CNWRA 91-016

EFFECTS OF VARIABLE HYDROLOGIC SATURATION ON 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

December 1991

CNWRA 91-016

EFFECTS OF VARIABLE HYDROLOGIC SATURATION ON SORPTION MODELING FOR HIGH-LEVEL WASTE PERFORMANCE ASSESSMENT: A LITERATURE REVIEW

Prepared for

Nuclear Regulatory Commission
Contract NRC-02-88-005

Prepared by

David R. Turner

Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

December 1991

9412050216 911219
PDR WASTE
WM-11 PDR

ABSTRACT

The ability of sorption processes to retard radionuclide migration to the accessible environment is a critical aspect of the performance assessment of the proposed high-level radioactive waste repository at Yucca Mountain, Nevada. Construction of the repository is currently planned for the unsaturated zone, and the effects of variable hydrologic saturation on sorption processes should be evaluated. 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 processes in radionuclide transport. Specifically, Subtask 1.2 of the project, "Literature Review and Development of Approach: Variable Saturation Sorption" is designed to consider the current status of research on sorption under hydrologically unsaturated conditions. Subtask 1.2 has been completed, and the results are presented in this report.

Based on experiments performed under hydrologically saturated conditions, the control exerted on sorption processes by the physical and chemical conditions of the repository environment are discussed. Chemistry of fluids from the saturated and unsaturated zones in the vicinity of Yucca Mountain are presented, and the effects of variable hydrologic saturation on critical controlling factors are discussed. Possible impact on sorption and radioactive transport are evaluated. Pronounced effects are generally considered likely only under conditions of extremely low water content. The basic flow and transport equations governing migration in the unsaturated zone are presented and discussed. Different techniques to modeling nonequilibrium reactive transport are presented, and common sorption models are summarized. Laboratory unsaturated column experiments are described and controlled field experiments are considered. The role of natural analogs in determining long time effects is also presented and evaluated. The findings of the literature review are summarized in the final section. The complexities of fluid flow in the unsaturated zone makes interpretation of the results of laboratory and field unsaturated experiments difficult. It seems unlikely that the effect of sorption processes can be isolated from other factors, given current levels of understanding.

TABLE OF CONTENTS

LIST OF FIGURES v
LIST OF TABLES vi
EXECUTIVE SUMMARY vii

1 INTRODUCTION 1-1

2 SORPTION PROCESSES AND MECHANISMS 2-1
2.1 CHEMICAL/PHYSICAL FACTORS CONTROLLING SORPTION PROCESSES 2-1
2.1.1 Substrate Properties Influencing Sorption 2-1
2.1.2 Solution Chemistry Controls Influencing Sorption 2-4
2.1.3 System Properties Influencing Sorption and Retardation 2-8
2.2 EFFECTS OF VARIABLE SATURATION ON CONTROLLING FACTORS 2-9
2.2.1 Yucca Mountain Groundwater Chemistry 2-9
2.2.2 Effects of Variable Saturation on Groundwater Chemistry . . 2-12
2.2.3 Effects of Variable Saturation on Flow Paths and Physical Transport 2-16

3 SOLUTE TRANSPORT – UNSATURATED FLOW CONDITIONS . . 3-1
3.1 SOLUTE TRANSPORT-UNSATURATED FLOW 3-1
3.2 SOLUTE TRANSPORT-NONEQUILIBRIUM TRANSPORT 3-4
3.2.1 Two-Region Transport 3-4
3.2.2 Two-Site Transport 3-7
3.2.3 Stochastic Models 3-8
3.3 SORPTION MODELS 3-8

4 EXPERIMENTAL AND FIELD STUDIES 4-1
4.1 EXPERIMENTAL SORPTION STUDIES 4-1
4.1.1 Hydrologically Saturated Column Experiments 4-1
4.1.2 Hydrologically Unsaturated Column Experiments 4-3
4.1.3 Intact Rock Experiments 4-4
4.2 FIELD EXPERIMENTS 4-5
4.2.1 *In Situ* Field Migration Experiments 4-5
4.2.2 Analog Migration Studies 4-7

5 SUMMARY AND CONCLUSIONS 5-1
5.1 SUMMARY 5-1
5.2 CONCLUSIONS 5-3

6 CITED REFERENCES 6-1

LIST OF FIGURES

Figure	Title	Page
3-1.	Early breakthrough and tailing observed for aggregated soils under unsaturated condtions	3-5

LIST OF TABLES

Table	Title	Page
2-1.	Element Concentrations in Ground Water from the Vicinity of Yucca Mountain	2-10
2-2.	Anionic Species Concentrations and Other Measurements for Ground Water from the Vicinity of Yucca Mountain	2-11
2-3.	Chemical Analyses of Fluids from the Unsaturated Tuffs in Drill Hole U12T3, Rainier Mesa, Nevada	2-13
2-4.	Chemical Analyses of Fluids from the Unsaturated Tuffs in Drill Hole UE-25, Yucca Mountain, Nevada	2-14
3-1.	Summary of Sorption Models, Equations, and Parameters	3-9

EXECUTIVE SUMMARY

The purpose of this report is to provide a survey of the recent literature on sorption processes and radionuclide transport under hydrologically unsaturated conditions.

In accordance with the Nuclear Waste Policy Act (as Amended 1987), Tertiary volcanic tuffs at Yucca Mountain, Nevada are being considered as a potential site for the construction of a geologic high-level radioactive waste repository. Current plans are to construct the repository in the unsaturated zone at a depth of some 300 m, well above the water table which is at a depth of about 500 to 750 m. As a result, the unsaturated zone at Yucca Mountain is likely to be a critical factor in the performance of the proposed high-level waste repository. Variable saturation may exercise a broad influence on a number of key parameters that control radionuclide transport. Unfortunately, due to the difficulty in extracting water samples from unsaturated rocks and in performing unsaturated transport experiments, the detailed characterization of many of these effects is currently understood only indirectly. As a result, a large number of simplifications are generally made in modeling reactive transport in the unsaturated zone.

The chemical and physical properties of the minerals, the speciation chemistry of the element of interest, the chemistry of the solution carrying the dissolved species through the geologic medium, and the physical conditions of the geologic environment all interact in a complex manner to control the solubility and the sorption of a given element in the saturated zone. In the unsaturated zone, these controls may be affected to varying degrees as a result of additional complications introduced by the effect of variable saturation such as changes in flow paths (e.g. fractured vs matrix flow), solution properties and access to adsorbent phases. Experiments under saturated conditions are often easier to interpret and have been used to determine the effect of physical and chemical system conditions on sorption processes. By distinguishing the effect of variable hydrologic saturation on physical and chemical parameters identified as key controls, it is possible to extrapolate the effects of variable hydrologic saturation on sorption processes and mechanisms. Although some physical and chemical variations can be attributed to partial saturation, many of these effects become pronounced only under extremely dry conditions. While such low saturation levels (probably 5 percent or less) may be reached in the near-field adjacent to a waste canister, the far-field at Yucca Mountain is unlikely to be dried to such an extent, given current saturation levels of 40-80 percent.

Reactive solute transport in the unsaturated zone is usually described using the classical convection-dispersion equation appropriate to the dimensionality of the problem. However, given the non-linear nature of hysteretic effects on moisture content, hydraulic conductivity, and other hydraulic properties in the unsaturated zone, there is considerable uncertainty in the applicability of this equation to transport under variably saturated conditions and in the validity of the assumption of local equilibrium. Assuming that the convection-dispersion equation is appropriate, modeling kinetic solute transport in the unsaturated zone has followed two basic approaches. The first approach involves dividing the flow regime into two physically distinct domains, mobile water actively engaged in flow and transport, and stagnant water isolated in

dead-end pore spaces. The second approach proposes two reaction sites, one of which obeys chemical equilibrium, and the second of which follows nonequilibrium (usually first-order kinetic) processes. Different approaches are used to model sorption in unsaturated transport, but the most common approach is the simple linear isotherm. Mechanistic surface complexation and ion exchange models have not generally been applied to the complexities of unsaturated flow and transport.

Given the spatial scale of most laboratory and field experiments, the effects of sorption processes at the microscale under unsaturated conditions tend to be lost in the uncertainty surrounding medium heterogeneities and complex fluid flow systematics. While such experiments may be useful in determining general transport behavior in the vadose zone, until the uncertainties inherent in unsaturated fluid flow can be better constrained, effort is perhaps better spent in understanding sorption under saturated conditions. Combined with a better understanding the chemistry of natural groundwaters in the unsaturated zone at Yucca Mountain, this approach can allow an evaluation of the specific role of sorption processes in retarding radionuclide migration. Once this role has been established, it may then be possible to extrapolate to radioelement transport under variable hydrologic saturation.

1 INTRODUCTION

In accordance with the Nuclear Waste Policy Act (as Amended 1987), Tertiary volcanic tuffs at Yucca Mountain, Nevada are being considered as a potential site for the construction of a geologic high-level radioactive waste repository. Current plans are to construct the repository in the unsaturated zone at a depth of some 300 m, well above the water table which is at a depth of about 500 to 750 m (DOE, 1988 - Ch. 3). This thick unsaturated zone is proposed as an additional natural barrier to radionuclide transport from the repository to the water table (Montazer and Wilson, 1984; DOE, 1988 - Ch.3). In order to evaluate the effectiveness of this barrier, it is necessary to gain some understanding of how different retardation processes operate in an unsaturated environment.

In meeting the EPA criteria outlined in 40 CFR Part 191, the sorption of radionuclides on the minerals of the geologic medium is specifically mentioned as a favorable condition in the regulations governing the licensing and performance of the repository (10 CFR Part 60.122(b)). In addition, 10 CFR Part 60.122(c) mentions the reduction of radionuclide sorption as a potentially adverse condition. Because of its potential importance as a retardation mechanism, a great deal of effort has been expended to investigate the sorption of contaminants, and a large body of data is available (Turner, 1991). Given the likely importance of the unsaturated zone in radionuclide migration from the repository to the accessible environment, it may be important to examine this data in an effort to understand the effects of hydrologic saturation on sorption processes.

The effects of variable saturation are difficult to assess, and work has been largely limited to macroscale studies of solute transport. In the laboratory, reactive solute transport is examined using dynamic column experiments. These experiments are difficult to perform, since stable conditions are difficult to maintain for the relatively long experimental times required. Additionally, interpretation of the results with regard to sorption is complicated by the effects of flow and transport in the unsaturated column. Well constrained field experiments are also performed in an attempt to model solute transport in the unsaturated zone, but these are subject to many of the same limitations as column experiments. Natural analogs are available, but scales are often quite large, and uncertainties exist in the reconstruction of the physicochemical environment.

One possible approach to evaluating sorption in the unsaturated zone is to determine the factors controlling sorption in saturated systems. A large body of data is available for these types of systems, from both batch equilibrium and dynamic laboratory experiments (Turner, 1991). Under saturated conditions, experiments are more readily conducted and simple systems can be defined to focus on the response of specific sorption mechanisms to changes in physical and chemical conditions. Once the roles of these parameters in controlling sorption processes have been established under hydrologically saturated conditions, it may then be possible to consider the effect of variable saturation on these controlling factors, and infer potential changes in sorptive behavior in the vadose zone.

The purpose of this report is to provide a survey of the recent literature on sorption processes applicable to solute transport in the unsaturated zone, particularly as related to radionuclide migration. The reader is referred to Turner (1991) for a more detailed discussion of sorption theory, sorption models, experimental and field data, and coupled hydrogeochemical transport of reactive solutes.

2 SORPTION PROCESSES AND MECHANISMS

2.1 CHEMICAL/PHYSICAL FACTORS CONTROLLING SORPTION PROCESSES

The chemical and physical properties of the minerals, the speciation chemistry of the element of interest, the chemistry of the solution carrying the dissolved species through the geologic medium, and the physical conditions of the geologic environment all interact in a complex manner to control the solubility and the sorption of a given element in the saturated zone. In the unsaturated zone, these controls may be affected to varying degrees as a result of additional complications introduced by the effect of variable saturation such as changes in flow paths (e.g. fractured vs matrix flow), solution properties and access to adsorbent phases.

2.1.1 Substrate Properties Influencing Sorption

For a given solute, a number of properties have been identified as affecting the adsorptive capacity of the substrate. Based on the discussion of Turner (1991), these include the following.

Specific Surface Area (SA). There is a general positive correlation between specific surface area (m^2/g) and sorptive capacity (Fuller and Davis, 1987). This is likely to be due, at least in part, to an increase in the total number of sorption sites available (Balistrieri and Murray, 1986; Allison et al., 1990). Ames et al. (1982) also identified a positive correlation between specific surface area and the cation exchange capacity (CEC) of secondary clays. Smith and Jenne (1988; 1991) indicate that the "goodness-of-fit" of the triple-layer surface complexation model is highly sensitive to the value chosen for specific surface area of the substrate. In addition, Davis and Leckie (1980) calculated that for a constant capacitance, surface charge (moles charge/liter) increases markedly for iron oxyhydroxide with increasing surface area, altering the systematics of ion/solid interaction. Given these relationships, the uncertainty inherent in experimentally determining specific surface area (e.g., 157-840 m^2/g for amorphous iron oxyhydroxide, depending on the method used) may lead to inaccurate modeling of adsorption (Davis and Leckie, 1978). The magnitude of the analytical uncertainty is even greater for low surface area minerals where N_2 BET methods cannot be used effectively (Davis and Kent, 1990). Davis and Leckie (1978) and Smith and Jenne (1988; 1991) have suggested that writing specific adsorption reactions in terms of surface complexation of hydrolytic complexes rather than adsorption of bare ions by surface sites minimizes this effect. Modeling of unsteady, unsaturated flow and transport in dynamic column experiments indicates that the phenomenon of anion exclusion, which serves to accelerate transport of anionic species, is also a function of surface area and charge density (Bond and Phillips, 1990b).

Surface Site Density (N_s). As the number of available sorption sites increases, the sorptive capacity of the adsorbent is also expected to increase. Electrostatic surface complexation models specifically require an estimate of N_s (number of sites/m^2) in order to calculate total site "concentration" [i.e., total sites (moles site/liter)$=(SA \times N_s \times C_s)/N_a$, where

SA is surface area (m^2/g adsorbent), C_s is adsorbent concentration (g adsorbent/ liter), and N_a is Avogadro's number (number sites/mole sites)]. For oxide surfaces, surface site density varies as a function of pH due to the hydrolysis reactions occurring at the solid/liquid interface (Means et al., 1978; Davis and Leckie, 1978; 1980; Kent et al., 1988). For fixed charge minerals such as micas, clays, and zeolites, surface site density is essentially unaffected by solution chemistry.

Cation Exchange Capacity (CEC). The cation exchange capacity (meq/g) is a measure of the affinity of a solid for dissolved species and reflects the availability of ion exchange sites. In addition to the properties of the mineral (solid solution, surface charge, etc.), the relative sizes (and charges) of the exchanging cations also influences exchange process. Comans and Middleburg (1987) have noted that similar ionic radii between the exchangeable and sorbing cations leads to increased CEC. Considering CEC as a function of pH, Rhue and Mansell (1988) observed a two- to three-fold increase between pH 4 and 8 for Cecil sandy loam. This may be due to either the large pH-dependent surface charge in the soils which results from the presence of organic matter, or to increased competition by H^+ for sites at low pH. Cation exchange is thought to increase with decreasing particle size (increased specific surface area) (Ames et al., 1982), although Meyer et al. (1986) report evidence for a lack of correlation. Similar to CEC, Ames et al. (1983c) observed that anion exchange capacity (AEC) increases with decreasing CEC, and 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.

Surface Charge and Potential. Aluminosilicates such as zeolite and clays exhibit a permanent negative charge due the substitution of Al^{3+} for Si^{4+} in tetrahedrally coordinated sites (Kent et al., 1988). This charge is independent of the solution chemistry. In clays, the negative charge is on the planar surfaces, while edge sites tend to exhibit pH-dependent variably-charged sites along crystal edges. For oxides, however, surface charge generally increases with decreasing pH (Davis et al., 1978; Davis and Leckie, 1978; Kent et al., 1988). Surface charge is also dependent on several properties of the substrate. At a given pH, assuming constant capacitance in the inner electrostatic layer adjacent to the surface, charge increases with increasing specific surface area of the adsorbent (Davis and Leckie, 1978). In a similar manner, The pH at which surface charge vanishes (i.e., zero point of charge=pH_{zpc}) is also important (Means et al., 1978; Middleburg and Comans, 1991). At pH < pH_{zpc}, the surface exhibits a positive charge, at pH > pH_{zpc}, the surface charge is negative. For a given surface in solution, pH_{zpc} is established through the uptake or release of potential determining ions (e.g., OH^- and H^+ for oxides). Through electrostatic repulsion and attraction, changing surface charge affects the amount of energy transferred at the solid/water interface according to the Boltzmann relationship, which in turn controls the electrostatic adsorption of charged species. McCarthy and Zachara (1989) indicated 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. Electrostatic sorption also depends on the chemistry of the species being sorbed. The hydrolyzation of the cations or the protonation of anions can

affect the pH dependence of the species through changes in the systematics of the release (or consumption) of protons at the solid/water interface (Davis and Leckie, 1978; 1980).

