PREPARATION OF COMPUTER PROGRAMS FOR IMPLEMENTING MATHEMATICAL MODELS OF THE TRANSPORT OF RADIONUCLIDES IN UNSATURATED WELDED TUFF

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Abstract

This report summarizes the progress of Subtask 2.13, Preparation of Computer Programs for Implementing Mathematical Models of the Transport of Radionuclides in Unsaturated Welded Tuff, of FIN A-1266 from June 1988 to March 1989. Initially, a short study to identify important physical and chemical processes for unsaturated-zone transport was done. Next, An evaluation of existing transport codes that simulate unsaturated-zone solute transport was completed. 71 codes were identified and a recommendation to modify the SNLA/NRC transport code NEFTRAN was made and accepted by the NRC Project Manager. Also completed was a strategy to carry out the NEFTRAN modification and identification of potential problems to test the resulting transport code.

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1. BACKGROUND, OBJECTIVES, AND STATUS

This work is being conducted under FIN A-1266, "Development of a Methodology for Performance Assessment of Nuclear Waste Isolation in Alternative Geologic Media." The purpose of FIN A-1266 is to develop a performance assessment methodology for media other than bedded salt. A methodology was initially developed for saturated, fractured basalt formations. Currently, a methodology is being assembled to treat unsaturated, fractured tuff.

To develop a methodology for tuff, techniques must be obtained or developed to simulate ground-water flow and radionuclide transport in unsaturated, fractured media. This report describes Subtask 2.13 of FIN A-1266, which is the preparation of computer programs for implementing mathematical models of radionuclide transport in tuff.

The objectives of Subtask 2.13, are as follows:

1) Locate and obtain existing computer programs that implement the appropriate radionuclide transport models, or (if such programs do not exist),

2) Prepare new computer programs that implement the appropriate models. Note that this step requires the approval of the NRC Project Manager.

The reader should note that the appropriate transport models are those mathematical models that represent the important processes that control radionuclide transport in tuff. These models are usually so complex and must be assessed over very large time and space scales that a numerical solution is needed. In turn, the numerical solutions need to be solved using a computer code and, hence, that is the reason this subtask is based on obtaining an appropriate transport code.

A summary of the objectives for Subtask 2.13 is for SNLA to deliver to NRC a transport code capable of simulating radionuclide transport in unsaturated, fractured media. This code could be one that already exists, if possible, or one that SNLA modifies or develops. To carry out these objectives, it was apparent that the work plan would be separated into two parts. The first part would be an evaluation of existing transport codes and a recommendation, based on the evaluation, to accept an existing code, modify an existing code, or develop a new code. Based on this recommendation, the second part of the work plan would consist of the actual modifications to an existing code or development of a new code.

Based on this overall work plan, the current status of Subtask 2.13 is as follows:

1) The code evaluation has been completed.

2) It has been recommended to modify the SNLA/NRC transport code NEFTRAN. This recommendation has been accepted by the NRC Project Manager.

3) A strategy for modifying NEFTRAN has been formulated.

In the following chapters the strategy employed for the code evaluation and the results obtained are presented. Next, the recommendation to modify NEFTRAN is discussed, along with the plan for the modification.

2. APPROACH FOR CODE EVALUATION

To carry out the first objective for Subtask 2.13, a strategy for conducting a transport code evaluation was formulated. The seven-part plan for the evaluation consisted of the following steps:

Identify important physical and chemical processes for unsaturated zone transport

To provide a basis for the evaluation of transport codes, important physical and chemical processes for unsaturated zone transport were identified. The results of this step are presented in Chapter 3.

Identify test problems

Potential test problems were identified to test and compare existing codes and, if necessary, for verification of a modified or newly developed transport code. These problems consist of analytical solutions and experimental results. The problems selected have a range of values for the transport parameters and cover an assortment of physical and chemical processes identified in Step 1 (e.g., radioactive decay and retardation). The transport problems have been selected based on their relevance to contaminant transport in unsaturated, welded tuff and to test salient features associated with disposal of HLW. The results of this step are presented in Chapter 4.

Identify transport codes

A list of transport codes was compiled and those codes most likely to model processes identified in Step 1 were to be selected for further evaluation. In chosing between codes with equal capability, availability, documentation, proprietorship, and/or country of origin were to be considered. In the event that none of the codes identified were capable of treating all of the important processes, a recommendation was to be made on whether to modify an existing code or develop an entirely new transport code. The results of this step are presented in Chapter 5.

Describe the codes

If more than one code was selected for further evaluation, a written description of the selected codes was to be compiled. This description was to include the governing transport equations, boundary conditions, assumptions, numerical algorithms, and known limitiations of the codes.

Simulation of the test problems

If more than one code was choosen for further evaluation, every selected test problem was to be simulated, if possible, with each of the selected codes. It was realized that some of the codes may not be able to simulate all the test problems because of the dimensionality of the problems and/or boundary conditions. For instance, a one-dimensional transport code may not be able to simulate a two-dimensional transport problem.

Compare/contrast the code predictions with the test problem results

If more than one code was chosen for further evaluation, the code predictions were to be compared or contrasted to the analytical solutions and to the experimental results. Differences between predictions and solutions/results were to be identified and the causes of the differences explained. Examples of numerical dispersion and overshoot were to be recognized along with reasons they could not be eliminated. Computational time was also going to be documented.

Recommend on whether to accept an existing code, modify an existing code, or develop a new code

The performance of each selected code was to be summarized and a recommendation on whether to accept one of the existing codes, modify one of the existing codes, or develop a new code was to be made based on actual predictions of each code compared to test problem results.

3. IMPORTANT PHYSICAL AND CHEMICAL PROCESSES FOR UNSATURATED ZONE TRANSPORT

The main focus of this chapter is on the transport of radionuclides through the unsaturated zone. Initially, this chapter discusses the governing equation for solute transport in ground water. Each term in the equation, along with the possible corresponding transport mechanism(s), is then examined. Included in these discussions are liquid-phase transport in both fractures and matrix as well as vapor-phase transport. Finally, the relative importance of each mechanism is assessed. The reader should note that the main focus of this chapter will be on processes associated with solute transport and specific modeling of each process will not be discussed.

Governing Equation

A governing equation for solute transport is based on solute conservation of mass. A qualitative statement of the conservation of mass equation is given as:

$$\begin{array}{cccccccc} \text{rate of} & & \text{rate of} & & \text{rate of} & & \text{loss or} & \\ \text{accumulation} & = & \text{solute} & - & \text{solute} & \pm & \text{gain of} & (1) \\ \text{of solute} & & \text{in} & & \text{out} & & \text{solute} & \end{array}$$

The term on the left hand side (LHS) of Eq. 1 is the rate of accumulation of solute. This term indicates whether the rate of change of solute mass is under steady-state or transient conditions. The first two terms on the right hand side (RHS) of Eq. 1, the rate, or flux, of solute are controlled by physical processes. The last term on the RHS, the loss or gain of the solute mass, is commonly referred to as the source/sink term. This source/sink term is often associated with chemical processes (e.g., radioactive decay, sorption) and the physical process of matrix diffusion. When this statement is put into mathematical form and combined with expressions for the flux of solute and loss or gain of solute, the resulting differential equation is called the convective-dispersion equation.

When this conservation-of-mass statement is transformed into a differential equation, a continuum is assumed. However, it should be noted that the continuum approach has not yet been shown to be valid for unsaturated, fractured media. The reader is referred to Bear (1979) for a detailed discussion of the continuum approach and the assumptions required to use it. For a more detailed discussion and presentation of the convective-dispersion transport equation in ground water the reader is referred to Freeze and Cherry (1979). Several other references present a more general discussion of the conservation-of-mass equation (e.g., Bird and others, 1960; Welty and others, 1969).

When applying the governing equation for transport to a particular system, properties of that system must be accounted for. For geologic media there are several characteristics, both physical and chemical, that need to be considered. The physical characteristics consist of whether the medium is heterogeneous or homogeneous, isotropic or anisotropic, saturated or unsaturated, and fractured or unfractured. The chemical characteristics include the chemical composition of the rock formation, the chemical composition of the ground water and the chemical interaction between the geologic medium, the ground water, and the solute being transported. For the analysis presented here, unsaturated, fractured tuff is the geologic medium of interest. However, the reader should also note that, although the geologic medium is in the unsaturated zone, local saturation conditions can also occur (e.g., perched water tables).

The primary mode of transport for solutes (radionuclides) may be via ground-water movement through the geologic medium. Depending on the temperature and pressure, this water will be in either the vapor and/or liquid phase. Consequently, vapor-phase transport must be considered. For this report the term ground-water flow will indicate both liquid and vapor-water movement. Initially, each physical and chemical process will be addressed in general terms and then the discussion will be extended to the system of concern (unsaturated, fractured tuff).

Physical Processes

The physical processes that govern the flux of solute, the first two terms on the RHS of the governing equation for solute transport, are convection and hydrodynamic dispersion. Transport by the bulk motion of the flowing fluid is known as convection. The average rate of solute transport by convection alone is equal to the average linear velocity of the flowing fluid times the concentration gradient in the direction of flow. Hydrodynamic dispersion is the tendency of the solute to spread out from the path it is expected to follow due to convection or, in other words, is the macroscopic outcome of the actual movement of individual solute particles (Bear, 1972). The result is dilution of the solute. Bear states that hydrodynamic dispersion includes two processes. These processes are mechanical dispersion and molecular diffusion. The reader should note that although Bear defines hydrodynamic dispersion in this manner, mechanical dispersion and molecular diffusion are two distinctly different mechanisms. However, Bear further states that the separation between the two processes is artificial.

The hydrodynamic dispersion process is represented in the governing equation by a hydrodynamic dispersion coefficient. This coefficient is often defined as:

$$D = D_m + \alpha V_w \tag{2}$$

Where D_m is the molecular diffusion coefficient, α is the dispersivity which is a function of the porous medium, and V_w is the average velocity of the ground water. The first term represents the molecular diffusion part of the hydrodynamic dispersion process, whereas the second term represents the mechanical dispersion mechanism. Although this equation indicates that the dispersion coefficient is only a function of velocity, recent studies (Codell and Duguid, 1983; Gelhar, 1986) indicate that the scale of the experiment also influences the dispersion coefficient. More specifically, the dispersivity is probably not only a function of the porous medium, but also of length scale and velocity.

The driving force for mechanical dispersion is mechanical mixing. Mechanical mixing occurs during convection and, when viewed on the microscopic level, is caused by the roughness of pore surfaces, the differences in pore sizes along the flow paths, and the branching of pore channels. Molecular diffusion is solute particle (ionic or molecular constituents) movement in the direction of a concentration gradient. This movement is due to the thermal-kinetic energy of the solute particles (i.e., random motion). Solutes will tend to move outward from a concentrated source even in the absence of fluid movement. Diffusion is the dominant process of hydrodynamic dispersion at extremely low velocities and mechanical dispersion dominates at high velocities. The dispersive process causes spreading of the solute in the longitudinal flow direction as well as directions transverse to flow. It has been shown (Freeze and Cherry, 1979; Sahimi and others, 1983) that longitudinal dispersion is always greater than transverse dispersion for a flowing fluid. Consequently, the dispersion process is anisotropic.

Convection is more complicated when more than one phase is present, as is the case for radionuclide transport in the unsaturated zone (the phases being air, liquid water, and, possibly, water vapor). It is conceivable for convection to transport the chemical species in both the gas and liquid phases. The bulk movement (i.e., average linear velocity) in the gas and liquid phase is not necessarily the same. Also, the flow paths of the two phases could be different and this lends to complicate the convection process for unsaturated zone transport.

