of significant phosphate, carbonate complexation will control U(VI) solution chemistry. Adsorption to goethite is dependent on pH and concentration at atmospheric P(CO$_2$), possibly due to hydroxy-carbonate species alone. Tripathi (1984) shows that there is very little difference between the extent of U-adsorption in ligand-free and phosphate-bearing systems. Using the approach of Hsi and Langmuir (1985) and considering only di- and tri-carbonato species in a triple layer surface complexation model does not match experimental results. This is due to the importance of UO$_2$CO$_3$ (monocarbonate) in the pH range 4.8-6.4. Including this species results in a much better fit to the data.

Penrose, W. R., W. L. Polzer, E. H. Essington, D. M. Nelson, and K. A. Orlandini. 1990. Mobility of plutonium and americium through a shallow aquifer in a semiarid region. *Environ Sci. Technol. 24*: 228-234.

The authors have monitored the migration of Plutonium and Americium through the Bandelier Tuff, Mortandad Canyon, Los Alamos National Lab, New Mexico. A series of four wells were used to sample anoxic groundwaters from 1900 to 3390 m from the believed input source of the waste effluent. Samples were ultrafiltered through 0.45 micrometers initially. Size fractions of 25, 5, and 2 nm filtrates were analyzed for ^{239,240}Pu, and ^{241}Am. Equilibrium water chemistry was calculated with distance from the source using the WATEQ code. A decrease in pH with distance was predicted, in addition to decreasing PO$_4$, Fe, NO$_3$, K, and increasing Ca, Mg. ^{241}Am concentrations remained relatively constant with distance, while [illegible] decreased exponentially. Time-scale fluctuations on the order of weeks resulted in [illegible] fold fluctuations in Pu concentrations. Both Pu and Am were preferentially associated with certain size fractions of the ultra-filtrate. 85% of the Pu was associated with colloidal particles > 25 nm, and 43 percent of the Am was associated with particles < 2 nm in diameter. [illegible]Pu and ^{243}Am were added to the water samples as tracers and allowed to equilibrate for two days. The authors believe that differences in ratios between ambient Pu/Am and added [illegible]Pu for different size fractions indicates a lack of equilibrium for plutonium colloids. [illegible]Am was actively sorbed for the >25 nm size fraction. Based on the spiked samples, Pu bound to colloids is believed not exchangeable for the 25-450 nm size fraction, and one half of the Am is found as nonexchangeable anionic species of < 2nm.

Phillips, I. R., and W. J. Bond. 1989. Extraction Procedure for Determining Solution and Exchangeable Ions on the Same Soil Sample. *Soil Sci. Soc. Amer. Jour.* 53: 1294-1297.

The study presents a method for determining solution and exchangeable ions on small soil samples. Water content can also be determined. The technique calls for centrifuging high density, water-immiscible organic liquids to displace soil pore solutions. The accuracy of the procedure was good, within experimental error. The technique may need more testing for soils with higher organic content.

Pickens, J. F., and R. W. Gillham. 1980. Finite element analysis of solute transport under hysteretic unsaturated flow conditions. *Water Resourc. Res. 16*: 1071-1078

The authors use finite element methods to simulate two-dimensional unsaturated zone water/solute transport allowing for hysteretic or non-hysteretic effects. The unsaturated hydraulic conductivity (K_u) was assumed non-hysteretic, and moisture content (theta) is calculated as an hysteric function. A hysteresis index was developed and applied at each node to indicate whether the soil was draining or wetting. Different boundary conditions were used to describe hysteresis (Dirichlet), flux (Neumann), and solute distribution (Cauchy). A Cauchy boundary was necessary for solute transport for at least the part of the boundary where infiltration occurs. Although the model was applied to a nonreactive tracer, it is able to accommodate linear reversible sorption and radioactive decay. The problem was solved for a range in transverse and longitudinal dispersivities. The model is also able to accommodate radioactive decay. Since pore velocity is a function of moisture content, errors in moisture lead to errors in velocity. Simulations show that hysteresis is relatively unimportant in concentration profiles for non-reactive solutes. The effect of hysteresis is shown to be most significant in pressure head and water content profiles, where it slightly retards solute transport. The differences between hysteretic and non-hysteretic profiles decrease with lower infiltration rates.

Pietrzak, R. F., K. S. Czyscinski, and A. J. Weiss. 1981. Sorption measurements performed under site-specific conditions - Maxey Flats, Kentucky and West Valley, New York disposal sites. *Nuclear and Chemical Waste Management* 2: 279-285

Sorption coefficients were measured for Low Level Radioactive Waste Repositories at Maxey Flats, KY and West Valley, NY. The authors stress that K_d values must be determined under conditions approaching "in situ" values. For these shallow repositories, bacterial reduction of nitrate and sulfates results in a typically anoxic water chemistry. Iron oxide is the dominant sorbent phase. A series of batch equilibrium experiments were designed to preserve the anoxic character of the soil/water system through use of an inert atmosphere. Experimental methods are described in detail. Untreated, disaggregated soils were used as the sorbent medium. Parameters varied included soil/solution ratio, contact time, pH, water composition, and soil composition. Gamma ray spectroscopy was used to detect ^{60}Co, ^{137}Cs, ^{152}Eu, and ^{85}Sr. Sorption was lowest for anoxic waters, and competition for sorption sites was observed. Co and Sr reached steady-state quickly, Cs took longer. Americium and ^{59}Fe are more unpredictable, redox is controlled by iron. Sorption of ^{137}Cs and ^{60}Co generally increased with pH. A water/soil ratio effect was also observed for Cs; for anoxic waters, sorption increased with decreasing water/soil ratio; for deionized waters, sorption increased with increasing water/soil ratio. The authors do not measure the water composition at the conclusion of the experiments.

Polzer, W. L., and R. Fuentes. 1991. Fitting a modified Langmuir isotherm to data from batch sorption experiments for radionuclides on tuffs. *Radiochim. Acta* 52/53: 177-179.

The authors used a modified Langmuir isotherm to fit batch sorption data on two size fractions of crushed Yucca Mountain tuff (< 75 and 75-500 microns). Two adjustable parameters are related to sorption heterogeneity (beta) and average retardation (K_d). The isotherm is used to calculate a "composite" free energy of sorption, assuming that Langmuir isotherms effectively represent sorption processes. This allows an estimation of relative selectivity when adsorption occurs by ion exchange. Curve-fitting determines the values for the parameters in the modified isotherm. K_d was observed to vary by as much as a factor of 30 with a one order of magnitude change in CEC. Beta, however, was only slightly affected. CEC is related to the maximum amount of sorbed solute. Unfortunately, CEC is not a single-valued property, and there are uncertainties associated with different methods for determining CEC. For Cs, Ba and Eu, changes in free energy due to particle-size were deemed insignificant by the authors. Regression analysis indicates that barium sorption is dependent on particle size, but not for europium. The differences may be due to variations in surface area/fluid volume ratios and different mineral distributions in the two size fractions.

Read, D., and T. W. Broyd. 1989. *The CHEMVAL Project Status Report March 1989*. Pacific Northwest Laboratory, Richland, WA.

The CHEMVAL project was undertaken to validate predictive models for radionuclide migration. CHEMVAL consists of four main stages including application of aqueous chemical speciation codes, validation of aqueous speciation models through comparison with field and lab experiments, verification of coupled hydrogeochemical codes, hydrogeochemical code validation against experimental data. Stage I developed a number of test cases for participants to run simulations using five codes with either "in house" data or the standard CHEMVAL data base. Agreement was generally good, and variation was attributed to improper or missing entries in the data base, operator decision, or software limitations. For Stage II, a number of test cases were developed for four candidate sites. Preliminary model simulations were made by the participants and compared to experimental results. The proposed Mol clay and Gorleben salt repository sites are examined in the report. For the clay site at Mol, organic complexation is believed more significant than inorganic ion exchange, and proposed as a key control on radionuclide migration. Plutonium, americium and neptunium colloids have been identified at the Gorleben site. Saline brines at the site present problems for the codes in correcting for high ionic strength of the solutions. Stage III evaluated two one-step (CHEMTARD, THCC) and two-step (CHEQMATE, STELE) hydrogeochemical models. Initially, the equilibrium chemistry and transport were evaluated separately, and agreement between the codes was good. Preliminary coupled simulations yield reasonable agreement, and show promise. Compilation of the CHEMVAL comprehensive thermodynamic data base continues, and in 1989, contained 521 aqueous complexes and 327 solids. Some organic data is also available.