Gels and Coatings on Mineral Grains. Amorphous oxyhydroxides of aluminum and iron, or organic compounds can coat permanently charged minerals such as clays and feldspar, reducing, neutralizing, or even reversing the permanent negative charge. For clays, the ease with which a coating may form is in the order kaolinite > illite > montmorillonite (Robert and Terce, 1989). The formation of the coatings is also dependent on the solution chemistry. For example, under oxidizing conditions at neutral to slightly acid pH (< 7), positively charged Fe-oxyhydroxides bond readily to the negatively charged clays. In general, coatings tend to increase the sorptive capacity of the clays, and the adsorption of cations and anions on the coated clay reflects the pH-dependence observed for the coating (e.g., Fe-oxyhydroxide) (Robert and Terce, 1989).

Site Type and Crystallographic Orientation. Benjamin and Leckie (1981) have proposed the existence of sorption sites of varying binding energy as a means of explaining non-Langmuir type behavior in transition metal sorption on goethite. Also working with goethite, Hiemstra et al. (1989a,b) observed heterogeneity in sorption site types that depended in part, on crystallographic orientation. For example, no triply-coordinated surface groups were associated with the (100) plane. Davis and Leckie (1980) considered site area (~ 0.1 nm^2) in determining the degree to which sorbed anions (about 0.3 nm^2 in radius) covered adjacent sites. In a similar fashion, Hsi and Langmuir (1985) used crystallographic arguments to support bi- and tri-dentate surface complexation for $(UO_2)_3(OH)_5^+$. Comans et al. (1991) noted that the presence of easily dehydrated ions such as K^+ allowed the illite structure to collapse, limiting access of Cs^+ to electrostatic sorption on charged edge sites. In contrast, larger, hydrated ions such as Ca^{2+} tended to "prop open" the crystal structure, enhancing Cs-diffusion to intraplanar sites that are more favorable to irreversible ion exchange. As a result, the degree of rapid desorption was reduced. Cs^+ and Sr^{2+} ion exchange in clinoptilolite is retarded perpendicular to (010) faces, apparently due to the absence of intracrystalline channels (Burns et al., 1989). In the case of ion exchange, crystallographic and/or charge constraints may limit access to favorable sites on specific crystal faces, and large diameter ions, highly charged species, asymmetric polynuclear species, and complexes of radioelements such as Pu or U may be excluded, resulting in reduced sorption and/or retardation.

Grain Size. In batch sorption experiments, finer grain size tends to result in increased specific surface area and site density, and therefore increased sorption (DiToro et al., 1986; Kent et al., 1988). In addition, the finer grain sizes tend to concentrate the more adsorptive clay fraction. Jardine and Sparks (1984) note that K-exchange selectivity in loamy soils increases as particle size decreases, presumably due to increased clay content. Kent et al. (1988) suggested that finer particles may dissolve more readily in solution, changing solution composition. Daniels et al. (1982), however, did not observe any correlation between sorption and particle size in batch experiments with Yucca Mountain tuffs. Meijer (1990) indicated that size fraction does not significantly affect sorption coefficients at sizes > 75 μm, and Beckman et al. (1988) reported a threshold value of 106 μm. For smaller size fractions below these cutoff

values, sorption increases. In contrast, Meijer et al. (1989), reported that grinding pure zeolite separates did not greatly affect Cs, Ba, and Sr sorption for any size fraction, presumably due to the presence of intracrystalline exchange sites.

2.1.2 Solution Chemistry Controls Influencing Sorption

Solution pH. For many substrates, adsorption is strongly pH dependent, with rapid changes in sorption over a narrow range in pH called the "sorption edge" (MacNaughton, 1973; Hsi and Langmuir, 1985; Sanchez et al., 1985; Davis et al., 1987; Hayes et al., 1989). As demonstrated by Davis and Leckie (1978), surface charge is sensitive to pH; increasing pH decreases the positive surface charge of the oxide, and cationic species are more readily adsorbed. As a result, cation sorption increases across the edge with increasing pH, while anionic species exhibit an inverse relationship between sorption and pH (Parks, 1990). The location of the sorption edge is a function of both the element sorbed [e.g., ranging from pH≈4-5 for Cr(II) to pH≈10 for Na(I) adsorption on SiO_2]), and 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). Also a function of surface charge, CEC also increases with increasing pH above pH_{zpc} (Stumm and Morgan, 1981). Murali and Aylmore (1983c) reported 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. For the actinides and other redox-sensitive elements, element speciation and complexation are very sensitive to solution pH. Because sorption is often dependent on the species present in solution, this has an effect on the sorption of a given element. 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). There is also experimental evidence that the dissolution of $UO_2(s)$, an analog for spent fuel, increases with decreasing pH (Bruno et al., 1991), which may have some bearing on the source term for radionuclide migration. Solution pH is subject to a variety of controls through rock-water-atmosphere interaction, including mineral buffers, $p(CO_2)$, and alkalinity.

Adsorbate Concentration. For dilute solutions, sorption has generally been observed to increase with increasing concentration (e.g., $\Sigma\ m_i$) of the species of interest (Dzombak and Morel, 1986). 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). For adsorption of transition metals on Fe-oxyhydroxide, several studies (Benjamin and Leckie, 1981; Dzombak and Morel, 1986) note that for dilute solutions at low concentration ratios of adsorbate/adsorbent, sorption is essentially independent of adsorbate concentration. However, above a species-dependent threshold value, average binding decreases with increasing adsorbate concentration at constant pH. In addition, if adsorbent concentration is held constant, the pH sorption edge shifts to more basic values with increasing adsorbate concentration. Both

Benjamin and Leckie (1981) and Dzombak and Morel (1986) attributed this to the existence of at least two types of binding sites at the surface/water interface. Dzombak and Morel (1986) further observed that the kinetics of adsorption slowed with increasing adsorbate/adsorbent ratios, and modified the equilibrium two-site model to incorporate the effects of surface precipitation as reactive surface sites become saturated at high adsorbate/adsorbent ratios.

Ionic Strength. 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. 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). Increasing ionic strength may also reflect different concentrations of complexing ligands, competing ions and colloidal particles in solution, which tend to reduce sorption and enhance contaminant migration (Ames et al., 1983a,b,c; McCarthy and Zachara, 1989; Liu et al., 1991). In some cases, however, there is no apparent effect of ionic strength on sorption (e.g., Th and Pu; LaFlamme and Murray, 1987; Sanchez et al., 1985). Parks (1990) has indicated that sorption densities tends to decrease with increasing ionic strength for those ions that are either weakly complexed or not readily hydrolyzed (e.g., Na^+, K^+, NO_3^-). For these nonspecifically bound electrolytes, binding energy depends on coulombic attraction. In contrast, specific adsorption of multivalent and/or readily hydrolyzable electrolytes (including UO_2^{2+} and most actinides) requires an additional chemical component of adsorption, and sorption density is largely unaffected by changes in ionic strength.

Saturation Index. Changes in a variety of physicochemical conditions (temperature, pH, Eh, ionic strength) may lead to the solution becoming saturated with respect to one or more solid phases. If the reaction kinetics can be overcome, the solution may begin to precipitate saturated phases, removing radionuclides either through the precipitation of stoichiometric compounds or through the coprecipitation of mineral phases that incorporate the radioelement in solid solution. Precipitation processes tend to be highly nonlinear, and they can greatly effect the uptake of solute from solution (Ku et al., 1991).

Inorganic Complexing Ligands/Speciation. 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) points out the importance of potential complexing ligands (Cl^-, HCO_3^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, etc.) in solution. Because of the importance of carbon-bearing species in most natural systems, $p(CO_2)$, pH, and ionic strength have a pronounced effect on complexation and contaminant migration. 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, and that uranium carbonate complexes are poorly, if at all, adsorbed. This is probably due to a reduction in charge and the associated electrostatic attraction (Serne et al., 1990), increases in exclusion effects due to increased ionic radii, and changes in adsorption mechanisms (Pabalan et al., 1991). 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 was, however, found to have minimal effect on radium adsorption (Ames et al., 1983b). Phosphate complexation of uranium was found to have minimal effect on sorption (Tripathi, 1984), but some natural analog systems such as the Koongarra uranium deposit in Australia indicate that phosphate has played a major role in the mobilization and migration of uranium (Payne et al., 1990a,b).

Organic Complexing Ligands/Speciation. In a similar manner to inorganic complexation, organo-metallic complexes tend to be either neutral or anionic molecules, resulting in reduced electrostatic attraction and enhanced radionuclide migration. Organic compounds can also serve as reductants for redox sensitive elements. This may enhance (e.g. Tc^{4+} vs. Tc^{7+}) retardation (Lieser and Bauscher, 1988) or, as in the case of Pu^{4+} (sorption edge at pH=2-4 for goethite) and Pu^{5+} (pH=5-7), change the pH-dependence for the sorption of an element (Sanchez et al., 1985). In addition, the presence of net positive charged sites on some insoluble organics may serve to attract anionic species such as $^{129}I^-$. However, organic compounds may also serve as colloidal particles or coatings to enhance transport through porous media (Robert and Terce, 1989), and Toste et al. (1984) have suggested that the presence of strong organic chelators in solution may be more important than the oxidation state for the migration of some radionuclides.

Redox Conditions/Speciation. Because electrostatic effects and complexation depend on species charge, hydrolysis, ionic radius, etc., sorption is sensitive to the oxidation state of an element (Sanchez et al., 1985; Hsi and Langmuir, 1985; Liu and Narasimhan, 1989a,b). Serne et al. (1990) suggest that some sorption mechanisms may only be important for a particular oxidation state. For example, Alemi et al. (1991) noted that selenate adsorption was greater under reducing conditions. In batch experiments performed on crushed tuff in a nitrogen atmosphere, Np, Pu, U, and Tc sorption were observed to increase relative to experiments performed under open-air conditions (Meijer, 1990), presumably due to the less oxidizing nature of the inert atmosphere. Toste et al. (1984) and Bock et al. (1989) identified the reduction of Tc^{7+} (readily transported as TcO_4^-) to Tc^{4+} as an important prerequisite to sorption. Choppin (1988) reported that the tendency for Pu to form complexes decreased from Pu(IV) > Pu(VI) > Pu(III) > Pu(V). Solubility is also dependent on the oxidation state of the species of interest (Langmuir, 1978a,b). For example, Choppin (1988) reported that for pH > 2-3, hydrolysis tends to remove Pu(IV) from solution through adsorption and decreased solubility. Finally, radiocolloid formation has also been shown to depend on oxidation state (McCarthy and Zachara, 1989; Orlandini et al., 1990).

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

Competitively Sorbing Species. In multi-species systems, it is possible that cumulative sorption of all species exceeds that of any individual element. Competition for a limited number of sorption sites, however, acts to reduce the sorption of a given species (Benjamin and Leckie, 1981; Murali and Aylmore, 1983a,b,c). For example, at low pH, H^+

may successfully compete for sorption sites (Rhue and Mansell, 1988). Even if the competing ion is poorly sorbed, it may be present in such large concentrations (e.g., Ca^{2+} and Mg^{2+} in natural waters), that it effectively swamps all of the available sorption sites, reducing sorption of the contaminant of interest (Bradbury and Baeyens, 1991). Davis and Leckie (1980) also point out that the influence of the swamping electrolyte is not simply a function of ion exchange or mass action, but rather due to changes in the electrostatic potential of the charged surface, altering the uptake of dilute solutes. Some sites may only be available to one type of competing ion (Benjamin and Leckie, 1981; Murali and Aylmore, 1983c). In addition, although a given species may not directly compete for sorption sites, it may "cover" more than one site, making the covered sites unavailable to the species of interest. This may be especially true for relatively large, anionic or hydrolyzed species (Davis and Leckie, 1980; Miklavic and Ninham, 1990).

Colloids, Particulates. Microscopic colloidal particles (< 450 nm in diameter) may bind and carry a contaminant in suspension in a mobile fluid phase (McCarthy and Zachara, 1989). Because species charge is decreased through binding, solute retardation due to interaction with the solid matrix tends to be reduced. Indeed, for many organic colloids, the surface charge is negative, leading to acceleration of the particles through negatively charged porous media. 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). Association with larger particles may act to filter radiocolloids from solution by micropores in the matrix (McCarthy, 1990), or through flocculation and settling (Shainberg, 1990). Conversely, the binding of ions to small colloidal particles may act to enhance migration. Depending on the type of colloidal particle, such as organic compounds or Fe-oxides, the affinity of radioelements tends to be pH-dependent. Colloidal stability and activity also depend on a number of physicochemical properties of the solution [Eh, pH, $p(CO_2)$, etc.]. For example, chemical gradients can lead to the precipitation of solid phases (e.g., Fe-oxides) that may act as mobile colloids (McCarthy and Zachara, 1989). Likewise, decreasing pH may lead to increased dispersion, stabilizing the colloids in suspension.

Temperature. The intensive property temperature is critical in many aspects of adsorption. Changes in adsorption at high temperatures have been used to explain variations in natural radionuclide concentrations in geothermal systems (Ku et al., 1991). However, due to the complex nature in which solubility, reaction kinetics, complexation, redox, pH, and electrostatic potential all depend on temperature, only a few experiments have attempted to address the effects of temperature on sorption, and an empirical approach has been relied on for most predictive studies. For U- and Ra-sorption on a number of substrates, at temperatures ranging from 5° to 65° C, Ames et al. (1982; 1983a,b,c) indicated that sorption coefficients tended to decrease with increasing temperature in a complex fashion, although there were numerous exceptions even to this general trend. These experiments were performed on natural minerals rather than pure end-members, and the lack of experimental control on pH and $p(CO_2)$ complicates the interpretation of the results. For SO_4^{2-} adsorption on clay soils, Hodges and Johnson (1987) observed a decrease both in the adsorption reaction rate coefficients and desorption rate with a temperature increase from 4-40° C. This leads to a progressive degradation of the solute plume through irreversible uptake. In contrast, Meijer (1990) reported

that measured sorption coefficients generally increase with temperature, although early high-temperature studies were complicated by dissolution and recrystallization of the substrate.

2.1.3 System Properties Influencing Sorption and Retardation

Composite Mineralogy. Because of the highly variable sorptive properties of different minerals, it is necessary to have some idea of the composite mineralogy of the sorptive medium along the fluid flow path. Sorption experiments with crushed rock may provide some insight into sorption, but sample preparation may either preferentially remove important sorbing minerals or free minerals which would otherwise not come in contact with the transport solution. In either case, a nonrepresentative suite of minerals is produced, and the extrapolation from crushed to intact rock *in situ* is problematic (Davis and Kent, 1990). Several authors (Serne and Relyea, 1982; Meijer, 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. Honeyman (1984) and Altmann (1984), however, indicated that predictions made in this fashion are often unreliable in a nonsystematic fashion.

Water/Rock (W/R) Ratio. Several batch studies have indicated that sorptive behavior depends to some degree on the concentration of the adsorbent (solid) phase in solution (Benjamin and Leckie, 1981; Honeyman, 1984; Dzombak and Morel, 1986; Fuller and Davis, 1987). Generally, sorption is observed to increase with adsorbent concentration at low overall particle concentrations. However, site concentration commonly varies in a nonlinear fashion with solid concentration (Dzombak and Morel, 1986) and extrapolation is uncertain. At constant adsorbate concentrations, Benjamin and Leckie (1981) observed that the sorption edge for transition metal sorption on Fe-oxyhydroxide shifted to more alkaline conditions with decreasing adsorbent concentration. Davis and Leckie (1978) also noted that for those metals that are monovalent and weakly charged (e.g., Ag(I)), the uptake of the metal depends more on the amount of solid present than on the pH of the solution. As a means of explaining the W/R effect, Murali and Aylmore (1983b) suggested that desorption of the "native" species from the adsorbent provides a source of competitive ions for the infiltrating element. 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 appears anomalously low through competition, leading to the perception of a W/R effect.

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 is inferred for those systems where the sorption rate is fast relative to the residence time of the solute, otherwise kinetic sorption is generally considered appropriate (Travis and Etnier, 1981). The rate of sorption is a function of the type of adsorbent (e.g., oxide vs. clay), and other factors such as temperature, pH and redox conditions. Residence time is a function of one or more 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. It should be noted that most experimental studies exhibit

a rapid stage of initial uptake that is on the order of hours, followed by a slow stage of gradual uptake that generally lasts on the order of days to several weeks (Dzombak and Morel, 1986).

Atmospheric Composition. Especially in the unsaturated zone, the atmosphere in contact with the system affects sorption processes, as well as solution properties such as pH, alkalinity, and Eh. The importance of the atmosphere is particularly pronounced with respect to the influence of $p(CO_2)$ on carbonate complexation (Hsi and Langmuir, 1985; Payne et al., 1990a; Carroll and Bruno, 1991) and redox sensitive elements (Toste et al., 1984; Sanchez et al., 1985). The 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 (McCarthy and Zachara, 1989).