Dispersion is also more complicated when more than one fluid phase is present. The presence of each phase can deny pore space to the other phase and, thus, alter flow and transport paths significantly. As saturation decreases for a phase, that phase ultimately loses its continuity because of capillary instabilities. Sahimi and others (1983) indicate that, for two immiscible fluids, the distribution of phases in the pore space is dictated by the pore-space morphology, the capillary and viscous forces at the interfaces, and the stability of the shape the interfaces assume in response to these capillary and viscous forces. Other factors that can influence the distribution of the two phases are the saturations, volume fractions, and the saturation history's (i.e., the way the saturations were reached). Sahimi and others only consider the case where one phase strongly wets the pore walls (i.e., the contact angle is much less than 90 degrees) and the other is non-wetting. In this case, the saturation history is important because if a saturation level was reached during drainage, the wetting phase preferentially occupies the larger pores. If the saturation level was obtained during imbibition, the wetting phase preferentially resides in the smaller pores. It has also been found by Sahimi and others, using a network model, that in two-phase flow, longitudinal dispersion in a given phase increases greatly as the saturation of that phase approaches its percolation threshold. Transverse dispersion also increases but more slowly. Smiles and others (1981) have given laboratory evidence that, for transport in the unsaturated zone, the hydrodynamic dispersion coefficient (both longitudinal and transverse) is a function of water content.

Convection in fractured geologic media is more complicated compared to unfractured media because of the presence of both a fracture system and a matrix system. Ground water in the unsaturated zone is preferentially drawn into the smallest pores due to surface tension forces. This leads to greater constrictivity and lower permeability in the matrix compared to the fractures. Matrix potential data from the Topopah Spring Member of the Paintbrush Tuff (Mroz and others, 1983) indicate that at saturations below 50, a pressure of -10 bars would be required to begin removing water from pores within the tuff matrix. Travis and others (1984a, 1984b) conducted numerical simulations and concluded that fracture flow in the unsaturated zone is unlikely, due to the high matrix potential of the welded tuff formation. This conclusion is based on many assumptions; including an assumed infiltration rate, an assumed crack length and the assertion that flux due to slug flow will be higher than that associated with film flow. These assumptions are not substantiated by laboratory or field data and, therefore, fracture flow cannot be ruled out as a possible path for radionuclide migration in unsaturated, fractured rocks.

Hydrodynamic dispersion in fractured geologic media is also more complicated compared to unfractured media. Fractured geologic media are highly anisotropic with respect to the orientation and frequency of fractures and, hence, dispersion becomes complex. Little is known about hydrodynamic dispersion in fractured media at this time, but it is possible that dispersion of solutes during transport through fractured rock cannot be described by the equations used for unfractured materials. For example, it is conceivable that the connectivity of the fracture network would have a significant influence on the magnitude of the dispersive effects. Evans and Nicholson (1987) propose that for a fractured rock mass the overall hydrodynamic dispersion coefficient is some functional relationship of the coefficients for the matrix and the fracture system.

As indicated earlier, at relatively low flow velocities, molecular diffusion will dominate. For unsaturated zone transport, molecular diffusion can occur in both the liquid and gas phase. When a fractured geologic medium is considered, molecular diffusion within the fractures, matrix or between the fracture/matrix system can occur.

Diffusion within the unfractured matrix will be affected by resistance from pore constrictions and branching pore channels. Because of these resistances, the path of the solute particles becomes tortuous. This tortuous path results in an overall longer diffusion length when diffusion within the unfractured matrix is compared to bulk diffusion. Also, there is a smaller cross-sectional area for diffusion to occur as compared to bulk diffusion. These characteristics that will decrease diffusion due to the porous medium are conventionally accounted for by using an effective diffusivity, D_e, which is usually defined as:

$$D_e = (\epsilon D_m)/ \tau \tag{3}$$

where ϵ is the porosity of the porous medium, D_m is the bulk molecular diffusion coefficient, and τ is the tortuosity factor.

Another transport mechanism that may occur with diffusion in the unfractured matrix is configurational diffusion. Configurational diffusion occurs when the size of the diffusing molecule is on the same order as the pore size (Froment and Bischoff, 1979). These conditions can occur when radionuclides diffuse into zeolites and clays that are contained in the welded tuff matrix. Configurational diffusion is very complex because information about the force fields of the molecules making up the pore walls and their interactions with the diffusing molecules is needed. As a result of this complexity, no comprehensive theory has been established for configurational diffusion.

Since fracture flow in unsaturated, fractured tuff cannot be discarded at this time, diffusion from the bulk fluid in the fracture to the matrix, which is commonly called matrix diffusion, should also be considered. This transport mechanism is often classified as a physical retardation process. This is because, when the solute diffuses into the matrix from the fracture, its migration to the accessible environment is delayed. In a sense, the rock matrix could act as a storage volume; thus, reducing the concentration of radionuclides discharged. The driving force for matrix diffusion is a concentration gradient, and net diffusion into the rock matrix will occur until the matrix concentration equals the fracture concentration (i.e., at equilibrium, net diffusion equals zero). Consequently, after the solute in the fracture passes, the solute in the matrix may diffuse back into the fracture.

When considering transport of solutes from the fracture to the porous matrix, the mass flux at the fracture/matrix interface must also be accounted for. This is often referred to as film-type mass transfer resistance (Satterfield, 1970) and a mass-transfer coefficient is needed to describe the boundary condition at the fracture/matrix interface. Consequently, mass transfer of a radionuclide from bulk flow in the fracture into the matrix becomes a two-step process (film mass transfer followed by diffusion into the matrix). The slower of these two steps controls the overall rate of mass transfer. The relative time scale for each step should be estimated and compared to the time scale of flow. Local equilibrium may be assumed if the time scale of a particular step is significantly shorter than the step preceding and following it. Hence, external mass transfer resistance may be insignificant in the overall mass transfer of radionuclides to the matrix from the fracture.

Chemical Processes

There are many chemical processes that can result in the loss or gain of the solute (the last term on the RHS of Eq. 1). These chemical processes can occur in the liquid phase, gas phase, or both phases simultaneously for unsaturated-zone transport. For fractured media, the chemical reactions can take place in both the fracture system and porous matrix.

When considering solute transport in a ground-water system, one of the most significant chemical processes that occurs is sorption. Sorption, for this study, will be considered a general (net) term for adsorption-desorption reactions. Adsorption is the transfer of solute mass from the ground water to the solid part of the geologic medium. Desorption is the opposite phenomenon. Solute species adsorb to the solid by forming bonds with molecules on the solid surface. The strength of these bonds and kinetics of the surface reactions depend on the size and charge of both solute and surface species, the degree of saturation of surface bonding sites, the acidity (pH), the oxidation/reduction potential (Eh or pE), and the temperature and pressure of the system (Morel, 1983).

Adsorption can occur by two different processes: physical adsorption and chemical adsorption. Physical adsorption is exothermic, and the heat of adsorption, being on the order of 1 to 15 kcal/mol, is relatively small (Fogler, 1986). With physical adsorption, the forces of attraction between the adsorbed atoms or molecules and the solid surface are weak (i.e., van der Waals forces). Consequently, physical adsorption is often considered a reversible process. Physical adsorption can also occur between the molecules adsorbed on the surface and other molecules; thus, multi-layers of adsorbed molecules can be formed. For chemical adsorption, the adsorbed atoms or molecules are held to the surface by valence forces. These valence forces are of the same type as those between bonded atoms in molecules and the heats of adsorption are generally of the same magnitude, 10 to 100 kcal/mole, as the heat of a chemical reaction (Fogler, 1986). Chemical adsorption, therefore, is often considered an irreversible reaction. Chemical adsorption occurs only with surface atoms; consequently, a monolayer of adsorbed molecules is formed. Similar to physical adsorption, chemical adsorption is an exothermic process.

Sorption reactions are normally very rapid relative to the velocity of the flowing fluid. The contact time for sorption is controlled by the ground-water velocity and the apparent diffusivity, D_a (Neretnieks, 1980). The apparent diffusivity takes into account the decrease in effective diffusivity due to sorption, but treats the nature of the process (i.e., bulk diffusion) the same. A similar parameter, the effective diffusivity, D_e, has been discussed previously. It should be noted that D_a is a function of D_e and is defined by Neretnieks as:

$$D_a = \frac{D_e}{K_a \rho_p} \tag{4}$$

Where K_a is the sorption ratio, which will be discussed subsequently, and ρ_p is the bulk density of the rock.

The amount of solute that is adsorbed by the solid is a function of the concentration of the solute in solution. Consequently, the distribution of solutes between the liquid and solid phases in a porous medium is often analyzed from a graphical plot of amount adsorbed versus concentration. Because the laboratory experiments used to obtain these plots are conducted at a constant temperature, the plots are called sorption isotherms. Sorption isotherms often exhibit a hysteresis effect (i.e., the isotherm is different depending on whether adsorption or desorption is occurring).

Another way that the sorption process is described, is by means of a distribution coefficient (K_d). There are several assumptions that are made when using distribution coefficients. These assumptions include instantaneous and reversible adsorption and desorption (equilibrium), linear sorption isotherms, and single-valued sorption isotherms (i.e., no hysteresis effect) (Rasmussen and Evans, 1985). If the solutes of interest in ground-water studies meet these requirements, then distribution coefficients become a convenient way of describing the division of the solute between the liquid solution and the solid. If solute adsorption/desorption cannot be described by equilibrium relations (i.e., K_d's), then information on the rates of the sorption reactions must be known or empirical sorption ratios may be utilized.

A sorption ratio is a measurement of a species' distribution between phases under specific conditions, although no approach to equilibrium is assumed. In other words, reversible equilibrium is not achieved. If equilibrium were established, sorption ratios would equal distribution coefficients. Different conditions (e.g., oxidizing, reducing, adsorbing, desorbing) can produce different sorption ratios for the same system. Many studies (Johnstone and Wolfsberg, 1980; Tien and others, 1983; and Daniels and others, 1982) report data as sorption ratios. These studies were done on tuffaceous rock and show large positive values of sorption ratios. This indicates that sorption is a mechanism that could be critical in modeling radionuclide transport in unsaturated, fractured tuff. Daniels and others also conclude that sorption on tuff is nonlinear, that sorption ratios from desorption experiments are higher than those from adsorption experiments and that lack of agreement between experimental and theoretical models suggest a more complex sorption mechanism than simple linear sorption. Brookins (1984) concludes that sorption ratios for chemically reducing conditions are larger than values for oxidizing conditions. This is relevant for the unsaturated zone because Daniels and others report that water in unsaturated tuff is oxidizing.

Values for distribution coefficients or sorption ratios are normally reported as milliliters per gram (i. e., mass of solute on the solid per unit mass of solid per concentration of solute in solution) and range from values near zero to 10^3 ml/g or greater (Freeze and Cherry, 1979). Conservative solutes are solutes which have distribution coefficients or sorption ratios close to zero. This means that the average velocity of the solutes is approximately the same as the average ground-water velocity and do not adsorb appreciably onto the solid. Non-conservative solutes have non-zero distribution coefficients or sorption ratios. This means that the average velocity of the solutes is lower than the average ground-water velocity due to adsorption onto the solid.

For the most part, K_d's are measured in batch reactors and these conditions may not be indicative of in-situ ground water conditions for two reasons. First, in a ground-water system, sorption is related to the velocity of the ground water (Neretnieks, 1980) and, therefore, in-situ conditions are dynamic. Conversely, in a batch reactor conditions are static. Second, when using a batch system to measure K_d's, the rock sample is crushed. By crushing the sample, the surface area per unit volume for sorption to occur on may be significantly different than that of the in-situ rock mass.