Reeves, H., and D. J. Kirkner. 1988. Multicomponent mass transport with homogeneous and heterogeneous chemical reactions: Effect of the chemistry on the choice of numerical algorithm. 2. Numerical results. *Water Resourc. Res.* *24*: 1730-1739

The efficiency of different computational schemes for multicomponent transport was evaluated using a Galerkin finite element model (FEM) and the theoretical development of Part 1 (Kirkner and Reeves, 1988). The iterative schemes evaluated include Picard iteration and two modified Newton-Raphson (NR) techniques. One modification replaces the Jacobian with a diagonal matrix of constants, uncoupling component equations. The second is the standard modified NR, with the Jacobian held constant for the time step. The rate of accumulation considered in terms of aqueous phase, sorption, and precipitation/dissolution. Sorption was treated either using an isotherm or a surface complexation model. Test problems were of two classes: (1) One component transport undergoing Langmuir adsorption; (2) Multicomponent transport using a two-component Langmuir isotherm. Both classes were run on an IBM 3033 for high- and low-sorption cases. For a given Courant number (Cr) for one component transport, a modified NR scheme is more efficient in terms of iterations/time step, and CPU time/pore volume. For a fine time step, however, the Picard is as efficient as the modified NR. Both approaches are less efficient at high Cr values. In general, a modified NR scheme is more efficient, but this will depend on chemical reactions considered (sorption, complexation, precipitation/dissolution). A chromatographic effect is also observed in the models due to competitive sorption, and resulting in elevated aqueous concentrations.

Rhue, R. D., and R. S. Mansell. 1988. The effect of pH on sodium-calcium and potassium-calcium exchange selectivity for Cecil soil. *Soil Sci. Soc. Am. J.* 52: 641-647.

The authors performed a series of experiments on sandy loam soils to evaluate the effect of pH on cation exchange. Cation exchange capacities (CEC) were measured for Ca, Na, and K over a pH range from 4 to 8. CEC increased from pH 4 to 7 for both Ca and Na, showing signs of leveling off at pH 8 to 9. The most rapid increase occurred between pH 6 and 7. In general, the CEC for Ca was greater than that for Na, although above pH [illegible] there was little difference. Ca exchange increased and accounted for most of the increase in overall cation exchange for the soil with increasing pH. The major source of pH dependent charge is thought to be organic material, and some of the apparent increase in sorption may be due to increased adsorption of CaCl+ compounds.

Robertson, J. B. 1975. Numerical modeling of subsurface radioactive solute transport from waste seepage ponds at the Idaho National Engineering Laboratory, Idaho. *[illegible]* 56 [illegible]

ABSTRACT - The Idaho National Engineering Laboratory has disposed of aqueous chemical and low-level radioactive effluents to seepage ponds since 1952. The solutions percolate toward the

Snake River Plain aquifer (135 m below) through inter-layered basalts and unconsolidated sediments and a large zone of perched ground water on a sedimentary layer about 40 m beneath the ponds. A three-segment numerical model was developed to simulate the system, including effects of convection, hydrodynamic dispersion, radioactive decay, and adsorption. The first segment uses an analytical solution to simulate transport from the ponds to the 25 meter-thick perched water lens, assuming steady vertical flow through a 15-m long saturated homogeneous column. The second segment simulates two-dimensional horizontal transport in the perched water body using finite-difference methods, assuming complete vertical mixing, with vertical leakage out the bottom. The third segment of the model simulates vertical transport from the perched water body toward the aquifer, by assuming unsaturated but steady water content in a series of contiguous, nonhomogeneous independent vertical columns. The transport equation is solved by a hop-scotch finite-difference scheme for each column. Simulated hydraulics and solute migration patterns for all segments agree adequately with limited observed field data. The model can be used to project subsurface distributions of waste solutes under a variety of assumed conditions for the future. Although chloride and tritium reached the aquifer several years ago, the model predicts that more sorbable solutes such as cesium-137 and strontium-90 will not reach the aquifer in detectable concentrations within 150 years under present disposal conditions.

Rubin, J. 1983. Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions. *Water Resourc. Res.* *19*: 1231-1252.

This is a survey article that describes six broad classes of reactive solute transport using the convection-dispersion equation. The author [illegible] a number of simplifying assumptions including unidirectional transport, isothermal [illegible] steady water flow, constant water content, and the effect of the solutes on the system is minimal. It is also assumed that the physical characteristics of the porous media remain constant through time. Finally, the local equilibrium assumption (LEA) is employed. The author introduces the concept of the Tenad, which is defined as a reacting or nonreacting chemical entity if its global mass is reaction dependent. Chemical reactions are divided into six classes based on whether it is reversible or irreversible, homogeneous or heterogeneous, and if it is heterogeneous, whether it is a surface (sorption, ion exchange) or classical (precipitation dissolution, redox, complexation) reaction. Equations governing basic transport are developed for each of the six classes [illegible] mass balance and the tenad concept, and examples of each class are discussed. Emphasis is placed on the mathematical differences that result from the chemical constraints of a given class. The techniques and limitations of one-step and two step coupling between transport and geochemical equilibrium are also discussed. Criteria for [illegible] mathematical differences of the six classes are given.

Rubin, J., and R. V. James. 1973. Dispersion affected transport of reacting solutes in saturated **porous media:** Galerkin method applied to equilibrium controlled exchange in unidirectional **steady** water flow. *Water Resourc. Res.* 9, 1332-1356.

One of the first studies to couple transport and equilibrium geochemistry equations to model reactive solute transport. The convection-dispersion transport equation, and the mass-action relationships for equilibrium ion exchange are developed. These equations are directly coupled (one-step) for the special case of homovalent binary ion exchange assuming local equilibrium, resulting in a set of nonlinear partial differential equations. The authors then describe the use of Galerkin finite element methods to solve these equations for one-dimensional transport. The operational equations are also developed for leaching of a homogeneous gypsiferous soil incorporating Na-Ca binary exchange, precipitation dissolution, and dissociation of $CaSO_4$ complexes. The numerical solution is not explicitly developed. Five computed examples of solute transport for saturated, steady-flow with dispersion are presented with grid-size based on minimizing mass balance errors and numerical oscillation. (1) Binary 1:1 ion exchange, homogeneous medium, with constant concentration of the initial solution. (2) The same as case (1), only a second layer is introduced that shows a greater affinity for ion 1. (3) The same as case (1), except that the concentration of the initial solution is allowed to vary with time and depth. (4) Leaching a soil with 1:2 binary exchange. (5) Ternary 1:1:1 exchange. The authors indicate that activity concentration and kinetic relations can easily be incorporated, and the model can be readily extended to two-and three dimensions. Hydrodynamic dispersion is important and may make the approach inapplicable if zones of preferential flow ("fingering") are present.

Rundberg, R., D. Janecky, and A. Mitchell. 1987. *Ion Exclusion in Yucca Mountain Tuff.* Los Alamos National Laboratory, LANL Milestone No. 315, Los Alamos, NM.

A report of the results of a series of column experiments investigating anion migration through crushed tuff of Yucca Mountain. Five tuff samples (75-500 microns) from Drill Holes USW-G1, G2, and G3. Samples ranged from glass with minor smectite, to 40-50 percent clinoptilolite with varying amounts of mordenite (2-18 percent), opal (0-17 percent), feldspar (1 to 29 percent), and quartz (5-9 percent). One sample was roughly equal parts analcime, feldspar, and quartz with minor (5 percent) smectite-illite. J-13 water was used as the solution with chloride, nitrate, sulphate, fluoride, iodine, and technetium (TcO_4) added as anion tracers. Tritiated water (HTO) established the free column volume and provided a baseline for anion breakthrough. With the exception of fluoride, anion breakthrough occurred at an earlier volume than tritium, and calculated retardation factors less than 1. Fluoride is thought to react with the tuff samples. The calculated excluded volume corresponds fairly well with the calculated volume of intracrystalline channels in the zeolite. This is corroborated by crystallographic calculations which suggest that these channels are too small to admit most of the anions. Although the effect is small in the column experiments, the authors anticipate that it could be greater in unsaturated porous media where water remaining as saturation decreases is increasingly drawn into the intracrystalline porosity by capillary suction. Pertechnetate partly retained by the tuff indicating some form of anion exchange. Finally, the authors indicate that current batch procedures may underestimate retardation due to anion exclusion effects.

Russo, D. 1988a. Numerical Analysis of the Nonsteady Transport of Interacting Solutes Through Unsaturated Soil: 1. Homogeneous Systems. *Water Resourc. Res. 24*: 271-284.