2.2 EFFECTS OF VARIABLE SATURATION ON CONTROLLING FACTORS

One possible approach to evaluating the degree to which variable saturation affects the coupling of flow and radionuclide transport at Yucca Mountain is to determine the spatial and temporal variations in physical and chemical parameters of the unsaturated zone, and compare them to parameters known to affect sorption in saturated environments. The validity of this approach is based on the assumption that the nature of different sorption mechanisms is not affected by variable saturation in a new and unpredictable way. For example, it is assumed that sorption as a function of pH behaves in a similar fashion for both saturated and unsaturated environments. Unfortunately, additional complications are introduced when considering the unsaturated zone. These include the transient nature of unsaturated flow, changes in flow path with changing saturation, the effect of thin fluid films on water properties at low saturation, the existence of a gas phase, and the fact that the unsaturated zone is essentially an open system with respect to the atmosphere.

2.2.1 Yucca Mountain Groundwater Chemistry

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 has commonly been used as a reference groundwater in site characterization activities (DOE, 1988 - Ch. 4). Chemical analyses of waters collected from the saturated zone at the Yucca Mountain site are available in numerous studies (Ogard and Kerrisk, 1984; Benson and McKinley, 1985; Raker and Jacobson, 1987; Kerrisk, 1987). Representative compositions are listed in Tables (2-1) and (2-2). The waters are generally neutral to slightly basic, and relatively dilute (TDS < 400 mg/liter), dominated by Na^+ and HCO_3^-. The total concentration of colloidal particles $< 0.4\ \mu m$ in diameter is about 2.7×10^{-5} g/liter for J-13 well water (DOE, 1988 - Ch. 4). Colloids are predominantly silica, iron, calcium, aluminum, and sodium, which suggests that the particles are made up of clays and iron oxide. Total organic carbon (Means et al., 1983) is a minor component of about 0.14 mg/liter 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).

TABLE 2-1. ELEMENT CONCENTRATIONS IN GROUND WATER FROM THE VICINTY 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	0.09	--[d]	--	--	23
USW H-6	7.4	5.5	0.22	74	2.1	0.10	0.12	0.04	0.12	20.0
USW H-3	9.4	0.8	0.01	124	1.5	0.22	0.13	0.01	0.51	16.9
USW H-5	7.1	1.1	0.03	54	2.3	0.04	0.01	--	0.17	17.4
USW G-4	7.1	9.2	0.15	56	2.5	0.08	0.04	0.02	0.02	19.6
USW H-1[e]	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	0.03	0.005	0.04	25.9
UE-25b#1	7.7	19.7	0.68	56	3.3	0.28	0.04	0.004	0.03	31.5
UE-25b#1[e]	7.2	18.4	0.68	46	2.5	0.30	0.69	0.36	0.04	28.7
UE-25b#1[f]	7.3	17.9	0.66	37	3.0	0.17	0.08	0.07	0.06	28.8
J-13	6.9	11.5	1.76	45	5.3	0.06	0.04	0.001	0.03	30.0
UE-29a#2	7.0	11.1	0.34	51	1.2	0.10	0.05	0.03	0.04	25.8
J-12[c]	7.1	14	2.1	38	5.1	--	--	--	--	25
UE-25p#1[g]	6.7	87.8	31.9	171	13.4	0.32	<0.1	<0.01	0.1	30

[a]Concentrations from Ogard and Kerrisk (1984) unless otherwise noted.
All samples are integral water samples unless otherwise noted.
[b]See DOE (1988)--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 2-2. ANIONIC SPECIES 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	>2	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	–	0.5	2.2	<0.1	2.7	-18
UE-25b#1[g]	1.2	6.6	20.3	–	–	4.5	1.8	0.02	160
J-13	2.1	6.4	18.1	143	–	10.1	5.7	–	–
UE-29a#2	0.56	8.3	22.7	–	–	18.7	5.7	–	305
J-12[d]	2.1	7.3	22	119	–	–	–	–	–
UE-25p#1[h]	3.5	37	129	698	–	<0.1	–	<0.2	360

[a]Concentrations from Ogard and Kerrisk (1984) unless otherwise noted.
All samples are integrated samples unless otherwise noted.
[b]See DOE (1988)--Figure 4-11 for location.
[c]mV versus H_2 electrode.
[d]Data from Benson et al. (1983).
[e]– indicates the species was not detected.
[f]Bullfrog zone, 4th day of pumping.
[g]Bullfrog zone, 28th day of pumping.
[h]From carbonate aquifer.

Although difficult to perform, experiments have been conducted to extract waters from the fractured, unsaturated tuffs in the vicinity of Yucca Mountain (White et al., 1980; Yang et al., 1988; Yang, 1991) (Table 2-3 and 2-4). Water samples are obtained either through centrifugation or compression of samples of unsaturated tuff. The data of White et al. (1980) (Table 2-3) indicate that unsaturated water compositions vary significantly at Rainier Mesa to the north of Yucca Mountain, and many analyses fall outside the range observed for saturated waters. Triaxial compression and centrifugation of drill core obtained using dry-drilling techniques, has provided chemical and isotopic analysis of fluids from unsaturated tuffs at Yucca Mountain (Yang et al., 1988; Yang, 1991) (Table 2-4). 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). Additional constraints on fluid composition may be obtainable through geochemical modeling (Murphy, 1989).

2.2.2 Effects of Variable Saturation on Groundwater Chemistry

The effects of partial saturation on water chemistry are uncertain due to the lack of data. Fluid compositions are largely buffered through interaction (e.g., precipitation/ dissolution) with minerals, and there are some indications (Hem, 1985; Yang et al., 1988) that total dissolved solids (TDS), and therefore ionic strength, is generally higher in vadose zone waters relative to waters from the saturated zone. Matric suction increases with decreasing water content (Yang et al., 1988), resulting in increased capillary forces. Sears and Langmuir (1982) proposed that as moisture content decreases, the amount of water held in small pores by capillary forces becomes an increasingly significant part of the total groundwater. Restricted to very slow migration due to a higher matric suction, this water can react longer with minerals in the medium, increasing TDS, perhaps significantly. As discussed above, this may result in reduced sorption density through the effects of increasing ionic strength. However, for the readily hydrolyzable actinides that are considered to be important in high-level waste (HLW), the effect may be minimal (Parks, 1990). It is possible, however, that the increased TDS may lead to increased competition for reactive sorption sites, reducing sorption of the dilute radionuclides. Higher TDS may also reflect an increase in ligands available for complexing. Flocculation of colloids, enhanced by higher ionic strengths can result in reduced colloid mobility through removal by filtration and settling.

As a result of pH-Eh dependence of speciation and hydrolization, the effects of pH are likely to be more critical for actinide sorption. Due to the prevalence of calcite in an arid environment, alkalinity and pH are linked through the dissolution of calcite. If a system is closed to CO_2, percolating fluids continue to dissolve calcite until CO_2 is exhausted; the system pH is buffered by bicarbonate to alkaline values on the order of 8 or higher (Stumm and Morgan, 1981). For arid systems such as Yucca Mountain where the unsaturated zone is open to carbon dioxide from the atmosphere ($p(CO_2) \approx 10^{-3.5}$ atm), calcite dissolves continuously and the pH of the groundwater is buffered by calcite saturation to neutral to slightly alkaline values 7-8 (Freeze and Cherry, 1979; Wikberg, 1991). Data of White et al. (1980) suggest that at the 60-65 percent saturation levels observed at Rainier Mesa, pH values are indeed neutral to

TABLE 2-3. CHEMICAL ANALYSES OF FLUIDS FROM THE UNSATURATED TUFFS IN DRILL HOLE U12T3, RAINIER MESA, NEVADA (FROM WHITE ET AL., 1980)

Well (depth-meters)	Concentrations (mg/L)								
	Ca	Mg	Na	K	SiO_2	Cl	SO_4	HCO_3	pH
U12T3 (134.4)	11	3	25	10	61	27	20	58	7.6
U12T3 (199.2)	23	6	43	10	57	27	40	137	7.7
U12T3 (257.6)	16	5	30	5	60	52	38	26	7.2
U12T3 (441.4)	9	1	46	14	49	20	52	67	7.6
U12T3 (291.4)	8	2	26	5	75	21	22	48	7.8
U12T3 (320.6)	18	2	32	8	55	35	--	35	7.8
U12T3 (350.8)	13	2	23	6	75	30	55	59	7.9
U12T3 (470.6)	<0.2	<0.05	40	1	45	10	21	56	7.9

TABLE 2-4. CHEMICAL ANALYSES OF FLUIDS FROM THE UNSATURATED TUFFS IN DRILL HOLE UE-25, YUCCA MOUNTAIN, NEVADA (FROM YANG et al., 1988)

Well (depth-meters)	Concentrations (mg/L)										
	Ca	Mg	Na	K	Si	Cl	SO_4	Fe	Mn	Sr	Zn
UZ5-TP-4 (31.6)	61	12	30	15	99	--	--	0.127	0.021	0.585	0.140
UZ5-TP-1 & -3 (30)	48	10	29	7	88	45	41	0.024	0.011	--	--
UZ5-TP-6 & -5 (36)	27	6	35	8	97	43	47	0.022	0.015	--	--
UZ5-TP-9 & -8 (94)	36	7	39	--	94	51	41	0.0001	0.0003	0.0005	0.048
UZ5-TP-14 & -15 (97)	63	13	54	--	89	--	--	0.005	0.021	--	--
UZ4-TP-1[a] (91.6)	100	19	70	14	90	101	161	0.011	0.017	1.325	0.009
UZ4-TP-4[a] (91.5)	101	18	70	14	96	91	151	0.005	0.029	1.276	0.004
UZ4-TP-5[a] (95.3)	71	13	40	14	85	92	147	0.086	0.021	0.892	0.071

a. Several water samples from the same axial and confining stress levels were combined to provide sufficient water for chemical analysis.

slightly alkaline for both the unsaturated and saturated zone waters. However, in an arid climate, CO_2 is controlled to a large extent by plant respiration in the soil zone (Cerling, 1984), and soil CO_2 is lost in varying amounts to the precipitation of soil carbonate. In addition, gas analyses at Yucca Mountain indicate that $p(CO_2)$ can vary significantly with both space and time (diurnal to seasonal variations) (Murphy, 1989). Therefore, it is possible that pH variations in the unsaturated zone at Yucca Mountain are significant, and changes in sorption behavior in response to pH shifts may be important (Murphy, 1989).

As water percolates through the unsaturated zone to the water table, interaction with minerals and organic matter are expected to produce gradients in alkalinity and Eh as a function of depth. As a result of calcite dissolution, the groundwaters tend to have high concentrations of dissolved calcium and bicarbonate. White et al. (1980) observed that the carbonate content of unsaturated zone waters from Rainier Mesa increased with depth. Solution alkalinity controls the amount of carbonate available in solution for complexation, which as discussed above, tends to reduce actinide (e.g., U, Pu) sorption. Abundant dissolved calcium, however, may compete effectively with trace concentrations of dissolved radioelements for available sorption sites (Bradbury and Baeyens, 1991). Conversely, as noted by Comans et al. (1991), readily hydrated Ca^{2+} acts to enhance access to favorable ion exchange sites in illites and other clays, resulting in increased radionuclide uptake.

Oxygen is consumed during active bacterial reduction and during dissolution of iron-bearing minerals such as biotite. Under closed system conditions oxygen is rapidly depleted by these processes, and both ferrous iron concentration and Eh decrease with depth (Wikberg, 1991). Under conditions open to the atmosphere, however, the oxidation state of the system is largely controlled by the oxygen that is continually supplied to the system. Although Fe^{2+} is present in the Yucca Mountain system (Bish and Vaniman, 1985), it is likely to be insufficient to act as a reducing buffer for the system. For this reason, oxidized species are of general interest in far-field transport, although the presence of reducing environments on a small scale cannot be discounted, especially near the metal canisters envisioned for the engineered system.

Fluctuations in Eh, pH, and $p(CO_2)$ in response to open system conditions may all lead to precipitation and stabilization of an inorganic colloidal phase (McCarthy and Zachara, 1989). Therefore, in the absence of filtration mechanisms, colloidal transport of radionuclides in solution could be enhanced. Unfortunately, given the intrusive nature of collecting water samples from unsaturated rock, little information is currently available on colloid concentrations in solution, and the ability of colloids to act as an efficient transport mechanism through the thin water films that are likely to occur in the unsaturated zone remains uncertain. Organic compounds and colloidal particles are present as minor constituents in saturated waters at Yucca Mountain (Means et al., 1983). If these phases are also present in the unsaturated zone, they may act as a mechanism for colloidal transport. However, organic matter at Yucca Mountain is poorly characterized at present, sorptive characteristics of many organic compounds are not well known, and changes in organic chemistry with depth are poorly constrained (DOE, 1988; Serne et al., 1990). In addition, the importance of organic matter introduced to the system

during the construction of the repository and emplacement of the waste canisters cannot be estimated with any degree of certainty at present.

At low saturations, water/rock ratios are likely to be small, and may lead to increased sorption as discussed above. For transition metal sorption on Fe-oxyhydroxide, the study of Benjamin and Leckie (1981) suggests that low adsorbate/adsorbent ratios may shift the pH sorption edge to more alkaline pH conditions. If these conditions are outside of the range in pH for commonly anticipated groundwaters, this would lead to reduced sorption and enhanced transport. However, the location of the sorption edge is highly dependent on the sorbing radionuclide. Given the fact that most sorption edges are found under slightly acidic conditions, this effect is likely to be diminished in neutral to alkaline groundwaters.

If flow through the unsaturated zone is by matrix flow, then the fluid residence time is likely to be long (on the order of years), and equilibrium assumptions are valid. This is especially true for rapid surface sorption processes, where experiments with transition metal adsorption on Fe-oxyhydroxides indicate equilibration in a matter of hours (e.g., Dzombak and Morel, 1986). Even the slow, diffusion-controlled steps observed in many sorption experiments (Fuller and Davis, 1987) reach effective equilibrium in days to weeks, short times relative to fluid residence times expected for matrix flow. Flow through fractures in the unsaturated zone (see Section 2.2.3), may be more rapid than matrix flow, depending on fracture properties such as connectivity, geometry, and conductivity. Given the low rates of infiltration proposed for the arid climate of Yucca Mountain (4.5 mm/yr or less, Travis and Nuttall, 1987), it seems unlikely that flow rates will be shorter than the rates of sorption reaction. However, without more information on flow systematics in the unsaturated zone, it is not possible to evaluate quantitatively the residence time of fluids under fracture flow conditions.

2.2.3 Effects of Variable Saturation on Flow Paths and Physical Transport

At Yucca Mountain, the minerals encountered by fluids will vary depending on whether flow is through the fractures or the matrix (Bish and Vaniman, 1985). Primary quartz and feldspar, as well as secondary opal, zeolite, clays, calcite, and iron- and manganese-oxides line fractures in the tuffs at Yucca Mountain. For these minerals, a combination of ion exchange and surface complexation are likely to be the principal sorption processes (Kent et al., 1988; Pabalan et al., 1991). In the matrix, primary mineral include quartz, plagioclase, biotite, hornblende, and glass. Secondary alteration minerals include zeolites, clays, and chlorite. The thick layer of zeolitized (primarily clinoptilolite) tuff between the proposed repository horizon and the water table is expected to provide the bulk of radionuclide retardation in the case of migration through the rock matrix (DOE, 1988 - Ch.4), and ion exchange is likely to be a major sorption mechanism (Kent et al., 1988; Pabalan et al., 1991). Adsorption on smectitic clays is likely to be controlled by rapid surface complexation on edge sites, followed by slower diffusion to and ion exchange on interlattice sites (Comans et al., 1991).

Whether fluid flow in the unsaturated zone occurs through the matrix or the fractures is likely to be a function of the degree of hydrologic saturation (Conca, 1990). When

the matrix 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 (Peters and Klavetter, 1988). 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 hydraulic conductivity of the matrix. Experimental data indicates that small-scale fractures may need to be saturated before larger fractures conduct water (Conca, 1990). Periodic wetting and drying of the geologic media also affects hydrologic properties through hysteresis. In addition, exchange between the matrix and the fractures is retarded by capillary barriers (Peters and Klavetter, 1988). Flow experiments 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. Bradbury et al. (1988) propose that flow from the matrix to the fractures, accompanied by evaporation, can serve to concentrate radionuclides at the fracture surface. This in turn suggests that transient fracture flow conditions can actually enhance radionuclide migration through the vadose zone.

In a porous medium, experimental evidence indicates that solute dispersion is also dependent on the degree of saturation. Barnes (1989) suggested that where hydraulic conductivity was modeled as a function of solute concentration, solute and moisture plumes separated more rapidly than for the case where solute and water movement were considered to be independent. Calculations based on experiments for nonreactive solute transport through saturated and unsaturated columns of glass beads indicate that at the scale of the experiments (3 m), dispersion increased much more rapidly with increasing pore water velocity under unsaturated conditions relative to saturated transport (de Smedt and Wierenga, 1984). For example, at pore water velocities of 500 cm/day, the calculated dispersion coefficient (D) was about 15 cm^2/day under saturated conditions, but approached 250 cm^2/day for unsaturated conditions. While this leads to greater spreading of a solute plume migrating through the unsaturated zone at a given velocity, slower water velocities can offset or perhaps even overcome this dispersive tendency to some extent. Experiments by Bond and Phillips (1990b) indicated that the degree to which anion exclusion occurred to accelerate solute transport increased with decreasing water content. For reactive solute transport in a simple Na-Ca-Cl system, stochastic modeling approaches led Russo (1989a,b) to conclude that decreasing the effective saturation tended to increase retardation and reduce the spatial variability in both moisture content and hydraulic conductivity.