When considering radionuclide transport in fractured, unsaturated media there are several aspects of K_d's or sorption ratios that must be addressed. For unsaturated-zone transport, it has been proposed that the distribution coefficient or sorption ratio will be a function of moisture content (Millington and Quirk, 1959; Dykhuizen, 1987). This functional relationship is due to the liquid phase not having access to all adsorption sites because of the presence of the gas phase. The complex relationship between sorption and saturation will depend on parameters such as groundwater chemistry, radionuclide, pore shape and size distribution, fracture shape and size distribution, and the distribution of liquid and gas phases in the geologic medium. For fractured porous media, as suggested by Burkholder (1976), it may be more appropriate to express the distribution coefficient on a per-unit-fracture-surface-area basis as opposed to the per-unit-mass basis for porous media. This is reasonable because sorption reactions are more closely related to the surface area of the medium than the mass. Fracture surface areas are often approximated assuming a planar fracture surface but, due to surface roughness and irregularities, the actual surface area with which the radionuclides interact could be significantly higher than that representing this planar approximation. This assumption is not necessarily harmful in that, by assuming a planar surface, a conservative estimate of sorption is achieved.

Another aspect of sorption that has been found to be very important in terms of radionuclide discharge (Bonano and others, 1989, Neretnieks, 1980) is matrix diffusion. Diffusion of the solute from the fracture into the porous matrix can cause sorption to occur on a much larger surface area than if the solute stayed entirely in the fracture. Therefore, when considering fracture flow, solute transport may be retarded due to both matrix diffusion and sorption. Hence, migration to the accessible environment may be delayed significantly.

Sorption is considered a chemical retardation process because the transport of solute to the accessible environment is retarded due the sorption process. This chemical retardation by sorption is often described by a retardation equation:

$$\frac{V_w}{V_s} = 1 + \frac{\rho K_d}{\epsilon} \qquad (5)$$

Where V_w is the average velocity of the ground water, V_s is the solute velocity, ρ is the bulk density of the rock and ϵ is the porosity of the porous medium. The RHS of the retardation equation is known as the retardation factor, R_d, and can be coupled with the convective-dispersion equation to model solute transport in geologic media. Because many of the chemical processes associated with solute transport are complex and hard to model, the analysis of radionuclide transport has often been simplified by assigning a constant retardation factor to each radionuclide. This lumps all the effects of the chemical processes into this factor. By using this retardation factor, the lumped chemical processes are assumed to be linear. The use of a retardation factor defined as V_w/V_s seems like a reasonable approximation, however when R_d is K_d based (i.e., Eq. 5), there is some question concerning its use, especially for transport in the unsaturated zone. Currently, for unsaturated transport, the retardation factor has been proposed to be a function of water content and is given by:

$$R_d = 1 + \frac{\rho K_d}{\theta} \tag{6}$$

Where θ is the fraction saturation.

Non-radioactive elements in solution common to the natural ground-water system can compete with radionuclides for sorption. Hence, the presence of these elements and their preference for adsorption could possibly enhance the rate of radionuclide transport. Consequently, the sorption properties of these elements may need to be known to properly predict the sorption, or retardation, of radionuclides to the accessible environment.

Another chemical process that can occur in a ground-water system that is related to sorption is ion exchange. In fact, some studies define ion exchange as a form of sorption (Travis and Etnier, 1981). In a repository setting it is hard to discern between sorption and ion exchange because the result of each process (i.e., retardation of solutes) is the same. One main difference between the two processes is that sorption is often considered reversible (i.e., adsorption/desorption), whereas, ion exchange is often considered irreversible.

Ion exchange is replacement of one ion by another. More specifically, it is a chemical reaction in which mobile ions of a solid are exchanged for ions of like charge in solution. The solid has an open, fish-net-like structure, and the mobile ions neutralize the charged, or potentially charged groups attached to the solid matrix (ion-exchanger). Ion exchange can also occur as isotopic exchange with the same element. In addition to ionic charge, important information that is relevant to ion exchange includes exchange rate, reaction order, rate constant, temperature dependence of rate, and equilibrium concentration. Surface charge on the solid is a result of imperfections, ionic substitutions, or dissociation reactions at the surface. These mechanisms cause a net positive or negative charge on the surface. This charge imbalance is compensated for by a surface accumulation of ions of opposite charge called counter-ions. Counter-ions in this layer of accumulation can be exchanged for other ions providing that the electrical-charge imbalance on the surface continues to be balanced. The nature of the surface charge is a function of pH. At low pH (<7) a positively charged surface prevails and at high pH a negatively charged surface exists. The tendency for adsorption of ions, therefore, depends on the pH of the solution. The cation exchange capacity (CEC) of a material is defined as the excess of counter-ions in the zone adjacent to the charged surface or layer which can be exchanged for other cations.

One aspect of ion exchange that can be applied to unsaturated, fractured tuff is that the zeolites that are in the tuff show high selectivity for specific cations (Drever, 1982). Consequently, zeolites could immobilize specific radionuclide elements and, therefore, contribute to the chemical retardation process. However, because zeolites have a rigid structure and the pore sizes are relatively small (i.e., on the order of 3×10^{-9} m to 9×10^{-9} m), counter ions are not very mobile. Consequently, zeolites can act as molecular sieves and ions which are larger than the pore sizes are excluded from the ion exchange process. For example, Helfferich (1962) states that, in zeolites, ion exchange can occur with Na^+ for Li^+, K^+, and Ag^+, but not for Cs^+. This molecular sieve effect may exclude some of the larger radionuclide ions from exchanging with counter ions contained on the zeolite surface in the porous matrix.

Ion-exchange processes can occur on colloid particles. A colloidal system consists of relatively large molecules or small particles (colloids) dispersed in a solvent. The colloids have at least one dimension within the size range 10^{-9} to 10^{-6} m (Shaw, 1970; Van Olphen, 1977; and Yariv and Cross, 1979). Because of the size of the colloid particles, interfacial forces control their behavior and they stay in suspension by Brownian motion. Colloids are good adsorbents because of their high ratio of surface area to volume and ion-exchange occurs easily because colloids have a large electrical charge relative to their surface areas. Besides facilitating ion-exchange, colloid particles can coalesce and may precipitate.

In porous geological materials that are composed of an appreciable percentage of colloidal-sized particles, ion-exchange occurs with ionic constituents adsorbed onto the particle surfaces. Clay minerals are of colloidal size and geochemical weathering products of rocks are often inorganic, amorphous (uncrystallized or poorly crystallized) colloids in a metastable state. Clays, ferric and aluminum hydroxide, and silicic acid polymers are frequently found suspended as colloids in ground water (Apps and others, 1982).

Because colloid formation is not uncommon in geologic systems, it is possible that radionuclides could adsorb onto the surface of these particles, or even themselves form colloids and be transported to the accessible environment by the particulates. Chemically and physically, colloids behave differently from dissolved species and the mechanisms controlling transport of colloids are quite different from those controlling dissolved species. In fact, it has been concluded by a number of investigators (Apps and others, 1982; Champ and others, 1982, and Bonano and Beyeler, 1985) that, on the average, radionuclides in colloidal form can be transported faster than the average velocity of radionuclides in dissolved form. On the other hand, colloids might increase retardation by means of filtration.

Colloid filtration depends on the relative sizes of the colloids and the pores. Colloid particles must be smaller than the fractures and/or pores in the geologic media to pass through them. Preliminary experimental work (Smith, 1988) indicates that pore sizes in the welded tuff matrix are relatively small (6 x 10^{-9} m to 7 x 10^{-9} m) and that transport of radioactive colloids will probably occur primarily in the fractures of the tuff. This is consistent with the conclusions of Tsang and Mangold (1984). Consequently, the question of fracture versus matrix flow has to be answered before the importance of colloid transport in the unsaturated zone can be ascertained. Colloidal particles may also aggregate into larger particles due to flocculation. By forming larger particles, the efficiency of colloid filtration increases.

The critical parameters when considering colloid transport include flow rate, ionic strength, particle size, and surface charge (Binnall and others, 1987; Bonano and Beyeler, 1985). Unfortunately, due to lack of experimental data, the exact nature, stability, and properties of radioactive colloids are difficult to predict. However, colloid transport is usually associated with relatively large flow rates and this condition is more applicable to saturated porous media. Apps and others (1982) conclude, from the small amount of available data, that concentrations of colloids are very low and, therefore, not a critical path for radionuclide transport. Bonano and Beyeler (1985) show that if the rate of appearance of colloids increases along the transport path so does their rate of capture and vice versa. This may be the reason colloid concentrations are low. A general conclusion that can be reached based on the above discussions would be that tranport of radioactive colloids is likely to be less significant than transport of dissolved radionuclides in the unsaturated zone.

An important chemical process that occurs with transport of radionuclides in a ground-water system is radioactive decay. Radioactive decay is the spontaneous transformation of a nuclide into one or more different nuclides, accompanied by either the emission of particles from the nucleus, nuclear capture, ejection of orbital electrons, or fission. Radioactive decay is important because many of the transport mechanisms depend on the concentration of the radionuclide elements. For example, a daughter nuclide may be sorbing while its parent may not or vice-versa. Radioactive decay is a first-order reaction, where the amount of radioactive element decaying is proportional to the amount present. The proportionality constant is called the decay constant (γ) and is specific for each radionuclide. Radioactive decay results in radioactive decay chains, which are a succession of nuclides, each of which transforms by radioactive disintegration into the next, until a stable nuclide is formed. Because a short-lived radionuclide parent can decay into long-lived radionuclide daughter, including radionuclide chains in the transport model is essential for determining which radionuclides reach the accessible environment (i.e., assessing compliance with the regulations). Also, for this same reason and because several different radioactive elements will be placed in the repository, transport of multiple species must be examined. The presence of more than one radionuclide would affect all the physical and chemical processes that occur in the ground-water system and a governing equation for each species would be required. With the presence of multiple radioactive species, multiple decay chains must also be considered.

Some specific chemical processes that are related to the initial concentration of the radionuclides in the ground water are leaching and dissolution. The combination of leaching from the waste form and dissolution into the liquid phase governs the amount of radioactive material that will be available for migration out of the repository and into the accessible environment. Leaching is the washing of a soluble compound from insoluble material with a solvent. When considering radionuclide transport, radionuclides become the soluble compound and ground water becomes the liquid solvent. Dissolution of the solid after leaching has occurred consists of the following reaction (Moeller and others, 1980):

$$M_xA_y(s) = xM^{m+} + yA^{n-} \tag{7}$$

The solid (M_xA_y) can be dissolved if the equilibrium concentration of either the cation or the anion, or both, can be decreased sufficiently. As the product concentration decreases, equilibrium shifts from the solid. The concentration of the cation can be decreased by complexation, oxidation, or reduction. These chemical reactions will be discussed subsequently. The concentration of the anion can be decreased by formation of a weak acid, complexation, oxidation, or reduction. Precipitation is the opposite of dissolution and is the appearance of a solid when a reaction occurs in a solution. The solid is called the precipitate.

Equilibrium solubility is the process that regulates the concentration of a solute in solution. The solute is in equilibrium with respect to a solid phase containing the solute as a major component (Drever, 1982). Solubility is a measure of the amount of solute that can dissolve in a given amount of solvent or the ability of a substance to form a solution with another substance. Solubility is usually expressed as mass or moles per volume. The solubility of the solid phase is determined by the activity coefficients of the ions involved and the activity coefficients are determined by the composition of the solution. Temperature and flow rate (i.e., time for equilibrium to be achieved) also affect solubility. Equilibrium solubility, leaching, dissolution, precipitation of the waste form are more important for modeling the source term in a performance assessment methodology and are not as significant for far-field transport analysis. However, these chemical processes can affect far-field migration indirectly.

In a ground-water system, the water comes into contact with the minerals in the rock and leaching, dissolution, and precipitation of these minerals can occur. These chemical processes continue until equilibrium concentrations are obtained in the ground water or until all the minerals are consumed. The surface of the rock is altered due to these chemical processes. Long-term dissolution can diminish or completely remove reactive mineral phases from the surface, while precipitation of minerals may coat the surface. Because the surface is altered, sorption of the radionuclides onto the rock matrix is affected and, therefore, radionuclide migration is also affected. For tuff, when the ground water interacts with the rock minerals, the formation of any number of zeolite phases can occur (Apps and others, 1982). In a fractured geologic system, precipitation of minerals can occur in the fractures to the point where the fractures become filled. This phenomenon could have a significant effect on solute transport in the fractured geologic medium.