A numerical finite-difference simulation of 1-dimensional vertical transport of Na-Ca solutions in saturated/unsaturated soils. Planar mixed-ion diffuse double-layer theory is used for reactive solute transport, requiring knowledge of electrical potential distribution, spacing of exchange surfaces, and anion adsorption (Cl^-). Soils considered are hypothetically homogeneous and isotropic, and contain montmorillonite clay fractions with constant effective surface charge density. The model calculates the soils hydraulic conductivity (K_s) relative to some inert reference state, and uses empirical relations to determine the diffusion-dispersion coefficient (D). Up to three solute species are considered. Boundary conditions for fluid flow include recharge at the surface and some maximum pressure head. Solute boundary conditions include solute concentrations in the recharge and initial soil solute concentrations. Input necessary for the model includes: Soil specific surface area, cation exchange capacity (CEC), bulk density,soil-water retention curve, K_s function under wetting conditions at some reference state. Three soil textures are considered: Loamy sand, Loam, and Clay loam. Soil/water interaction affects both K_s and solute retention, and both the wetting and solute fronts are highly dependent on soil texture. Effects of soil matrix-soil solution interaction increase as soil-water pressure and water content increase. As water content increases, the differences between a reactive and nonreactive solute profile decrease. For given soil and boundary conditions, effects of matrix-solution interaction are to reduce water flow velocity relative to an inert reference soil. For solute transport, interactions may act in two opposing directions: (1) Retardation due to reductions in hydraulic conductivity and cation exchange; (2) Acceleration due to anion exclusion. Both effects increase as either soil or solution concentration decreases, as sodium adsorption ratios (SAR) increase, or as infiltration rates increase. The rate of change of retardation is different from changes in acceleration. As clay fraction increases or a soil texture becomes finer, retardation of water flow increases. Although retardation of solute transport becomes smaller, it comes to dominate acceleration due to anion exclusion. This indicates that there are threshold limits for SAR to reduce hydraulic conductivity by 25 percent.

Russo, D. 1988b. Numerical analysis of the nonsteady transport of interacting solutes through unsaturated soil: 2. Layered systems. *Water Resourc. Res.* 24: 285-290.

This study modifies the model of Russo (1988a) to study layered systems, assuming a regular interface between the layers, and local homogeneity at the interface. The simulation is applied to 3-layer models of loamy sand, loam, and clay loam in two basic configurations: fine textured soils over coarser soils, and the reverse case of a coarse soil over a fine soil layer. In general, the effect of water/soil interaction is greater for the case of a fine-over-coarse configuration. The degree of retardation versus a reference inert state is dependent on the initial sodium adsorption ratio (SAR) profile in the different layers. The author discusses the application of the model to the field scale using the concept of parallel vertical columns that do not interact. Applying a layered model to these columns would increase the spatial variability of water and solute observed on a field scale relative to the case where water/soil interactions are not considered.

Russo, D. 1989a. Field-scale transport of interacting solutes through the unsaturated zone: 1. Analysis of the spatial variability of the transport properties. *Water Resourc. Res.* 25: 2475-2485.

The author considers soil interaction terms such as hydraulic conductivity, soil water content, cation exchange equilibria, and anion exclusion and their dependence on soil water pressure, solution ionic concentration and composition for stochastic modeling. Precipitation/ dissolution reactions are not modeled, and only Na, Ca, and Cl ionic species are considered. Soil hydrodynamic properties vary in space, which is dealt with as a continuum with no fracture flow. The author defines retardation (R_f) and elution (E_f) factors for Na/Ca exchange and Cl exclusion, respectively, relative to non-reactive solute transport. These factors are functions of head, C(Na)/C(Ca) = R, and total ionic concentration. Hydraulic conductivity [K_s] is presented as a function of degree of saturation. Effective saturation is a power function of head, and unsaturated conductivity (K_r) is a function of head and tortuosity. The approach was tested for a soil from Israel using the method of Russo (1988a,b) using inert solute transport as a reference state. The effects of ionic concentration increase as sodium adsorption ratio (SAR) increase. Increasing SAR and decreasing concentration (C) reduces the mean values for K_s, porosity, E_f, and increases mean effective saturation, head, and R_f. R_f and E_f are also affected by the degree of water saturation. For a given SAR and C, the effect of decreasing effective saturation is to increase the mean value of R_f and decrease the mean value of E_f. In contrast, this decreases the mean adsorption water content, increases mean exclusion water content, and decreases variability. Soil solution concentration and composition most affect K_s, which also exhibits the most spatial variability. Reduced soil saturation reduces relative variability of both moisture content and K_s, and increases relative mean K_s, and decreases the effective saturation relative to saturated conditions. Under field conditions, where both solute concentrations and water content vary spatially, the spatial distribution of hydraulic properties cannot be estimated, and only the effects of water content and salinity will be apparent.

Russo, D. 1989b. Field scale transport of interacting solutes through the unsaturated zone: 2. Analysis of the spatial variability of the field response. *Water Resourc. Res.* 25: 2487-2495.

The author takes the stochastic model developed in Russo (1989a) part I, and applies it to a given set of boundary and initial conditions. The model is a simplified, one-dimensional model of vertical Na-Ca-Cl transport perpendicular to heterogeneities in an unsaturated porous medium. Boundary and initial conditions include rainfall/irrigation rates and initial soil ionic concentrations. A short term model is subjected to a rainstorm for five hours. The model results are expressed as profiles of field-scale dependent variables at a given elapsed time. Field-average values and a coefficient of variation are determined. Interaction between soil solution and soil matrix is based on a mixed-ion diffuse double layer using experimental data on clay structure at the pore scale. Model results are compared to the Bet Dagan field study in Israel. Modeling vertical transport in one-dimension is supported by the field evidence. For low infiltration or high evaporation, however, this may not be a valid assumption and a three-dimensional model should be used. Comparison indicates that modeling spatial variation may lead to increased retardation relative to homogeneous simulations (10-15 percent additional retardation of the wetting and chloride fronts, respectively) and increased variabilities in the positions of these fronts. Interactions are also dependent on initial conditions chosen. The combination of high water content, low ionic concentrations, and high sodium adsorption ratios (SAR) will generally retard movement of solutes and water, and increase the variability of the dependent variables in the horizontal plane.

Salbu, B., H. E. Bjornstad, E. Lyderson, and A. C. Pappas. 1987. Determination of radionuclides associated with colloids in natural waters. *Jour. Radioanal. Nuclear Chem. 115*: 113-123.

The article presents the results of an ultrafiltration study of radiocolloids in Norway and Sweden. Size distribution for a given radionuclide depends on the origin of the water and the precipitation history of the solute. In addition, the size distribution is dependent on the radionuclide itself. Hollow fibre ultrafiltration is used to filter colloids of less than 0.45 microns. A brief description is given of experimental design for a continuous mixing and separation system to separate colloids according to a limited size fraction. In the Norway experiment, radionuclides of Co, Zn, and Mn are observed to be largely associated with colloids, with less than 20 percent present as simple ions. The authors indicate that radionuclide reactivity with colloids will lead to seasonal variations of radioelement concentrations. However, the chemically inert nature of corrosion or activation products entering the waste waters tends to counteract these seasonal effects.

Sanchez, A. L., J. W. Murray, and T. H. Sibley. 1985. The adsorption of plutonium IV and V on goethite. *Geochim. Cosmochim. Acta 49*: 2297 - 2307.

The authors examine adsorption of Pu(IV) and Pu(V) on goethite. The adsorption edge of Pu(IV) is at pH 3 to 5. The adsorption edge for Pu(V) is 5 to 7, shifting to lower pH with time, as it is reduced to Pu(IV). Pu(IV) adsorption is unaffected by increased ionic strength (I), but decreases with increased dissolved organic carbon (DOC) and alkalinity. Synthetic goethite experiments are used to study the effects of variable pH, I, alkalinity (alk) and DOC on Pu-adsorption. Pu(IV) is observed to achieve equilibrium in about 1 hour, while Pu(V) does not achieve equilibrium for times up to 20 days as it is reduced to the more easily hydrolizable Pu(IV). In addition, the adsorption edge shifts to higher pH for greater Pu concentrations. Ionic strength does not effect adsorption. Alkalinity effects become more pronounced for values >

100 meq/L, and adsorption is totally inhibited at 1000 meq/L, probably due to increased formation of carbonate complexes. DOC only slightly decreases Pu-adsorption. A modified version of the geochemical code MINEQL is used to model adsorption of Pu(IV) using a triple layer model with parameters fitted to the data. Pu(V) was not modeled because equilibrium was not obtained. Modeling suggests that hydrolytic species of Pu(IV) adsorb onto goethite. Best fit to the data is achieved for Pu-carbonate complexes forming ternary complexes with goethite surfaces.

Selim, H. M. September 1978. Transport of Reactive Solutes During Transient, Unsaturated Water Flow in Multilayered Soils. *Soil Science 126*: 127-135.

The author develops an explicit/implicit FD approximation to solve water and solute transport equations simultaneously. The test case is transient transport in an unsaturated, multilayered (clay, sand, loam) soil. The conceptual model is one-dimensional vertical transport of a single solute. The water flow equation is solved prior to solute transport. Mass balance is used as a check on numerical results. Linear and nonlinear adsorption isotherms and first order reversible and irreversible kinetic reactions are incorporated by the model. The nonlinear sorption model used does not account for site competition, and sorption increases infinitely with concentration. The rate constants used in the model are not based on any particular data. Rather, sorption is assumed to be slightly irreversible. The model shows that the solute distribution is dependent on the ordering of layers of variable sorbency. Breakthrough is predicted to be earlier if the most sorptive layer was encountered first by the solution.

Selim, H. M., R. S. Mansell, L. A. Gaston, H. Fluhler, and R. Schulin. 1990. Prediction of cation transport in soils using cation exchange reactions. *Field-Scale Solute and Water Transport Through Soil*. Birkhauser Verlag, Basel, Switzerland. 223-238.

