

SOLUTE TRANSPORT IN SATURATED FRACTURED MEDIA

by

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ABSTRACT

The accidental release of radiochemicals from a repository designed for the storage of high-level radioactive wastes within saturated geologic media is modeled by applying a Discrete-State Compartment (DSC) model to the advection-dispersion (AD) equation. The DSC model is applied to problems concerning matrix diffusion, variable time-dependent sorption and desorption processes, heat transport, and chemical and radioactive decay of radiochemicals. The parameters required for the operation of the DSC model are related to aquifer parameters, such as diffusion, dispersion, heat capacity and the specific heat conductivity. It is shown that by the selection of compartment sizes and an appropriate time step, the DSC solution closely approximates the AD solution. The DSC solution is more powerful than a standard cells-in-series (CIS) solution because variable parameters can be incorporated into the DSC model. A CIS solution allows for only uniform cell attributes and sizes throughout the system.

Matrix diffusion is shown to penetrate several metres into a rock matrix when solvent transport is along a fracture. Sorption and desorption of the radiochemicals was modeled by using a thermodynamic equilibrium constant with the option for allowing for transient conditions before equilibrium. The transient condition was modeled using a first-order linear differential equation.

CHAPTER 1

PROBLEM STATEMENT

High-level radioactive wastes (HLRW) result from nuclear power generation and nuclear weapons development. The disposal of HLRW has become a major impediment to the full scale development of the nuclear power industry. The decision by then-President Carter to suspend the development of both nuclear reprocessing of spent fuel rods and the Clinch River Breeder Reactor has resulted in the accumulation of HLRW. The extraction of the wastes by means of nuclear reprocessing and the subsequent use in a reactor would have resulted in the recycling of a major fraction of the HLRW (Angino, 1977).

Storage of HLRW has become a major national issue, resulting in one state (California) refusing to license additional nuclear power plants until the question of waste disposal is resolved. California law requires proof that developed waste technology exists and can be demonstrated and approved before any additional nuclear power plants are licensed in that state. To demonstrate the feasibility of nuclear waste disposal, the Department of Energy (DOE) is presently developing the Waste Isolation Pilot Plant (WIPP), currently located near Carlsbad, New Mexico (Metz, 1978). The disposal of the wastes is also hampered by the fact that since March 1977 more than 15 states have enacted laws that regulate storage or forbid disposal of radioactive wastes within their borders (Lee, 1980). The resolution of this problem will require that difficult political decisions be made at the federal level.

A variety of storage strategies have been proposed. Included are disposal in outer space, in the ocean, in salt domes and bedded salts, in stable igneous formations, and in bedded shales. Each of these strategies has inherent weaknesses, the major weakness being the possibility of leakage or contamination of the surrounding medium. A primary requirement for a suitable location is the absence of a transport mechanism for the movement of the radiochemicals in the event of a failure of the integrity of the nuclear repository.

Geologic disposal of HLRW raises the fundamental question of whether it is feasible to store radioactive wastes safely underground for long periods of time and, if so, what geologic medium is the safest for long-term burial. Some of the factors that need to be considered in selecting a rock formation as a burial site are (Angino, 1977):

- Wide distribution, availability and horizontal extent.
- High structural strength, heat capacity, good thermal conductivity.
- Low seismicity and high tectonic stability.
- Relatively impermeable, porosity must be known.
- Undisturbed structurally.
- Thickness great enough to allow burial at least 300 m below surface.
- Monomineralic or homogeneous rock unit.
- Reasonably plastic in event of a breach at the burial site.
- Absence of subsurface water, knowledge of ground water hydrology.

Salt formations have been considered to be the most attractive disposal sites for several reasons. Salt formations lack fractures and, because the salt flows under pressure, fractures within the salt deposit should seal themselves if they do form. Salt is one of the most

impermeable rocks in nature, yet readily conducts heat, an advantage because of the high temperatures associated with high-level radioactive waste storage. Salt is approximately equal to concrete in its ability to shield harmful radiation (NAS, 1970). Disadvantages associated with storage in salt include the high solubility of the salt, a problem if ground water flow should pass through or near the salt deposits, the highly corrosive nature of salt in solution, and the low adsorption capacity of salt for transuranic elements (Boffey, 1975; Kerr, 1979).

Another alternative being investigated is the use of massive clay deposits. The thickness, plasticity, large lateral extent, low permeability, high ion exchange capacity, and other properties of clay would ensure preservation of any escaping waste in event of subsequent faulting (Gera, et al., 1976). Disposal of HLRW in red clays in deep ocean basins has been considered because of the stability of these formations for periods of over 70 million years and because the areas extend hundreds of kilometres (Kerr, 1979). A difficulty cited by Walton (1980) with the deep sea disposal of nuclear wastes is the inability to predict what would happen if radioactivity escapes and begins traveling through the environment and the food chain. In addition, the retrievability of wastes disposed in deep sea formations would be more difficult than in land-based facilities. DOE has begun to study the question of subseabed disposal of nuclear wastes but field tests will not begin until about the year 2010.

Deep sea dumping of nuclear wastes is currently controlled by an international treaty, the London Convention, which has been signed by 41 nations, including the United States. The convention requires that all

radioactive packages be placed at a depth of at least 4000 m. The international implications of deep sea disposal is a topic of discussion at the Law of the Sea Treaty negotiations.

On a final note, non-geologic alternatives exist to the entire problem of HLRW disposal. For example, present waste extraction processes provide for 99.5 percent removal of plutonium and uranium. Angino (1977) has calculated that if there were 99.9 percent removal of plutonium, uranium, and neptunium, and 99 percent of americium and curium, then the long-term activity of the remaining wastes would be reduced by a factor of 100 and the waste problem, according to Angino, would be a concern for only 700 to 1000 years; a time period much more tractable from man's frame of reference. The extracted plutonium, uranium, neptunium, americium and curium would be used as a fuel source in nuclear power production.

Problems associated with the disposal of HLRW have required hydrologists and geologists to begin formulating conceptual and computer models which will accurately describe the movement of radiochemicals in the event of a loss of integrity in the containment structure. As de Marsily, et al. (1977) have found, "neither the thickness of the geologic formation nor its low permeability are major factors in the confining of radionuclides with very long half-lives over periods of time on the geological scale." The question arises, then, what processes exist within the geologic environment which would retard the movement of the possibly hazardous substances found in high-level nuclear wastes. De Marsily suggests that the ion exchange capacity for each toxic element is the most important factor.

The purpose of this investigation is to present the techniques whereby a Discrete-State Model (DSC) model can be applied to problems of radionuclide transport in ground water. The DSC model is related to the advection-dispersion (AD) equation in such a way that the aquifer parameters required in the AD equation can be used to generate parameters required by the DSC model.

A discussion of radionuclide transport processes, including matrix diffusion, sorption-desorption processes, chemical and radioactive decay, and heat transfer is first presented in Chapter 2. A conceptual transport model is presented in that chapter along with the flow equations used to describe solute transport.

The DSC model is introduced in Chapter 3 and the choice of this particular model is explained. A brief description of the algorithms used to model solute transport movement is included.

Chapter 4 presents the techniques whereby the DSC model can be used to model the transport processes. The inclusion of sorption-desorption processes under equilibrium and transient conditions is also shown to be an application of the computer model.

In Chapter 5, the computer model is shown to accurately reproduce the analytic solution of solute transport through a fractured medium when matrix diffusion is included. The model is also shown to reproduce the conduction and convection of thermal energy from a heat source at a great depth. In addition, applications of the model to four cases are presented and the failure of the model to apply to three of the cases is explained.

CHAPTER 2
DESCRIPTION OF GROUND WATER TRANSPORT PROCESSES

The leaching of stored radiochemicals by ground water and the subsequent migration of these radiochemicals is the major event of concern with regard to the disposal of high-level nuclear wastes (HLRW) (Nuclear Fuel Safety Project, 1978). The purpose of this chapter to describe the processes and mechanisms whereby dissolved radiochemicals are transported from the initial disposal site through geologic media. The discussion will concentrate on the processes and mechanisms which could mitigate the rate of migration of HLRW.

Discussion of Transport Processes

Three transport processes; advection, hydro-mechanical dispersion, and diffusion can be identified which describe the movement of a solute within a medium; porous or fractured. Advection is the mass transport of a solute as a result of the movement of the solvent in response to a pressure or head gradient.

Advection:
$$\Omega \frac{\partial C}{\partial t} = - \frac{\partial (\Omega C v)}{\partial x} \quad (2-1)$$

- where Ω - porosity (L^0)
 C - solution concentration (M/L^3)
 v - fluid flux density (L/T)
 t - time dimension (T)
 x - space dimension (L)

Diffusion is the movement of a dissolved constituent as a result of a concentration gradient within the solvent.

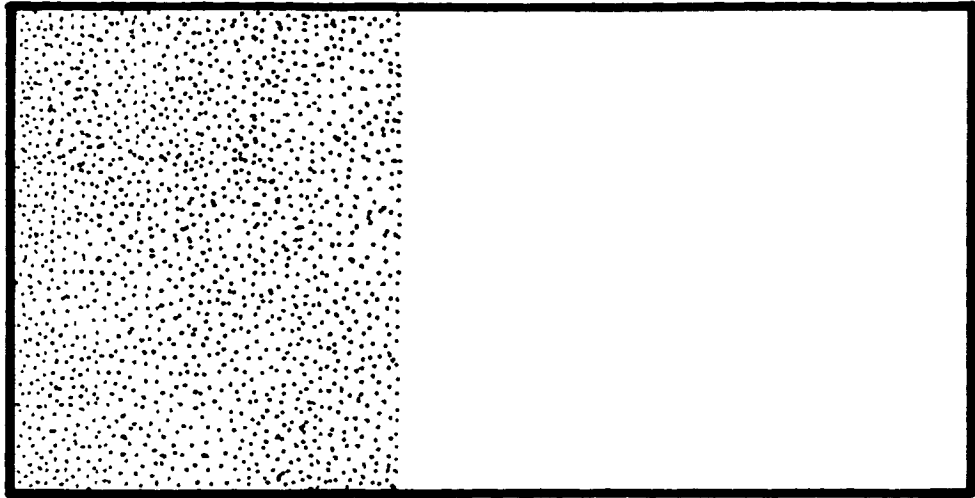
$$\text{Diffusion:} \quad \frac{\partial C}{\partial t} = D \left(\frac{\partial C}{\partial x} \right) \quad (2-2)$$

where D - diffusion coefficient (L^2/T)

A diagrammatic representation of advection and diffusion is presented in Figures 2-1 and 2-2. The upper illustration in Figure 2-1 shows the distribution of a number of hypothetical tracer particles as the result of pure advection with no diffusion. Essentially, the tracer is immobile with respect to the fluid transporting it. No variability is observed either in front of the sharp tracer boundary or behind it. The lower set of graphs in Figure 2-1 present the variation in space (left) and in time (right) as the result of a uniformly increasing concentration of tracer. The increase in concentration of tracer with time (right) would be a function of the velocity field, v .