An important point that should be considered when ascertaining the importance of leaching, dissolution, and precipitation during far-field migration is the time scale for these processes. For example, if the equilibrium concentrations are obtained relatively quickly, these processes would not affect long-term migration significantly. Consequently, for the time scales of interest for a repository, these chemical processes may be insignificant. Also, as indicated earlier, the effects of these chemical processes are often lumped into a single retardation coefficient for each radionuclide.

Another chemical reaction that can occur in the ground-water/geologic-medium system involves the transfer of electrons between dissolved, gaseous, or solid constituents. More specifically, reduction/oxidation (redox) reactions often take place. Redox reactions are equilibrium reactions that represent the summation of two electron-transfer equilibria. One involves the loss of electrons in the oxidation of a chemical species, the other involves the gain of electrons in the reduction of a chemical species.

A parameter that is associated with redox reactions is the redox potential, pE (or Eh). The redox potentional is used in determining the initial concentration of radionuclides in solution (i.e., modeling the source term). pE is of primary importance in determining the solubility of many transition metal radionuclides. Metals are more soluble, when in a higher oxidation state then when in a lower oxidation state. Daniels and others (1983) report that water in unsaturated tuff may be oxidizing. If this is true, then higher solubilities for a number of radionuclide elements would occur compared to solubilities under mildly to strongly reducing conditions. Again, redox reactions seem to be more important for modeling the source term, however they can indirectly affect transport in the far-field. For example, sorption can be affected by oxidizing conditions in that sorption ratios for chemically reducing conditions are larger than values for oxidizing conditions (Brookins, 1984).

Radionuclide speciation is another chemical process that can occur in a ground-water system. Radionuclide speciation is the formation of various oxidation states of radionuclide elements and the formation of radionuclide complexes (Kerrisk, 1984). In other words, it is the chemical form of the dissolved radionuclide species in the liquid ground water. In addition to pE and pH, the species present will also depend on the concentration of complexing ions. A complex is formed between a metal atom or ion that accepts one or more electron pairs and ions or neutral molecules that donate electrons. The molecule or ion that contains the donor atom is called the ligand and a positively or negatively charged complex is called a complex ion. Complexation involves the bonding of ligands to a metal atom or ion due to the valence of the metal atom. The formation of complexes in solution is a function of the activity coefficients of the ions involved. In turn, the activity coefficients are determined by the composition of the solution. Radionuclide speciation seems to be more relevant for determining which radionuclides are available for transport to the accessible environment, as opposed to actual radionuclide transport through the geosphere.

One way geosphere transport may be affected is in the formation of radioactive complexes. Many metal ion radionuclide species form very strong complexes with materials contained in ground water (e.g., polycarboxylic and amino carboxylic compounds) (Apps and others, 1982). Transport of dissolved radionuclides complexed with these ligands may be significantly different than transport of uncomplexed radionuclides. For example, radionuclides in complex form may have different affinities for sorption compared to uncomplexed radionuclides. Also, the mobility of the radionuclide complex may change depending on the solubility of the complex formed relative to its constituents. There is also the possibility that the radionuclide species will form a complex with solid phase molecules (i.e., a form of chemical adsorption). The formation of organic radionuclide complexes will depend on the concentration of organics in the ground water. Unfortunately, the basic chemistry of complexation of radionuclides with ligands and migration of these complexes is poorly understood and, therefore, radionuclide transport by complexation cannot be predicted at this time.

As indicated earlier, the presence of a vapor phase in unsaturated tuff implies that a second path for radionuclide transport to the accessible environment may exist. There have been several studies that have investigated this possibility. These studies include works by Tien and others (1985), Smith and others (1986), Binnall and others (1987), Rasmussen and Evans (1987), and Green and Evans (1987). A analysis of these studies is warranted to ascertain the importance of radionuclide transport in the vapor phase.

Tien and others (1985) and Binnall and others (1987) determined the parameters that would indicate whether or not vapor phase transport would be a significant mechanism for radionuclide transport. These parameters are: radionuclide vapor pressure, radionuclide liquid phase mole fraction and activity coefficient, percent saturation, relative liquid and vapor phase transport rates, and relative liquid and vapor phase retardation. Based on these parameters, Tien and others suggested calculations that should be made for each radionuclide to determine the possibility of radionuclide transport in the vapor phase.

Rasmussen and Evans (1987) identified and examined potential vapor phase transport mechanisms and processes. These mechanisms include ordinary diffusion, self and binary diffusion, Knudsen diffusion, viscous flow, pressure flow, slip flow, forced diffusion, aerosol transport, solubility of gas in liquid, free convection, thermal diffusion, and thermophoresis. The reader is referred to Rasmussen and Evans for a detailed account of these processes. Green and Evans (1987) also investigated potential mechanisms of radionuclide transport as vapor in unsaturated, fractured media. They studied these mechanisms under both isothermal and non-isothermal conditions. They concluded that transport mechanism which are thought to be important near a repository (i.e, in the near-field) were ordinary diffusion, viscous flow and additional mechanisms whose driving forces arise from heat pulses. They also concluded that radionuclide transport as an aerosol could be a potentially important mechanism.

Smith and others (1986) assessed radionuclide vapor-phase transport in unsaturated tuff. They examined aerosol formation and convection/diffusion of volatile species. For aerosol transport, they considered the formation of aerosols from the liquid phase contained on the fracture wall. This was justified in that aerosol formation will not occur in the rock matrix since a liquid film and air space overlying the liquid film is required for aerosol production. To form an aerosol, the ground water must become supersaturated with air components and, if the degree of supersaturation is high enough, gas bubbles will be formed. These air bubbles will then migrate to the surface of the liquid ground-water film if the film thickness is large as compared to the air bubble size. Then, if the bubble velocity is high enough, the bubble will collapse and aerosols will be produced. For repository conditions, it is possible that the ground water will become supersaturated with air during the "heat pipe" effect that occurs near the high-level waste. This effect consists of liquid-film-ground-water movement towards the nuclear waste where high temperatures exist, vaporization of the ground water and movement of the vapor away from the waste to a region of lower temperatures. The solubility of air components in the liquid ground water will decrease as the temperature increases and, if the air components cannot diffuse quickly enough into the vapor phase, the liquid film may become supersaturated with the air components.

The strategy employed by Smith and others (1986) consisted of analyzing air diffusional transport in a stagnant liquid film to determine the degree of supersaturation in the liquid ground water film. This was a conservative analysis, in that, by assuming a stagnant liquid film and transport by molecular diffusion only, the effects of turbulence and other transport mechanisms were not accounted for. These other processes would only lend to increase transport in the liquid film. From their analysis, Smith and others concluded that the air transport rate is high, such that supersaturation does not occur, and, in turn, gas bubbles are not formed and aerosols are not produced. This conclusion was reached for all expected repository conditions. Green and Evans (1987) also come to the conclusion that aerosol production from bubble formation should not exist under expected repository conditions. However, they believe that processes other than bubble formation may exist to produce aerosols. One process they suggest is the rupture of thin films (i.e., 5×10^{-8} m to 5×10^{-7} m). Unfortunately, they do not give any information on the processes involved. It is questionable whether or not this phenomenon will occur and, if it does occur, under what conditions.

It should be noted that Smith and others (1986) also point out that if gas bubbles actually did form, it is unlikely that the liquid film would be of adequate thickness for bubbles to be accelerated to sufficient velocities for aerosol production. Day (1964), using a diffusion cloud chamber, determined that aerosol particles are not ejected by gas bubbles that have a radius less than 1×10^{-4} m. Therefore, the minimum film thickness needed for bubble formation to occur is 1×10^{-4} m, which corresponds to a minimum fracture aperture on the order of 2×10^{-4} m. Ogard and others (1983) measured fracture apertures for six tuff samples in the range of approximately 6 x 10^{-5} m to 2.5 x 10^{-4} m. From these measurements the possibility of adequate liquid film thickness is greatly reduced. However, Green and Evans (1987) point out that the six core samples tested by Ogard and others do not adequately characterize the entire zone of canister placement for a HLW repository. They also state that the heat from the HLW could alter the fractures in such a way that the apertures are enlarged significantly. It should be noted that this question of aerosol formation is primarily relevant for the near-field and not for far-field radionuclide migration.

Smith and others (1986) also analyzed the transport of volatile radionuclides in the gas phase by convection/diffusion. Conservative bounding calculations were done which consisted of calculating the gas flow rate relative to the liquid flow rate (i.e., mobility ratios) due to convection/diffusion for expected repository conditions. From the magnitude of these mobility ratios it was concluded that, except for the immediate region near the canister, transport in the liquid phase will be dominant for radionuclides such as cesium and heavier species. The authors also note that near the waste canister, vapor phase transport of ^{129}I may be important.

Transport of gaseous radionuclides, such as ^{14}C in the form of $^{14}CO_2$ or $^{14}CH_4$, may also occur in the unsaturated zone. This is a research area where little work has been done to ascertain its importance, although, recently, some studies have been conducted concerning gaseous ^{14}C migration (Van Konynenburg, 1985; Knapp, 1987; Amter and others, 1988; Ross, 1988).

In high-level waste (i.e., spent fuel) ^{14}C is found on the interior of fuel rods and on the interior and exterior of fuel assembly structural components (Van Konynenburg and others, 1985). Initially, when the waste package is breached and contacted with air, the ^{14}C contained in the external structural components will be released rapidly in the form of gaseous CO_2. Van Konynenburg and others (1985) conclude that this initial release of ^{14}C will not excede the proposed EPA standard but that further research is needed to account for slower ^{14}C release (i.e., oxidation of the internal components of the fuel assembly) and transport of this CO_2 through the geosphere.

There are several different driving forces for gas flow in the geosphere. Diffusion occurs down a concentration gradient. Density diffferences drive convective gas flow. The density difference between gases below the surface and the atmosphere are caused by temperature and pressure differences (i.e., the land surface is warm in the summer and cool in the winter). Because of seasonal temperature flucuations, gas moves upward in the winter and downward in the summer and this phenomena has been observed in boreholes at Yucca Mountain (Weeks, 1987). Due to daily pressure changes, gas can also move upward and downward. Consequently, the possibility of gas phase radionuclide migration to the surface due to the oscillating flows must be considered. Amter and others (1988) conclude that, for CO_2 migration, transport due to the seasonal gas flow is much less than migration of CO_2 due to diffusion, and, therefore, is negligible.

Besides diffusion and convection, there are several chemical processes that must be considered for CO_2 gas phase transport. These chemical processes include isotopic exchange, radioactive decay, sorption and water-carbonate mineral reactions (Knapp, 1988). These water-carbonate mineral reactions may provide a sink for removal of ^{14}C from the gas phase (Ross, 1988). Due to these complicated chemical processes, analyzing gaseous CO_2 migration becomes very complicated.

The analyses on CO_2 gas transport that have been done for Yucca Mountain (Knapp, 1988 and Amter and others, 1988) assume an equivalent porous medium and, therefore do not account for fractures in the tuff. Conceptually, it seems that gas would migrate predominately through the path of least resistance (i.e., the fractures) and assuming an equivalent porous medium for gas transport seems questionable. Also, the presence of the liquid phase needs to be considered. For example, if one assumes that gas flow occurs primarily in the matrix than the liquid flow would have to occur in the fractures and vice versa. Another aspect that needs to be considered is that, if there is a continuous path for gas phase transport from the repository to the land surface (i.e., the accessible environment) then there is also a continuous path for water infiltration and this may prove to have a greater impact then gas phase transport.