At the solid/water interface, water properties may be affected due to the interaction between dipolar water molecules and charged particles in the geologic media (Nielsen et al., 1986). In response to the surface charge, water molecules at the solid/solution interface become progressively more ordered and layered (Mulla, 1986; Giese and Costanzo, 1986), forming first an inner layer binding to the silicate substrate, with an associated outer layer hydrogen-bonded to the first. From Monte Carlo simulations and molecular dynamic studies, water density and hydrogen bonding are thought to decrease near the solid surface as a result of this ordering; the dielectric constant also decreases, as does the self-diffusion coefficient of water at the solid/liquid interface (Mulla, 1986). Polar water bound to the charged particle also

becomes less mobile than the bulk water several molecules removed from the surface (Giese and Costanzo, 1986). The thickness of the electrical double layer (EDL) is a function of solution composition, and the net surface charge of the medium. At high ionic strengths, or for multivalent ions the EDL is compressed, extending some 5 nm into the pores. For dilute solutions or monovalent ions, the EDL may expand to more than 20 nm in thickness (Nielsen et al., 1986). Under partially saturated conditions, the effects of these interactions at the solid/water interface become more pronounced as the medium becomes drier. Under extremely dry conditions, water films may only be 10-20 water molecules thick and interaction between cations and anions in solution becomes increasingly restricted as the water film at the interface becomes progressively thinner with decreasing moisture content. Since solute transport is assumed to be possible only where the film is continuous, a discontinuous water film tends to retard transport of a radionuclide by requiring a more tortuous travel path between those pores that remain connected (Butters and Jury, 1989; Butters et al., 1989). It should be noted that these types of severe effects on water properties only become pronounced at exceedingly low moisture contents (Nielsen et al., 1986). With water saturation at 40-80 percent in the Yucca Mountain tuffs (Montazer and Wilson, 1984; DOE, 1988 - Ch.3), it seems unlikely that necessary extreme conditions would be encountered in the far-field. In the near-field, however, where the heat of the canisters can possibly dry out the rock, saturation may become low enough to reach the point where water properties are affected (Pruess et al., 1990).

In the presence of poorly hydrolyzed cations such as Na^+, the electrical double layer around charged particles extends further into the solution. This can cause the expansion of swelling clays, and also tends to promote clay dispersion. This in turn clogs pores with fine particles, shifting the pore-size distribution to smaller diameter pores, and reduces the permeability, hydraulic conductivity (K), and water diffusivity (D) (Siyag et al., 1983; Nielsen et al., 1986) of the soil. Called the salinity effect by Nielsen et al. (1986), this phenomenon has been documented in numerous studies of unsaturated soils under arid and semi-arid conditions (Suarez et al., 1984; Russo, 1989b; Goldberg et al., 1991). Even under saturated conditions, K can be reduced by an order of magnitude or more (Laryea et al., 1982; Nielsen et al., 1986). As a relative measure of the salinity effect, the sodium adsorption ratio (SAR) has been developed such that $SAR = Na/(Mg+Ca)^{1/2}$ for electrolyte concentrations in mmol/liter. High SAR values (i.e., relatively high Na-concentrations) reflect an increased salinity effect.

Variations in overall solution chemistry and moisture content also influence the magnitude of the salinity effect. For constant SAR values, Suarez et al. (1984) noted decreasing hydraulic conductivities with increasing pH. This is likely due to the fact that at low pH, the surface charge is high, and edge-surface bonding of clays, as well as bonding of positively charged oxides to negatively charged clay surfaces, occurs. Under these conditions, clay dispersion is low, and the adverse effect on hydraulic conductivity is minimal. As the pH increases, the surface charge decreases, clay dispersion is enhanced, and the salinity effect is amplified (Suarez et al., 1984). In a similar manner, at low ionic strengths or with predominantly monovalent cations, the EDL expands outward from particle surfaces into the pores, leading to a more pronounced salinity effect with decreasing electrolyte concentration (Nielsen et al., 1986). Finally, as the moisture content decreases, the water film becomes

thinner, and the thickness of the EDL becomes relatively more important. Under drying conditions, reductions in D and K due to the salinity effect become more pronounced, with decreases of as much as 3 orders of magnitude, as the moisture content declines from 0.5 cm^3/cm^3 to 0.3 cm^3/cm^3 (Siyag et al., 1983).

Most of these studies have been conducted in soils, and the extent to which the treatment is applicable to intact rock, such as the volcanic tuffs at Yucca Mountain, is very uncertain. However, expandable smectitic clays are present as alteration products of the various tuff units (Broxton et al., 1987), and possibly as colloidal particles as well (Means et al., 1983). Given the arid climate of southern Nevada, it is possible that a correlation between solution chemistry and hydraulic properties of the geologic media, similar to that outlined above for soils, may exist at Yucca Mountain. Using the values in Table (2-1), SAR values for saturated waters are as high as ~40 (Well USW H-3; 3.3 for J-13 water). This is low in comparison to values of the 20-250 used in most soil experiments (Siyag et al, 1983), and suggests that if a salinity effect is possible in intact rock, it is likely to be small.

Because dry rock has a lower thermal conductivity than saturated rock, the temperature perturbations due to high-level waste emplacement may increase with decreasing moisture content. For alluvium, Wollenberg et al. (1983) estimate that the temperature increase may be on the order of 1.6 times higher for dry versus saturated conditions. The authors point out that this is likely to be only significant in the near-field, since significant decreases in thermal conductivity due to drying will only occur near the waste canisters. One phenomenon which may mediate temperature changes due to waste emplacement is the development of a heat pipe effect. In a steady-state heat pipe, heat transport is by convection. As water evaporates adjacent to the hot canisters, it moves to the ambient region as vapor, cools and condenses, and returns to the repository as liquid (Evans and Huang, 1983). Using numerical simulations of the proposed repository horizon at Yucca Mountain, Pruess et al. (1990) reported that as long as water can move through fractures, a strong heat pipe effect will be maintained and peak temperatures will be on the order of 100° C. If water cannot move through the fractures, however, the medium will dry out. Under these conditions, heat transfer is predominantly conductive, and temperatures may reach 200° C or more. Increased temperatures serve to affect the geochemistry of the rock-water system in a complex manner as discussed above. Laboratory experiments with crushed Yucca Mountain tuff (Rimstidt et al., 1989) and numerical simulations (Travis and Nuttall, 1987) indicate that there is significant dissolution, mobilization, and reprecipitation associated with the heat pipe effect. Geochemical equilibria modeling may be appropriate to simulate these effects, and in turn evaluate the influence these changes might have on radionuclide sorption. In addition, water viscosity and surface tension decreases with increasing temperature, allowing water to wet the medium more effectively and provide a more continuous water film.

Gas flow in the vadose zone may act to enhance transport of certain radionuclides, particularly ^{14}C in carbon dioxide. Murphy et al. (1991) have developed a simplified one-dimensional model that addresses the nonisothermal transport of $^{14}CO_2$ at Yucca Mountain. By coupling chemistry and moisture flow, this model takes into consideration the

exchange of carbon between the gas, liquid and solid phases. The equilibria and reaction rates of the aqueous speciation and gas solubilities that govern this exchange are a function of temperature and solution chemistry. Temperature varies either due to the natural geothermal gradients or radioactive waste emplacement, while solution chemistry is a function of a number of interacting process, as discussed above.

3 SOLUTE TRANSPORT -- UNSATURATED FLOW CONDITIONS

3.1 SOLUTE TRANSPORT-UNSATURATED FLOW

In mathematical terms, transient fluid flow under unsaturated conditions is generally defined using the Richards' equation (Richards, 1931) for the vertical coordinate z positive downwards:

$$C(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z}\right] - \frac{\partial K(h)}{\partial z} + \Phi \qquad (3\text{-}1)$$

where θ is the volumetric moisture content of the media (m^3/m^3), h is water pressure head (m), $C(h) = \partial\theta/\partial h$ is the water capacity of the medium, K is hydraulic conductivity (m/s), t is time (s), and Φ represents sources and sinks of the system. This equation assumes a rigid medium, and that Darcy's Law and all of its assumptions (Freeze and Cherry, 1979) are valid. The equation neglects compressibility in the matrix and the fluid, spatial variations in fluid density as a function of solute concentrations or temperature, and the effects of the air phase. In practice, infiltration in the unsaturated zone is complicated by the fact that hydrologic parameters, particularly the hydraulic conductivity (K), are non-linear functions of the moisture content of the medium. In addition, this dependence differs depending on whether the medium is being wetted or drained.

Neglecting molecular diffusion and assuming that solute is only transported in the liquid phase, the classical deterministic convection-dispersion equation has been used in many studies to model nonreactive solute transport (e.g., Nielsen et al., 1986; Selim et al., 1990) in the unsaturated zone. For reactive solute transport in one-dimension, the general equation is modified to account for the effects water/rock interaction such that:

$$\frac{\partial}{\partial t}\left(C + \frac{(1-\eta)}{\theta}\rho S\right) = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x} - vC\right) + \Phi \qquad (3\text{-}2)$$

where C is the solute concentration (g/ml) in the liquid, and η and θ (m^3/m^3) are the porosity and volumetric water content, respectively, of the medium. D is the hydrodynamic dispersion coefficient (m^2/s), v is the mean pore velocity (m/s), S is the solute concentration (g/g) adsorbed on the solid phase, ρ (g/m^3) is the mean density of the medium, and Φ represents solute sources and sinks in the system other than sorption (Nielsen et al., 1986). Eqn. (3-2) is frequently simplified by substituting the dry bulk density $\rho_b = (1-\eta)\rho$ and fluid flux $q = \theta v$ for ρ and v, respectively.

For steady-state flow conditions, and assuming that the medium is homogeneous and incompressible with respect to material properties, η, ρ, v, and D can be treated as constants. If equilibrium sorption is the only attenuation mechanism other than dispersion considered, $\Phi=0$, and Eqn. (3-2) simplifies to:

$$\frac{\partial}{\partial t}\left(C + \frac{(1-\eta)}{\theta}\rho S\right) = \left(D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x}\right) \quad . \tag{3-3}$$

$\partial S/\partial t$ depends on the type of sorption model used (Domenico and Schwarz, 1990). For the simplest case of a linear sorption isotherm, and assuming instantaneous equilibrium, $S = K_d C$. Under these conditions, Eqn. (3-3) simplifies further such that:

$$\frac{\partial}{\partial t}\left[C\left(1 + \frac{(1-\eta)}{\theta}\rho K_d\right)\right] = \left(D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x}\right) \quad . \tag{3-4}$$

To reflect the attenuation of solute transport relative to water velocity (or to the transport of a non-reactive solute), a retardation factor, R_f can be defined such that:

$$R_f = \left(1 + \frac{(1-\eta)}{\theta}\rho K_d\right) \quad . \tag{3-5}$$

and Eqn. (3-4) is modified such that:

$$\frac{\partial}{\partial t}R_f C = \left(D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x}\right) \quad . \tag{3-6}$$

In addition to sorption, several mechanisms can contribute to the retardation of solute transport, including precipitation/dissolution, diffusion, fluid mixing, and radioactive decay. Under these conditions, $\Phi \neq 0$, and retardation behaves in a much more complex manner than can be described using the simple R_f approach in Eqns. (3-4) through (3-6) (McKinley and Alexander, 1991). A complex coupling of geochemical relations with transport equations is then required to account for the various mechanisms controlling contaminant transport (e.g., Krishnaswami et al., 1982; Ku et al., 1991).

Returning to the assumption that $\Phi=0$, Eqn. (3-2) can be adapted to two- and three-dimensional transport in the general form:

$$\frac{\partial}{\partial t}\left(C + \frac{(1-\eta)}{\theta}\rho S\right) = \nabla(\underline{\underline{D}}\nabla C - \underline{v}C) \quad . \tag{3-7}$$

which can be modified in a fashion similar to the development outlined above in Eqns. (3-2) through (3-6). From Eqn. 3-5, if θ does not vary with time, R_f can be considered constant for an homogeneous, incompressible medium. Under saturated conditions, $\theta = \eta$, and this is likely to be a valid assumption. In the unsaturated zone, however, volumetric moisture content varies as a complex function of both time and space, and θ cannot be considered constant. As a

result, R_f must also be evaluated as a function of time. Eqn. (3-7) also assumes that all available surfaces will be wetted, regardless of hydrologic saturation, and that mass transport through the volume is by piston displacement (i.e., no preferential zones of flow) (Clothier, 1984). Tritium experiments by Bond et al. (1982) suggested that piston displacement may be obtainable in unsaturated column experiments. In practice, however, most geological media are heterogeneous, and preferential flow and transport through permeable layers and fractures all serve to complicate the application of a simplified model (Ababou, 1991).

In general, solution of the convection-dispersion equation requires numerical solution and simple analytical solutions are not readily derived. Bond and Phillips (1990a) developed a one-dimensional analytical solution for cation transport. The solution assumes a general non-linear adsorption isotherm, although the exact approach depends on the shape of the isotherm. The model has been applied to column experiments in the Ca-Na-K system using isotherms determined by batch experiments with fairly good agreement, except at short times.

In practice, diffusion along chemical gradients is generally neglected in Eqn. (3-7), and advective transport is assumed to be the principle mode of solute transport within permeable layers. The spreading of a nonreactive solute plume by mechanical dispersion during advective transport through a heterogeneous, layered medium requires complex velocity distributions. Gillham et al. (1984) proposed an advection/diffusion model that minimizes this complexity by invoking molecular diffusion along chemical gradients between layers of contrasting hydraulic conductivities. In this fashion, less permeable layers tend to act as temporary storage cells; solutes are concentrated at the expense of the more permeable layers, and contaminant transport is attenuated. This molecular interpretation requires knowledge of the contrast in unit hydraulic conductivities of the layers, layer thickness, and the molecular diffusion coefficient for the solute. Unfortunately, these parameters are not always known with any degree of certainty, and Gillham et al. (1984) were required to use empirical estimation techniques. Travis and Nuttall (1987) also suggested that at the slow flow rates anticipated in the unsaturated zone at Yucca Mountain (< 1 cm/yr), diffusion may become relatively more important as the magnitude of advective transport diminishes.

Fracturing of geologic media leads to heterogeneity at a variety of scales, greatly complicating the modeling of fluid flow and transport. Deterministic modeling approaches have been modified for fracture flow in two basic ways. In the 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. (3-2 through 3-6). An additional term is required to consider cross-flow and transport between the fractures and the unfractured rock matrix. 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. Wilson and Dudley (1986) and Dykhuizen (1987) used this approach to describe one-dimensional transport in the unsaturated zone at Yucca Mountain. Neretnieks and Rasmuson (1984) also

modified the approach to include radioactive decay during radionuclide transport in a fractured medium with varying velocity and block-size.

The second deterministic 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) proposed that this is perhaps a more computationally efficient approach than dual porosity, and 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.

3.2 SOLUTE TRANSPORT-NONEQUILIBRIUM TRANSPORT

Reactive solute transport in the unsaturated zone is usually described using the convection-dispersion equation appropriate to the dimensionality of the problem (Eqn. 3-7). For example, Nair et al. (1990) modified the convection-dispersion equation to develop a one-dimensional transport model for the three phase (gas-liquid-solid) system in the unsaturated zone. However, given the non-linear nature of hysteretic effects, moisture content, hydraulic conductivity, and other hydraulic properties in the unsaturated zone, there is considerable uncertainty in the applicability of this equation to transport under variably saturated conditions and in the validity of the assumption of local equilibrium (Valocchi, 1985). If the assumption of equilibrium is valid, and if the convection-dispersion equation is adequate to describe solute transport in an unsaturated column experiment, it is expected that the eluted pulse of the solute will be roughly symmetrical in shape, increasing in concentration from zero to some maximum and decreasing back to zero. In practice, however, soils exhibit some structure, and elution curves from column experiments of both nonreactive and reactive solute transport are frequently asymmetrical (showing early breakthrough), and exhibit extensive tailing (Figure 3-1), asymptotically approaching some minimum, non-zero concentration. Van Genuchten and Wierenga (1976) also noted that tailing at larger pore volumes generally increases as porewater velocity decreases. Assuming that the convection-dispersion equation is appropriate, modeling kinetic solute transport in the unsaturated zone has followed two basic approaches. The first approach involves dividing the flow regime into two physically distinct domains. The second approach relies on chemical kinetics to reproduce observed profiles. Two reaction sites are proposed, one of which obeys chemical equilibrium, and the second of which follows nonequilibrium (usually first-order kinetic) processes.