The corresponding illustration for diffusion is presented in Figure 2-2. In this example there is no velocity field; the fluid is immobile with respect to the surrounding medium. As the result of Brownian motion, movement of the tracer from a region of higher concentrations to regions of lower concentrations will occur. The lower pair of figures illustrate the change in concentration with respect to space (left) and time (right). The relation follows a Gaussian distribution (Silliman, 1981).

It is important to note that another process, hydro-mechanical dispersion, will result as a consequence of variable flow paths or from



MOVING SOLVENT · NO DIFFUSION

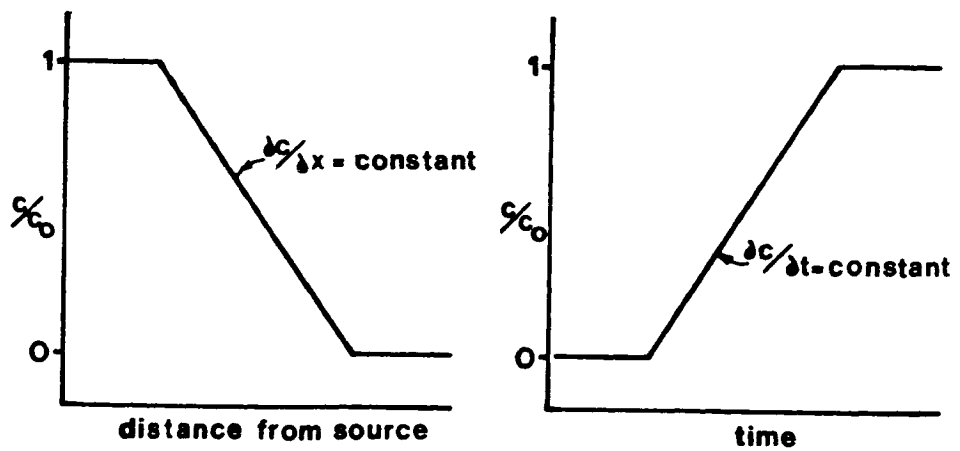
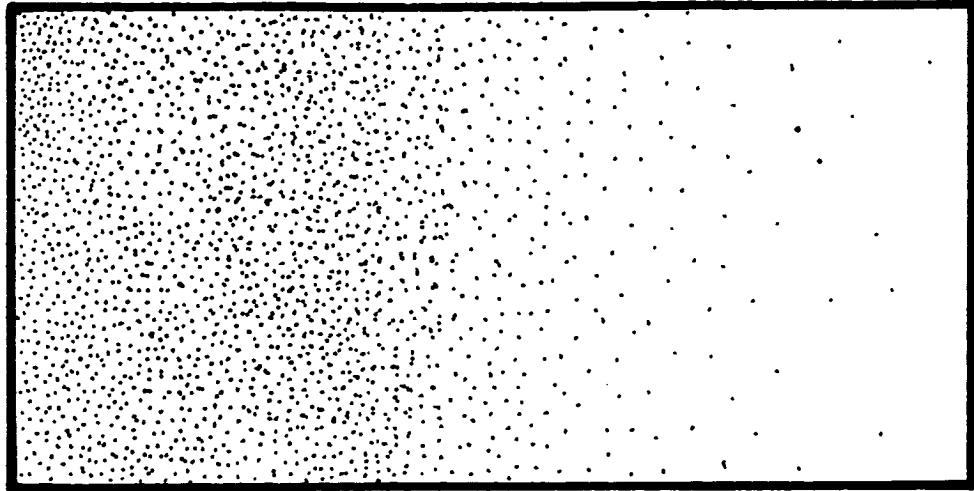


Figure 2-1: Movement of a tracer by advection only.



NON-MOVING SOLVENT · DIFFUSION ONLY

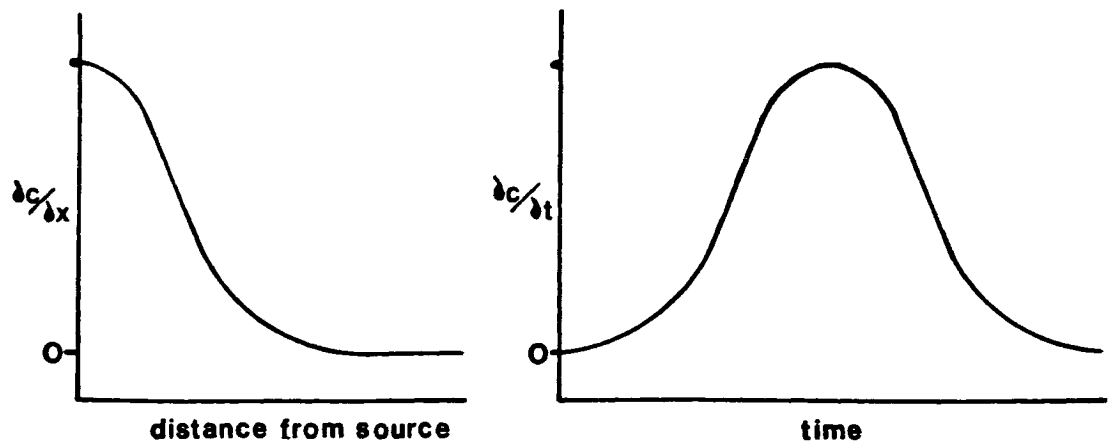


Figure 2-2: Movement of tracer by diffusion only.

the presence of large voids in direct communication with the flow channel. Within a fracture system, alternate flow paths exist which tend to result in an effect which smears the sharp, smooth front associated with pure advective transport. A diagrammatic representation of hydro-mechanical dispersion within a hypothetical fracture system is presented in Figure 2-3. The flow equation which incorporates hydro-mechanical dispersion would be identical to the flow equation for diffusion as the number of alternate flow paths approaches a very large number. The diffusion coefficient can then be replaced by the coefficient of hydrodynamic dispersion, which is the combination of the diffusion and hydro-mechanical dispersion coefficients. (Bear, 1972)

A measure of the magnitude of the advection component relative to the dispersion component can be made by using the Peclet number, P_e , a dimensionless variable of the form:

$$P_e = v \Delta x / D \quad (2-3)$$

The Peclet number can also be obtained by multiplying the Reynold's number, R_e , by the Schmidt number, S_c , where:

$$R_e = v \Delta x \rho / \mu \quad (2-4)$$

where μ is the viscosity (M/LT), and the Schmidt number is given by:

$$S_c = \mu / \rho D \quad (2-5)$$

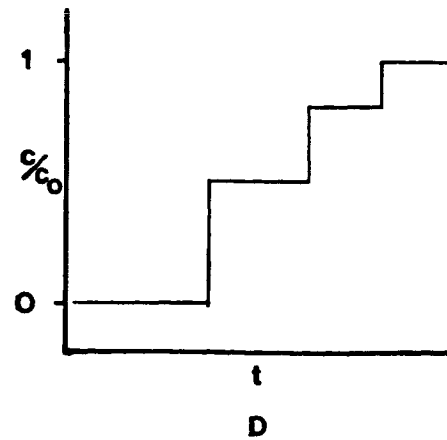
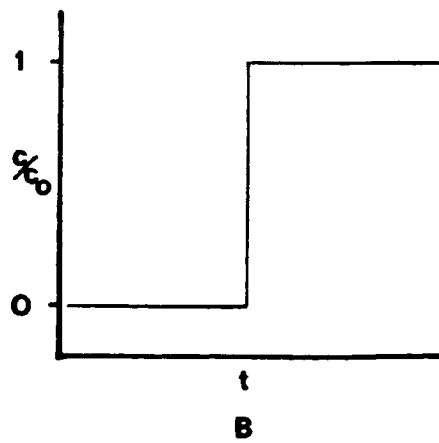
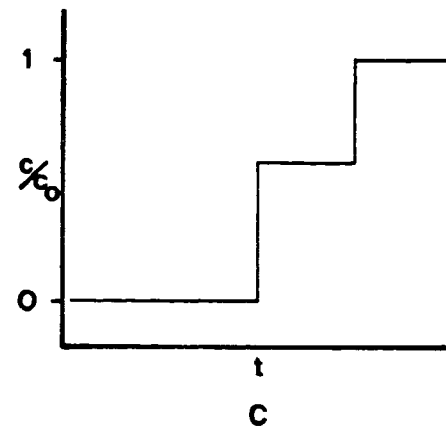
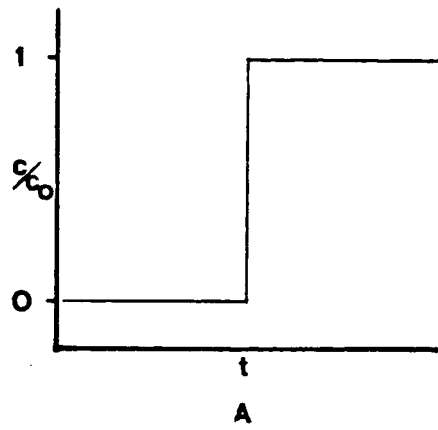
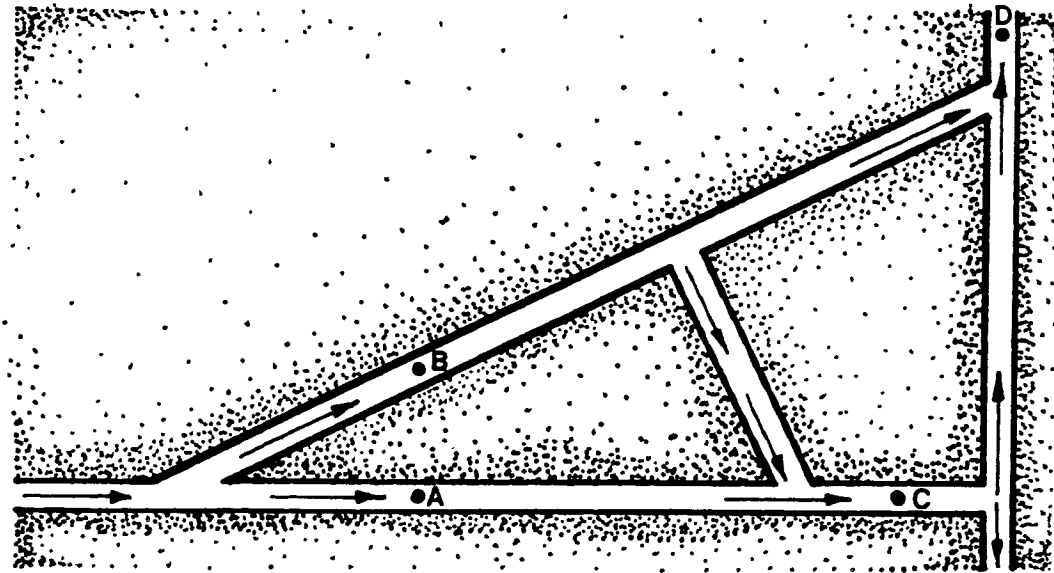