Conclusions

The following physical and chemical processes have been identified as pertinent to transport of radionuclides in unsaturated, fractured, tuff: convection, dispersion, diffusion, sorption, radioactive decay, speciation, complexation, ion-exchange, leaching, dissolution, precipitation, and redox reactions. The possibility of vapor-phase transport and colloid transport has also been considered. It is apparent from the literature that many factors concerning transport in an unsaturated, fractured geologic medium are disputable. These factors include whether the fractured geologic medium can be considered a continuum, whether fracture flow will occur, whether colloid transport will occur, whether vapor-phase transport will occur, and how to handle geochemical retardation. The reader should also realize that different scenarios (e.g., changes in infiltration and recharge to aquifers, drilling through the repository, faulting or increased fracturing through the repository) may also affect which transport processes will be important in the unsaturated zone. However, from the above discussions, it is evident that some processes will, in general, be more significant than others.

From the governing equation for solute transport, it is apparent that the physical processes (i.e., convection, dispersion, and diffusion) are the foundation of solute movement. It would be extremely difficult to present conditions where convection, dispersion, or diffusion would not occur during transport of solutes in a ground-water system. One exception to this may be that if flow occurs predominantly in the matrix, then transport by diffusion would be more significant than transport by convection. However, since there has been no conclusive evidence to prove that matrix flow will dominate at all times during the regulatory period, it will be assumed that flow can occur in both the matrix and the fractures. Therefore, all three physical processes are assumed to occur. Consequently, convection, dispersion, and diffusion must be modeled when analyzing radionuclide transport in unsaturated, fractured tuff and can be considered the most important processes for unsaturated-zone transport.

It is difficult to establish the important chemical processes that can occur in unsaturated, fractured tuff because of lack of experimental, laboratory and field data. In general, studies investigating which geochemical processes are likely to occur in unsaturated, fractured tuff have not been performed. Nonetheless, it is evident, from the preliminary work of Johnstone and Wolfsberg (1980) and Daniels and others (1982), that sorption is a critical mechanism that must be modeled when considering radionuclide transport in unsaturated, fractured tuff. In fact, retardation by sorption is one of the main justifications for containment of nuclear waste in a geologic repository. Hence, sorption is considered as the most important chemical process for transport in the unsaturated zone. Also, since it is hard to distinguish between sorption and ion exchange under repository conditions, the ion-exchange process will be considered as part of the sorption process. This can be justified in that, if sorption ratios are measured under dynamic conditions (i.e., ground water flowing through a tuff sample), then both ion exchange and sorption will be accounted for in the measured sorption ratio.

The next important chemical process affecting transport of radionuclides in the unsaturated zone is radioactive decay. Radioactive decay is important because the decay process establishes, over time, which radionuclides will be transported to the accessible environment. If this is not known, one cannot accurately predict the concentrations of radionuclides that will reach the accessible environment, no matter how accurately the transport processes are modeled. Modeling multiple constituents and multiple decay chains is also essential for assessing which radionuclides reach the accessible environment (i.e, compliance with the regulations).

The remaining chemical processes (leaching, dissolution, precipitation, speciation, complexation, redox reactions) seem to be more important for consideration in a source term model than for far-field radionuclide transport modeling. These processes can affect migration indirectly, (i.e., changing the surface for sorption to occur on), however, their primary importance will be to establish the initial concentration of radionuclides for transport through the geosphere.

Based on the research done at this time, vapor-phase transport will not be considered as an important process for radionuclide transport in the far-field. This is based on the study by Smith and others (1986), which concludes that liquid phase transport will be dominant for most radionuclide species (e.g., ^{134}Cs and heavier) for far-field migration. The reader should note that this low ranking of importance for vapor-phase transport is specific to the far-field and that, in the near-field, vapor-phase transport may become more significant. Also, it should be noted that there is a significant need to address vapor-phase transport with laboratory and field experiments.

Colloid transport can be considered the least important transport process for radionuclide transport in the unsaturated zone. This is based on low colloid concentrations in ground-water systems (Apps and others, 1982) and the study by Bonano and Beyeler (1985). This study indicates that the dynamic balance between the appearance and capture of colloids will probably keep the concentration of colloids low. Also, relatively high ground-water velocities are necessary to transport colloids and these velocities are more pertinent to saturated-zone transport than to unsaturated zone transport.

In summary, the chemical and physical processes identified as important for unsaturated zone transport are listed as follows: convection, dispersion, diffusion, sorption, and radioactive decay. It is interesting to note that these processes are the same processes that are important for transport in the saturated zone. However, how these processes occur in the unsaturated zone may be very different compared to how these processes occur in the saturated zone. The current approach to modeling unsaturated-zone transport is based on a very simple modification to the convective-dispersion equation for saturated-zone transport (i.e., replacing porosity by moisture content). This does not seem to be justified by experimental field or laboratory results. Therefore, in general, there is some question about the applicability of the convective-dispersion equation for simulating transport in the unsaturated zone.

4. POTENTIAL TEST PROBLEMS

A preliminary literature search was done to identify potential test problems for use in the transport code comparison and, if necesary, for verification of a modified or newly developed transport code. This list is presented in Table 4.1.

Test problems were defined as problems with either analytical solutions or results from experiments. Finding test problems that are completely representative of conditions in unsaturated, fractured tuff is probably not possible. Instead, test problems were chosen to test various aspects of the transport codes. Consequently, the test problems can only be expected to represent some simplification of conditions in unsaturated, fractured tuff. Also, if the codes cannot adequately simulate simple transport processes, then it can be concluded that they will be unable to simulate relatively complex processes expected for transport in unsaturated, fractured tuff.

Some other posssible test problems that were not included in Table 4.1 are test cases from INTRAVAL, the international transport validation study. The Las Cruces Trench Experiment (Test Case 10) and the Apache Leap Block Experiment (Test Case 11a), which involve unsaturated-zone transport seem most appropriate. However, as discussed in Chapter 3, since the difference between transport in the unsaturated and saturated zones is based on the numerical solution of the transport equations, the INTRAVAL saturated-zone test cases could also be potential test problems.

Table 4.1
List of Potential Test Problems

Reference(s)	Summary
Cameron, D.R., and Klute, A., 1977, Convective-Dispersive Solute Transport With a Combined Equilibrium Adsorption Model: Water Resour. Res., v. 13, no. 1, pp. 183-188	An analytical solution to the 1-D convective-dispersive transport equation with a combination Freundlich isotherm and first-order reversible kinetic adsorption model is presented. A constant moisture content is assumed.
Dykhuizen, R.C., 1988, Transport of Solutes Through Unsaturated Fractured Media: Sandia National Laboratories, SAND86-0940, Alb., NM, 16 pp.	A numerical model that is thought to represent transport through a highly fractured, unsaturated, porous medium. A sample calculation to illustrate the model is presented.
Erickson, K.L., and Fortney, D.R., 1981, Preliminary Transport Analyses for Design of the Tuff Radionuclide Migration Field Experiment: Sandia National Laboratories, SAND81-1253, Alb., NM, 56 pp.	Transport analyses were conducted on a hypothetical experiment involving an idealized joint. The experiment is modeled as two semi-infinite, parallel plates confining an aqueous solution in 1-D, laminar flow. Breakthrough curves are given for this hypothetical experiment.
Eriksen, T.E., 1985, A Laboratory Study on Radionuclide Migration in a Single Natural Granitic Fissures: Nuclear Tech., v. 70, pp. 261-267. Eriksen, T.E., 1983, Radionuclide Transport in a Single Fissure - A Laboratory Study, SKFB/KBS, Technical Report TR 83-01, Stockholm, Sweden 23 pp.	Results of laboratory experiments for radionuclide migration in a single fissure oriented parallel to the axis of a granitic drill core are presented.

Table 4.1 (cont.)
List of Potential Test Problems

Reference(s)	Summary
Gureghian, A.B., 1981, A Two-Dimensional Finite-Element Solution for the Simultaneous Transport of Water and Multiple Solutes Through a Non-homogeneous Aquifer Under Transient Saturated-Unsaturated Flow Conditions: in The Science of the Total Environment, v. 21, pp. 329-337.	A 2-D solution is presented. The model was tested by comparing predictive values with analytical solutions and experimental results for transient flow.
Huyakorn, P.S., Mercer, J.W., and Ward, D.S., 1985, Finite Element and Matrix and Mass Balance Computational Schemes for Transport in Variably Saturated Porous Media: Water Resour. Res., v. 21., no. 3, pp. 346-358.	A model and computational schemes are presented. Three examples are provided to verify and demonstrate the utility of the model for two dimensions.
James, R.V., and Rubin, J., 1979, Applicability of the Local Equilibrium Assumption to Transport Through Soils Affected by Ion Exchange: Chemical Modeling in Aqueous Systems Am. Chem. Soc. Symp. Series V Vol. 93, pp. 225-235.	Effluent concentration histories were obtained for calcium and chloride ions during miscible displacement of CaCl solutions through vertical columns containing homogeneous, repacked sandy soil that was saturated.
Lester, D.H., Jansen, G., and Burkholder, H.C., 1975, Migration of Radionuclide Chains Through an Adsorbing Medium: Adsorption and Ion Exchange AICHE Symposium Series Volume 71 Number 152, pp. 202-213.	Numerical calculations of the analytical solutions that model the migration of radionuclide chains through a saturated soil column are presented.
Lung, H.C., Chambre, P.L., Pigford, T.H., and Lee, W.W.L., 1987, Transport of Radioactive Decay Chains in Finite and Semi-Infinte Porous Media: Lawrence Berkeley Laboratory, LBL-23987, Berkeley, Cal., 101 pp.	This report presents analytical solutions for transport of radioactive decay chains of arbitrary length in porous media of limited and unlimited extent.

Table 4.1 (cont.)
List of Potential Test Problems

Reference(s)	Summary
Pickens, J.F., and Gillham, R.W., 1980, Finite Element Analysis of Solute Transport Under Hysteretic Unsaturated Flow Conditions: Water Resour. Res., v. 16, no. 6, pp. 1071-1078.	A model for the 2-D simulation of the transient movement of water and solutes in saturated-unsaturated soils is presented. The model is applied to a hypothetical 1-D case involving vertical infiltration and redistribution of a slug of water containing a non-reactive tracer in a column of sand.
Pigford, T.H., et. al., 1980, Migration of Radionuclides Through Sorbing Media Analytical Solutions - II: Lawrence Berkeley Laboratory, LBL-11616, Berkeley, Cal.	Analytical solutions are presented for radionuclide transport in a 1-D flow field with transverse dispersion and for transport in multi-dimensional flow.
Prickett, T.A., Michael, P.E., Voorhees, L., and Herzog, B.L., 1980, Comparison of One-, Two-, and Three-Dimensional Models of Mass Transport of Radionuclides: Camp, Dresser, and McKee Inc., UCRL-15210, Champaign, Il., 95 pp.	A review of analytical and numerical models is presented in conjunction with a comparison of 1-, 2-, and 3-D models of mass transport of radionuclides in ground water under saturated conditions.
Travis, B.J., Hodson, S.W., Nuttall, H.E., Cook, T.L., and Rundberg, R.S., 1984, Numerical Simulation of Flow and Transport in Fractured Tuff: Mat. Res., Soc. Symp. Proc., v. 26, pp. 1039-1046.	A modeling study of flow and transport in unsaturated, fractured tuff of Yucca Mt. is presented. Analytical solutions were used to estimate migration times through the formation. Concentration histories are presented.