3.2.1 Two-Region Transport

Two-region (or two-component) transport models are based on the existence of two physically distinct regions in a porous medium (Coats and Smith, 1964; van Genuchten and Wierenga, 1976). 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:

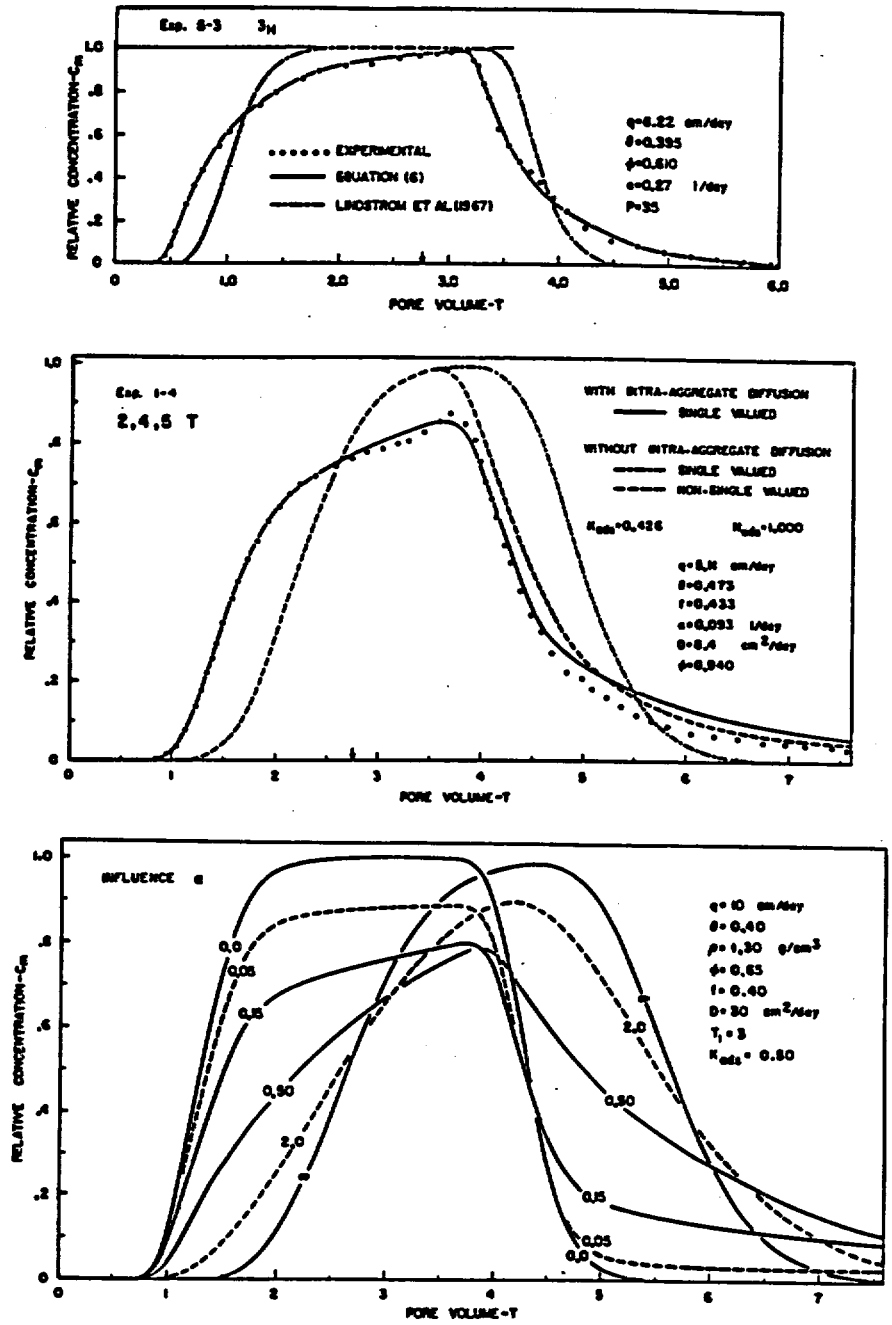

Figure 3-1. Early breakthrough and tailing observed for aggregared soils under unsaturated conditions. (a) Nonreactive tritium (^3H) breakthrough and theoretical predictions based on the assumption of one-region transport and two-region transport (from van Genuchten and Wierenga (1976); (b) Experimental reactive transport of the pesticide 2,4,5 T and theoretical conditions based on one-region (without intra-aggregate diffusion) and two-region (with intra-aggregate diffusion, from van Genuchten and Wierenga, 1977); (c) The effect of the mass transfer coefficient (α) on transport using the two-region model, from van Genuchten et al., 1977).

$$\theta_m \frac{\partial C_m}{\partial t} + f\rho_b \frac{\partial S_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} + (1-f)\rho_b \frac{\partial S_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - \theta_m v \frac{\partial C_m}{\partial x} \tag{3-8}$$

where the subscripts m and im represent 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 dry bulk density as defined in Section 3-1. Diffusion between the mobile and immobile regions is controlled by the relationship:

$$\theta_{im} \frac{\partial C_{im}}{\partial t} + (1-f)\rho_b \frac{\partial S_{im}}{\partial t} = \alpha (C_m - C_{im}) \tag{3-9}$$

where α is an empirical mass transfer coefficient (s^{-1}) between the stagnant and mobile waters. The degree of nonequilibrium represented in the system decreases as the rate of exchange between the two regions (α) increases relative to the rate of solute advection. It is important to note that local equilibrium is assumed to govern relationships in the mobile and immobile regions of the system. The two-region model as defined by Eqns. (3-8) and (3-9), is therefore not a model limited by reaction kinetics, but rather uses concentration gradients at points along the direction of flow to simulate disequilibrium (W. Murphy, personal communication).

The two-region approach has been used in a number of studies (van Eijkeren and Loch, 1984; de Smedt and Wierenga, 1984; Jinzhong, 1988; Mansell et al., 1988; Selim et al., 1990). Immobile water has been inferred from unsaturated column experiments that exhibit early breakthrough and asymmetric breakthrough curves (Bond and Wierenga, 1990). Skopp et al. (1981) noted that the fraction of stagnant water and the magnitude of the mass transfer coefficient are only defined by the results of experiments conducted under certain conditions; knowledge of the geometry and hydrologic properties of the medium is insufficient to predict the necessary parameters. De Smedt and Wierenga (1979) suggested that immobile water is present if fitting unsaturated transport data requires the use of a dispersion coefficient much larger than that predicted for saturated fluid flow. De Smedt and Wierenga (1984) noted a roughly linear increase in α with increasing pore water velocity (v_m) based on nonreactive transport column experiments. De Smedt and Wierenga (1984) also noted a positive linear correlation between mobile water (θ_m) and total water content ($\theta = \theta_m + \theta_{im}$) of the medium. Bond and Wierenga (1990) conducted nonreactive solute transport experiments under both steady and unsteady unsaturated conditions to evaluate the two-site model. Under steady flow, early breakthrough and asymmetric breakthrough curves indicated the presence of small amounts of immobile water. Under unsteady flow conditions, however, the data was adequately described without invoking two regions. Bond and Wierenga (1990) attributed this to the differences in wetting patterns between the two cases. In the case of steady flow, water flow is already

established and biased towards preferential flow paths, resulting in dead-end pore space. In contrast, wetting of the soil during the unsteady experiments carried the tracer into the wetted pore space by advection alone, with little or no contribution from diffusive mass transfer between mobile and immobile water. Mansell et al. (1991) incorporated a mobile/immobile two-region approach to nonequilibrium transport into the direct-coupled model of Valocchi et al. (1981a,b). Selectivity coefficients are allowed to vary in space and time as a function of changes in solution normality and composition. The authors reported that the model was successful in predicting Na^+ and Mg^{2+} transport in laboratory experiments.

Skopp et al. (1981) further modified the two-region model to consider two homogeneous flow regions. One region consists of relatively rapid flow through macropores; the second region is governed by much slower matrix flow. Exchange between the two regions is modeled using a linear interaction coefficient. If the interaction coefficient is sufficiently large, the model reduces to the classical convection dispersion equation. In general, structured soils require large coefficient values, possibly due to flow channeling or clay dispersion. Reinterpreting the data of van Genuchten and Wierenga (1976) using this approach, Skopp et al. (1981) suggested that the mean diffusion path exceeds the average aggregate size, suggesting that the mobile/immobile assumption is inadequate.

3.2.2 Two-Site Transport

Many studies (Selim et al., 1976; Cameron and Klute, 1977; Jennings and Kirkner, 1984; Parker and Jardine, 1986; Kool et al., 1987) have proposed a two-site approach to modeling early breakthrough curves. One site is assumed to be governed by equilibrium sorption, and the second site assumes kinetic sorption reactions. As discussed by Nkedi-Kizza et al. (1984), adsorption on the equilibrium site (site 1) is governed by a linear sorption isotherm, while sorption at the nonequilibrium site (site 2) is governed by first-order, linear kinetics. Expressed in terms of adsorption at the nonequilibrium sites, the overall governing transport equation is:

$$\left[1+\frac{f\rho_b K_d}{\theta}\right]\frac{\partial C}{\partial t} + \frac{\rho_b \alpha_2}{\theta}[(1-f)K_d C - S_2] = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \qquad (3\text{-}10)$$

where f is the fraction of sites that are governed by equilibrium sorption, K_d is the linear sorption coefficient that is assumed valid for both sites, α_2 is a first-order kinetic rate constant for the nonequilibrium sorption sites, and other variables (S, C, ρ_b, D, v) are as defined previously.

Nkedi-Kizza et al. (1984) used a dimensionless parameterization of both the two-region and two-site models to demonstrate a mathematical equivalence of their dimensionless forms in terms of addressing nonequilibrium solute transport. Breakthrough curves (BTC) for ^{45}Ca, ^{3}H, and ^{36}Cl transport in water saturated column experiments were fit reasonably well by

the models, including the tailing observed for the different BTCs. The authors noted, however, that because only the forms of the dimensionless equations are directly comparable, this equivalence is only valid for simulations of the net effect of retardation at a macroscale. Since dependent dimensionless variables (e.g., one dimensionless variable, c_2 measures either solution concentrations in the immobile water for the two-region model, or the sorbed concentration at the kinetic site in the two-site model) differ in the two models, microscopic measurements (unspecified by the authors) are necessary for discrimination between the conceptual models. It is also important to note that the authors use a linear sorption isotherm to describe the sorption/concentration relationships in the transport models.

3.2.3 Stochastic Models

Recent studies suggest inadequacies in the deterministic, convection-dispersion approach to simulating solute transport in the unsaturated zone (e.g., Jury et al., 1983, 1986; Sposito et al., 1986). Alemi et al. (1991) also indicated that retardation factors based on K_d values from batch equilibrium experiments were inadequate to fit the results of selenium transport through unsaturated soil columns. As a result, recent efforts to model fracture and permeability induced heterogeneities and unsaturated transport have centered about the development of stochastic models. These models rely on performing large numbers of calculations to generate population statistics for of hydraulic and transport properties. Statistical treatments of these probability distribution functions are then used to simulate heterogeneities at any scale. The specifics of the stochastic model techniques are beyond the scope of this text, and the reader is referred to other reviews (Dagan, 1986; van Genuchten and Jury, 1987; Ababou, 1991) for a more detailed discussion of stochastic models.

At present, stochastic approaches have been largely limited to nonreactive solute transport (e.g., Bresler and Dagan, 1981). Those studies that do deal with reactive transport have generally modeled retardation using a linear K_d approach (Jury et al., 1983). However, some studies have attempted to use more sophisticated sorption models (Section 3.3). Russo (1989a,b) developed a one-dimensional stochastic model using a mixed-ion diffuse double layer to simulate solid/solution interaction for a simplified Na-Ca-Cl system. Comparison of predicted results to field data from an arid soil site at Bet Dagan, Israel, suggested that interactions between soil and solutions may affect transport under transient conditions, and increase the hydrologic heterogeneity of the medium. Cvetkovic and Shapiro (1990) used a first-order kinetic approach to account for retardation in their stochastic models, although at equilibrium, the model reduces to a linear K_d. Van der Zee (1990) and van der Zee and Bolt (1991) attempted to address a maximum sorption limit using the Langmuir isotherm. The applicability of this approach is somewhat restricted, however, in that it does not allow for desorption.

3.3 SORPTION MODELS

Table (3-1) is intended as a general summary of the adsorbed concentration/solution concentration relationships used to model sorption effects in geologic media. The reader is referred to Turner (1991) for a more detailed description of the derivation and applications of

TABLE 3-1. SUMMARY OF SORPTION MODELS, EQUATIONS, AND PARAMETERS (AFTER TURNER, 1991)

MODEL-EQUATION/REACTION	EQUILIBRIUM MASS-ACTION EXPRESSION CHARGE/POTENTIAL RELATIONSHIPS	ADJUSTABLE PARAMETERS
I. Empirical Sorption Isotherms		
A. Linear: $S = K_d C$		K_d
B. Freundlich: $S = K_{Fr} C^n$		K_{Fr}, n
C. Langmuir: $S = \frac{bK_{La}C}{(1 + K_{La}C)}$		K_{La}, b
D. Dubinin-Radushkevich: $S = b[\exp(K_{DR}[RT\ln(1 + \frac{1}{C})]^2)]$		K_{DR}, b
II. Mechanistic Models		
A. Ion Exchange: $SOH \cdot M_1 + M_2^+ = SOH \cdot M_2 + M_1^+$	$K_{ex} = \left(\frac{[M_1^+][SOH \cdot M_2]}{[M_2^+][SOH \cdot M_1]}\right)$	

TABLE 3-1.(CONTINUED)

MODEL EQUATION/REACTION	EQUILIBRIUM MASS-ACTION EXPRESSION CHARGE/POTENTIAL RELATIONSHIPS	ADJUSTABLE PARAMETERS[a]
B. Electrostatic Models-Surface Complexation:		
1. Diffuse-Layer:		
$SOH_2^+ = H^+ + SOH$ (K^+)	$-\sigma_o = \sigma_d = -0.1174\sqrt{I}\,\sinh\left(\frac{zF\Psi_d}{2RT}\right)$	K^+, K^-, N_s
$SOH = SO^- + H^+$ (K^-)	$\Psi_o = \Psi_d$	
$SOH + M^+ = SOM + H^+$ (K_M+)		
2. Constant Capacitance:		
$SOH_2^+ = H^+ + SOH$ (K^+)	$\sigma_o = -\sigma_d$	K^+, K^-, N_s, C_1
$SOH = SO^- + H^+$ (K^-)	$\sigma_o = C_1\Psi_d$	
$SOH + M^+ = SOM + H^+$ (K_M+)	$\Psi_o = \Psi_d$	
3. Triple-Layer:		
$SOH_2^+ = H^+ + SOH$ (K^+)	$-\sigma_o = \sigma_d = -0.1174\sqrt{I}\,\sinh\left(\frac{zF\Psi_d}{2RT}\right)$	K^+, K^-, K_{Cat}, K_{An}, N_s, C_1, C_2
$SOH = SO^- + H^+$ (K^-)	$\Psi_o = \Psi_d$	
$SOH + C^+ = SO^- - C^+ + H^+$ (K_{Cat})		
$SOH + A^- + H^+ = SOH_2 - A^-$ (K_{An})		

a. Parameters are: K_d, K_{Fr}, K_{Lm}, K_{DR} = Distribution, Freundlich, Langmuir, and Dubinin-Radushkevich empirical coefficients, respectively; n = Empirical coefficient; b = Maximum sorption limit; K^+, K^- = Protonation and Deprotonation equilibrium constants, respectively; K_M+, K_{Cat}, K_{An} = Intrinsic equilibrium constant for metals, cations, and anions, respectively; N_s = surface site density; C_1, C_2 = Capacitance for inner and outer electrostatic layers.

the various models presented. In general, as the sophistication and mechanistic basis increases, so does the complexity of the model and the number of adjustable parameters involved. Linear and nonlinear isotherm models tend to be determined by fitting one or more empirical parameters to a particular dataset. In contrast, mechanistic approaches are more flexible and robust enough for extrapolation to a variety of conditions, providing that the necessary parameters are defined. If independent data are not available, multiparameter models commonly reduce to curve-fitting of one or more variables to a specific dataset. If this is the case, an additional uncertainty is introduced through the possibility of nonunique solutions. This limits the predictive capability of the model in that extrapolation beyond the experimental conditions for the fitted data may lead to divergent results, depending on the initial set of parameters chosen. Even in the absence of hard data, however, it may be possible to eliminate one or more of the solutions based on chemical constraints. For example, if an excessively high specific surface area is required to fit one set of parameters to the dataset, this possible solution may be discounted.

4 EXPERIMENTAL AND FIELD STUDIES

4.1 EXPERIMENTAL SORPTION STUDIES

The details of sorption experimental design is necessarily specific to a given laboratory and a given set of experiments. Some common methodologies exist, however, and are described below.

4.1.1 Hydrologically Saturated Column Experiments

Under essentially static system conditions, batch sorption experiments involve adding a known mass of solid to a fluid which is spiked with a known concentration of the element of interest. The mixture is generally agitated during the experiment to ensure adequate contact between the solid and liquid phases, for a time chosen to ensure that sorption equilibrium is reached. Experiments of different duration are also used to investigate sorption reaction rates. The adsorbent is separated from the solution phase through filtration or centrifugation, and the concentrations of the spiked element associated with the solid and liquid phases are measured. In this way, the distribution of the solute between the solution and solid phase is monitored. Due to the immediate and intimate contact of solution with the solid phase, several studies have indicated that batch experiments tend to overestimate sorption relative to more dynamic experiments (Jury et al., 1983; Hodges and Johnson, 1987). In contrast to static batch experiments, column experiments simulate a dynamic environment by passing the spiked solution through a volume of material. The chemistry of the solution eluted through the column is monitored, and in most cases, the solid phase is analyzed to determine the distribution of the spiked element with time.