Figure 2-3: Hydro-mechanical dispersion in fractures (no diffusion).

Discussion of Physical System

A medium can have two porosities; primary and secondary. Primary porosity, or bulk porosity, is the percentage volume of pores within a volume of rock or alluvium. Secondary porosity is the percentage volume of fissures and micro-fissures within the total rock volume. Figure 2-4 is a pictorial representation of primary porosity (upper illustration) and secondary porosity (lower illustration). The primary porosity is composed of voids with blunted ends at either end of the cavity while the secondary porosity is indicated by a set of intersecting fractures.

Matrix Diffusion

The transport of solute through the host rock, or matrix, surrounding a fracture system could occur as a result of either hydrodynamic dispersion, advection, or both. If the hydrostatic gradient is such that all flow lines are parallel to the fracture system, no movement of solute would occur normal to the fracture system. The only movement normal to the fracture system would be as a result of diffusion, which occurs in response to a concentration gradient. Two types of diffusion would occur; through the fracture dead spaces (secondary porosity), and/or through the host rock itself (primary porosity). This second type of diffusion is termed matrix diffusion.

Neretnieks (1980) postulates that the diffusion of the nuclides into the rock matrix is one of the main mechanisms retarding migration from a repository. His opinion is that the observed rate of diffusion (about $1 \times 10^{-10} \text{ m}^2/\text{s}$) into a non-sorbing granitic matrix will retard the velocity of a radiochemical by a factor of 700.

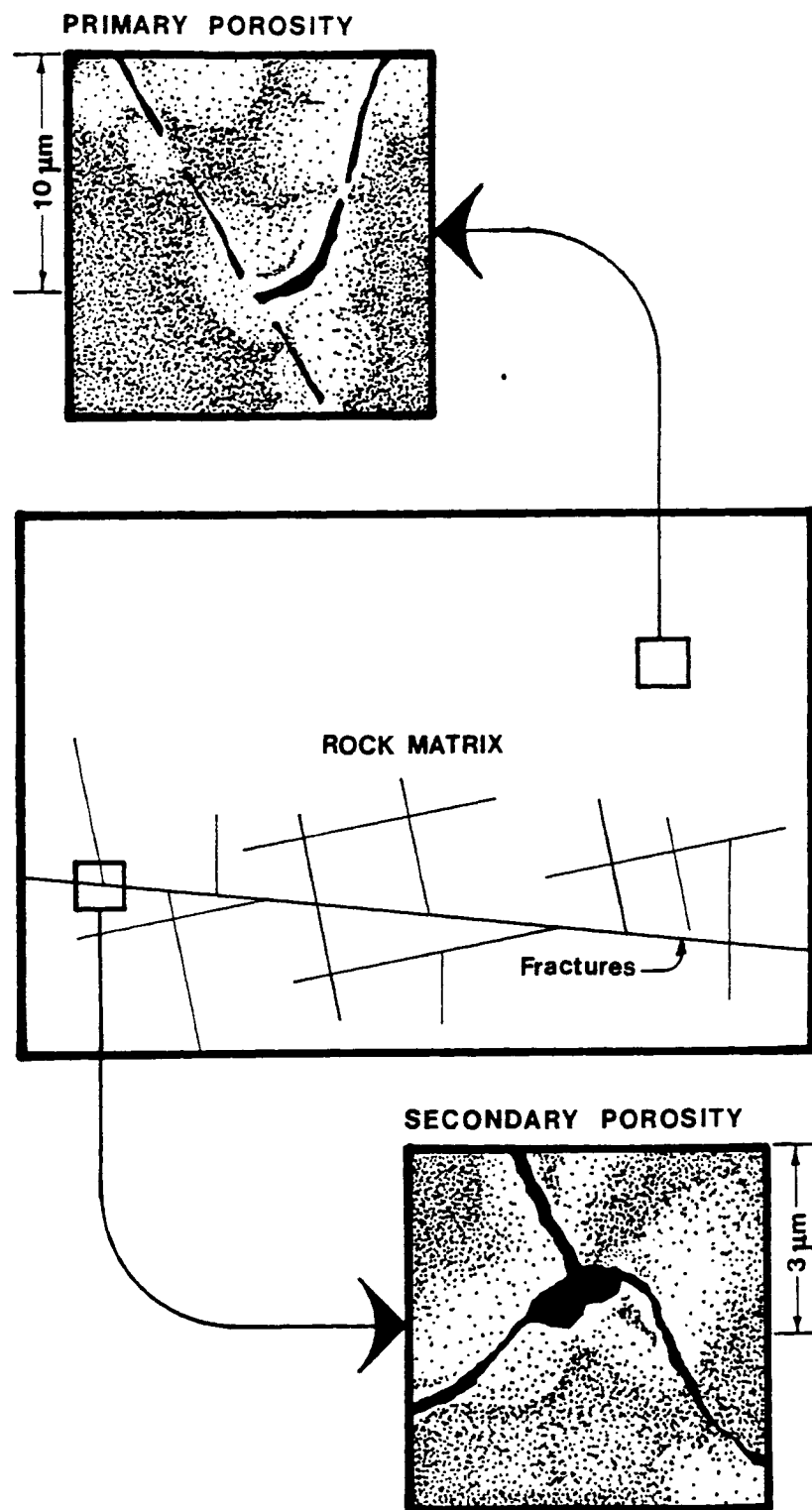


Figure 2-4: Primary porosity (Sprunt and Brace, 1974, pg. 144) and secondary porosity (Kranz, 1979, pg. 43)

Sorption-Desorption Processes

A distribution coefficient has been defined as the ratio of the concentration of a tracer dissolved in a solute, C_W , versus the concentration of the tracer sorbed on a solid, C_S . For some concentrations of C_W versus C_S , a linear relation holds such that:

$$C_S = K_d C_W \quad (2-7)$$

where C_S - Mass of tracer on solid per mass of solid (M°)
 C_W - Mass of tracer in solution per volume of solution (M/L^3)
 K_d - distribution coefficient (L^3/M)

A retardation factor, R , can be defined such that the velocity of the tracer is a fraction of the velocity of the water, or;

$$v_t = v_w / R \quad (2-8)$$

where v_t - velocity of tracer (L/T)
 v_w - velocity of water (L/T)
 R - retardation factor (unitless)

The retardation factor can be related to the distribution coefficient by the expression;

$$R = 1 + \rho/\Omega K_d \quad (2-9)$$

where ρ - porous medium bulk density (M/L^3)
 Ω - primary porosity (L°)

A new dispersion coefficient can be calculated, $D' = D / R$, such that D' represents the dispersion about some mean velocity front, v_t ,

resulting from an instantaneous injection of tracer. A new advection-dispersion equation can be written relating the concentration of a tracer in a sorbing environment;

$$\frac{\partial C}{\partial t} = D' \frac{\partial^2 C}{\partial x^2} - v_t \frac{\partial C}{\partial x} \quad (2-10)$$

assuming local chemical equilibrium exists everywhere, and the concentration of the tracer in solution is a function only of concentration on the solid phase (Simpson, lecture notes).

Chemical and Radioactive Decay

Radioactive isotopes decay through a variety of processes. The rate of decay has been found to be proportional to the amount of radioactive material present. The general form of the equation for chemical and radioactive decay would be:

$$\frac{dC}{dt} = - [\alpha R C + \beta \rho S] \quad (2-11)$$

where α - first-order liquid phase decay constant (1/T)
 β - first-order solid phase decay constant (1/T)
 ρ - porous medium bulk density (M/L³)
 S - adsorbed concentration (M^o)

When the liquid and solid phase decay constants are equal (they are unequal for some instances of chemical decay, but are equal for radioactive decay), then the above equation can be reduced to the form:

$$\frac{dC}{dt} = - \Omega R C \quad (2-12)$$

Heat Transport

Associated with the decay of radioactive isotopes is the production of heat. Heat flux can be considered to be similar to fluid flux in that both mechanisms behave according to the same physical process as described by the equation;

$$Q = K A t \frac{dT}{dx} \quad (2-13)$$

where Q - heat (calories)

K - specific heat conductivity (calories/cm-sec-°C)

T - temperature (°C)

A - cross-sectional area (cm²)

t - time (sec)

The thermal conductivity, K, relates the time rate of transfer of heat by conduction, through a unit thickness, across a unit area for a unit difference in temperature.