Table 4.1 (cont.)
List of Potential Test Problems

Reference(s)	Summary
van Genuchten, M.T., 1980, Determining Transport Parameters from Solute Displacement Experiments: USDA Science and Education Administration U.S. Salinity Laboratory, Research Report No. 118, Riverside, Cal., 37 pp.	Analytical solutions to the 1-D convective-dispersive transport eq. assuming steady-state flow a constant water content, and excluding radionuclide decay are presented. An appendix lists five analytical solutions for different initial and boundary conditions.
van Genuchten, M.T., 1982, One-Dimensional Analytical Transport Modeling: in Proceedings of the Symposium on Unsaturated Flow and Transport Modeling, U.S. Nuclear Regulatory Commission, NUREG/CP-0030, Washington, D.C., pp. 233-248.	1-D analytical solutions are given assuming a constant volumetric moisture content and steady-state flow, a semi-infinite media, and that the systems are initially free of solute. Three different formulations are considered: 1) single-ion equilibrium transport w/ and w/o decay, 2) single ion non-equilibrium transport w/ and w/o decay, and 3) multi-ion equilibrium transport in which the ions form an an interactive chain.
van Genuchten, M.T., and Alves, W.J., Analytical Solutions of the One-Dimensional Convective-Dispersive Solute Transport Equation: U.S. Dept. of Agriculture, Technical Bulletin no. 1661, 151 pp.	Numerous analytical solutions of the general solute transport equation are presented assuming a a constant volumetric water content.
van Genuchten, M.T., and Wierenga, P.J., 1976, Mass Transfer Studies in Sorbing Porous Media I. Analytical Solutions: Soil Sci. Soc. of Am. J., v. 40, no. 4, pp. 473-480.	An analytical solution is presented for the movement of chemicals through a sorbing porous medium with lateral or intra-aggregate diffusion. The liquid phase in the porous medium is divided into mobile and immobile regions.

Table 4.1 (cont.)
List of Potential Test Problems

Reference(s)	Summary
Walter, G.R., 1982, Theoretical and Experimental Determination of Matrix Diffusion and Related Solute Transport Properties of Fractured Tuffs from the Nevada Test Site: Los Alamos National Laboratory, LA-9471-MS, Los Alamos, NM, 132 pp.	The results of diffusion experiments on tuff are presented, as well as, a theoretical and numerical evaluation of multi-component effects on diffusional transport.
Yates, S.R., 1988, Three-Dimensional Radial Dispersion in a Variable Velocity Flow Field: Water Resour. Res., v. 24, no. 7, pp. 1083-1090.	An analytical solution is is developed which provides a 3-D solution for the rate and transport of contaminants in a variable velocity and axially symmetric flow field.
Yu, C., Jester, W.A., and Jurnett, A.R., 1985, A General Solute Transport Model and Its Applications in Contaminant Migration Analysis: Argonne National Laboratories, CONF-850893-1, Argonne, Il., 20 pp.	A general solute transport model is presented to simulate solute movement in both homogeneous and non-homogeneous media and the model can be used for both saturated and unsaturated conditions. The model is compared to experimental breathrough curves obtained under homogeneous saturated conditions.

5. SUMMARY OF COMPUTER CODES FOR MODELING TRANSPORT IN THE UNSATURATED ZONE

A master list of 71 computer codes that simulate transport in unsaturated or unsaturated/saturated media is presented in Table 5.1. This list was compiled with information found in the literature and does not reflect actual use of the codes. Consequently, the information reported in Table 5.1 can be termed as "advertised" and may or may not be representative of the actual code. Due to lack of documentation, some of the listed codes do not have complete sets of information (i.e., author, code name, numerical characteristics, fluid flow characteristics, solute transport characteristics, special features, and code availability).

The mathematical model that is the basis for all of the codes listed in Table 5.1 is the convective-dispersion equation for solute transport, which has previously been discussed in Chapter 3. The codes do differ in the solute transport processes included in the convective-dispersion equation, as well as the numerical technique for solving the equation. The numerical solution techniques include finite difference, finite element, method of characteristics and the radom-walk method. Dimensionality of the transport codes also varies among the codes.

The criteria that were used to select/screen the codes that were to be further evaluated is as follows:

1. Solute Transport Processes - The codes to be further evaluated should model at least convection, dispersion, diffusion, sorption and radioactive decay. These processes had previously been determined as most significant for unsaturated zone transport (Chapter 3). A more specific criterion related to the process of radioactive decay is that the code must be able to simulate radionuclide chains with more than three members and multiple radionuclide chains. This criterion is needed since the final code will be used in a performance assessment of a high-level waste repository in tuff. Unfortunately, none of the codes listed in Table 5.1 include this feature.

2. Numerical Characteristics - If transport in one or two dimensions is clearly dominant, then simplifying the three-dimensional geologic system into a one- or two-dimensional model may be possible. Unfortunately, there is no conclusive experimental evidence that indicates transport is primarily in one or two dimensions, for unsaturated, fractured tuff. Therefore, it seems that at least two or three dimensions will be necessary to model the system accurately. Consequently, only those codes that model two or three dimensions should be evaluated further. However, to test this assumption, one code should be chosen that models one-dimensional transport. Also,

those codes that use lumped mass transport models do not seem to be appropriate because of the presence of fractures in unsaturated tuff.

3. Availability - The code should be available for use in this study, have references and/or a user's manual, and be accepted by the technical community.

4. Miscellaneous - Codes that model both heat and solute transport are probably too complicated for modeling only solute transport in the far-field, as we are assuming isothermal conditions.

The following six codes have been identified from the master list of codes as those which appear to meet the above requirements except for the specific radioactive decay criterion: 3-D SATURATED/UNSATURATED TRANSPORT MODEL, SATURN, SUTRA, TRACER3D, TRIPM, and INEL-TRA-POND (one-dimensional). These codes are presented in Table 5.2. Again, it should be noted that none of the codes in Table 5.2 model multiple decay chains and only two of these codes model decay chains (TRIPM and TRACER3D) at all.

Table 5.1.
Master List of Transport Codes

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
Y. Bachmat Chetborn	BACHMAT	1-D; FD	Unsaturated		Predicts nitrogen conc. in surface water	Available Foreign code (Israel)
Baehr (1987)		1-D	Unsaturated Homogeneous isotropic porous medium Steady-state Isothermal	Dispersion Diffusion Adsorption	Hydrocarbon transport (vapor phase transport)	
Bresler		2-D	Saturated/ unsaturated	Diffusion Non-reactive solute		
A. Mercado	CAREQ (1976)	Iterative procedure (Lumped mass transport)	Saturated/ unsaturated Steady-state Homogeneous isotropic aquifer	Multiple constituents Chemical reactions Precipitation Dissolution Ion-exchange	Prediction of changes in water quality in a carbonatic system	Available References User's instr. Foreign code (Israel)
H. Fluhler W. A. Jury	DISPEQ/ DISPER (1983)	1-D vertical FD	Unsaturated Steady-state Isotropic heterogenous soil	Convection Dispersion Adsorption Ion-exchange Chemical reactions		Available References User's instr. Foreign code (Switzerland)
J. O. Duguid M. Reeves	Dissolved Constituent Transport Code (1976)	2-D vertical Galerkin FE Linear basis functions; L-U decomposition	Saturated/ unsaturated Transient Anisotropic heterogeneous porous medium	Convection Dispersion Diffusion Adsorption First-order decay	superceded by FEMWASTE/ FECWASTE Velocities required as input	Available References User's instr.
J. O. Duguid M. Reeves	DUGUID-REEVES (1976)	2-D Galerkin FE Linear basis functions	Saturated/ unsaturated Homogeneous porous medium	Convection Dispersion Sorption Decay Ion-exchange	Modified by FEMWASTE Uses flow fields from REEVES-DUGUID	Available References User's instr.

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
R. G. Baca, et. al.	FECTRA	2-D; Galerkin FE; Adams-Moulton predictor correlator algorithm	Unsaturated or saturated Porous medium w/ complicated or arbitrary geometry	First order decay Sorption	Transport w/ heat transfer and fracture flow	Available User's instr.
G. T. Yeh D. S. Ward	FEMWASTE-FECWASTE (1981)	2-D areal or cross-section Upstream weighting Quadrilateral bilinear elements Galerkin FE	Saturated/unsaturated Density as a function of moisture content Steady-state or transient Anisotropic heterogeneous porous medium	Convection Dispersion Diffusion Non-linear adsorption First order decay	Heads required as input are computed by flow model FEMWATER or FECWATER	Available References User's instr.
R. J. Hanks S. W. Childs	HANKS	1-D; FD	Unsaturated	Root uptake	Designed for soil-water-salinity flow and crop production	Available References
Intera Environmental Consultants, Inc.	MCTM (1975)	1, 2, or 3-D or axisymmetric Method of characteristics for convection; FD	Saturated/unsaturated Transient Anisotropic heterogenous porous medium	Convection Dispersion Diffusion Sorption First-order decay	Variable grid spacing; Mine dewatering needs	Proprietary References User's instr.
J. B. Robertson D. B. Grove	INEL-TRA-POND (1976)	1-D vertical unsaturated; 2-D horizontal saturated FD	Unsaturated or saturated Steady-state or transient Anisotropic heterogenous porous medium	Multiple constituents Convection Dispersion Adsorption Ion-exchange First order decay Chemical reactions	With variably saturated perched water	Available References

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
M. A. Marino	Infiltration FEM (1977)	2-D horizontal or vertical FE	Saturated/unsaturated Transient Single phase homogeneous fluid; Isotropic homogeneous aquifer	Convection Dispersion Mass conserved (no reactions or phase changes)	Solute introduced as a constituent of artificial recharge	Proprietary supported References
M. A. Marino	MARINO (1981)	2-D Galerkin FE	Unsaturated /saturated	First order reactions (Decay)		Available References
R. A. McCann L. E. Wiles	MCCANN (1981)	2-D; FD	Unsaturated Transient		Coupled heat and mass transport	Available References
A. E. Reisenauer, et. al.	MLTRAN (1982)	1 or 2-D; FE Kinematic pathline model	Unsaturated Fracture flow	Convection Sorption	Uses TRUST for flow field Mass flux output not conc.	Available References User's instr.
W. Ahlstrom M. P. Foote R. C. Arnett C. R. Cole R. J. Serne	MMT (1977)	2-D; Monte Carlo for dispersion (discrete-parcel-random walk approach)	Saturated/unsaturated 1-D ground water	Convection Dispersion Adsorption Decay Ion-exchange Precipitation Dissolution Multiple constituents	Second generation of three generations of code	Available References User's instr.
W. Ahlstrom M. P. Foote	MMT-1D (1976)	1-D	Saturated/unsaturated Homogeneous porous medium Steady-state	Dispersion Sorption Decay Multiple constituents	First generation of three generations of code	Available References User's instr.