Solids are prepared in a variety of ways for column sorption experiments. Disaggregated samples are generally used to provide for measurable flow and transport in relatively short times (days to months). If the sample is not naturally disaggregated (i.e. rock *vs.* soils and sediments), the sample is crushed and sieved. Grinding is generally avoided to reduce the possibility of creating nonrepresentative reactive grain surfaces (Kent et al., 1988). Minimum particle sizes on the order of 75-100μm (Beckman et al., 1988; Meijer, 1990) are used to minimize particle effects. For experiments using pure minerals, physical mineral separation and ultrasonic cleaning are used to produce a pure mineral separate. Whole rock samples are carefully split to reduce the possibility of bias resulting from the techniques used for sample preparation. The solid is characterized using a variety 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. In some cases, to study specific processes such as ion exchange on zeolites, the sample is pretreated to produce homoionic mineral forms (Pabalan, 1991). For those experiments with redox-sensitive elements, samples are kept in a controlled atmosphere (Hakenen and Lindberg, 1991).

Waters can include simple solutions (e.g., Na-Cl solutions), natural waters or synthetic groundwaters prepared to approximate conditions in the field. 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^{2-}, SO_4^{2-}, EDTA, etc.) to the solution in varying concentrations. Low concentrations of the spike (commonly 10^{-7} M) are used to remain below chemical saturation with respect to stoichiometric compounds of the spiked element(s) and to avoid the complicating factors of precipitation (Meijer, 1990). At the same time, however, the introduction of an aqueous solution may promote dissolution of the solid phase(s), especially if the particles are fine-grained (Kent et al., 1988). Geochemical modeling can be used in some degree to simulate the extent of this effect. For many redox-sensitive elements, such as the actinides, solution pH and Eh are externally controlled to the extent possible through the addition of buffers for many redox-sensitive elements in order to characterize and maintain oxidation states and speciation. For species where carbonate complexation is important (U, Pu, Am, etc.), it may be necessary to perform experiments under an inert atmosphere (usually N_2 gas) or in an atmosphere where $p(CO_2)$ can be externally controlled, to minimize the effect of atmospheric CO_2 on solution alkalinity.

In setting up the experiment, crushed material (or soil) is packed into a column (commonly acrylic) which is usually on the scale of tens of millimeters to several meters in length. Care is taken to load the material as uniformly as possible to avoid introducing heterogeneities into the system. Many of the columns are constructed of thin rings bolted together to build a column of the desired length (e.g., Siyag et al., 1983; Bond and Wierenga, 1990). Although these types of experiments are generally conducted in a vertical column, the column can be oriented at any angle (Bond and Wierenga, 1990). Samples are equilibrated with the unspiked water prior to the sorption experiment (Thomas, 1987; Triay et al., 1991). 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 (m^2/s) in 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. In many soil experiments, the feed solution contains a dissolved salt such as $CaCl_2$ to saturate exchange sites in the medium.

After flow has reached a steady state, the spiked feed solution is introduced at one end of the column. Generally, the input is in the form of a pulse, although a gradual input can also be applied. After input, the unspiked feed solution is maintained to flush the spike through the system. In many experiments, a nonreactive solute such as tritium is first eluted through the column to determine 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 (Triay, Personal Communication). 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 (or the walls of the column). If the column is composed of sections, the apparatus is disassembled following the sorption experiments, and the chemistry of the solid in each section is analyzed and characterized. High resolution analytical methods may be applicable for identifying principle adsorbent phases, and characterizing the surface of the solids. Several studies (Phillips and Bond, 1989; Bond and Phillips, 1990c) have described a nondestructive method involving centrifugation of the column material using a high-density, water-immiscible organic liquid to displace pore fluids in the column materials for analysis.

By adjusting flow rates in the column apparatus, it is possible to evaluate the migration mechanisms in a dynamic system, and to evaluate the possible effects of geochemical processes (e.g., anion exclusion and slow sorption kinetics) on solute breakthrough (Wierenga et al., 1986; Bond and Phillips, 1990b). Column experiments also offer a simple, dynamic, essentially one-dimensional model against which to validate hydrogeochemical transport codes. Because no two columns are identical with respect to interconnected porosity and other physical characteristics, however, replication of results tends to be poor. 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 evaluation of the relative importance of a single factor difficult if not impossible for column experiments (Meijer, 1990).

4.1.2 Hydrologically Unsaturated Column Experiments

The effects of variable saturation can also be investigated using unsaturated column experiments (Gaudet et al., 1977; Wierenga et al.,1986; Bond and Phillips, 1990b,c; Bond and Wierenga, 1990). In these experiments, steady unsaturated flow is obtained either by applying a controlled suction at the base or positive pressure at the top 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; Wierenga et al., 1986) and fix the location of the solution front. These probes must, however, be calibrated individually as a function of water content and ion concentration, which in turn depends on whether the column is draining or being wetted. Gamma-ray densitometers are used to determine the saturation profiles in the column as a function of depth. Several studies (Bond, 1986; Wierenga et al., 1986; Bond and Wierenga, 1990) describe unsteady, unsaturated flow experiments using variable flow rates. Procedures are similar to saturated column experiments, with the introduction of a nonreactive solute, and the analysis of the eluted solution.

Hydrologically unsaturated column experiments have been largely restricted to soil science applications. As a result, the investigated media are soils, and the transported species are usually either inert (van Genuchten and Wierenga, 1977; Bond, 1986; Bond and Wierenga, 1990), pesticides (van Genuchten et al., 1977) or common ions such as Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} (Gaudet et al., 1977; Bond et al., 1982; Siyag et al., 1983; Bond and Phillips, 1990b). Modeling of the results usually assumes that sorption is adequately represented by either a linear or Freundlich isotherm. While some of these species may be useful as analogs to some

radioelements, little or no data is available from unsaturated column experiments performed using radionuclides that are potentially important in the high-level waste repository. Alemi et al. (1991) performed batch and unsaturated column experiments to examine selenium transport. Their results indicated that convection-dispersion modeling using the Freundlich isotherms derived from the batch experiments were inadequate to fit the elution data. Complex fluid flow systematics in unsaturated column experiments such as these tend to mask the contribution of sorption processes at the microscale. This makes evaluation of the effects of different parameters on sorption difficult if not impossible. For more complex chemistries such as those encountered for the actinide series radioelements, these uncertainties become even more critical.

4.1.3 Intact Rock Experiments

In the proposed deep geologic repository at Yucca Mountain, the medium is not a disaggregated material, but intact fractured rock. Extrapolation of results from crushed rock experiments to intact rock is complicated by uncertainties in how representative the mineral suite is, whether or not the mineral surfaces in the crushed material are typical of those in the natural environment, and how fluid flow is controlled through the intact medium versus the crushed rock experiment. In the optimal case, a solid rock column is used to achieve a more accurate representation of the geological environment. Flow experiments with intact rock are difficult to conduct (Meijer, 1990), and can only be performed under high pressure gradients for either highly permeable rock or relatively nonreactive elements in order to achieve breakthrough in laboratory time scales. In addition, intact rock experiments are subject to many of the same limitations of crushed rock experiments in that the hydrological transport in the experiment must be tightly constrained before any information can be gained regarding the contributions of different geochemical processes to radionuclide migration. Conca (1990) 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.

Thin wafers on the order of 1-2 mm thick have been used instead of crushed rock in batch type experiments to provide a more accurate representation of a composite material (Meijer, 1990; Hakenen and Lindberg, 1991). These experiments are essentially diffusion experiments, and to date, success has been largely limited to more permeable rock (Meijer, 1990). Thompson and Wolfsberg (1979) report on the use of autoradiography to ascertain the continuity of the U- and Am-sorbing phases (such as clays) in tuffs, tuffaceous alluvium, and sedimentary rocks from the Yucca Mountain area. In a similar fashion, Liu et al. (1991) immersed polished wafers of andesite and coral limestone in a radionuclide-spiked solution (^{137}Cs, ^{90}Sr, and ^{60}Co) for one week. Following immersion, the samples were rinsed in deionized water, and exposed to X-ray film for a period of two weeks. Comparison to transmitted and reflected light petrography allowed for the qualitative determination of the sorbing phase(s) in the rock.

4.2 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, 1991). Field experiments also provide a valuable method for the calibration and validation of reactive transport modeling codes. 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.

4.2.1 *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 kilometers. Several studies (Jury et al., 1983; Butters and Jury, 1989; Butters et al., 1989) have conducted field experiments to investigate reactive solute transport in a soil system. In general, a relatively small plot of land (~ 1 hectare) is instrumented on a grid pattern. Neutron access tubes are used to measure moisture content at depth, and solution samplers and suction lysimeters are used to extract soil solutions at varying depths. The site is irrigated either by trickle (drip) irrigation or a sprinkler system for an extended period until a quasi-steady state flow is achieved. A solution pulse is introduced, and irrigation with unspiked water continues; the migration of the solute plume is monitored through the instrumentation. In some cases, drilling is used to take soil cores for analysis. In small pores, capillary pressure tends to be greater than the suction applied by the solution sampler. These pore fluids are essentially unavailable for analysis. In fine-grained media, these pore fluids represent a greater proportion of the soil water, and capillary pressures are even higher. As a result of these complications, samples may underrepresent fluids from small pores and fractures, and be inherently biased towards the more accessible "gravitational" water in macropores and large fractures (Sears and Langmuir, 1982).

Trench experiments of the type conducted by INTRAVAL (Wierenga et al., 1986) at Las Cruces, NM, are slightly different in construction 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 water movement and solute transport are monitored through the instrumentation installed in the trench face and in a series of wells. Tritium and bromide migration has been investigated at the Las Cruces Trench site (Sagar and Wittmeyer, 1991), and tests have also been recently performed with chromium as a reactive tracer.

Transport through an aquifer is studied in a similar fashion (Avogadro, 1990; Williams et al., 1991). In these experiments, a dense sampling through drill holes or trenching

allows a relatively fine discretization of the physical properties (porosity, permeability, hydraulic conductivity, etc.) 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, although the influence of a pumped well is 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 (Waldrop et al., 1985; Fuentes et al., 1989). Experiment scale is relatively small (tens of meters) in most cases, to limit the effects of external processes on the experiment, and to keep the time scales relatively short.

Assuming that steady flow has been achieved, 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 recommended (Gschwend, 1990) in order to minimize the introduction of well material into the water samples. Fluid characteristics (e.g., pH, Eh, TDS) 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 (Fuentes and 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.

4.2.2 Analog Migration Studies

Natural analog studies provide a method for evaluating solute migration at geologic scales space, and offer the only method in which to examine transport over geologic time. 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 and 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, 1991). Despite these limitations, these studies are 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; Leslie, 1991).

Analogs can vary in size from centimeter-scale processes to the kilometer-scale of ore deposits and mining districts (Pearcy and Murphy, 1991). The migration of depleted uranium from expended artillery shells was investigated under both wet and semi-arid conditions (Ebinger et al., 1990). Under the relatively wet conditions of the Aberdeen Proving Ground in Maryland, Ebinger et al. (1990) indicated that uranium transport was by dissolution, transport, and reprecipitation. In the arid climate of the Yuma Proving Ground in Arizona, physical erosion and transport were proposed as the dominant processes. On a larger scale, the Koongarra system in the Alligator Rivers region has received particular attention with regard to the mobilization, transport, and adsorption of uranium under saturated conditions during the weathering of the ore body (Short et al., 1988; Payne et al., 1990a,b). 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 the uranium in the dispersion fan (Payne et al., 1990b; Payne and Waite, 1991). Gvirtzman et al. (1988) reported an *in situ* field application of the mobile/immobile model of van Genuchten and Wierenga (1976) which modeled bomb tritium migration in unsaturated soils in Israel. By introducing an empirical factor to account for the salinity effect (clay dispersion), the model was able to adequately reproduce observed profiles.

An example of an intermediate-scale anthropogenic natural analog to reactive solute transport is the series of field studies conducted at the Nevada Test Site in rocks similar to those at Yucca Mountain (Coles and Ramspott, 1982). In this case, water was pumped from a monitoring well near (91m) the Cambric detonation site on the Nevada Test Site. Tritium, ^{36}Cl, ^{85}Kr, ^{106}Ru, and ^{129}I were monitored. Anionic species (e.g., RuO_4^{2-}) arrived nearly as quickly as tritium, and in the case of ^{36}Cl and ^{129}I, the pulses preceded the tritium pulse (Thompson, 1985), suggesting anion exclusion. Cationic species such as ^{90}Sr and ^{137}Cs were not detected, even after 10 years of pumping. Coles and Ramspott (1982) used the Cambric site to

illustrate some of the drawbacks of the K_d approach to sorption. Assuming that the K_d approach is valid, the relatively rapid migration of Ru as an anionic compound suggests K_d values on the order of 0.3. However, experimental batch sorption K_d values for Ru range from 10 to 8,000. The discrepancy between laboratory and field results indicates that these experimental values are not adequate to model retardation under field conditions that may vary considerably from those in the laboratory (Coles and Ramspott, 1982).

Unlike a controlled field-experiment, a natural analog provides, in essence, a "snapshot" of the net effects of transport processes. Unraveling 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. It is unlikely that the heterogeneities of scale will allow for any detailed quantitative investigation of the effect of unsaturated flow on individual chemical retardation processes such as sorption. The reader is referred to Pearcy and Murphy (1991) and references therein for a detailed discussion of geochemical analogs pertinent to radionuclide transport.

5 SUMMARY AND CONCLUSIONS

5.1 SUMMARY

The unsaturated zone at Yucca Mountain is likely to be a critical factor in the performance of the proposed high-level waste repository. Variable saturation may exercise a broad influence on a number of key parameters that control radionuclide transport. Unfortunately, due to the difficulty in extracting water samples from unsaturated rocks and in performing unsaturated transport experiments, the detailed characterization of these effects is currently understood only in a general sense. As a result, a large number of simplifications are generally made in modeling reactive transport in the unsaturated zone.

Sorption behavior as a function of the physical and chemical conditions of the experimental system has been studied using batch and saturated column sorption experiments, and there is little experimental evidence to indicate that sorption processes are radically affected by variable saturation. Assuming that sorption processes are similar at the microscale, observations and calculations of changes in the physicochemical conditions of the system due to variable saturation can be used to infer the retardation behavior of radioelements in the unsaturated zone.

It seems that higher ionic strength solutions will be produced as meteoric waters percolate through the unsaturated zone (Sears and Langmuir, 1982; Hem, 1985; Yang et al., 1988; Meijer, 1990). Under these conditions, the electrical double layer is compressed, charged particles (e.g., clays) flocculate, and the salinity effect reducing hydraulic conductivity is diminished. Parks (1990) suggested that electrostatic effects such as these are most critical for monovalent, poorly hydrolyzed ions. In the case of increased ionic strength, competition between ions for sorption sites increases, possibly reducing radionuclide sorption. Increased ionic strength may also reflect the presence of complexing ligands such as CO_3^{2-} and PO_4^{3-} which also serve to reduce cation adsorption (Sanchez et al., 1985). Conversely, higher TDS may lead to supersaturation with respect to one more mineral phases. In this case, trace contaminants can be removed from solution through coprecipitation (Ku et al., 1991). This possibility is further enhanced given the slow rates of flow and long fluid residence times considered likely for matrix flow through the unsaturated zone at Yucca Mountain (Travis and Nuttall, 1987; Peters and Klavetter, 1988; DOE, 1988).

One key characteristic of the unsaturated zone is that it is open to the atmosphere. In the absence of significant microbial activity under these conditions, the geochemical environment is oxidizing. Under the oxidizing conditions anticipated at Yucca Mountain, many of the redox sensitive radionuclides are likely to be multivalent. Many of these highly charged ions (e.g., Tc^{7+}, Pu^{6+}) are readily hydrolyzed to form polymeric species (Choppin and Mathur, 1991), and may be transported as colloids (Travis and Nuttall, 1987). Also, in the presence of complexing ligands, these species form complexes that reduce the charge and increase the molecular size, perhaps leading to reduced retardation. Because the Yucca Mountain system is open to

atmospheric CO_2, soil calcite is dissolved, solution bicarbonate increases, and the pH of the groundwater is buffered to neutral to slightly alkaline values of 7-8. In an arid climate such as at Yucca Mountain, $p(CO_2)$ is controlled by plant respiration in the soil zone, and may vary as a function of vegetative cover and time of year. Precipitation of soil carbonate reflects this control, and may serve as a relatively large sink for carbon in arid climates. There are indications (Murphy, 1989) that $p(CO_2)$ indeed varies significantly with time and space at Yucca Mountain, and therefore the pH, which is controlled by carbonate equilibria, may vary as well. The sorptive behavior of an element depends on its speciation, which in turn is controlled to a large extent by its redox conditions.