CHAPTER 3
DISCRETE-STATE COMPARTMENT MODEL

In some situations, a distributed model can provide solutions to problems that an analytic solution could not provide. In a homogeneous system, analytic solutions can be developed to describe the distribution of head, concentration or flux. Under field conditions, however, few systems are homogeneous. A distributed model is able to simulate complex systems including variable matrix porosities, diffusion coefficients, fracture flow velocities and apertures. A compartmental model allows a complex system to be described by assuming uniform properties over a relatively small region.

The concept of using small compartments, or cells, to characterize local regions was first applied to a hydrologic system by Zoch (1937), according to Chow (1964, pg. 14-28). He used a linear reservoir model to describe runoff hydrographs. Zoch's work was soon followed by a number of papers (Turner and Burdoin, 1941; Clark, 1945; and O'Kelly, 1955) who expanded the concept to include the identification of the linear storage coefficient and the instantaneous unit hydrograph (IUH). Nash (1957) was the first to explicitly propose the conceptual model of identical linear reservoirs in series. By routing a unit inflow through the reservoirs, an equation for the IUH can be obtained:

$$U(t) = \frac{1}{K (n-1)!} \left(\frac{t}{K}\right)^{n-1} e^{-t/K} \quad (3-1)$$

where K - linear storage coefficient (1/T)
 n - number of reservoirs in series (L^0)
 t - time dimension (T)

The linear reservoirs can be considered to be a special case of the cells-in-series (CIS) model used by chemical engineers. The CIS model has been described by Levenspiel (1972). In addition to the simple CIS model, more complicated geometries can be described. Himmelblau and Bischoff (1968, p. 73) present an analytic solution for a model consisting of two parallel streams, each with a given number of perfectly mixed tanks in series (see Figure 3-1). If flow can occur through either stream, then an equation describing the relative ages, or concentrations of a pulsed input, would be:

$$E(t) = f \frac{n^n}{(n-1)!} \frac{t^{n-1}}{(t_1)^n} e^{-nt/t_1} + (1-f) \frac{m^m}{(m-1)!} \frac{t^{m-1}}{(t_2)^m} e^{-mt/t_2} \quad (3-2)$$

where: f - fraction of flow to branch 1

t_i - mean residence time for branches 1 and 2 as indicated

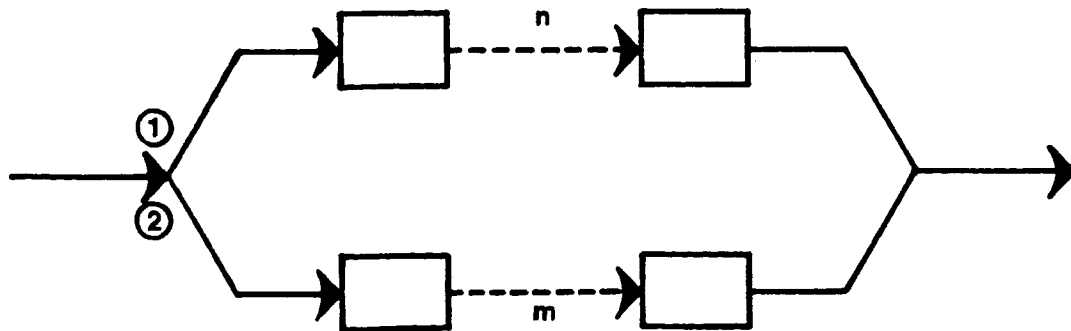


Figure 3-1: Schematic diagram of two parallel series of cells with variable cell numbers.

The existence of multiple flow paths, can be modeled by a simple mathematical expression relating the geometry to the residence time distribution. By introducing fractures into the rock matrix, a bypassing mechanism is established which will force the flow through one series of fractures, allowing for the rapid penetration of the rock mass by some tracer.

The utility of a compartmental model lies in its simplicity and ease of application. By discretizing the system into logical subunits and applying known geophysical data to the subunits, results can be achieved which are similar to those obtained from more sophisticated models (Llamas and Martinez Alfaro, 1981). Because the model is non-dimensional (the modeler specifies the arrangement of the cells according to his/her perception of the system), the resulting geometry can replicate a three-dimensional system. It can even represent a system that varies over time such that volume and boundary conditions can be varied. Such versatility in modeling state variables dynamically allows for greater flexibility in solving problems. Such flexibility is accomplished with little loss of accuracy. A loss in efficiency can be expected in comparison to a powerful finite difference or finite element model, but the extra cost of computer time is offset by the reduced user programming time.

A further refinement of the CIS model has been developed at the University of Arizona at Tucson by Dr. E. S. Simpson. The new model has been named the Discrete-State Compartment (DSC) model. The DSC model is a modification of the CIS model which allows for non-uniform cell characteristics. Rather than obtaining an analytic solution for the

CIS, the DSC model provides a solution by using a recursive algorithm which satisfies the equation of continuity. The first application was made while Dr. Simpson was on sabbatical leave at the International Atomic Energy Commission in Vienna, Austria during 1971.

The computer code for the DSC model was developed in conjunction with M. E. Campana at the University of Arizona in 1975 and is still being used with modifications. Simpson (lecture notes, 1979) subsequently proposed applications for heat flow through porous media. Mike Osborne, a graduate student at the University of Arizona, is currently applying the model to problems of dipole heat flow. Dr. M. R. Llamas of the University of Madrid, Spain, is presently applying the DSC model to problems of fluid and heat flow in the extensive alluvial aquifer which underlies the Madrid basin in Spain.

Operation of the Discrete State Model

The DSC model assumes that each compartment, or mixing cell, is uniformly mixed during each iteration. A series of cells can represent a hydrologic system such that variability within the system is distributed between the compartments or cells. A recursive equation can be written such that the inputs, outputs, as well as sources and sinks within the cell are combined in a mass balance equation which conserves the equation of continuity. The model has been developed to consider problems where the cells contain a fixed volume between iterations, as well as problems of non-steady volume. Only the steady volume case will be presented. The basic equation used by the DSC model is:

$$S(n) = S(n-1) + [BRV(n) \times BRC(n)] - [BDV(n) \times BDC(n)] \pm R(n) \quad (3-3)$$

where

S - mass or amount of tracer in cell

BRV - boundary recharge volume (input volume of water to cell)

BRC - boundary recharge concentration (input concentration of tracer)

BDV - boundary discharge volume (output volume of water from cell)

BDC - boundary discharge concentration (output concentration of tracer)

R - tracer source or sink within cell

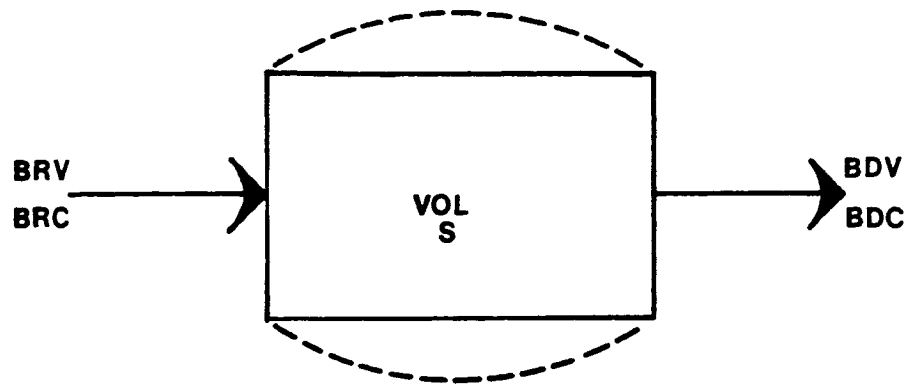
n - iteration number

The term tracer is used to indicate any measurable substance dissolved in water. The model can be used to simulate flow in a system which is defined by the modeler and can vary in volume, porosity, geometry, and diffusivity.

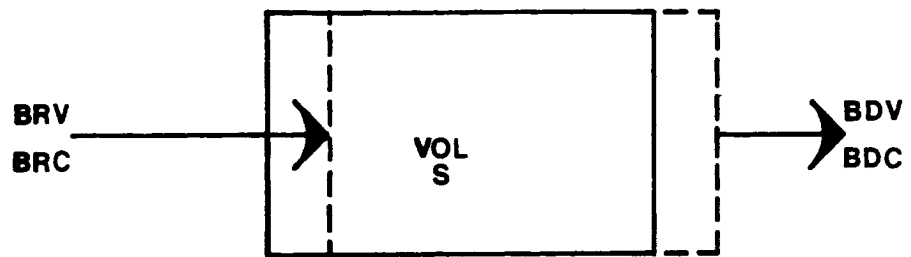
A computer code using the standard FORTRAN was used to simulate transport phenomena. The computer model incorporates the major elements of the Discrete-State Model and was written by Michael E. Campana (1975) of the Department of Hydrology and Water Resources at the University of Arizona. The algorithms used by the model to solve transport processes are described below.

Advective transport

Two alternate algorithms are available for solving the boundary discharge concentration (BDC) from each compartment or cell. The first equation is termed the Simple Mixing Cell (SMC) algorithm. The BDC at each time step is obtained by assuming that at each iteration the cell walls expand to accommodate the incoming water (Figure 3-2, upper illustration). The tracer and incoming water completely mix with the



SIMPLE MIXING CELL, SMC.



MODIFIED MIXING CELL, MMC.