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
F. E. Kaszeta C. S. Simmons C. R. Cole S. W. Ahlstrom M. P. Foote R. J. Serne	MMT-DPRW (1D/3D) (1980)	1- or 2-D vertical or horizontal, or 3-D Discrete parcel random walk	Unsaturated /saturated Steady-state or transient Isotropic heterogenous porous medium	Multiple constituents Convection Dispersion Adsorption Ion-exchange Radioactive decay Chemical reactions	Third generation of three generations of code	Available References User's instr.
Ph. Couchat G. Le Cardinal P. Moutonnet	MOBIDIC (1976)	1- or 2-D vertical FD Runge-Kutta method	Unsaturated Transient Homogenous isotropic 2-D or layered 1-D soil	Convection Dispersion Quadratic adsorption Plant uptake	Predicts water transfer from soil to plants	Proprietary References User's instr. Foreign code (France)
R. J. Wagenet	NFLUX (1980)	1-D vertical FD	Unsaturated Steady-state or transient Isotropic homogeneous soil	Convection Dispersion Diffusion Adsorption Ion-exchange Chemical reactions	Nitrogen transport and transformations	Proprietary References
D. B. Oakes	NIMBUS (1976)	1-D vertical FD Method of characteristics	Unsaturated Transient Single homogeneous fluid phase Isotropic homogeneous soil	Convection Dispersion Mass conserved (no reactions or phase changes)	Prediction of heads, water content, nitrate flux and nitrate balance in soils	Available References User's instr. Foreign code (U.K.)
G. W. Kruh	Nitrogen Dynamics in Soil (1976)	1-D vertical FD	Unsaturated /saturated Steady-state or transient Flow of air and water Isotropic heterogenous soil	Convection Dispersion Diffusion Chemical reactions	Nitrogen transport and transformations	Available References User's instr. Foreign code (Israel)

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
H. M. Selim Davidson	NMODEL	1-D; FD	Unsaturated Transient or steady-state Homogeneous or multi-layered soil		Predicts water and nitrogen transport and transformation	Available
D. Lester	NRC-SLB (1981)	1-D; FD Analytic for sat.	Unsaturated /saturated		For shallow land burial; Includes atmos. transport	References User's instr.
Union Carbide	ODMOD (1985)	1-D vertical	Unsaturated Layered Soil moisture zone	Convection Linear sorption Tracer amounts	Lateral flow treated as sinks	Available References
F. Lindstrom W. Piver	ODWHCX/ OD2WHCX (1985)	1-D or 2-D	Simple aquifer		For the microcomputer	References
J. A. Korver	OGRE (1970)	2-D axi-symmetric 3-D ADI; FD	Saturated/ unsaturated Transient Homogeneous porous medium	Convection Dispersion Adsorption		Available References
R. J. Serne R. C. Routson	PERCOL (1972)	1-D vertical FD	Saturated/ unsaturated Steady-state Isotropic heterogenous soil	Convection Adsorption Ion-exchange Chemical reactions	Superceded by other USGS codes For soil columns	Available References User's instr.
H. Fluhler W. A. Jury	PISTON (1983)	1-D vertical FD	Unsaturated Steady-state Isotropic heterogenous soil	Convection Adsorption Ion-exchange Chemical reactions		Available References User's instr. Foreign code (Switzerland)

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
H. M. Selim	PMODEL (1978)	1-D FD	Unsaturated Steady-state or transient Isotropic heterogeneous soil Evapotranspiration	Convection Dispersion Diffusion Non-linear adsorption Ion-exchange Chemical reactions Immobilization Mineralization	Phosphorus transport and transformations	Available References
Carsel et. al.	PRZM (1982)	1-D FD Soil compartments	Saturated/ unsaturated Steady-state or transient Homogeneous isotropic porous medium Single phase Evapotranspiration	Convection Dispersion Sorption Decay Plant uptake	Pesticide root zone model	User's instr.
D. E. Evenson	GWQUAN/ GWQUAL (1975)	2-D horizontal FD	Saturated/ unsaturated Transient Single phase homogeneous fluid Anisotropic heterogeneous porous medium	Convection Dispersion Mass conserved (no reactions or phase changes)	QUAN submodel generates velocity field for QUAL submodel	Proprietary References
Donigian et. al.	RAPCON (1971)	1-D Analytic	Unsaturated Homogeneous porous medium Single phase	Convection Dispersion Sorption Decay		References
G. R. Dutt M.J. Shaffer W.J. Moore	Salt Transport in Irrigated Soils (1972)	1-D vertical coupled with chemistry model; FD	Unsaturated Transient Homogeneous isotropic soil Evapotranspiration	Ion-exchange Convection Plant uptake	Includes sulfate and nitrogen	Available References User's instr.

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
P. S. Huyakorn S. D. Thomas J. W. Mercer B. H. Lester	SATURN (1983)	2-D; Galerkin FE Linear shape functions Complex geometry	Unsaturated /saturated Steady-state or transient Single phase Homogeneous porous medium	Convection Dispersion Sorption Decay	May simulate flow through fractured rock Simulates flow or transport or both	Proprietary References
C. A. Oster	SCAT 1-D, 2-D (1981)	1-D, 2-D; Stochastic model for dispersion; FD	Unsaturated	Dispersion	Produces velocity fields; User inputs velocity covariance functions	Available References
G. Segol	SEGOL (1976)	3-D Galerkin FE Isoparametric hexahedral elements	Saturated/ unsaturated Transient Homogeneous porous medium	Convection Dispersion Diffusion Sorption Decay	2-D form of code also available	Available User's instr.
M. Bonazountas J. M. Wagner	SESOIL (1981)	1-D Analytic Vertical compartments	Unsaturated Homogeneous layered medium Evapotranspiration Infiltration Percolation	Ion-exchange Sorption Decay Volatilization Precipitation Complexation	Solute can exist in either phase	References User's instr.
M. Vauclin	SHAMTU (1878)	1-D Implicit FD	Unsaturated	Evaporation	Coupled heat and mass transfer	Available User's instr. Foreign Code (France)
E. Elzy T. Lindstrom L. Boersma R. Sweet P. Wicks	SLM-1 (1974)	Mass Balance (Lumped mass transport)	Saturated/ unsaturated Steady-state or transient Homogeneous isotropic soil and aquifer	Multiple constituents Convection Dispersion Diffusion Adsorption Chemical reactions First-order biodegradation	Pollutant migration from a landfill	Available F. References User's instr.

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
Milly	SLPASHWATR (1980)	1-D; FE	Unsaturated Steady-state or transient Isotropic heterogenous non-deformable Evapotranspiration	Hysteresis Diffusion		
R. J. Hanks S. W. Childs	Soil Water Salinity Flow and Crop Production Model (1975)	1-D vertical FD	Unsaturated Transient Single phase homogeneous fluid; Isotropic layered soil	Convection Diffusion Mass conserved (no reactions or phase changes)	Calculation of soil water and salinity profiles	Proprietary References
M. A. Marino	Stream Stage FEM (1977)	2-D vertical or horizontal FE	Unsaturated /saturated Transient Anisotropic homogenous soil	Convection Dispersion Diffusion Adsorption Radioactive decay Chemical reactions	Soil in contact with stream	Proprietary References
M. Th. van Genuchten	SUMATRA-1 (1978)	1-D vertical Hermatian (cubic) FE	Unsaturated /saturated Transient Isotropic heterogenous soil	Convection Dispersion Linear adsorption Ion-exchange First-order and zero order decay	Hysteresis not considered Only single ion equilibrium transport occurs	Available References User's instr.
C. Voss	SUTRA (1984)	2 or 3-D Hybrid FE and IFD	Saturated/ unsaturated	Convection Diffusion Dispersion Decay Sorption	Transport of either energy or solute; Density variations considered Single solute	Available References
D. Sharma	TARGET (1980)	1,2 or 3-D IFD Freundlich sorption	Unsaturated /saturated Transient Multilayered soils	Zero and first order decay Dispersion Sorption	Coupled flow, heat, and chemical species transport	Proprietary References

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
A. L. Dudley R. R. Peters M. S. Tierney E. A. Klavetter J. H. Gauthier M. L. Wilson	TOSPAC (1987)	1-D	Saturated/ unsaturated Fractured medium	Convection Dispersion Sorption Decay	Matrix-fracture coupling	References (unpublished)
B. J. Travis	TRACER3D (1984)	1, 2,or 3-D; IFD Freundlich and Langmuir sorption models Gauss-Seidel iteration procedure	Unsaturated 1 or 2 phase Deformable heterogeneous porous/fractured medium; Transient or steady-state	Convection Dispersion Diffusion Sorption Decay Multiple constituents	Tracer in either phase	Available References User's instr.
W. Walker, et. al.	TRANS (1981)	2-D Galerkin FE Axisymmetric	Unsaturated Transient Soils or aquifers		Coupled heat and mass transfer	Available References
M. Th Van Genuchten	TRANSONE (1976)	1-D vertical or horizontal Hermitian FE with Galerkin approximation	Saturated/ unsaturated Transient Single phase homogeneous fluid; Isotropic layered soil	Convection Diffusion Mass conserved (no reactions or phase changes)		
A. Shapiro G. F. Pinder	TRANSTWO (1976)	2-D horizontal or vertical FD	Saturated/ unsaturated Transient Single phase homogeneous fluid; Isotropic heterogeneous porous medium	Convection Dispersion Mass conserved (no reactions or phase changes)		Available

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
J. F. Pickens R. W. Gillham	TRANUSAT (1977)	2-D vertical Galerkin FE	Unsaturated /saturated Transient Anisotropic heterogeneous aquifer or soil Evapotranspiration	Convection Dispersion Diffusion Adsorption Ion-exchange First-order decay Chemical reactions		Proprietary References Foreign code (Canada)
A. B. Gureghian	TRIPM (1981)	2-D; FE Velocity and migration modules	Saturated/ unsaturated Transient or steady state Evapotranspiration Homogeneous isotropic porous medium	Convection Dispersion Diffusion Sorption Decay Multiple constituents	Includes 3-membered radionuclide decay chains Modules may be used independently	Available References
M. Av-Ron	TRNMDL (1975)	1-D vertical FD	Unsaturated Transient Isotropic homogeneous soil	Convection Adsorption First-order decay	Computes flux of water and solutes into phreatic aquifer	Proprietary References Foreign code (Israel)
T. N. Narasimhan A. E. Reisenauer K.T. Key R.W. Nelson	TRUST+ FLUX/MILTVL (1982)	IFDM; 3-D Complex geometry Pathline solutions	Saturated/ unsaturated Deformable porous medium	Convection	Soil columns Field consolidation	Available References
I. Kapuler	UNFLW (1976)	1-D vertical FD	Unsaturated Transient Single homogeneous fluid phase Isotropic layered soil	Convection Dispersion Mass conserved (no reactions or phase changes)	Simulation of vertical movement of water and solutes in layered soils	Proprietary References User's instr. Foreign code (Israel)
J. F. Pickens	UNFLOWHYS (1977)	2-D vertical FE	Unsaturated /saturated Steady-state or transient Isotropic heterogeneous aquifer or soil Evapotranspiration	Convection Dispersion Diffusion Adsorption Ion-exchange First-order decay Chemical reactions	Flow hysteresis	Proprietary References Foreign code (Canada)

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
M. Th. van Genuchten Alves	USDA (1982)	1-D Analytic	Unsaturated		Flow and transport	
EPA	VHS (1985)	Analytic	Unsaturated		Flow and transport	
	VSFAST		Saturated/ unsaturated	Radionuclide migration		
B. J. Travis	WAFE	1 or 2-D FD	Unsaturated 2 phase flow		Coupled heat and mass transport	Available Unpublished user's instr.
H. M. Selim J. M. Davidson	WASTEN (1976)	1-D vertical FD	Unsaturated Steady-state or transient Isotropic heterogenous soil	Convection Dispersion Diffusion Adsorption Ion-exchange Chemical reactions Immobilization Mineralization Plant uptake of water and nitrogen	Nitrogen transport and transformations	Available References User's instr.
J. P. Gaudet R. Haverkamp	WATSOL (1977)	1-D vertical FD	Unsaturated Transient Isotropic homogeneous soil	Convection Dispersion Diffusion Ion-exchange	Predicts water flow w/ or w/out solute	Available References Foreign code (France)
E. A. Crooks G. T. Yeh	WHC (1981)	1, 2, or 3-D Integrated compartment method	Unsaturated /saturated Complex aquifer systems Anisotropic Transient Nonisothermal	Convection Dispersion Decay Diffusion Sorption Biological degradation	Coupled water, heat, and chemical transport	Available References User's instr.

Table 5.1 (cont.)