This article is a good survey of methods and models of reactive solute transport. The authors develop a modified chromatographic approach (after Valocchi et al., 1981a,b) to incorporate 2-region (mobile/immobile) methods. Valocchi et al (1981a,b) showed that use of ion concentration rather than activities does not restrict the predictive capability of the model. The approach presented initially assumes that total solution normality remains constant, which leads to an expression for adsorbed phase equivalent fraction (S_1) vs. concentration (c_1). A retardation factor is developed which incorporates the ion selectivity coefficient (K_{12}) which is similar, but not equivalent to K_d. The use of mobile/immobile water zones assumes that K_{12} is constant and equal for both regions. Using the data of Lai et al. (1978), an empirical relationship between K_{12} and c for Ca and Mg is developed such that $\log(K_{12}) = a + bc$. The model is a good predictor for early breakthrough, but it is less satisfactory for the observed tailing in concentration. The authors indicate that some of the discrepancy may be due to neglecting complexes of the solutes of interest and in the assumption of local equilibrium. Kinetic effects in ion exchange are specifically considered. Ion exchange is modeled using a two-site approach (one site at equilibrium, and one site using first-order kinetics). Kinetic desorption coefficients are empirically determined for the batch data of Lai et al. (1978). The two-site model improves prediction of the Ca breakthrough and tailing. Some of the remaining discrepancy may be due to the fact that the model is developed for static water, and is not directly applicable to transient water flow.

Serne, R. J., R. C. Arthur, and K. M. Krupka. 1990. *Review of Geochemical Processes and Codes for Assessment of Radionuclide Migration Potential at Commercial LLW Sites*. U.S. Nuclear Regulatory Commission, NUREG/CR-5548; PNL-7285, Washington, D. C.

A literature review of radionuclide migration from LLW repositories indicates that some radionuclides are mobile in anionic or neutral form, but relatively immobile as cations (Co, Tc, I, Ru, Sb, Fe, and Ni). Some elements exist predominantly as less mobile cations including Mn, Sr, Np, Ba, La, Ce, Pu, and Am. Organic matter will also affect the mobility of radionuclides, either through increasing element solubility or diminishing the charge of dissolved species, thereby reducing sorption. The authors summarize available data for six LLW repositories (Barnwell, SC; Sheffield, IL; West Valley, NY; Maxey Flats, KY; Hanford, WA, and Beatty, NV). Most of the data are site-specific, and include mineralogy, water chemistries, head distributions, and the results of studies that used geochemical equilibrium programs to model water/rock interaction. Data limitations and recommendations are given for the separate sites. The study identifies a large number of geochemical codes. MINTEQ (using the mathematics of MINEQL with the thermodynamic database of WATEQ) is identified as the only code meeting basic criteria that contains adsorption algorithms. From a given starting point, the results obtained from MINTEQ and EQ3/EQ6 are similar. Analytical uncertainty will propagate through computer calculations and there is uncertainty in applying MINTEQ to high-I solutions of the unsaturated zone. The authors stress the need for thermodynamic data for organic ligands and stress the importance of speciation in characterization of geochemical processes. Fluid bulk composition will affect speciation, and therefore sorption. Mixing processes in turn are important because of resulting changes in solution chemistry. Adsorption potential is sensitive to valence state of a redox-sensitive elements, and some mechanisms may only be important for a particular oxidation state. Organic compounds reduce electrostatic charge, and therefore adsorption. They can also adsorb anionic species, and act as a reductant to change redox conditions. Solution alkalinity is important as a pH buffer, which in turn minimizes $Fe(OH)_3$ solubility. The study describes experimental procedures to measure radionuclide attenuation. Sorption models are presented. Empirical models include multinomial K_d, Freundlich, Langmuir, and Dubinin-Radushkevich isotherms. These isotherms neglect contaminant speciation. Mass-action cation exchange and surface-complexation (diffuse layer, constant capacitance, triple-layer) models are also discussed. These models include a variety of adjustable parameters, but their use is principally limited to systems known ionic strength. The FASTCHEM code suggests using a one-layer, no electrostatic model to minimize numerical instability. Kinetics appear to be considerable (weeks) and heterogeneous systems create problems. ^{60}Co is anionic and strongly associated with organics. A final section lists recommendations: Eh and pH are identified as critical parameters, quantitative descriptions of mineralogies and coatings are necessary, organic chelating ligands are likely to be important but additional thermodynamic data is needed to evaluate the extent of this effect

Shaffer, M. J. 1975. Predicting solute reactions and transport in the unsaturated zone. *EOS 56*: 980.

ABSTRACT - A computer model has been developed which simulates chemical, mass transport, and dispersion processes affecting the ionic composition of water percolating through unsaturated soils. Constituents considered include Ca^{2+}, Mg^{2+}, Na^{+}, NH_4^{+}, HCO_3^{-}, CO_3^{2-}, Cl^{-}, SO_4^{2-}, and NO_3^{-}. The model combines subroutines simulating one-dimensional unsaturated flow with chemical equilibrium and kinetic routines to predict constituent concentrations in the soil profile and deep percolation. Verification has been achieved under both laboratory and field conditions. Built-in model flexibility and detailed user's manuals allow application to a variety of problems.

Short, S. A., R. T. Lowson, and J. Ellis. 1988. U-234/U-238 and Th-230/U-234 activity ratios in the colloidal phases of aquifers in lateritic weathered zones. *Geochim. Cosmochim. Acta 52*: 2555-2563.

The authors investigate the transport of uranium by colloids at Narbalek and Koongarra, Alligator Rivers, Australia. Water samples were collected, and hollow-fibre filters were used to collect colloidal particles (1 micrometer to 18 nanometers). The filtrate was analyzed for $^{234,238}U$ and $^{230,232}Th$. Colloids were determined to be predominantly ferrihydrites and silicates. Excess silica was shown to stabilize Fe-silicate colloids, and suppress adsorption of anionic U-complexes on Fe-oxide surfaces. Only minor portions of both ^{234}U and ^{238}U occurred in the colloidal phase, while $^{230,232}Th$ strongly sorbed to colloids, with quick adsorption and slow desorption. Colloidal U decreased with distance from the ore body down gradient. Solute U also decreased logarithmically, although the colloids were generally more depleted in ^{234}U than the solute. $^{230}Th/^{234}U$ was always greater in the colloids than the solutes, and the complexing of ^{232}Th appeared to suppress the solubility of ^{230}Th. The paper gives a good description of field sampling and lab techniques that are possible in this type of study

Siegel, M. D., R. Rechard, K. L. Erickson, J. O. Leckie, D. B Kent, and D. A. Grover et al. 1989. *Progress in Development of a Methodology for Geochemical Sensitivity Analysis for Performance Assessment. Volume 2: Speciation, Sorption, and Transport in Fractured Media.* Division of High Level Waste Management, Office of Nuclear Regulatory Research, U. S. Nuclear Regulatory Commission, NUREG/CR-5085 V.2, Washington, D. C.

The study begins with a discussion of the compilation of thermodynamic and sorption data for radionuclides and associated database files. These include the Aqueous Solutions Database (ASD), and the Sandia Sorption Data Management System (SSDMS). Data estimation techniques are described, and quality indices are assigned to evaluate the reliability of the various data. Most of the data presented have been determined for basalt. The surface complexation triple-layer model (TLM) is described, and methods of experimentally estimating parameters for the model are discussed. Theoretical K_d values are estimated using TLM methods, particularly for the case of uranium and neptunium speciation and sorption. Sensitivity analyses are considered, and a method for approximating solute transport in fractured porous media is discussed. Modeling assumptions and potentially important complicating factors are also considered. Radionuclide transport codes such as NEFTRAN and SWIFT II are discussed, and the suitability of the more comprehensive TRANQL hydrogeochemical code is also considered. As it is currently configured, TRANQL is relatively inflexible, and expensive to run. The study includes simulation exercise for uranium and neptunium migration through a basalt host. Organic and carbonate-complexing effects are considered, and a generic surface-complexation model is used to calculate theoretical sorption ratios (K_d) for radioelement sorption onto a goethite substrate.

Siegel, M. D., J. O. Leckie, S. W. Park, S. L. Phillips, and T. Sewards. 1990. Studies of *Radionuclides Sorption by Clays in the Culebra Dolomite at the Waste Isolation Pilot Plant Site, Southeastern New Mexico.* Sandia National Laboratories, SAND89-[illegible] Albuquerque, NM.