Variable hydrologic saturation controls whether flow from the repository to the accessible environment is through fractures or through matrix flow. Above some threshold value of moisture content, fracture flow becomes more important (Peters and Klavetter, 1988; Conca, 1990). In this case, secondary fracture-lining minerals such as oxides, zeolites, clays, and calcite would control sorption processes, predominantly through surface adsorption and ion exchange. At lower hydrologic saturation, matrix flow is predominant, and sorption by ion exchange with zeolitized tuff is anticipated to be a key control on radionuclide migration. Under low flow conditions through small fractures and the rock matrix, transport may be slow enough that kinetic effects on sorption processes are negligible, and diffusion along chemical gradients would become significant relative to advective transport. If saturation reaches the point at which larger fractures begin to conduct water, transport may be rapid enough that sorption kinetics becomes significant. However, batch experiments suggest that sorption equilibrium is reached in times on the order of weeks to months in most systems. Ages of 1,000 years or more for waters from the unsaturated zone at Yucca Mountain (Yang, 1991), suggest that fluid residence times are long enough that sorption kinetics, even through fractures, will not inhibit radionuclide retardation. Finally, transport through large fractures may enhance colloidal transport, where flow through the matrix or microfractures tends to remove colloids from solution due to filtration by small pores (Travis and Nuttall, 1987).

Water/rock (W/R) ratios in the unsaturated zone are expected to be low, certainly much lower than the typical ratios of 10/1 or more used in batch equilibrium experiments. At lower W/R ratios, there should be a surplus of adsorption sites, and a general increase in sorption density (Benjamin and Leckie, 1981; Dzombak and Morel, 1986). The manner in which sorption behavior is controlled by solution pH may also be affected by a decreased W/R ratio, with the pH sorption edge for transition metals shifting to more alkaline conditions at constant electrolyte concentrations (Benjamin and Leckie, 1981).

Under extremely dry conditions, the water film surrounding grains in the geologic medium becomes thinner, and water properties may also be affected. This is mainly due to the effects of the electrical double layer surrounding charged particles in the medium, particularly clays (Hem, 1985; Nielsen et al., 1986). In response to the surface charge, water molecules at the solid/solution interface become progressively more ordered and layered (Mulla, 1986; Giese and Costanzo, 1986), forming first an inner layer binding to the silicate substrate, with an associated outer layer hydrogen-bonded to the first. From Monte Carlo simulations and

molecular dynamic studies, water density and hydrogen bonding are thought to decrease near the solid surface; the dielectric constant also decreases, as does the self-diffusion coefficient of water at the solid/liquid interface (Mulla, 1986). Polar water bound to the charged particle also becomes less mobile than the bulk water several molecules removed from the surface (Giese and Costanzo, 1986). As the medium dries and the water film becomes more discontinuous, ion interaction with the medium becomes progressively restricted to a thinner and thinner layer. Since contaminant transport in solution is only possible where the film is continuous, then a discontinuous water film would tend to retard transport of a radionuclide by requiring a more tortuous travel path between those pores that remain connected.

There is also evidence to suggest that there is a complex interdependence between the solution chemistry and the hydrologic properties of the medium. Interaction between the electrically charged minerals and the electrolyte solution may lead to clay dispersion accompanied by a reduction in permeability and hydraulic conductivity (Nielsen et al., 1986). For soils in arid regions, this interaction has been demonstrated to be a function of the relative concentrations of Na^+ relative to Ca^{2+} and Mg^{2+}, pH, and moisture content (Laryea et al., 1982; Siyag et al., 1983; Suarez et al., 1984). It is uncertain to what extent that this salinity effect may occur in the intact rocks of the unsaturated zone at Yucca Mountain.

A limited number of column and controlled field experiments have been conducted to examine the effect of unsaturated transport through soils. These studies are largely limited to the transport of common cations and anions through soils and synthetic materials, and serve to demonstrate some of the complexities of data interpretation. In column experiments, early, asymmetric breakthrough and extensive tailing has been observed for both inert and reactive transport (van Genuchten and Wierenga, 1976, 1977; van Genuchten et al., 1977; Bond and Wierenga, 1990). These results have required modification of the standard convection-dispersion approach to solute transport, and different approaches have been used to fit the data. In most cases, the interaction between the liquid and the solid phase has been modeled with either a K_d approach or a nonlinear sorption isotherm, but some two-site models have used linear first-order reaction kinetics. K_d values determined from batch experiments tend to overestimate adsorption relative to column experiments (Jury et al., 1983; Hodges and Johnson, 1987), and the use of the K_d approach has been shown to be inadequate for modeling the results of dynamic experiments (Alemi et al., 1991). It has been argued (Jury et al., 1983; Roth et al., 1990; Alemi et al., 1991) that the convection-dispersion equation is perhaps insufficient to model heterogeneous flow and transport under variable hydrologic saturation, and that probabilistic stochastic models will be needed.

5.2 CONCLUSIONS

Many of the effects of variable hydrologic saturation must be indirectly modeled through the extrapolation of observations conducted under saturated conditions. Although some physical and chemical variations can be attributed to partial saturation, most of these effects become pronounced only under extremely dry conditions. While such low saturation levels (probably 5 percent or less) may be reached in the near-field adjacent to a waste canister (Travis and

Nuttall, 1987), the far-field at Yucca Mountain is unlikely to be dried to such an extent, given current saturation levels of 40-80 percent (Montazer and Wilson, 1984; DOE, 1988 - Ch. 3).

Perhaps the most important use of column experiments is in the validation of coupled hydrogeochemical models. A variety of approaches have been used to model the results of column experiments. In most cases, the complexity of the flow problem has prompted the use of a simple linear sorption model or a nonlinear sorption isotherm to simplify the problem for numerical analysis (Bond and Phillips, 1990a,b; Alemi et al., 1991), but even at the small scale of most laboratory experiments, the K_d approach has been demonstrated to be inadequate (Alemi et al., 1991). The assumption of local equilibrium in a single mobile flow region has also been shown to be inadequate, and several different schemes (two-region, two-site) have been used to model experimental results. The effects of hysteresis on column transport experiments have generally been avoided. An additional complication is that most modeling efforts have focused on fitting a particular dataset. If a large number of adjustable parameters are used, the possibility of a non-unique fit is achieved. If this is the case, then the predictive capability of the model is restricted, as the different distinct parameter combinations diverge beyond the conditions of the fitted experiment.

In most experimental and geological systems, heterogeneities exist at a variety of scales (Ababou, 1991). In the unsaturated zone, transport is further complicated by the dependence of hydraulic properties on the degree of saturation. Results from column experiments are therefore of limited use in examining the effect of field-scale heterogeneities on radionuclide transport (van der Zee and Bolt, 1991). Most of these studies have been restricted to the transport of common ions such as Na, Ca, Mg, Cl, and Br. Although these experiments may be used as analogs in a first-order approximation, the direct extrapolation of the results of laboratory and field experiments to radionuclide migration is likely to be unjustifiable given the complex chemistries of multivalent redox-sensitive radioelements. Environmental considerations make it unlikely that such controlled field experiments will be conducted using radioelements considered to be important in high-level waste.

Given the spatial scale of most laboratory and field experiments, processes at the microscale under unsaturated conditions tend to be lost in the uncertainty surrounding medium heterogeneities and complex fluid flow systematics. As a result of this uncertainty, the usefulness of unsaturated experiments in isolating the effects of variable saturation on sorption is limited. While such experiments may be useful in determining general transport behavior in the vadose zone, until the uncertainties inherent in unsaturated fluid flow can be better constrained, effort is perhaps better spent in understanding sorption under saturated conditions. Combined with a better understanding the chemistry of natural groundwaters in the unsaturated zone at Yucca Mountain, this approach can allow an evaluation of the specific role of sorption processes in retarding radionuclide migration. Once this role has been established, it may then be possible to extrapolate to transport under variable hydrologic saturation.

6 CITED REFERENCES

Ababou, R. 1991. *Approaches to Large Scale Unsaturated Flow in Heterogeneous, Stratified, and Fractured Geologic Media.* U. S. Nuclear Regulatory Commission, NUREG/CR-5743. Washington, D. C.

Alemi, M. H., D. A. Goldhamer, and D. R. Nielsen. 1991. Modeling selenium transport in steady-state, unsaturated soil columns. *Jour. Environ. Qual. 20*: 89-95.

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, Georgia.

Altmann, S. A. 1984. *Copper Binding in Heterogeneous, Multicomponent Aqueous Systems: Mathematical and Experimental Modeling.* Ph.D. Dissertation. Stanford University. Stanford, California.

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.

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.

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.

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.

Avogadro, A. 1990. *CEC Project Mirage - Second Phase on Migration of Radionuclides in the Geosphere. Third (and Final) Summary Progress Report (Work Period 1989).* In situ migration experiments and development of measuring techniques, Commission of the European Communities, Nuclear Science and Technology, EUR 12858 EN. Brussels, Belgium.

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.

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

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, New Mexico.

Benjamin, M. M., and J. O. Leckie. 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *Jour. Coll. Interface Sci.* *79*: 209-221.

Benson, L. V., and P. W. McKinley. 1985. *Chemical Composition of Ground Water in the Yucca Mountain Area, Nevada, 1971-1984.* U. S. Geological Survey Open File Report, USGS-OFR-85-484. Denver, Colorado.

Benson, L. V., J. H. Robison, R. K. Blankennagel, and A. E. Ogard. 1983. *Chemical Composition of Ground Water and the Locations of Permeable Zones in the Yucca Mountain Area, Nevada.* U. S. Geol. Survey Open-File Report, USGS-OFR-83-854. Denver, Colorado.

Bish, D. L., and D. T. Vaniman. 1985. *Mineralogic Summary of Yucca Mountain, Nevada.* Los Alamos National Laboratory, LA-10543-MS. Los Alamos, New Mexico.

Bock, W. D., H. Bruhl, C. Trapp, and A. Winkler. 1989. Sorption properties of natural sulfides with respect to technetium. in: W. Lutze and R. C. Ewing, (eds.). *Scientific Basis for Nuclear Waste Management XII*, Materials Research Society, Pittsburgh, PA: 973-977.

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

Bond, W. J., B. N. Gardiner, and D. E. Smiles. 1982. Constant-flux adsorption of a tritiated calcium chloride solution by a clay soil with anion exclusion. *Soil Sci. Soc. Am. Jour.* *46*: 1133-1137.

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

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

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

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

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

Bradbury, M. H., and B. Baeyens. 1991. A mechanistic approach to the generation of sorption databases. Draft Report, *NEA Sorption Workshop '91*. Interlaken, Switzerland.

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

Broxton, D. E., D. L. Bish, and R. G. Warren. 1987. Distribution and chemistry of diagenetic minerals at Yucca Mountain, Nye County, Nevada. *Clays Clay Mineral. 35*: 89-110.

Bruno, J., I. Casas, and I. Puigdomenech. 1991. The kinetics of dissolution of UO_2 under reducing conditions and the influence of an oxidized surface layer (UO_{2+x}): Application of a continuous flow-through reactor. *Geochim. Cosmochim. Acta 55*: 647-658.

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.

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

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

Cameron, D. R., and A. Klute. 1977. Convective-dispersive solute transport with a combined equilibrium and kinetic adsorption model. *Water Resourc. Res. 13*: 183-188.

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

Cerling, T. E. 1984. The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth Planet. Sci. Letters 71*: 229-240.

Choppin, G. R. 1988. Chemistry of actinides in the environment. *Radiochim. Acta 43*: 82-83.

Choppin, G. R., and J. N. Mathur. 1991. Hydrolysis of actinyl (VI) cations. *Radiochim. Acta 52/53*: 25-28.

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

Coats, K. H., and B. D. Smith. 1964. Dead-end pore volume and dispersion in porous media. *Soc. Pet. Eng. Jour. 4*: 73-84.

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.

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.

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.

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

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

Dagan, G. 1986. Statistical theory of groundwater flow and transport: Pore to laboratory, laboratory to formation, and formation to regional scale. *Water Resourc. Res. 22*: 120S-134S.

Daniels, W. R., K. Wolfsberg, and R. S. Rundberg et al. 1982. *Summary Report on the Geochemistry of Yucca Mountain and Environs*. Los Alamos National Laboratory, LA-9328-MS. Los Alamos, New Mexico.

Davis, J. A., and D. B. Kent. 1990. Surface complexation modeling in aqueous geochemistry. in: M. F. Hochella, Jr. and A. F. White (eds.) *Reviews in Mineralogy: Volume 23. Mineral-Water Interface Geochemistry*. Mineralogical Society of America, Washington, D. C.

Davis, J. A., and J. O. Leckie. 1978. Surface ionization and complexation at the oxide/water interface 2. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *Jour. Coll. Interface Sci. 67*: 90-107.

Davis, J. A., and J. O. Leckie. 1980. Surface ionization and complexation at the oxide/water interface 3. Adsorption of anions. *Jour. Coll. Interface Sci. 74*: 32-43.

Davis, J. A., R. O. James, and J. O. Leckie. 1978. Surface ionization and complexation at the oxide/water interface 1. Computation of electrical double layer properties in simple electrolytes. *Jour. Coll. Interface Sci. 63*: 480-499.

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.

de Smedt, F., and P. J. Wierenga. 1979. Mass transfer in porous media with immobile water. *Jour. Hydrol. 41*: 59-67.

de Smedt, F., and P. J. Wierenga. 1984. Solute Transfer Through Columns of Glass Beads. *Water Resourc. Res. 20*: 225-232.

Department of Energy (DOE). 1988. *Site Characterization Plan: Yucca Mountain Site, Nevada Research and Development Area, Nevada*. Office of Civilian Radioactive Waste Management (OCRWM), DOE/RW-0199. Washington, D. C.

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.

Domenico, P. A., and F. W. Schwarz. 1990. *Physical and Chemical Hydrogeology*. John Wiley and Sons, New York.

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

Dzombak, D. A., and F. M. M. Morel. 1986. Sorption of cadmium on hydrous ferric oxide at high sorbate/sorbent ratios: Equilibrium, kinetics, and modelling. *Jour. Coll. Interface Sci. 112*: 588-598.

Ebinger, M. H., E. H. Essington, E. S. Gladney, B. D. Newman, and C. L. Reynolds. 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, New Mexico.

Environmental Protection Agency (EPA) (40 CFR Part 191). 1991. *Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes*. Title 40, Protection of Environment, Part 191, U. S. Government Printing Office, Washington, D. C.

Evans, D. D., and C. Huang. 1983. Role of desaturation on transport through fractured rock. in: J. W. Mercer, P. S. C. Rao, and I. W. Marine (eds.). *Role of the Unsaturated Zone in Radioactive and Hazardous Waste Disposal*. Ann Arbor Science, Ann Arbor, Michigan.

Finnegan, D. L., and F. A. Bryant. 1987. *Methods for Obtaining Sorption Data from Uranium-Series Disequilibria*. Los Alamos National Laboratory, LA-11162-MS, Los Alamos, New Mexico.

Freeze, R. A., and J. A. Cherry. 1979. *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Fuentes, H. R., and W. L. Polzer. 1987. *Interpretive Analysis of Data for Solute Transport in the Unsaturated Zone*. LA-10817-MS, NUREG/CR-4737. Los Alamos National Laboratory, Los Alamos, New Mexico.

Fuentes, H. R., W. L. Polzer, E. H. Essington, and B. D. Newman. 1989. *Characterization of Reactive Tracers for C-Wells Field Experiments I: Electrostatic Sorption Mechanism, Lithium*. LA-11691-MS. Los Alamos National Laboratory.

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.

Garrels, R. M., and C. L. Christ. 1965. *Solutions, Minerals, and Equilibria*. Freeman, Cooper and Company, San Francisco, California.

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. Am. Jour. 41*: 665-671.

Giese, R. F., Jr., and P. M. Costanzo. 1986. Behavior of water on the surface of kaolin minerals. in: J. A. Davis and K. F. Hayes (eds.). *American Chemical Society Symposium Series 323: Geochemical Processes at Mineral Surfaces*. American Chemical Society, Washington, D. C.

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 Resourc. Res. 20*: 369-378.

Goldberg, S., H. S. Forster, and E. L. Heick. 1991. Flocculation of illite/kaolinite and illite/montmorillonite mixtures as affected by sodium adsorption ratio and pH. *Clays Clay Minerals 39*: 375-380.

Green, R. T., and F. T. Dodge. 1991. Thermohydrology, Ch. 3. in: *Report on Research Activities for the Quarter January 1 Through March 31, 1991*. Center for Nuclear Waste Regulatory Analyses, CNWRA 91-01Q. San Antonio, Texas.

Gschwend, P. M. (abs.) 1990. Measurement and characterization of colloids in groundwater. *Soil Sci. Soc. Am. 82nd Annual Meeting 123*.

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

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

Hayes, K. F., G. Redden, W. Ela, and J. O. Leckie. 1989. *Application of Surface Complexation Models for Radionuclide Adsorption: Sensitivity Analysis of Model Input Parameters*. U. S. Nuclear Regulatory Commission, NUREG/CR-5547 PNL-7239. Washington, D. C.

Hem, J. D. 1985. *Study and Interpretation of the Chemical Characteristics of Natural Water*. U.S. Geological Survey, Water-Supply Paper 2254. Alexandria, Virginia.

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. Coll. Interface Sci. 133*: 91-104.

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. Coll. Interface Sci. 133*: 105-117.

Hodges, S. C., and G. C. Johnson. 1987. Kinetics of sulfate adsorption and desorption by Cecil soil using miscible displacement. *Soil Sci. Soc. Am. Jour. 51*: 323-331.

Honeyman, B. E. 1984. *Cation and Anion Adsorption at the Oxide/Solution Interface in Systems Containing Binary Mixtures of Adsorbents: An Investigation of the Concept of Additivity*. Ph.D. Dissertation, Stanford University. Stanford, California.