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
A. Mercado	WQSWG/ . HEVMET (1975)	Mass balance (Lumped mass transport)	Saturated/ unsaturated Steady-state Homogeneous isotropic aquifer	Multiple constituents Adsorption 1st-order decay Retention in unsaturated zone	Prediction of pollutant conc. in a uni-cell system	Proprietary References Foreign code (Israel)
G. Segol E. O. Frind	3D Saturated/ Unsaturated Transport Model (1976)	3-D Isoparametric elements Galerkin FE	Saturated/ unsaturated Transient or steady state Free surface Anisotropic heterogenous aquifer	Convection Dispersion Diffusion Adsorption First-order decay	Flow from ponds	Available References User's instr. Foreign code (Canada)

Table 5.2
Summary of Selected Transport Codes

Author(s)	Code Name	Numerical Characteristics	Fluid Flow Characteristics	Solute Transport Processes	Special Features	Code Availability
J. B. Robertson D. B. Grove	INEL-TRA-POND (1976)	1-D vertical unsaturated; 2-D horizontal saturated FD	Unsaturated or saturated Steady-state or transient Anisotropic heterogenous porous medium	Multiple constituents Convection Dispersion/Diffusion Adsorption Ion-exchange First order decay Chemical reactions	With variably saturated perched water	Available References
P. S. Huyakorn S. D. Thomas J. W. Mercer B. H. Lester	SATURN (1983)	2-D; Galerkin FE Linear shape functions Complex geometry	Unsaturated /saturated Steady-state or transient Single phase Homogeneous porous medium	Convection Dispersion Diffusion Sorption Decay	May simulate flow through fractured rock Simulates flow or transport or both	Proprietary References
C. Voss	SUTRA (1984)	2 or 3-D Hybrid FE and IFD	Saturated/ unsaturated	Convection Diffusion Dispersion Decay Sorption	Transport of either energy or solute; Density variations considered Single solute	Available References
B. J. Travis	TRACER3D (1984)	1, 2,or 3-D; IFD Freundlich and Langmuir sorption models Gauss-Seidel iteration procedure	Unsaturated 1 or 2 phase Deformable heterogeneous porous/fractured medium; Transient or steady-state	Convection Dispersion Diffusion Sorption Decay Multiple constituents	Tracer in either phase	Available References User's instr.
A. B. Gureghian	TRIPM (1981)	2-D; FE Velocity and migration modules	Saturated/ unsaturated Transient or steady state Evapotranspiration Homogeneous isotropic porous medium	Convection Dispersion Diffusion Sorption Decay Multiple constituents	Includes 3-membered radionuclide decay chains Modules may be used independently	Available References
G. Segol E. O. Frind	3D Saturated/ Unsaturated Transport Model (1976)	3-D Isoparametric elements Galerkin FE	Saturated/ unsaturated Transient or steady state Free surface Anisotropic heterogenous aquifer	Convection Dispersion Diffusion Adsorption First-order decay	Flow from ponds	Available References User's instr. Foreign code (Canada)

6. RECOMMENDATION

After reviewing the results of the first steps of the code comparison (Chapters 3, 4, and 5) and looking at the documentation for the selected codes, a recommendation was made on whether to accept a transport code as it exists, modify a code, or develop a new code without completing the remaining parts of the code evaluation. These remaining steps include simulating each test problem with each of the selected codes, and comparing the code predictions with the test problems solutions/results.

We feel that none of the codes as they exist now would be adequate for simulating transport of radionuclides in unsaturated, fractured tuff. The primary reason for this assertion is that these codes, as advertised, do not simulate radionuclide chains with more than three members and/or they do not simulate multiple decay chains. We felt that these attributes are essential for a transport code that is to be part of an overall performance assessment methodology used to evaluate the adequacy of a HLW repository. This is because radionuclide chains with more than three members are often found in HLW (e.g., actinides) and, to assess compliance with the EPA standard, multiple decay chains must also be considered.

Modifying an already existing code to contain these attributes is not a trivial task, and given the time constraints (completing the comparison by the end of FY89, and modifying the "best" code by the end of FY90), it is probably an unrealistic ambition. Even if a code could be modified to include these characteristics, the efficiency of this modification would be questionable because the code did not contain these attributes initially. This is especially relevant for uncertainty and sensitivity analysis in the performance assessment, where, due to numerous simulations, an efficient treatment of radioactive decay is crucial.

The option which had the most merit is modifying the existing NRC/SNLA code NEFTRAN developed in FIN A-1266. NEFTRAN currently models transport of multiple, n-membered radionuclide chains in saturated, fractured media and would be modified to do the same in unsaturated, fractured media. In addition to modeling multiple n-membered radionuclide chains, there are several other advantages in choosing this option. First, since NEFTRAN is a code developed at SNLA for the NRC, there are SNLA and NRC staff members who are familiar with the code. Second, NEFTRAN's efficient treatment of the radioactive decay process is such that it would be relatively easy to integrate the modified version of the code into the overall performance assessment methodology. Also, the SNLA staff believe that by beginning work at this time, the necessary modifications can be accomplished effectively by the end of FY90. The final product provided to the NRC would be the modified version of the code with the appropriate documentation.

7. APPROACH TO MODIFYING NEFTRAN

For the unsaturated zone, transport parameters are time dependent. For example, moisture content is a function of time and, therefore, the retardation factor, velocity, and hydraulic conductivity, as they are functions of moisture content, are also a function of time. Consequently, NEFTRAN needs to be modified to simulate radionuclide transport under transient flow conditions. Unsaturated, fractured-zone transport also implies the possibility of matrix to matrix transfer. Therefore, adding this capability to NEFTRAN also needs to be investigated. Other characteristics of NEFTRAN that need to be addressed but are not related directly to unsaturated-zone transport are a time-step criterion based on matrix diffusion and modifying the data input subroutine for more "user friendly" data input and editing.

Based on the above needs, SNLA has prepared a detailed plan for modifying NEFTRAN, consisting of two parts, Phase I and Phase II. A short discussion on the existing code, a detailed work plan for Phase I, and a discussion of possible tasks for Phase II follows.

Current Version of NEFTRAN

The NEFTRAN code has been modified since the publication of the Users Manual (NUREG/CR-4766). Many of the enhancements are believed to be beneficial for application to performance assessment and will be included in the base code used as the starting point for the modifications in Phase I and Phase II. These changes to the documented version of NEFTRAN to create this base code plus those modifications to the base code implemented in Phase I and Phase II will be documented as part of Phase II. The enhancements currently included in the base code are:

1) The source module has been decoupled from the transport module.

- The source calculations are performed using a time step independent of the transport. Coding is in place that automatically determines a suitable time step if the user does not input a value.

- Source rates are written to a separate disc file to be read subsequently by the transport module. Although not currently in place, it will be feasible to add the capability to incorporate source rates determined by other source codes.

- The transport module reads source rates from the disc file and integrates over the transport time steps.

- A decay chain can be included for only source calculations and not be transported.

2) The source module has enhanced capabilities.

- Solubility is input and treated as a property of an element. The code apportions solubility to each isotope of the element according to mass fractions. As these are determined internally, the user need not estimate such fractions for input.

- Both constant and exponential leach rate modules are available and can be accessed at the users option.

3) Additional output is available.

- Time-dependent concentrations at the discharge point can be reported for each isotope.

- Normalized discharges for each isotope and the total over all isotopes are reported. In particular, if the user inputs EPA normalization factors, the normalized discharge can be directly compared to EPA sums.

Work Plan for Phase I

As was stated earlier retardation factors, velocity, and hydraulic conductivity are time-dependent due to changes in moisture content. Consequently, a capability needs to be developed to treat this time dependency. The first capability that will be added to NEFTRAN is a multiple steady-state feature in order to treat this time dependency. To add this capability to NEFTRAN the following tasks must be completed:

Transport

- Add to NEFTRAN the capability to read time-dependent velocities and moisture contents for each leg in the network from an external file. The frequency of velocity fields appearing on the file will correspond to the occurrence of significant changes in the velocity field during the regulatory period. NEFTRAN will assume that velocities are constant until a new field is read.

- For each new velocity field the transport, source, and discharge fractions of the Distributed Velocity Method (DVM) algorithm will have to be regenerated.

- The time step will be allowed to change for each new velocity field.

- A constant space step that corresponds to the minimum space step for each leg for all the velocity fields will be found. This avoids the problem of particle redistribution caused by regridding. If this approach causes unacceptable execution times, regridding may be implemented in Phase II.

Source

- Add to NEFTRAN the capability to read time dependent source flow rates from an external file of flow rates.

- Since the source flow rates are changing with time, the fraction of the inventory that can dissolve will also change with time. Consequently, this will have to be implemented into the source model.

- A time-step criterion for the source calculations will be defined. The time step will depend on the time between the successive occurrences of time dependent source flow rates, but will not be dependent on the transport time step since the two models are independent of each other.

The second set of enhancements to NEFTRAN for Phase I involve input and accuracy. Subroutine FLOWIN of NEFTRAN currently reads the input file and places data into the appropriate common blocks. FLOWIN will have to be modified to accept input data, external files, required by the enhancements to NEFTRAN discussed in Section II. In addition, FLOWIN will be modified to make data input and editing easier. Accuracy will be potentially increased for problems simulating transport of radionuclides through media characterized by the presence of both mobile and immobile fluid i.e., matrix diffusion). NEFTRAN models diffusional exchange between such fluids using first-order approximations to both the space and time derivatives of concentration. Currently, this time-derivative approximation is not addressed by subroutine DXDT in determining an appropriate time step for transport. The tasks associated with this second set of enhancements are as follows:

Input

- Input hydraulic conductivity, mass-transfer exchange coefficients, and retardation factors by rock-type.

- Input by element, retardation factors and solubilities.

- Input all properties for a leg or junction in a separate record.

- Input normalizing factors (e.g., EPA factors).

- Decay chains on input file should be designated to be used for source and transport, source only, or not at all.

Diffusional Accuracy

- Investigate the relationship between mobile-immobile diffusion and the time step for transport.

- Modify subroutine DXDT, as necessary, to increase the accuracy of the matrix diffusion model.

Possible Tasks for Phase II

There are several tasks that may be addressed in Phase II of Subtask 2.13. Two tasks that must be completed are the writing of user's manual and verification of the resulting code. In verification of the resulting code, the test problems identified in Chapter 4, along with results from some of the codes listed in Chapter 5 will be used. Time and available funding permitting, other possible areas of investigation for Phase II consist of the following:

Matrix diffusion - Enhance the treatment of matrix diffusion to account for diffusion depth.

Simultaneous matrix and fracture transport - At the completion of Phase I, NEFTRAN will be able to simulate unsaturated zone transport for either matrix or fracture transport, but not simultaneous matrix and fracture transport. NEFTRAN can be modified to simulate simultaneous matrix and fracture transport. This could be done by adding matrix-to-matrix transport in the matrix diffusion model, or by using a two-dimensional DVM numerical scheme. This scheme could be implemented assuming only right angle velocities or a fully 2-D velocity field. Since this modification is not trivial, a preliminary analysis is needed to ascertain the importance of simultaneous matrix and fracture transport in the unsaturated zone.

Multiple paths for migration - At the completion of Phase I, NEFTRAN will simulate unsaturated-zone transport assuming there is one dominant migration path from the repository to the accessible environment. If it is found that there are multiple paths for a given release scenario, NEFTRAN will have to be modified to treat multiple migration paths. One possible way of simulating this would be to set up a global network that contained all the possible paths. Then, each path would act as a transport path separately and results would be combined for output. If some legs occur in more than one migration path, then flow potentially splits at leg junctions. NEFTRAN will assume that radionuclide mass is apportioned in the same ratio as flow. To implement this, the leg-to-leg transfer fractions would have to be reduced according to a mass balance at each junction.

Dynamic Gridding - As mentioned in Phase I, space steps will be determined for each leg before a transport simulation and these will remain constant throughout the entire simulation time. They will be small enough so that numerical dispersion criteria will be met for all velocity fields. Since execution time increases with the number of grid blocks and since other velocity fields may allow for fewer grid blocks, it may be desirable to regrid each leg for each velocity field. An algorithm would have to be developed that partitions the particles into the new grid for each leg.

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