Figure 3-2: Stepwise operation of two advection algorithms by DSC model

contents of the cell. Following that, the cell walls contract to their original volume and the cell discharges a volume of water equal to the volume which entered. The BDC will be equal to the concentration in the cell in its expanded condition. The operation is an 'input-mix-output' scheme and the BDC would be:

$$\text{BDC}(n) = \frac{S(n-1) + [\text{BRV}(n) \times \text{BRC}(n)]}{\text{Vol} + \text{BRV}(n)} \quad (3-4)$$

where Vol is the volume of the cell. Alternatively, the model can solve for the BDC by using a modified mixing cell (MMC) algorithm which assumes that at each iteration the incoming water first displaces a volume of cell water equal to the incoming volume, and then the incoming water mixes with the remaining cell contents (Figure 3-2, lower illustration). The operation is an 'input-output-mix' scheme and the BDC can be calculated from:

$$\text{BDC}(n) = S(n-1) / \text{Vol} \quad (3-5)$$

Dispersive transport

Additionally, an exchange algorithm has been incorporated into the model which allows for modeling processes where no water transport is observed. The algorithm allows for such processes as heat and tracer movement as the result of conduction and diffusion, respectively. Because no movement of solvent need occur, the solute can be modeled without any net movement of water. Again there are two possibilities for exchange. Using the SMC algorithm, a volume of water and tracer is first moved from one cell and mixed with the next (Figure 3-3, upper illustration). After mixing, an equivalent amount of water and the new

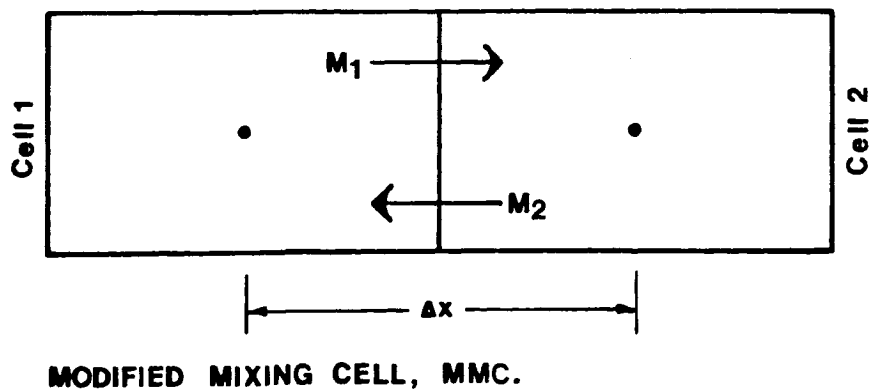
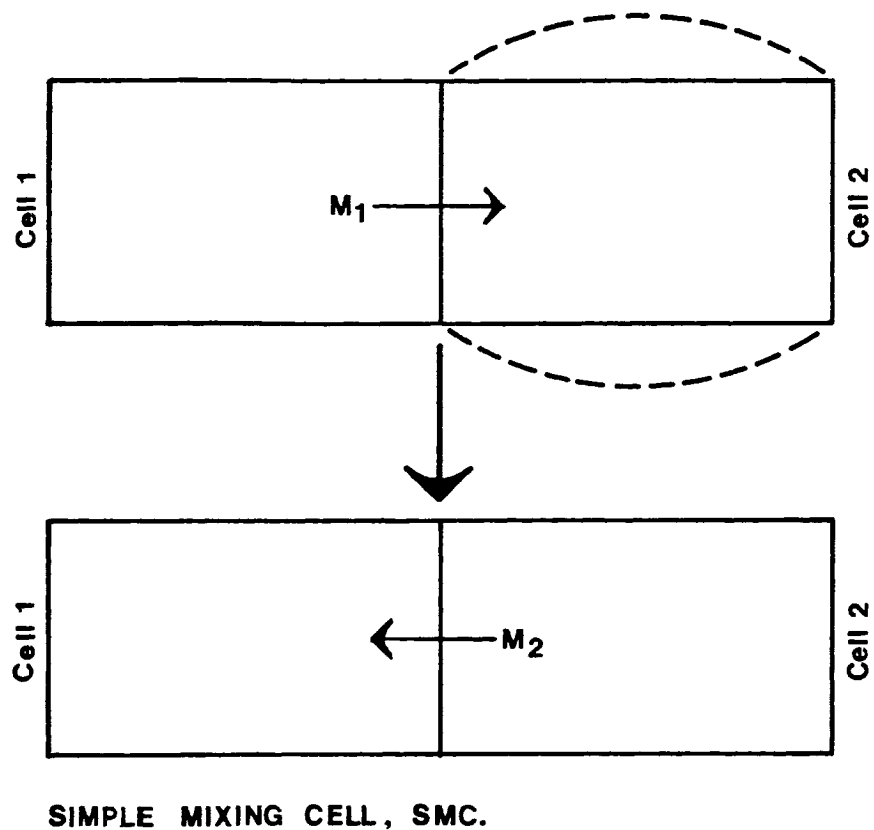


Figure 3-3: Stepwise operation of two exchange algorithms by DSC model

concentration of tracer are moved back to the original cell and mixed. The operation would be an 'input-mix-output-mix' scheme. The operation can be described analytically by taking the difference between the mass transported from the first cell to the second cell and subtracting the mass transported back from the second cell to the first as indicated below:

$$\text{Mass flux} = M_1 - M_2 \quad (3-6)$$

$$M_1 = C_1(n) \times \text{Vol}_1 \times \text{FAC}_1 \quad (3-7)$$

$$M_2 = \frac{(M_1 + C_2(n) \times \text{Vol}_2)}{(\text{Vol}_1 \times \text{FAC}_1 + \text{Vol}_2)} \times \text{Vol}_1 \times \text{FAC}_1 \quad (3-8)$$

$$\text{Mass flux} = \text{FAC}_1 \times \text{Vol}_1 \times \text{Vol}_2 \times \frac{[C_1(n) - C_2(n)]}{(\text{Vol}_1 \times \text{FAC}_1 + \text{Vol}_2)} \quad (3-9)$$

where FAC is the volumetric fraction of the first cell that is transported to the second.

The second option would be to use the MMC algorithm to calculate the mass flux. In this case the operation would be to exchange equal volumes before mixing and then to mix after the exchanges take place (Figure 3-3, lower illustration). The procedure would be an 'input-output-mix-mix' scheme, as indicated below:

$$M_1 = C_1(n) \times \text{Vol}_1 \times \text{FAC}_1 \quad (3-10)$$

$$M_2 = C_2(n) \times \text{Vol}_1 \times \text{FAC}_1 \quad (3-11)$$

$$\text{Mass flux} = \text{FAC}_1 \times \text{Vol}_1 \times [C_1(n) - C_2(n)] \quad (3-12)$$

CHAPTER 4

MODEL FORMULATION

This chapter will present the various modeling techniques which can be used to simulate the physical processes described in Chapter 2. The major elements to be discussed are matrix diffusion, sorption-desorption and heat transfer processes. The intent of the simulation is to develop a model which can accurately replicate a system as described by a set of analytic equations. The ability of the model to yield results consistent with the analytic solutions will be presented in Chapter 5.

Matrix Diffusion

The process of diffusion can be described mathematically using Fick's law. Fick's law states that the rate at which a solute is transported between two points is directly related to the concentration gradient between the two points. When using Fick's law, the assumption is made that no advective transport of solute is occurring. Fick's law can be written as;

$$F = - D \frac{dC}{dx} \quad (4-1)$$

where F is the mass flux per unit area ($M/L^2/T$), D is the coefficient of molecular diffusion (L^2/T), x is a spatial component (L) and C is the concentration (M/L^3).

Assuming that the above equation can be approximated by a finite difference equation for a small time interval, Δt , then the following equation can be written;

$$\Delta M = D \frac{\Delta C}{\Delta x} A \Omega \Delta t \quad (4-2)$$

where ΔM is the mass transported across the interval Δx , A is the cross-sectional area normal to x (L^2), and Ω is the matrix (primary) porosity.

Substituting discrete concentrations yields;

$$\Delta M = D \frac{(C_1 - C_2)}{\Delta x} A \Omega \Delta t \quad (4-3)$$

where C_1 and C_2 are average concentrations at two points separated by the distance between the two points, Δx .

Relation of DSC to Fick's law

As mentioned in Chapter 3, an algorithm has been developed which describes solute transport between compartments of a multi-compartmental model using a mixing fraction coefficient. The purpose of this section is to relate the coefficients used by Fick's law to the parameters required by the DSC model using the governing equations of the two approaches.

The use of a compartmental model requires the arbitrary identification of compartmental shapes and volumes. Mass flow between compartments can be described as the fraction of the volume of one cell that is transported to an adjacent one. In order to conserve volumes, however, an exchange from the second to the first cell occurs, after the initial volume is mixed with the second cell. This is required when

using the simple mixing cell model. This type of mixing uses the simplified mixing cell, SMC, approach, as described in Chapter 3.

The net flux, therefore, is the initial mass transported, M_1 , minus the mass transported back to the original cell, M_2 . The process can be described by the following equations;

$$\text{Mass flux} = M_1 - M_2 \quad (4-4)$$

$$M_1 = C_1 \text{ Vol}_1 \text{ FAC}_1 \quad (4-5)$$

$$M_2 = \frac{(M_1 + C_2 \text{ Vol}_2)}{(\text{Vol}_1 \text{ FAC}_1 + \text{Vol}_2)} \text{ Vol}_1 \text{ FAC}_1 \quad (4-6)$$

Substituting M_1 and M_2 in the upper equation and simplifying yields;

$$\text{Mass flux} = \text{FAC}_1 \text{ Vol}_1 \text{ Vol}_2 \frac{(C_1 - C_2)}{(\text{Vol}_1 \text{ FAC}_1 + \text{Vol}_2)} \quad (4-7)$$

By setting the net mass flow obtained by means of Fick's law equal to the net mass flow equation obtained above, the relationship between D and FAC can be established.

$$D \frac{(C_1 - C_2)}{\Delta x} A \Omega \Delta t = \text{FAC}_1 \text{ Vol}_1 \text{ Vol}_2 \frac{(C_1 - C_2)}{(\text{Vol}_1 \text{ FAC}_1 + \text{Vol}_2)} \quad (4-8)$$

Simplifying and rearranging yields;

$$\text{FAC}_1 = \frac{\text{Vol}_2 D A \Omega \Delta t}{\text{Vol}_1 (\text{Vol}_2 \Delta x - D A \Omega \Delta t)} \quad (4-9)$$

When the compartmental volumes are equal, then the substitution $\text{Vol} = \text{Vol}_1 = \text{Vol}_2$ can be made:

$$FAC_1 = \frac{D A \Omega \Delta t}{(Vol \Delta x - D A \Omega \Delta t)} \quad (4-10)$$