The authors have studied radionuclide migration through the Culebra Dolomite [illegible] above the Waste Isolation Pilot Plant (WIPP) in New Mexico. Radionuclide-clay interactions are possible mechanisms for attenuation of the solute plume, and Plutonium and Uranium sorption to clays in the host rock. Because the K_d (linear isotherm) approach lumps attenuation processes, its application to a variety of systems is limited. If the effects of sorption [illegible] separated out, performance assessment calculations using a defensible model [illegible] radionuclide retardation will have some basis in theory. In order to determine retardation due to sorption, it is necessary to: (1) characterize the clay and groundwater compositions along the flow paths; (2) measure the surface complexation constants for U, Pu in solution with the clays; (3) develop a database of equilibrium constants and interaction parameters. Possible radionuclide release scenarios at WIPP include unintentional drilling through the repository, into the underlying pressurized brines. The mineralogy along potential flow paths is listed. The principal clay is corrensite (smectite-chlorite). Pre-emplacement water compositions are discussed, and speciation is calculated using the code PHRQPITZ for saturation indices. The Culebra Dolomite is at partial equilibrium. Reaction path modeling along the flow path and fluid mixing was also performed using PHRQPITZ. Fluid mixing is based on fluid fluxes calculated using hydraulic gradients and measured transmissivities. Future modeling will indicate a [illegible] range of mixing compositions. For sorption, the goal is to obtain the surface complexation constants necessary to calculate K_d over the predicted range of solution compositions. These are calculated from radionuclide concentrations, surface sites, etc., using the method of Kent et al. (1988). The code HYDRAQL is used to calculate sorption curves and surface complexation constants at a given pH. Activity-concentration relationships calculated using the Davies equation are only valid for low solution ionic strength [illegible]. The authors use the Bronsted-Guggenheim interaction theory to extend the calculations to [illegible] ionic strengths [illegible] note that the extended Debye-Huckel approach is also possible. A stripping voltammetry technique is used to measure U-sorption on corrensite. Sorption is a strong function of pH and carbonate concentration. Total sorption decreases with increasing carbonate concentration, and reaches a maximum in the pH range of about 4.5 to 7.5.

Smith, R. W., and E. A. Jenne. 1991. Recalculation, evaluation, and prediction of surface complexation constants for metal adsorption on iron and manganese oxides. *Environ. Sci. Technol. 25*: 525-531.

There are several necessary parameters for application of a triple-layer surface complexation model: activities of uncomplexed species, model parameters [pK(int,a1), pK(int,a2), p*K(int)] for each element, surface properties of adsorbent. The reactions and mass-action equations for a TLM are presented. Tables of experimentally determined TLM parameters are presented for Fe- and Mn-oxides. The authors stress that there are limited data available for p*K(int) for cation adsorption onto Fe- and Mn-oxides, and there are frequent discrepancies. This may be due to the density and total number of sites, fraction of occupied sites (site loading), and inner and outer-sphere complexation. Uncertainties in the site density lead to substantial differences in calculated pK(int,a1) and pK(int,a2). These uncertainties are largely due to differences between experimental methods. Site loading only becomes significant when the most energetic sites are filled. The lack of ionic strength dependence suggests inner- rather than outer-sphere complexation. For Cd2+, there is a slight ionic strength dependence. By using the relationship between effective nuclear charge, hydrolysis constant (b(1,n)) and ionic size, p*K(int) can be predicted. The authors present a linear equation for log b(1,n)-charge (z), and a table with the necessary constants for Fe(III) and Mn(IV) oxides. Using this equation, progressive surface loading and inner sphere complexing are shown to be negligible in most groundwaters. The authors set up equations for determining p*K(int, Me(OH)n) from pK(int,a2), K(sc), b(1,n), and ion size. Comparison of estimated values with experimental data for silver shows good agreement for n=1 or 2, but it is less accurate for higher values of n.

Sposito, G., and W. A. Jury. 1986. Group invariance and field-scale solute transport. *Water Resourc. Res. 22*: 1743-1748.

The authors evaluate the hypothesis that in a field-scale vadose zone, the Convection-Dispersion Equation (CDE) governs solute transport locally. They evaluate the data of Biggar and Nelson (1976) using coordinate transform theory. The development only deals with transformation variables for the one-dimensional, unsaturated general case. Dispersion(D) and pore water velocity(u) are related at different locations in the vadose zone through scaling transformations. The authors maintain that the resulting six non-trivial transformed equations are the only way to relate different spatial points in the zone continuously to one another at different times in a way that is consistent with the differential equations assumed to govern solute transport locally. Lognormal statistical properties should be the rule for the transport coefficients D and u.

Sposito, G., R. E. White, P. R. Darrah, and W. A. Jury. 1986. A transfer function model of solute transport through soil. 3. The convection-dispersion equation. *Water Resourc. Re* 255-262.

The classic convection-dispersion equation (CDE) is presented as a special case of the function model developed in part one of the study (Jury et al., 1986). The specifi one-dimensional solute movement with steady flow and linear, non-specific sorp addressed. A two-component model similar to the mobile/immobile model of van G and Wierenga (1976) is presented. The basic equation of the model is a fun dimensionless time and space with four adjustable parameters: relative retardation (B) retardation (R), sorption kinetics (W), and the Peclet number (P). Three cases are con (1) A mobile/immobile model with positive sorption in both regions, and exchange regions governed by a linear mass transfer coefficient. Convection and dispersion only in the mobile phase; (2) Differs from case (1) in that no sorption occurs in the mob Negative sorption (exclusion) occurs in the immobile phase; and (3) All volumetric w the mobile region. Only rapid and slow sorption occurs. The authors indicate that this model is a special case of the two-component model. The authors discuss the effects of parameters on travel-time probability density function (pdf). Increasing Peclet number sharp the peak of the pdf, while heterogeneous velocities tend to smear out the pdf. The authors that positive sorption can readily counteract the asymmetric effects of the immobile pha tends to make the tranvel-time pdf symmetric. Two-component and two site models observed to have the same general effect. Total mobile water is considered critical determined directly from experimental travel-time pdf's and median solute travel time.

Szatkowski, A., and C. T. Miller. 1989. An investigation of mass transfer at the unsaturated-saturated zone interface. *EOS 70*: 325-326

ABSTRACT - The transport of volatile organic chemicals (VOC's) in the vapor phase of unsaturated zone has received increasing attention in the literature of late. The presence VOC's in the vapor phase affects the distribution and overall transport of contaminants subsurface. New methods for the monitoring and the rehabilitation of aquifers, which rely the presence of these compounds in the vapor phase, are affected by the rate at which transfer occurs from the aqueous phase to the vapor phase. A common assumption is aqueous and vapor phase are at equilibrium. This work examines the propriety of assumption. A new experimental apparatus was developed to measure mass transfer boundary between a saturated region and an unsaturated region. The experimental method allows for isolation of mass transfer at the saturated and unsaturated region interface and allow for a complete system mass balance to be performed. Experimental results show the eff of aqueous-phase velocity in the saturated zone on the interphase mass transfer coefficient the solutes perchloroethylene and toluene, in porous media of either glass beads or material. The results are shown in dimensionless form and compared to mass-transfer from related systems. The results are interpreted with the aid of a new two-dimensional element model, which simulates concentrations in three phases: aqueous, vapor, and the rate of interphase mass transfer. The mathematical model is used to derive results showing conditions that determine the direction of mass transfer, as a function of the source conditions, media properties, and solute properties. The model is also used to derive criteria under which the assumption of local equilibrium between the vapor and aqueous phase is appropriate.

[illegible]oste, A. P., L. J. Kirby, W. H. Rickard, and D. W. Robertson. 1984. Radionuclid[illegible] characterization, migration and monitoring at a commercial low-level waste disposal site. *[illegible] Waste Management 5*: 213-226.

At the LLW Repository at Maxey Flats, KY, the most abundant radionuclides are tritium, [illegible] Sr, [illegible] ^{240}Pu, and ^{241}Am. ^{60}Co and ^{238}Pu are primarily mobile as anionic species unde[illegible] anoxic conditions. Under oxic conditions, only a small fraction of ^{60}Co is anionic, while [illegible] [illegible] 1/2 cationic, 1/4 anionic, and 1/4 non-ionic. The anionic state is mo[illegible] [illegible] species tend to be more mobile, and the presence of a strong chelator ma[illegible] [illegible] than the oxidation state for radionuclide migration. Tables report on the org[illegible] [illegible] found in groundwaters from Maxey Flats. A section also reports on environment[illegible] [illegible] in forests at the site.

[illegible] 1984. *TRACR3D: A Model of Flow and Transport in Porous/Fractured Media*. Lo[illegible] [illegible] Laboratory, LA-9667-MS, Los Alamos, NM.

[illegible] solute transport code for transient, two-phase, multicomponent flow throu[illegible] [illegible] porous/fractured media. An implicit finite difference scheme is used. Isothermal [illegible] and unsaturated flow in one to three dimensions can be simulated. Radionuclide decay [illegible] be incorporated, and the number of tracers is limited by the memory of the compute[illegible] [illegible] modeled by either a K_d approach, or a first order rate-controlled process. The code [illegible] AN and is currently set up to run on a CRAY machine and comes with graphi[illegible] [illegible] code does not explicitly treat geochemical equilibrium, and therefore does [illegible] [illegible] ility to handle speciation, complexation, precipitation/dissolution, surfa[illegible] [illegible] or ion exchange. The report includes a user's guide to TRACR3D, with samp[illegible] [illegible] put decks and examples of the code's graphic capability.