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.

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.

Jardine, P. M., and D. L. Sparks. 1984. Potassium-calcium exchange in a multireactive soil system: II. Thermodynamics. *Soil Sci. Soc. Am. Jour. 48*: 45-50.

Jennings, A. A., and D. J. Kirkner. 1984. Instantaneous equilibrium approximation analysis. *Jour. Hydraul. Div. Am. Soc. Civ. Eng. 110*: 1700-1717.

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

Jury, W. A., H. El Abd, and T. Collins. 1983. Field scale transport of nonadsorbing and adsorbing chemicals applied to the soil surface. in: D. M. Nielsen and M. Curl (eds.). *Proceedings of the National Water Well Association/U. S. Environmental Protection Agency Conference on Characterization and Monitoring of the Vadose (Unsaturated) Zone*. Las Vegas, Nevada.

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

Kent, D. B., V. S. Tripathi, N. B. Ball, J. O. Leckie, and M. D. Siegel. 1988. *Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments*. Sandia National Laboratory. NUREG/CR-4807, SAND86-7175. Washington, D.C.

Kerrisk, J. F. 1987. *Groundwater Chemistry at Yucca Mountain, Nevada, and Vicinity*. Los Alamos National Laboratory, LA-10929-MS. Los Alamos, New Mexico.

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.

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 Resourc. Res. 18*: 1633-1675.

Ku, T. L., S. Luo, B. W. Leslie, and D. E. Hammond. 1991. Decay-series disequilibria applied to the study of rock-water interaction and geothermal systems. in: M. Ivanovich and R. S. Harmon (eds.). *Uranium-Series Disequilibrium: Application to Environmental Problems*, 2nd edition, Oxford Univ. Press.

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.

Langmuir, D. 1978a. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta 42*: 547-569.

Langmuir, D. 1978b. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. in: M. M. Kimberley (ed.). *Short Course in Uranium Deposits: Their Mineralogy and Origin*. Mineralogical Association of Canada, Toronto, Ontario: 17-55.

Laryea, D. B., D. E. Elrick, and M. J. L. Robin. 1982. Hydrodynamic dispersion involving cationic adsorption during unsaturated transient water flow in soil. *Soil Sci. Amer. Jour. 46*: 667-671.

Leslie, B. W. (abs.) 1991. Modeling water-rock interactions using uranium-series isotopes: A critical assessment and examples from active continental geothermal systems. *7th Int. Symp. Water-Rock Interaction*. (in submission).

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.

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

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.

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.

MacNaughton, M. G. 1973. *Adsorption of Mercury(II) at the Solid-Water Interface.* Ph.D. Dissertation, Stanford University. Stanford, California.

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

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).*

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

McCarthy, J. F. (abs.) 1990. Subsurface transport of contaminants: Role of mobile colloidal particles. *Agronomy Abstracts, Soil Sci. Soc. Am. 82nd Annual Meeting, San Antonio, Texas*: 233-234.

McKinley, I. G., and W. R. Alexander. 1991. Constraints on the applicability of in situ distribution coefficient values. *Jour. Environ. Radiochem. (in press).*

Means, J. L., D. A. Crerar, M. P. Borcsik, and J. O. Duguid. 1978. Adsorption of Co and selected actinides by Mn and Fe oxides in soils and sediments. *Geochim. Cosmochim. Acta 42*: 1763-1773.

Means, J. L., A. S. Maest, and D. A. Crerar. 1983. *Organic Geochemistry of Deep Ground Waters and Radionuclide Partitioning Experiments Under Hydrothermal Conditions.* Office of Nuclear Waste Isolation, ONWI-448. Columbus, Ohio.

Meijer, A. 1990. *Yucca Mountain Project Far-Field Sorption Studies and Data Needs.* LA-11671-MS/UC-510. Los Alamos, New Mexico.

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

Meyer, R. E., W. D. Arnold, J. G. Blencoe, G. D. O'Kelley, R. I. Case, and J. F. Land et al. 1986. *Progress in Evaluation of Radionuclide geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Semi-Annual Report for October 1985 - March 1986.* U.S. Nuclear Regulatory Commission, NUREG/CR-4708. Washington, D. C.

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

Miklavic, S. J., and B. W. Ninham. 1990. Competition for adsorption sites by hydrated ions. *Jour. Coll. Interface Sci. 134*: 305-311.

Montazer, P., and W. E. Wilson. 1984. *Conceptual Hydrologic Model of Flow in the Unsaturated Zone, Yucca Mountain, Nevada.* U. S. Geological Survey Water-Resources Investigations, USGS-WRI-84-4345. Lakewood, Colorado.

Mulla, D. J. 1986. Simulating liquid water near mineral surfaces: Current methods and limitations. in: J. A. Davis and K. F. Hayes (eds.). *American Chemical Society Symposium Series 323: Geochemical Processes at Mineral Surfaces.* American Chemical Society, Washington, D. C.

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

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.

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.

Murphy, W. M. 1989. *Constraints on the Chemistry of Groundwater in the Unsaturated Zone at Yucca Mountain, Nevada, and in the Proposed Repository at that Site.* Center for Nuclear Waste Regulatory Analyses, Draft Report. San Antonio, Texas.

Murphy, W. M., R. T. Green, and G. W. Wittmeyer. (abs.) 1991. Thermodynamic and kinetic analysis of the retardation of ^{14}C transport under nonisothermal conditions in the proposed high-level waste repository at Yucca Mountain, Nevada. *Third International Conference on Chemistry and Migration Behavior of Actinides in the Geosphere.* Jerez de la Frontera, Spain. 272-273.

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

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.

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.

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

Nuclear Regulatory Commission (NRC) (10 CFR Part 60). 1991. *Disposal of High-Level Radioactive Wastes in Geologic Repositories*. Title 10, Energy, Part 60, U. S. Government Printing Office, Washington, D. C.

Nuclear Waste Policy Act as Amended. 1987. Public Law 100-203, Title 42, Section 10101, United States Code.

Ogard, A. E., and J. F. Kerrisk. 1984. *Groundwater Chemistry Along Flow Paths Between a Proposed Repository Site and the Accessible Environment*. Los Alamos National Laboratory, LA-10188-MS. Los Alamos, New Mexico.

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.

Pabalan, R. T. 1991. Nonideality effects on the ion exchange behavior of the zeolite mineral clinoptilolite. T. Abrajano, Jr. and L. Johnson (eds.) *Scientific Basis for Nuclear Waste Management XIV*. Materials Research Society, Pittsburgh, PA 559-567.

Pabalan, R. T., J. D. Prikryl, and P. M. Muller. (abs.) 1991. Experimental study of U^{6+} sorption on the zeolite mineral clinoptilolite. *7th Int. Symp. Water-Rock Interaction*. (in submission).

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

Parks, G. A. 1990. Surface energy and adsorption at mineral/water interfaces: An introduction. in: Hochella, Jr. and A. F. White (eds.) *Reviews in Mineralogy: Volume 23. Mineral-Water Interface Geochemistry*. Mineralogical Society of America, Washington, D. C.

Payne, T. E., J. A. Davis, and T. D. Waite. 1990a. Modelling 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.

Payne, T. E., T. D. Waite, J. A. Davis, and K. Sekine. 1990b. Experimental Study of Uranium Sorption. in: P. Duerden (ed.). *Alligator Rivers Analogue Project Progress Report (June 1, 1990 to August 31, 1990)*. Austral. Nucl. Sci. Technol. Organization: 139-160.

Payne, T. E., and T. D. Waite. 1991. Surface complexation modelling of uranium sorption data obtained by isotope exchange techniques. *Radiochim. Acta 52/53*: 487-493.

Pearcy, E. C., and W. M. Murphy. 1991. *Geochemical Natural Analogs Literature Review*. Center for Nuclear Waste Regulatory Analyses, CNWRA 90-008. San Antonio, Texas.

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.

Peters, R. R., and E. A. Klavetter. 1988. A continuum model for water movement in an unsaturated fractured rock mass. *Water Resourc. Res. 24*: 416-430.

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

Pruess, K., J. S. Y. Wang, and Y. W. Tsang. 1990. On thermohydrologic conditions near high-level nuclear wastes emplaced in partially saturated fractured tuff. 1. Simulation studies with explicit consideration of fracture effects. *Water Resour. Res. 26*: 1235-1248.

Raker, S. L., and R. L. Jacobson. 1987. *Chemistry of Groundwater in Tuffaceous Rocks, Central Nevada*. State of Nevada Agency for Nuclear Projects/Nuclear Waste Project Office, NWPO-TR-006-87.

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. Jour. 52*: 641-647.

Richards, L. A. 1931. Capillary conduction of liquids in porous mediums. *Physics 1*: 318-333.

Rimstidt, J. D., W. D. Newcomb, and D. L. Shettel, Jr. 1989. A vertical thermal gradient experiment to simulate conditions in vapor dominated geothermal systems, epithermal gold deposits, and high level radioactive repositories in unsaturated media. in Miles (ed.) *Water-Rock Interaction*. Baikema, Rotterdam.

Robert, M., and M. Terce. 1989. Effect of gels and coatings on clay mineral chemical properties. in: B. Bar-Yosef, N. J. Barrow, and J. Goldshmid (eds.) *Inorganic Contaminants in the Vadose Zone. Ecological Studies, Volume 74*. Springer-Verlag, New York.

Roth, K., W. A. Jury, and H. Flühler. (abs.) 1990. Solute transport through unsaturated soil: The field evidence. *Agronomy Abstracts, Soil Sci. Soc. Am. 82nd Annual Meeting, San Antonio, Texas*: 218.

Rundberg, R., D. Janecky, and A. Mitchell. 1987. *Anion Exclusion in Yucca Mountain Tuff*. Los Alamos National Laboratory, LANL Milestone No. 313. Los Alamos, New Mexico.

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.

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.

Sagar, B., and G. Wittmeyer. 1991. Performance Assessment Research, Ch. 8, Phase 2 INTRAVAL project: Las Cruces Trench solute transport modeling study, Plot 2, Experiment A. in: *Report on Research Activities for the Quarter January 1 Through March 31, 1991*. Center for Nuclear Waste Regulatory Analyses, CNWRA 91-01Q. San Antonio, Texas.

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.

Sears, S. O., and D. Langmuir. 1982. Sorption and mineral equilibria controls on moisture chemistry in a C-horizon soil. *Jour. Hydrol. 56*: 287-308.

Selim, H. M., J. M. Davidson, and R. S. Mansell. 1976. Evaluation of a 2-site adsorption-desorption model for describing solute transport in soils. in: *1976 Summer Computer Simulation Conference*, (Simulation Councils, Inc., La Jolla, CA, 1976): 444-448.

Selim, H. M., R. S. Mansell, L. A. Gaston, H. Fluhler, and R. Schulin. 1990. *Field-Scale Solute and Water Transport Through Soil.* K. Roth, H. Fluhler, W. A. Jury, and J. C. Parker (eds.). Prediction of cation transport in soils using cation exchange reactions, Birkhauser Verlag, Basel, Switzerland: 223-238.

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.* PNL, PNL-7285. Richland, Washington.

Serne, R. J., and J. F. Relyea. 1982. *The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program.* Pacific Northwest Laboratory, PNL-3997. Richland, Washington.

Shainberg, I. (abs.) 1990. Dispersion processes in semi-arid region soils. *Agronomy Abstracts, Soil Sci. Soc. Am. 82nd Annual Meeting, San Antonio, Texas*: 237.

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.

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 for United States Department of Energy, SAN89-2387, UC-721. Albuquerque, New Mexico.

Siyag, R. S., R. Pal, and S. R. Poonia. 1983. Water transmission of unsaturated soil samples in relation to mixed Na-(Ca + Mg) solutions. *Geoderma 31*: 107-116.

Skopp, J., W. R. Gardner, and E. J. Tyler. 1981. Solute movement in structured soils: Two-region model with small interaction. *Soil Sci. Soc. Am. Jour. 45*: 837-842.

Smith, R. W., and Jenne, E. A. 1988. *Compilation, Evaluation, and Prediction of Triple-Layer Model Constants for Ions on Fe(III) and Mn(IV) Hydrous Oxides.* Pacific Northwest Laboratory, PNL-6754/UC-11. Richland, Washington.

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

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. Res.* *22*: 255-262.

Stumm, W., and J. J. Morgan. 1981. *Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters*. John Wiley and Sons, New York.

Suarez, D. L., J. D. Rhoades, R. Lavado, and C. M. Grieve. 1984. Effect of pH on saturated hydraulic conductivity and soil dispersion. *Soil Sci. Soc. Amer. Jour.* *48*: 50-55.

Thomas, K. 1987. *Summary of Sorption Measurements Performed with Yucca Mountain, Nevada, Tuff Samples and Water from Well J-13*. Los Alamos National Laboratory, LA-10960-MS. Los Alamos, New Mexico.

Thompson, J. L. (comp.). 1985. *Laboratory and Field Studies Related to the Radionuclide Migration Project, October 1, 1983-September 30, 1984*. Los Alamos National Laboratory, LA-10372-PR. Los Alamos, New Mexico.

Thompson, J. L., and K. Wolfsberg. 1979. *Applicability of Microautoradiography to Sorption Studies*. Los Alamos National Laboratory, LA-7609-MS. Los Alamos, New Mexico.

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

Travis, B. J., and H. E. Nuttall. 1987. *Two-Dimensional Numerical Simulation of Geochemical Transport in Yucca Mountain*. Los Alamos National Laboratory, LA-10532-MS. Los Alamos, New Mexico.

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

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. *Radiochim. Acta* *52/53*: 141-145.

Tripathi, V. S. 1984. *Uranium(VI) Transport Modeling: Geochemical Data and Submodels*. Ph.D. Dissertation, Stanford University. Stanford, California.

Turner, D. R. 1991. *Sorption Modeling for High-Level Waste Performance Assessment: A Literature Review*. Center for Nuclear Waste Regulatory Analyses, CNWRA 91-011. San Antonio, Texas.

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

Valocchi, A. J., P. V. Roberts, G. A. Parks, and R. L. Street. 1981a. Simulation of the transport of ion-exchanging solutes using laboratory-determined chemical parameter values. *Ground Water 19*: 600-607.

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.

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

van der Zee, S. E. A. T. M., and G. H. Bolt. 1991. Deterministic and stochastic modeling of reactive solute transport. *Jour. Contam. Hydrol. 7*: 75-93.

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.

van Genuchten, M. T., and P. J. Wierenga. 1976. Mass transfer studies in sorbing porous media, 1. Analytical solutions. *Soil Sci. Soc. Am. Jour. 40*: 473-480.

van Genuchten, M. T., and P. J. Wierenga. 1977. Mass transfer studies in sorbing porous media: II. Experimental evaluation with tritium (^3H_2O). *Soil Sci. Soc. Am. Jour. 41*: 272-278.

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

van Genuchten, M. T., P. J. Wierenga, and G. A. O'Connor. 1977. Mass transfer studies in sorbing porous media: III. Experimental evaluation with 2,4,5-T. *Soil Sci. Soc. Am. Jour. 41*: 278-285.

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

White, A. F., H. C. Claassen, and L. V. Benson. 1980. *The Effect of Dissolution of Volcanic Glass on the Water Chemistry in a Tuffaceous Aquifer, Rainier Mesa, Nevada.* U. S. Geol. Survey Water Supply Paper 1535-Q. Washington, D. C.

Wierenga, P. J., L. W. Gelhar, C. S. Simmons, G. W. Gee, and T. J. Nicholson. 1986. *Validation of Stochastic Flow and Transport Models for Unsaturated Soils: A Comprehensive Field Study*. U. S. Nuclear Regulatory Commission, NUREG/CR-4622 PNL-5875. Washington, D. C.

Wikberg, P. 1991. Laboratory Eh simulations in relation to the redox conditions in natural granitic groundwaters. Draft Report, *NEA Sorption Workshop '91*. Interlaken, Switzerland.

Williams, G. M., J. J. W. Higgo, M. A. Sen, W. E. Falck, D. J. Noy, and G. P. Wealthall et al. 1991. The influence of organics in field migration experiments: Part 1. In situ tracer tests and preliminary modelling. *Radiochim. Acta 52/53*: 457-463.

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

Wollenberg, H. A., J. S. Y. Wang, and G. Korbin. 1983. Nuclear waste isolation in the unsaturated zone of arid regions. in: J. W. Mercer, P. S. C. Rao, and I. W. Marine (eds.). *Role of the Unsaturated Zone in Radioactive and Hazardous Waste Disposal*. Ann Arbor Science, Ann Arbor, Michigan.

Yang, I. 1991. Flow and transport through unsaturated rock--Isotopic data from unsaturated-zone drill holes in Pagany Wash, Yucca Mountain, Nevada. in: *Workshop V on Flow and Transport Through Unsaturated Fractured Rocks as Related to High-Level Radioactive Waste*

Yang, I. C., A. K. Turner, T. M. Sayre, and P. Montazer. 1988. *Triaxial-Compression Extraction of Pore Water from Unsaturated Tuff, Yucca Mountain, Nevada*. U. S. Geol. Survey Water-Resources Invest. Rept., USGS-WRI-88-4189.