If additional assumptions are made which specify that the compartments are square in two dimensions and of unit thickness in the third, of unit porosity (or the effective diffusion coefficient, D_e , is used), and the mixing fraction is small in comparison with the total volume, then the following relation can be obtained:

$$FAC_1 = D_e \Delta t / (\Delta x)^2 \quad (4-11)$$

For the modified mixing cell (MMC) algorithm, equation 4-6 becomes:

$$M_2 = C_2 Vol_1 FAC_1 \quad (4-12)$$

Equation 4-7 becomes:

$$Mass = FAC_1 Vol_1 (C_1 - C_2) \quad (4-13)$$

Equation 4-8 becomes:

$$D \frac{(C_1 - C_2)}{\Delta x} A \Omega \Delta t = FAC_1 Vol_1 (C_1 - C_2) \quad (4-14)$$

Solving for FAC_1 yields:

$$FAC_1 = \frac{D A \Omega \Delta t}{Vol_1 \Delta x} \quad (4-15)$$

For equal volume cells, the equation simplifies to equation 4-11.

$$FAC_1 = D_e \Delta t / (\Delta x)^2 \quad (4-16)$$

Apparent diffusivity vs. the effective diffusivity

Confusion may arise as to the precise definition of the diffusivity coefficient. To avoid any ambiguity, the following relations are defined (Neretnieks, 1980):

$$D_a = \frac{D_v \Omega C_d}{t_o^2 K_d \rho} = \frac{D_p \Omega}{K_d \rho} = \frac{D_e}{K_d \rho} = \frac{D_p}{R'} \quad (4-17)$$

where $R' = K_d \rho / \Omega = R$ (when $R' \gg 1$)

D_a - apparent diffusivity (L^2/T)

D_v - diffusivity in water (L^2/T)

D_p - diffusivity in water in pores (L^2/T)

D_e - effective diffusivity (L^2/T)

Ω - porosity (L^0)

C_d - constrictivity (L^0)

t_o - tortuosity (L^0)

$K_d \rho$ - volumetric sorption equilibrium constant (L^0)

As will be shown below, the apparent diffusivity coefficient, D_a , may be used in the situation where sorption-desorption processes become important.

Sorption-Desorption

The processes of sorption and desorption can be modeled using a thermodynamic distribution coefficient, K_d . The distribution coefficient relates the concentration of the ion on the solid (number of ions/gm) to that in the solvent (number of ions/cm³).

$$K_d = \frac{C_s}{C_w} = \frac{\text{no. ions on solid/gram of solid}}{\text{no. ions in solution/volume of solution}} \quad (4-18)$$

The distribution coefficient is often corrected for dimensions (the bulk density, ρ , and the porosity, Ω) to yield a dimensionless coefficient, termed the retardation factor, R .

$$R = 1 + \rho/\Omega K_d \quad (4-19)$$

Steady-state conditions

In situations where the ions can be assumed to sorb or desorb instantaneously to maintain a constant K_d , sorption and desorption can be modeled using the apparent diffusivity coefficient, D_a . In other words, sorption can be modeled by assuming that diffusion proceeds at a slower rate. The definition of the apparent diffusivity coefficient, D_a , was given in the preceding section.

Transient conditions

On occasion, as during a tracer test, the rate of sorption and desorption can not be assumed to proceed instantaneously. Studies (McKinley and West, 1981) have indicated that from several days to a month may be required for a solute to be fully sorbed onto a particle. Short-term differences can be expected between the observed concentrations in the solution and the expected concentrations when using instantaneous sorption rate assumptions. The rate of sorption (and desorption) can be modeled by using a first-order linear differential equation which relates the rate of sorption to the gradient between the concentration of the ion on the particle and the concentration of the ion in the solution. The process of sorption can be expressed by the following equation:

$$\frac{dC_w}{dt} = -\frac{1}{K_+} (C_w - C_s / K_d) \quad \text{for } C_s < K_d C_w \quad (4-20)$$

Similarly, the process of desorption can be expressed by the following equation:

$$\frac{dC_w}{dt} = \frac{1}{K_-} (C_w - C_s / K_d) \quad \text{for } C_s > K_d C_w \quad (4-21)$$

where C_w - number of ions in solution/volume of solution (M/L³)

C_s - number of ions on solid/gram of solid (M^o)

ρ - bulk density of the medium, dry mass (M/L³)

Ω - porosity of the medium (L^o)

K_d - thermodynamic equilibrium coefficient (L³/M)

K_+ - Sorption rate coefficient (T)

K_- - Desorption rate coefficient (T)

The analytic solution for the equations above (considering only the sorption process) for C_w versus time has been obtained (see Appendix B) and is of the form:

$$\frac{C_w}{C_t} = F / R \quad (4-22)$$

where C_t is the initial ionic concentration or activity before sorption occurs and F is the time-dependent correction factor of the form:

$$F = 1 + \rho/\Omega K_d e^{-t/K_+} \quad (4-23)$$

The transient condition can be modeled using the DSC by adding a complementary cell for each cell representing the liquid phase. The

complementary cells would represent the solid phase of the tracer. The volumes of the complementary cells represent the storage capacity of the medium, and are determined by:

$$V_S = \rho/\Omega K_d V_W \quad (4-24)$$

where V_S - Volume of cells representing the medium

V_W - Volume of cells representing the solution

The parameter FAC can then be obtained from the following relation:

$$FAC_1 = \frac{R \Delta t}{K_+ - \Delta t} \quad (4-25)$$

Heat Transport

Heat can be conducted or convected through a series of cells using a formulation equivalent to that applied to fluid flow and contaminant transport. Each cell can be defined such that its total heat content represents its state. Likewise, the flux can be described in terms of two components; conducted heat and convected heat. The heat content of the cell is the sum of the heat content of the water (expressed in calories) plus the heat content of the solids (also expressed in calories). It should be noted that at zero degrees Celsius, the cell is assumed to contain zero calories. The heat content of the water can be expressed as:

$$H_W = HC_W V \Omega D_W T_W \quad (4-26)$$

where H_W - heat content of water (calories)
 HC_W - heat capacity of water (calories/gm/°C)
 V - volume of cell (cm³)
 Ω - porosity of porous medium
 D_W - density of water (gm/cm³)
 T_W - temperature of water (°C)

Similarly, the heat content of the solid can be expressed as;

$$H_S = HC_S V (1-\Omega) D_S T_S \quad (4-27)$$

where H_S - heat content of solid (calories)
 HC_S - heat capacity of solid (calories/gm/°C)
 D_S - density of solid (gm/cm³)
 T_S - temperature of solid (°C)

The total heat content of the cell would be;

$$H_t = H_W + H_S \quad (4-28)$$

The heat flux across a cell boundary would equal the the heat content of the flow volume plus the heat conduction. The heat content of the flow volume can be expressed by;

$$H_f = BRMH T_W \quad (4-29)$$

where BRMH is the boundary recharge mass heat capacity (calories/°C). The heat flux associated with heat conduction can be calculated using the exchange mechanism described in Chapter 3. Heat conductivity can be modeled in a manner analogous to diffusion. FAC can be calculated

assuming equal-sized cells by the equation:

$$FAC_1 = \frac{K \Delta t}{H' \Delta x^2} \quad (4-30)$$

where $H' = [HC_W \Omega D_W + HC_S (1 - \Omega) D_S]$

K - specific heat conductivity (calories/cm-sec-°C)

CHAPTER 5
RESULTS AND DISCUSSION

The derivation of the relation between FAC and parameters related to the physical nature of a medium allows for the opportunity to test the compartmental model against known, analytic solutions of simple physical systems. Once the model has been shown to accurately reproduce the analytic solution for a homogeneous matrix and fracture, then the model can be applied to configurations for which analytic solutions are not available.

Matrix Diffusion

The system modeled will be one similar to that initially described by Grisak and Pickens (1981) in which the analytic solution was developed for modeling solute transport through fractured media with matrix diffusion.

A simple system can be described such that a planar fracture is bounded by a matrix of very low permeability. As a solute is introduced into the fracture at one boundary, an equation can be used to define the expected concentration of that solute over time at any point within the fracture and at any distance normal to it.

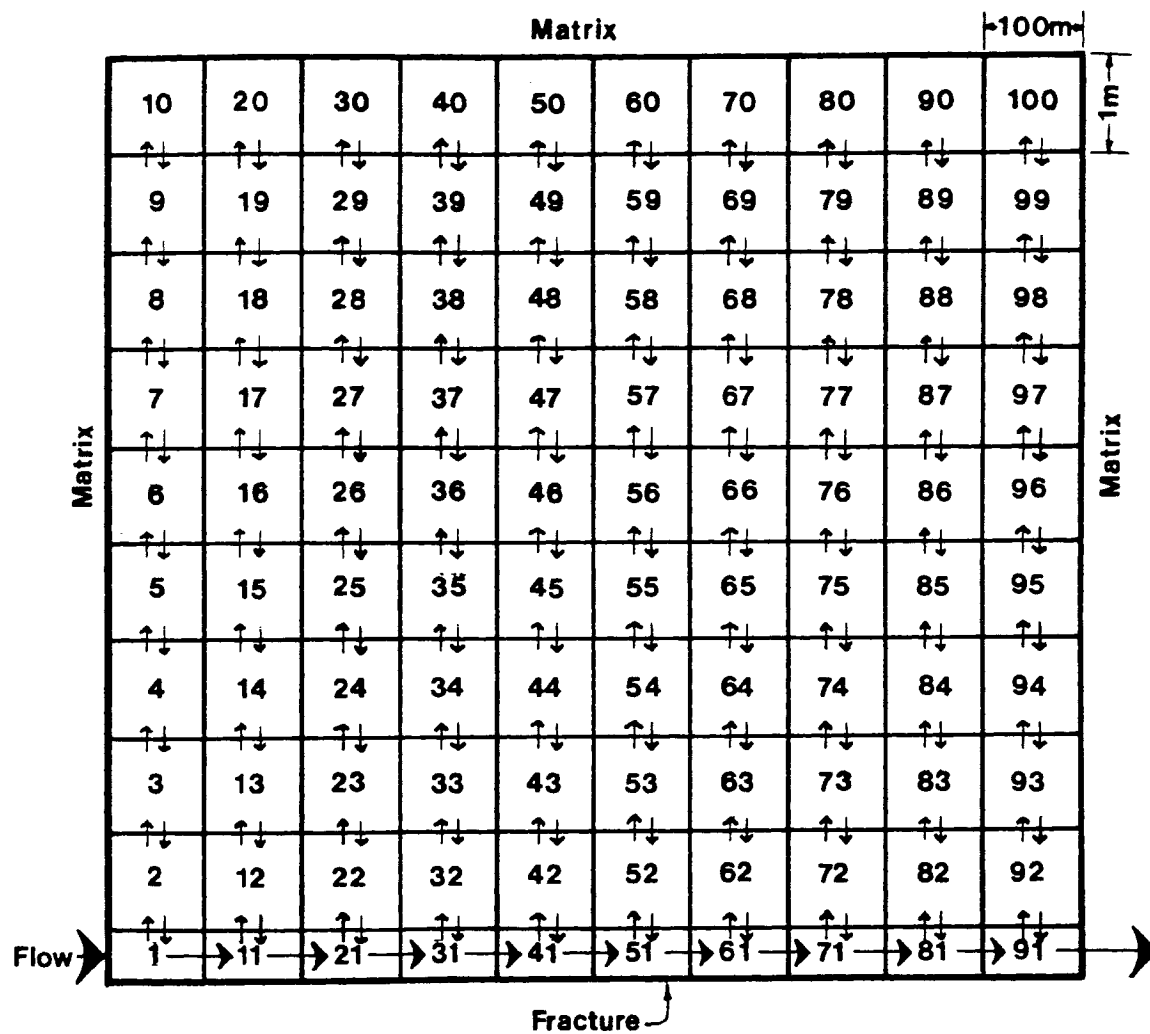
The form of the analytic solution can be given as:

$$\frac{C}{C_0} = \operatorname{erfc} \frac{[\Omega D^* / (V b)] X + Y}{2[D^*(t - X / V)]^{1/2}} \quad (5-1)$$

where b - fracture half-aperture width
 C_0 - initial solute concentration
 C - solute concentration in the matrix or fracture
 D^* - effective molecular diffusion coefficient of the solute
 erfc - complementary error function
 t - time
 V - water velocity in the fracture
 X - direction of fracture
 Y - direction normal to the fracture
 Ω - porosity

The compartmental model was compared against the analytic solution for a geometry described in Figure 5-1. The results of the trials are presented in Tables 5-1 and 5-2. Table 5-1 presents the calculated concentration at various points along the fracture using both the analytic and compartmental model solutions. The two techniques agree very well in this case and the error is, in all cases, less than three percent.

Table 5-2 presents the calculated concentration at various points normal to the fracture using both the analytic and compartmental model solutions. The agreement between the two techniques is generally excellent except at large distances from the fracture. The percentage difference at these distances is great, yet the actual magnitude of the discrepancy is minimal.



Matrix Diffusion Coefficient = 10^{-6} cm²/sec

Matrix Cell Porosity = 0.003

Fracture Cell Porosity = 1.0

Fracture Flow Velocity = 100 m/yr

Figure 5-1: System of cells used by DSC model to simulate matrix diffusion

Table 5-1: Calculated concentrations in various cells along a fracture using both the analytic and compartmental model solutions.

Cell	DSC -----Solution-----	Analytic	Difference	Error (Percent)
1	0.939	0.940	- 0.001	- 0.1
11	0.879	0.880	- 0.001	- 0.2
21	0.819	0.820	- 0.001	- 0.2
31	0.762	0.763	- 0.001	- 0.1
41	0.706	0.706	0.000	0.0
51	0.652	0.651	+ 0.001	+ 0.2
61	0.600	0.597	+ 0.003	+ 0.5
71	0.550	0.545	+ 0.005	+ 1.0
81	0.504	0.496	+ 0.008	+ 1.6
91	0.459	0.449	+ 0.010	+ 2.3

Table 5-2: Calculated concentrations in cells normal to the fracture using both the analytic and compartmental model solutions

Cell	DSC -----Solution-----	Analytic	Difference	Error (Percent)
1	0.939	0.940	- 0.001	- 0.1
2	0.779	0.784	- 0.005	- 0.6
3	0.492	0.501	- 0.009	- 1.7
4	0.277	0.284	- 0.007	- 2.5
5	0.139	0.142	- 0.003	- 2.0
6	0.062	0.062	0.000	0.0
7	0.025	0.023	+ 0.002	+ 6.9
8	0.009	0.008	+ 0.001	+ 18.5
9	0.003	0.002	+ 0.001	+ 40.7
10	0.001	0.001	+ 0.001	+ 116.2

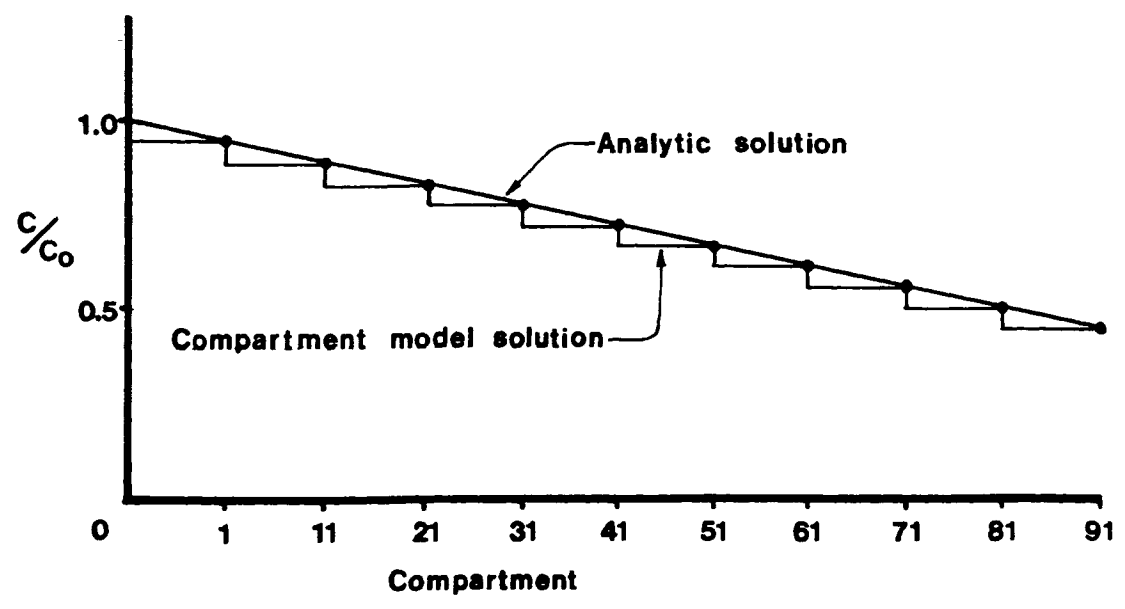
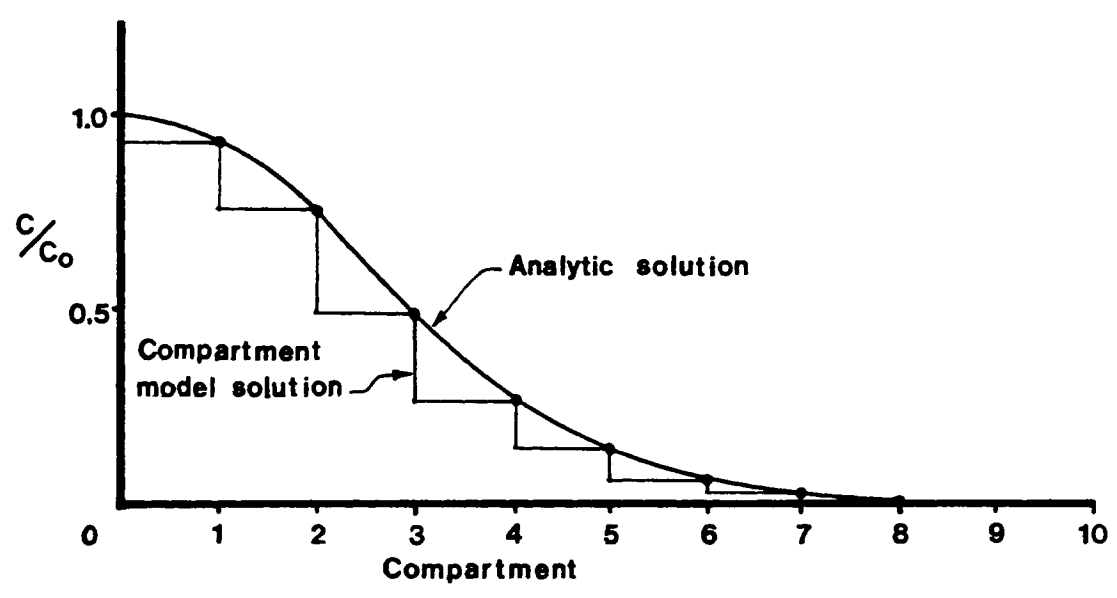


Figure 5-2: Comparison of analytic to DSC model solutions for cells normal to fracture (above) and cells along fracture (below)

Combined Advection and Diffusion Components

To validate the DSC model under as wide a range of conditions as possible, four examples provided by Neuman and Sorek (no date, in preparation) were evaluated. The first example solves the problem:

$$\frac{\partial C}{\partial t} = D^* \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (5-2)$$

for initial and boundary conditions:

$$C(x,0) = 0$$

$$C(0,t) = 1$$

$$C(x_R,t) = 0$$

The analytic solution for such a system is given by:

$$C(x,t) = 1/2 \left[\operatorname{erfc}\left(\frac{x - vt}{2(D^*t)^{1/2}}\right) + \exp\left(\frac{vx}{D^*}\right) \operatorname{erfc}\left(\frac{x + vt}{2(D^*t)^{1/2}}\right) \right] \quad (5-3)$$

The first example has been so specified such that:

$$D^* = 0.01$$

$$v = 0.05$$

$$x_R = 2.5$$

where all parameters are measured in a consistent set of units. This first example would require that a grid system be established so that the flux through the system would equal the volume of each cell during each iteration. In this way the advective component can be accurately modeled. By defining such a cell size, the value of the time step, Δt ,

can be related to the velocity and the cell length, Δx :

$$\Delta t = \Delta x / v \quad (5-4)$$

The cell length can be calculated from equation 4-11, which relates the value of FAC to Δx :

$$FAC = D^* \Delta t / \Delta x^2 \quad (5-5)$$

Substituting equation 5-4 into equation 5-5 and solving for Δx yields:

$$\Delta x = D^* / (v FAC) \quad (5-6)$$

The value of FAC must be equal to or less than 1.0 for reasons of stability. An arbitrary value of FAC equal to 0.4 results in a value of Δx of 0.5. This grid spacing is not as fine as the spacing (0.05) presented in the examples by Neuman and Sorek, yet allows for a solution of the problem.