[illegible]vis, B. J., and H. E. Nuttall. 1987. *Two-Dimensional Numerical Simulation of Geochemi[illegible] [illegible] Yucca Mountain*. Los Alamos National Laboratory, LA-10532-MS, Los Alam[illegible]

[illegible] report results of two-dimensional simulations using the TRACR3D solute transp[illegible] [illegible] and hydrologic properties appropriate to radionuclide transport at Yucca Moun[illegible] [illegible] simulations. Vertical and horizontal radionuclide transport through the frac[illegible] [illegible] severely attenuated, with ^{99}Tc the first to arrive at the water table after 1[illegible] [illegible] thermal behavior analogous to the elevated temperatures resulting are mo[illegible] for silica transport and deposition using J-13 water compositions. The result is a net dissolution and reprecipitation of silica away from the waste canisters. Colloid-aided radionuclide migration is also modeled. Colloid transport will mostly be confined to fractures, and small pore filtration, gravity settling, and diffusion into the solid phase will all act to decrease its effects. The report very useful for its tabulations of data relevant to high-level waste and the Yucca Mountain environment.

Travis, C. C., and E. L. Etnier. 1981. A survey of sorption relationships for reactive solutes in soil. *Jour. Environ. Qual. 10*: 8-17.

An excellent survey of existing (pre-1981) theoretical models of sorption relationships. Sorption is defined as the uptake and storage of solute species. Adsorption, chemisorption, and ion exchange are identified as the principle means. Process models are divided into equilibrium and kinetic models. It is stressed that equilibrium sorption isotherms cannot be used to model kinetic sorption, and cannot distinguish between adsorption and secondary precipitation. Equilibrium sorption is defined as that case where the rate of sorption is much greater than the rate of change in solute concentration due to other processes. Equilibrium models include a number of empirical adsorption isotherms. Linear and Freundlich adsorption isotherms allow for easy curve-fitting of data, but are not properly extrapolated beyond the experimental points. Also, there is no maximum adsorption concentration. Shayan and Davis (1978) have modified a Freundlich isotherm to include a critical concentration. The Langmuir, Langmuir Two-Surface, and Competitive Langmuir isotherms include a measure of sorptive bond strength, and incorporate a maximum amount of sorbed solute. The monolayer theory breaks down, however, where free energy of adsorption is not constant, which may be the case where the heat of adsorption is dependent on the number of occupied sites. Frequently, separate Langmuir isotherms are applied to account for different stages of adsorption. Kinetic models include a variety of approaches. The Reversible Linear and Nonlinear Models require first-order rate constants for adsorption and desorption, and can be applied to unsaturated systems, but there is no maximum concentration. The Kinetic Product Model is empirical and has no theoretical basis. In addition, it also has no limit on adsorption. Bilinear Adsorption is a kinetic version of the Langmuir equilibrium isotherm, incorporating a maximum quantity of adsorbed solute. The Mass Transfer Model is a more general case of the Bilinear and Reversible Linear models, depending on how the liquid phase concentration is defined. The Elovich model uses empirical parameters, and models the fraction of occupied adsorption sites. The Fava and Eyring model uses a first-order kinetic approach to predict the distance from equilibrium sorption. Finally, the Two-Site Kinetic Model incorporates one "fast" equilibrium site and one "slow" kinetic site. For fast water flow, the residence time of the solute is low and the fast site is dominant. At low velocities, overall sorption is greater due to increased participation of slow sorption reactions.

Triay, I. R., A. Meijer, M. R. Cisneros, G. G. Miller, A. J. Mitchell, and M. A. Ott et al., 1991. Sorption of Americium in Tuff and Pure Minerals Using Synthetic and Natural Groundwaters. *Radiochimica Acta* 52/53: 141-145.

Batch equilibrium experiments were performed to study americium sorption by crushed tuff, and pure clinoptilolite and romanechite. Natural J-13 water from the Yucca Mountain saturated zone, and synthetic groundwater. Spikes of Am(III) are used with an original molarity of 1.3 x 10^{-7}. For buffered solutions, pH was originally measured at [illegible]. The experiments are carefully described, particularly fluid preparation and storage. Up to 79% of the original Am was lost to glass containers, with maximum loss for J-13 waters. In contrast, the synthetic solution lost the greatest percentage of Am to teflon containers. Minerals were equilibrated with the appropriate groundwater prior to the sorption experiments. During 21-day experimental runs, water/rock ratios were held at 100 ml to 1 g. The solution was continuously shaken. Kd values were determined, assuming equilibrium sorption. Kd values range from 4900 for clinoptilolite and 330000 for romanechite with synthetic groundwater, to 12000 for J-13 water and Yucca Mountain tuff. The authors indicate that the dilute solutions used preclude precipitation/dissolution, and that the lower Kd value for clinoptilolite may be due to the large size of $AmCO_3^+$ which is unable to fit into the clinoptilolite structure.

Valocchi, A. J. 1984. Describing the transport of ion exchanging contaminants using an effective K_d approach. *Water Resourc. Res.* 20: 499-503.

Calculated distribution coefficients (K_d) are frequently observed to change across a solute migration front. An effective K_d approach is developed to address this problem for simple one-dimensional transport in a homogeneous porous medium. Local equilibrium and a sharp migration front are also assumed. The effective K_d is formulated using simple mass balance across a finite step along the advancing solute front. In contrast to simple K_d, the effective K_d is not a unique property of the medium since it depends on the aqueous concentration of the fluid. Mathematically, for the case of simple, binary, homovalent ion exchange, this approach requires knowledge of K_{12}, the selectivity coefficient between the two ions. This approach can also be applied to multispecies transport by finding an effective K_d for each migrating front. The approach breaks down for multi-ion, heterovalent exchange. The method is then applied to a field problem at the Palo Alto Baylands, for Ca^{2+}, Mg^{2+}, NH_4^+, and Na^+ migration. Using an effective K_d reproduces the observed breakthrough of NH_4^+, despite apparent disequilibrium sorption in the field experiment. In order to apply the method, the aqueous and sorbed phase composition must be known upstream and downstream of the solute front. Therefore, the effective K_d is not a unique soil property. The author concludes that it is possible to include precipitation/dissolution and surface complexation processes, and stresses that the approach is invalid if either hydrodynamic dispersion is important, or the assumption of local equilibrium is violated.

Valocchi, A. J. 1985. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. *Water Resourc. Res.* 21: 808-820.

The author presents criteria to evaluate the validity of the local equilibrium assumption (LEA) for sorption processes for one-dimensional, steady flow in homogeneous soils. He comments that models based on LEA do not accurately simulate the sorbing solute. A list of experimental studies in saturated soils indicates several investigations where the LEA proved successful for hydrodynamic dispersion > > molecular diffusion (10^{-6} cm^2/s). Two classes of models are discussed: (1) physical non-equilibrium where the sorption rate is controlled by diffusion between mobile and immobile water (two-region); (2) chemical non equilibrium, where all pore fluid is considered mobile and overall sorption is governed by the rate of reaction at the soil/solution interface (two-site). Chemical non-equilibrium models usually incorporate kinetics as a diffusion equation describing concentration profiles within particles, an adsorption rate expression, and an equation linking microscopic concentrations at the particle boundary with macroscopic aqueous concentrations. The rate-controlling step is either: (1) transport to and from soil surfaces, or (2) rates of reaction. For physical non-equilibrium models, several studies have used first order rate equations for exchange between mobile and immobile waters. From time moment analysis, the author demonstrates that non equilibrium does not influence the mean breakthrough time of the solute pulse, and gives a series of expressions to use in determining the validity of LEA. The author concludes that the validity of LEA depends upon all system parameters and the assumed form of the non equilibrium submodel. LEA is generally valid when the rate of microscopic sorption processes is much faster than bulk flow processes, and is more appropriate for gradual input of the contaminant rather than for an instantaneous pulse.

Valocchi, A. J. 1989. Spatial moment analysis of the transport of kinetically adsorbing solutes through stratified aquifers. *Water Resourc. Res.* 25: 273-279.

The author uses spatial moment analysis to model the long time behavior of reactive solute transport in a vertically stratified aquifer. A first order rate law is used to describe adsorption reactions, deemed by the author as a better approach than a two domain (mobile-immobile) approach. From moment analysis, an effective dispersion coefficient (D) governing transport in a one-dimensional, saturated, homogeneous medium is defined. This coefficient is made up of three components. (1) local hydrodynamic dispersion; (2) Taylor dispersion due to vertical variation in pore fluid velocity and retardation factors; (3) dispersion due to the kinetics of adsorption reactions. Taylor dispersion depends on the correlation between retardation factor and pore water velocity. A negative correlation is reflected in increased Taylor dispersion. Slow adsorption kinetics also increases the dispersion of the solute plume. The author then develops a non-equilibrium index as a measure of the importance of adsorption equilibrium. Like Taylor dispersion, deviations from equilibrium also depend on the spatial variability of velocity and retardation factor. Increased pore fluid heterogeneity leads to a decreasing deviation from local equilibrium.

Valocchi, A. J., R. L. Street, and P. V. Roberts. 1981b. Transport of ion-exchanging solutes in groundwater: Chromatographic theory and field simulation. *Water Resourc. Res.* *17*: 1517-1527.

The authors address multispecies, heterovalent solute transfer using chromatographic theory. The finite-element model presented is for steady, one-dimensional flow in saturated homogeneous medium, assuming that ion-exchange is the only chemical reaction occurring to any appreciable degree. The model also ignores solution phase activity corrections, and combines the solute transport/water transport equations into one system of interdependent non-linear equations. Mass balance checks the accuracy of the numerical solution. Results of modeling indicate that dispersion-induced ion exchange is only a second-order effect. For binary or ternary systems, there is the possibility of either self-sharpening or spreading solute front depending on whether the infiltrating ion is preferentially adsorbed relative to the native ion. Variations in total solution normality, (Ct) are observed to travel at the pore velocity. Th model was applied to a field problem at Palo Alto, CA. Inverse modeling obtained the physica parameters, and batch lab experiments were used to determine ion exchange capacity and io exchange selectivity. The system was modeled for Na, Mg, and Ca breakthrough at thre observation wells. The model matched the observed data fairly closely, while selectivity coefficients were ordered such that Ca > Mg > Na. The model provides no information on the time necessary to achieve calculated concentration profiles. Profiles developed quickly in this study, but the authors were unsure of the results for larger dispersivities. The model also assumes local chemical equilibrium, which is only valid for low enough pore velocities.

van der Zee, S. E. A. T. M. 1990. Analysis of solute redistribution in a heterogeneous field. *Water Resourc. Res.* *26*: 273-278.

The author uses a one-dimensional stochastic model to simulate solute redistribution in the vertical direction. A two-dimensional field is represented as a collection of parallel columns with random sorption parameters and saturated layer thicknesses. Adsorption is modeled according to empirical Langmuir isotherms, which are transformed into dimensionless variables. Desorption is not incorporated into the model. Soil chemical properties are randomly distributed, and local chemical equilibrium is assumed. Solute distribution in each column in the model is calculated separately, and a field-averaged front was obtained by arithmetically averaging concentrations at some depth. There was no coupling in the horizontal direction. Due to nonlinear adsorption, the solute front decreased in steepness with time. Heterogeneous field properties resulted in a smearing out of the field-averaged front. Sensitivity analysis was performed by randomly varying each transport parameter in turn. Flow properties were assumed nonrandom. Results suggest that pore-scale dispersion is of less importance than spatia variability. At large distribution times, if the field-averaged concentration is small enough adsorption approaches linearity, and pore scale dispersion is increasingly important, compared to nonlinear sorption which tends to counter dispersional effects. If linear adsorption assumed, the relative importance of pore dispersion and spatial variability can be compared f constant input concentration. The author derives a length scale criteria for which spati variability controls the field-averaged concentration front. The author concludes with the intuitive statement that when adsorption is nonlinear, a simple analytical treatment of solute transport is not feasible.

van Duijn, C. J., and S. E. A. T. M. van der Zee. 1986. Solute transport parallel to an interface separating two different porous materials. *Water Resourc. Res.* 22: 1779-1789.

The authors address the diffusion between zones of mobile/immobile waters as proposed in the model of van Genuchten and Wierenga (1976). They develop an approximate analytical solution, that treats the problem as diffusion across an interface separating two fluids that are moving at different velocities. Linear adsorption is assumed for the 2-dimensional solution. The resulting solutions are compared to an unconditionally stable finite-difference solution using a central-differencing approach and a Neumann boundary condition (prescribed flux). The retardation factors were matched to the permeability/velocity, such that regions with the highest velocities were given the smallest retardation factor (R). Dispersion anisotropy of 10:1 was used in the numerical models. Agreement is good for large values of (R),but the differences become greater for smaller values. The authors believe that some of the discrepancy is due to the assumption of an infinitely thick impermeable region in the analytical solution. If restrictions in thickness are met, the concentration profiles are in good agreement except for first breakthrough. Because of restrictions on thicknesses of the two regions, and the assumption of zero longitudinal dispersion coefficient, the applicability of the solution is limited to short travel distances in domains consisting of different, homogeneous layers.

van Eijkeren, J. C. H., and J. P. G. Loch. 1984. Transport of cationic solutes in sorbing porous media. *Water Resourc. Res. 20*: 714-718.

The authors study the transport of reactive cations through a saturated sorbing porous medium. A mobile/immobile model is used with steady-state convection-dispersion model. The dispersion term includes both molecular diffusion and hydrodynamic dispersion. Transport velocity increases as mobile water decreases for a given water flux/total water content. Earlier breakthrough results, but is partially offset by lateral diffusion from mobile to immobile liquid. Non-linear, equilibrium cation sorption is assumed. The authors develop a mathematical model which includes charge balance. The Gapon equation is used for exchangeable sorption in a two-ion, heterovalent system. Although initial development is for two ions, the authors indicate that the approach is not limited in this respect. In the numerical treatment, one-step coupling is used, resulting in non-linear partial differential equations. Galerkin finite element methods are used with Crank-Nicholson time discretization. The numerical model predicts solute breakthrough in Na-K column experiments fairly well.

van Genuchten, M. T., and W. A. Jury. 1987. Progress in unsaturated flow and transport modeling. *Rev. Geophys.* 25: 135-140.

This is a survey paper of methods and techniques employed in modeling solute transport and unsaturated flow. It provides an excellent summary of a variety of approaches used through 1986. The authors begin by developing of Richard's equation for unsaturated transport and describe several analytical, approximate analytical, and numerical approaches for solving these equations. A retardation factor is used to represent equilibrium adsorption or exchange. There is some disagreement over whether or not deterministic solutions of Richard's equations can accurately represent transfer processes. One-step and two-step coupling approaches for hydrogeochemical transport, are discussed. The two-step approach is more efficient, particularly for multicomponent transport. The authors then address the question of non-equilibrium adsorption and discuss the two-site (partial equilibrium) and two-region (mobile-immobile) approaches. The two-site approach assumes one equilibrium sorption site and one first-order kinetic site, while the two-region model assumes that sorption kinetics are controlled by mass transfer between mobile water in equilibrium with immobile water in dead end pore spaces. Transport in heterogeneous, structured soils is also discussed using two-domain, two-region, or bicontinuum approaches. The authors conclude with a discussion of stochastic modeling methods, especially as applied to two-region models of kinetics.

van Ommen, H. C., J. W. Hopmans, and S. E. A. T. M. van der Zee. 1989. Prediction of solute breakthrough from scaled soil physical properties. *Jour. Hydrol.* 105: 263-273.

The authors have used the stochastic transfer function concept of Jury (1982) to measure overall response of a heterogeneous system. The response to an impulse input is a lognormally distributed residence time. Heterogeneity is lumped into a variance of the residence time. The authors use the scaling theory of similar media to give the physical background and quantify the residence time distribution. A scaling factor (delta) is defined for a characteristic length to relate the unsaturated and mean hydraulic conductivity, such that K = (delta)^2*K. The derived probability density functions (PDF) for the scaling factor allow full characterization of the hydraulic properties. The model that follows assumes gravity flow, steady-state flow, a uniform soil profile, and purely convective vertical transport. It is determined that variability in travel time is primarily variability in the downward flux as opposed to moisture content. An analytical approximation is then derived for travel time as a function of the PDF's for the scaling factor. The model was then applied to a field study. Measured breakthrough consistently occurs sooner than predicted, and agreement was poor for realistic measured scale factors and soil water pressure head. The authors suggest that the approach might be more successful under different experimental conditions, although they give no indication what these conditions might be.

von Breymann, M. T., R. Collier, and E. Suess. 1990. Magnesium adsorption and ion exchange in marine sediments: A multi-component model. *Geochim. Cosmochim. Acta* 54: 3295-3313.

The authors investigate the systematics of Mg adsorption and desorption in marine sediments, and the effect it has on the Mg-composition of seawater. Free Mg^{2+} activity is decreased by increasing carbonate complexation, and therefore, higher total dissolved CO_2 reduces adsorption. Higher Mg-carbonate complexation is initially compensated by sulfate loss (another Mg-ligand). Carbonate complexation effects are most pronounced in sulfate-depleted systems. Ammonium $(NH_4)^+$ also desorbs Mg^{2+} through site competition. A computer model is developed using MINEQL for speciation which matches data observed for natural seawaters fairly well. The model includes complexation, NH_4^+/Mg^{2+} exchange, and ligand competition for magnesium. A Langmuir isotherm fits data determined for sediments from the Bransfield Strait, the Gulf of California, and the coast of Peru. Total exchangeable magnesium generally equals 40 percent of total cation exchange capacity (CEC) for the sediments, and maxima Mg activity in pore waters coincides with minima in CEC. Therefore, changes in CEC during anoxic diagenesis are reflected in anomalous dissolved Mg^{2+}/depth profiles.

Waldrop, W. R., L. W. Gelhar, A. Mantoglou, C. Welty, and K. R. Rehfeldt. 1985. Water Systems Development Branch. *A Review of Field-Scale Physical Solute Transport Processes in Saturated and Unsaturated Porous Media*. Electric Power Research Institute, EA 4190, Palo Alto, CA.

The authors present a critical review of available data (pre-1985) on field-scale solute transport. These include sites in both the saturated and unsaturated zones. The report includes development of deterministic transport equations for a nonreactive solute. The dispersion coefficient is identified as a key element of the equation. The validity of the approach has been demonstrated in the laboratory for homogeneous media, but in moving to field-scale, dispersion coefficients are orders of magnitude larger than those predicted in the lab. This is probably due to large-scale heterogeneities that are difficult to simulate in the laboratory. The authors present three approaches to modeling field-scale dispersion, including perfect layering, specified spatial statistics of a heterogeneous velocity field, and statistical description of the variability of hydraulic conductivity. The third option is chosen as the best approach for field experiment design. Saturated and unsaturated transport processes are described, and tables containing descriptions of field and lab studies and calculated site parameters (dispersivity, field scale, transmissivity, etc.) are presented. Detailed analysis of the Canadian Borden, and Bonnaud, France are presented to demonstrate the use of second moment analysis in determining 3-D dispersion characteristics, spatial variability in hydraulic conductivity to predict dispersivity. Models of unsaturated transport are critically discussed, and it is suggested that classical flow and transport models will be inadequate to address the lateral and preferential flow observed in these environments. The authors conclude that heterogeneity in field-scale transport is critically important, and that both lateral flow and preferential flow have been observed in field experiments as a result of these features. The authors recommend a series of experiments in a variety of field settings to evaluate the characteristics of these different processes. Stochastic theory is proposed as the best approach to extending small-scale observations to the field-scale.

White, R. E., J. S. Dyson, R. A. Hag[illegible] and G. Sposito. 1986. A transfer function model of solute transport through soil. 2 [illegible] applications. *Water Resourc. Res.* 22: 248-254.

The transfer function model developed in part I of the study (Jury et al., 1986) is applied to field- and lab-scale studies of Br, Cl, and bacteria transport through unsaturated, heterogeneous porous media. Only net effect is considered in this approach. Field tracer experiments on Br-transport indicate a two-component transport mechanism (mobile/immobile) through clay during unsteady, unsaturated flow. Fast transport occurs through large porous zones, while slow transport dominates fine, dense soil zones. A lognormal probability density function (pdf) may be inadequate to predict transport. Parameter fitting is used to determine an appropriate travel-time density function. Different parameter estimation methods are observed to give different results. Soil type, initial water content, and solution input all affected observed travel times. Soil column experiments (for Cl, bacteria transport) indicate that not all of the available fluid volume is involved in solute transport, supporting the application of a two-component model. Calculations indicate that the fraction of the water participating in solute transport varied from 14 percent up to 90 percent of the total water content of the soil, values which increased with the rate of solution input.

Wilson, M. L., and A. L. Dudley. 1986. *Radionuclide Transport in an Unsaturated, Fractured Medium.* Sandia National Laboratory, SAND--86-7017C, Albuquerque, NM

The authors develop a fractured media transport model, which considers both advective and diffusive processes. The code (TOSPAC) is a one dimensional, composite porosity model, which approximates the matrix fracture system as an equivalent porous medium. Solute and water transport are solved using a two-step approach. Water transport is solved first, and the resultant velocity field is passed on to the solute transport model. Solute transport is calculated separately for the fracture and matrix flow components of the water transport model. The two regions then exchange through a dispersive coupling term (X), assuming a discontinuous gradient at the fracture/matrix boundary. Retardation is tied up in the coupling of transfer between the fractures and the matrix. The coupling time is proportional to the retardation factor for fracture and matrix transport (R_f and R_m, respectively). The model can handle constant K_d sorption and radioactive decay, but it is strictly a transport code and cannot model geochemical equilibria. Transport is modeled at Yucca Mountain assuming a vertical fracture network, although for such an arid region, infiltration is probably so low that fracture flow is low, and matrix transport is the dominant mechanism. Retardation is assumed to be 1 for the fractures. Distribution coefficients and mineral modes are used to determine R_m. ^{129}I is assumed to be a non-reactive tracer, and R_m is set at 40 for ^{238}U. A simple, congruent leach model is used for a source term, and radionuclide concentrations are assumed zero at the surface and at the water table. The effect of coupling is to drastically increase groundwater travel-time. The degree of coupling at Yucca Mountain is unknown because R, is unknown and a source of uncertainty. Breakthrough depends on the infiltration rate chosen, and the units assumed. [illegible] most instances, breakthrough was on the order of 1000 to 20000 years. The fully uncoupled [illegible] is considered a conservative limit for solute transport.

Wood, W. W., T. F. Kraemer, and P. P. Jr. Hearn. 1990. Intragranular diffusion: An important mechanism influencing solute transport in clastic aquifers? *Science* 247: 1569-1572.

The authors find that intragranular diffusion is an important mechanism for solute transport, at least in the sand from Cape Cod that is considered in the article. The authors performed experiments with the Cape Cod soil and Li^+ tagged groundwater. The results indicate that Li uptake for times on the order of 10 minutes was by ion exchange at the surface, while at times greater than 100 minutes, diffusion into grains was the rate controlling process. Approximately 80% of the Li was removed from solution in this way. The authors filtered the samples at 450nm, but did not analyze the filtrate for Li, and removal of Li from solution by colloids in the size range 450nm-1000nm was not considered. The authors conclude that diffusion into the grains is time-dependent, and can lead to chemical disequilibrium that will result in the increased dispersion of the solute plume.

Yeh, G. T. 1985. Comparisons of successive iteration and direct methods to solve finite element equations of aquifer contaminant transport. *Water Resourc. Res.* 21: 272-280.

Successive iteration techniques in finite element analysis offer a substantial savings in both CPU memory and calculation time requirements relative to direct elimination schemes, even for simple problems. The author discusses the theory of iterative techniques and the types and ranges of relaxation factors used. The different methods were tested against analytical solutions of one-dimensional transient transport from an upstream concentration, and two-dimensional transient transport from a two-dimensional upstream strip source. The paper presents a comparison of iteration schemes with respect to CPU memory and calculation time requirements, program complexity, and numerical stability. Only the successive underrelaxation (SUR) and Gauss-Seidel (G-S) solutions converge in systems for Peclet numbers (Pe) greater than one. For the two-dimensional case, the SUR technique is more efficient for advection dominated systems with larger Pe. For small Pe, the G-S is shown to be more efficient. The successive overrelaxation technique (SOR) diverges for Pe > 1, and is not appropriate for transient problems where Pe may change over space and time. An orthogonal-upstream weighting scheme, however, will allow SOR to be applied for all values of Pe, but CPU calculation time will double relative to the G-S method. The author also suggests compressing the coefficient matrix to contain only non-zero values in a pointer array to improve memory and calculation efficiency.

Yeh, G. T., and V. S. Tripathi. 1989. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resour. Res.* 25: 93-108.

The authors identify three basic approaches to hydrogeochemical modeling: (1) Mixed differential and algebraic substitution (DAE), (2) Direct substitution (DSA), or one-step coupling, and; (3) Sequential iteration (SIA) between hydrologic transport and geochemical equilibria, or two-step coupling. The six identified primary dependent variables (PDV's) are: (1) Concentrations of all species; (2) Concentrations of all component species and precipitated species; (3) Total analytical concentrations of all aqueous components; (4) Total dissolved concentrations of aqueous components; (5) The concentrations of the aqueous component species, and (6) Hybrid concentrations. These PDV's are combined with the different approaches in order to evaluate the strengths and weaknesses of each model. The DAE technique can incorporate PDV's 1 and 2; the DSA approach can use PDV's 1-4, and the SIA method can employ PDV's 1-3. The authors present the basic hydrologic transport equations for N(a) aqueous components and N(s) sorbent components. Chemical equilibria equations for complexation, surface complexation, ion exchange, and precipitation dissolution are presented. These equations assume that the activity of the solids is unity, that local equilibria is valid, and that chemical reactions are fast and reversible. For a given mathematical strategy, complexation, redox, acid/base, sorption, and precipitation dissolution reactions need to be solved simultaneously. The authors feel that at current levels of understanding and technology the SIA method is the best approach in terms of efficient solution, while the DAE and DSA approaches are generally not feasible for even small two- and three-dimensional problems because of excessive computer memory requirements. SIA models that employ PDV 1 cannot deal simultaneously with precipitation dissolution, complexation and sorption. SIA models with PDV 2 cannot handle precipitation dissolution reactions. SIA techniques using PDV 3, however, can handle the entire range of geochemical reactions, and can readily incorporate kinetic effects. This approach is therefore recommended by the authors for future research.

APPENDIX B:

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