The second example solves the same problem as the first. The initial and boundary conditions are identical. The parameters for the second example have been changed to:

$$D^* = 1.0$$

$$v = 10,000$$

$$x_R = 1.0$$

$$\Delta x = 0.02$$

By using a grid size identical to that presented by Neuman and Sorek and a time interval such that plug flow can be reproduced, FAC can be found:

$$FAC = 0.0025$$

The third and fourth examples evaluate the movement of a rectangular wave as it moves through the medium. The third example has been described by Equation 5-2 such that:

$$\begin{aligned} C(x,0) &= 1 && \text{when } 0.1 < x < 0.2 \\ C(x,0) &= 0 && \text{when } 0 < x < 0.1 \text{ and } 0.2 < x < 1.0 \\ C(0,t) &= C(1,t) = 0 \end{aligned}$$

The analytic solution is given by the equation:

$$C(x,t) = 1/2 \left[\operatorname{erf}\left(\frac{b-x+vt}{2(D^*t)^{1/2}}\right) + \operatorname{erf}\left(\frac{b+x-vt}{2(D^*t)^{1/2}}\right) \right] \quad (5-7)$$

where $2b = 0.1$ is the half width of the rectangular wave. A solution for the third example was obtained using the values of the parameters:

$$\begin{aligned} D^* &= 1.0 \\ v &= 1000 \\ \Delta x &= 0.02 \\ t &= 0.0006 \end{aligned}$$

For this example the parameter FAC was computed and found to be 0.060. A value of this magnitude should be easily incorporated into the model using the exchange mechanism.

When the DSC model was used to evaluate the three examples presented above, no reasonable results were obtained. To determine the cause of the unsatisfactory results for the first three examples, a simple network of advection along a fracture and dispersion into an

adjoining dead cell was postulated. Plug flow was prescribed for the fracture (cells one through three) and a mixing factor (FAC) equal to 0.5 was entered for the dispersion between one of the fracture cells (cell two) and the dead cell (cell four), as indicated in Figure 5-3. The results are presented in Table 5-3. The concentration in cell two becomes negative after the third iteration. It appears that the computer program is not able to accurately model both dispersion and advection during the same time step. It is evident that subroutines which are responsible for both advective transport and exchange transport need to be revised.

Table 5-3: Transport of a hypothetical tracer through a fracture (cells one through three) and into a dead cell (cell four).

Iteration Number -	1	2	3
Cell	State	State	State
1	1.0	0.0	0.0
2	0.0	1.0	- 0.5
3	0.0	0.0	1.0
4	0.0	0.0	0.5

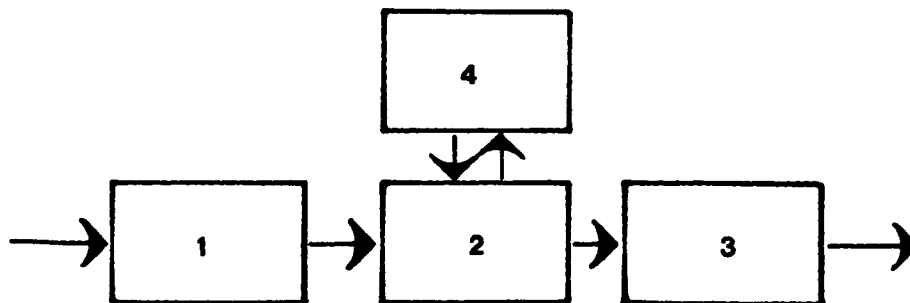


Figure 5-3: System of four cells with advective transport in cells 1, 2, and 3 with diffusion between cells 2 and 4.

The fourth example is solely concerned with the advective component of the advection-dispersion equation. For this example the following parameters have been set:

$$D^* = 0.0$$

$$v = 1$$

$$\Delta x = 0.02$$

$$t = 0.6$$

The value of the parameter FAC is zero for this example. Because the compartment model is superb at modeling pure piston flow, the results (presented in Table 5-4) are perfect for this example.

Table 5-4: Results of example four; pure piston flow.

Distance (x) :	0.68	0.70	0.72	0.74	0.76	0.78	0.80	0.82
State (C) :	0.0	0.0	1.0	1.0	1.0	1.0	1.0	0.0

Heat Transport

The movement of heat through subsurface geologic formations can be modeled using both convection and conduction components. A simple two-dimensional arrangement of cells was used to simulate the movement of heat from an isothermal body at a depth of 2800 m to the surface. Density, viscosity and specific heat were all considered to be independent of the temperature of the water. While this assumption introduces a minor error into the calculation, the model was considered valid for obtaining estimates of the thermal gradients in the subsurface.

Two scenarios were developed. The first assumes that no convective transport of heat occurs and that the entire heat movement is the result of conduction through the rock and the water within the pores of the rock. A hypothetical thermal conductivity of 5.45×10^{-3} cal/cm/sec/°C was used. The value represents a mean of observations found to be representative of the Tucson basin in Arizona (Sass et al., 1971). The results of the first scenario are presented in Figure 5-4 and show that the lines of equal temperatures correspond well with a hypothetical gradient of 3.0° C/100m.

The second scenario assumes that recharge in the highland areas on either side of the stream course moves downward and toward the center. It then moves upward, finally emerging along the stream channel. As can be observed in Figure 5-5, the lines of equal temperature indicate that lower temperatures predominate where water is moving downward. The highest temperatures are observed where the water is moving upward, transporting the deep, geo-thermal heat to the surface.

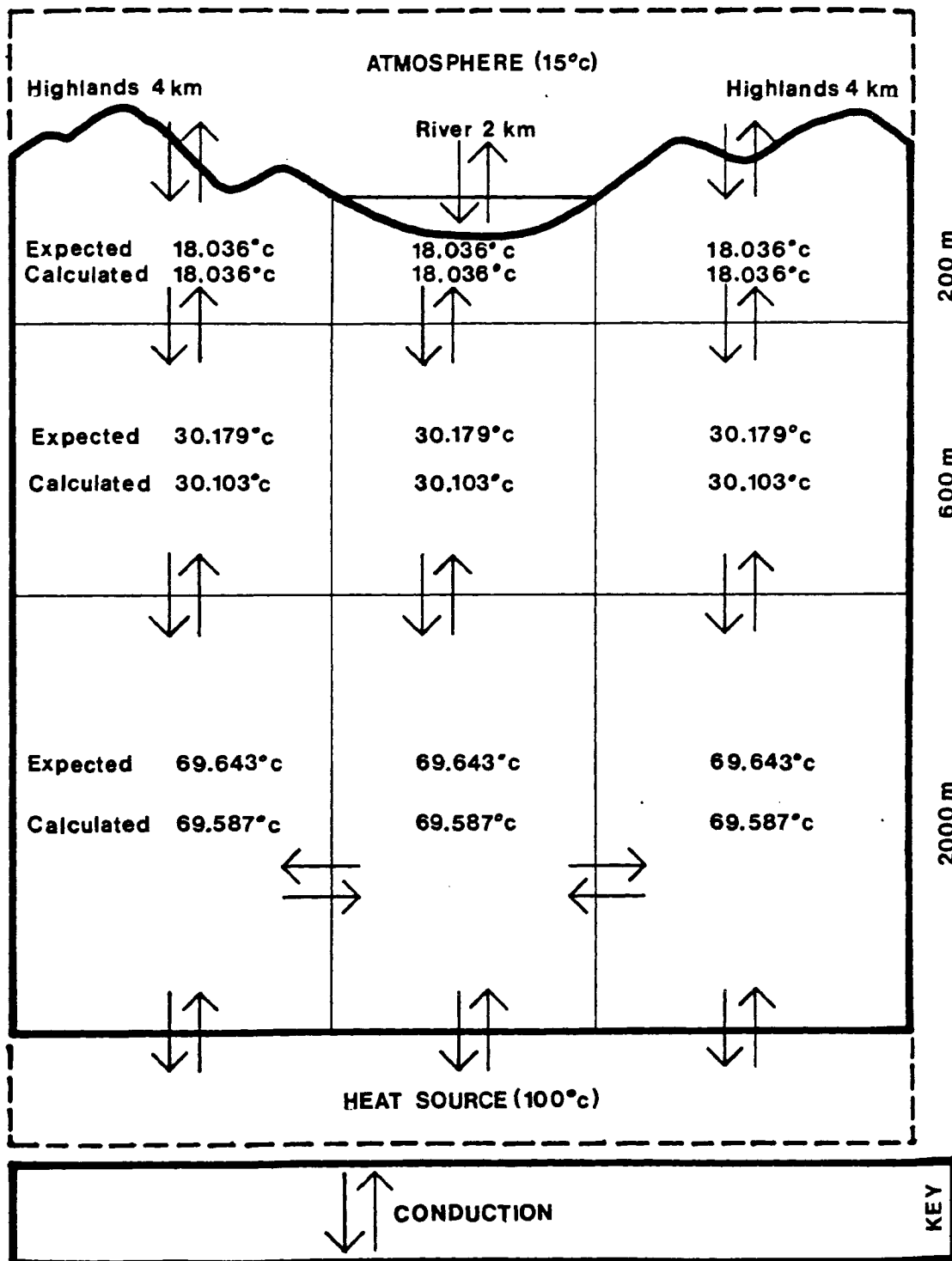


Figure 5-4: Heat flow in a hypothetical aquifer including only conduction of heat.

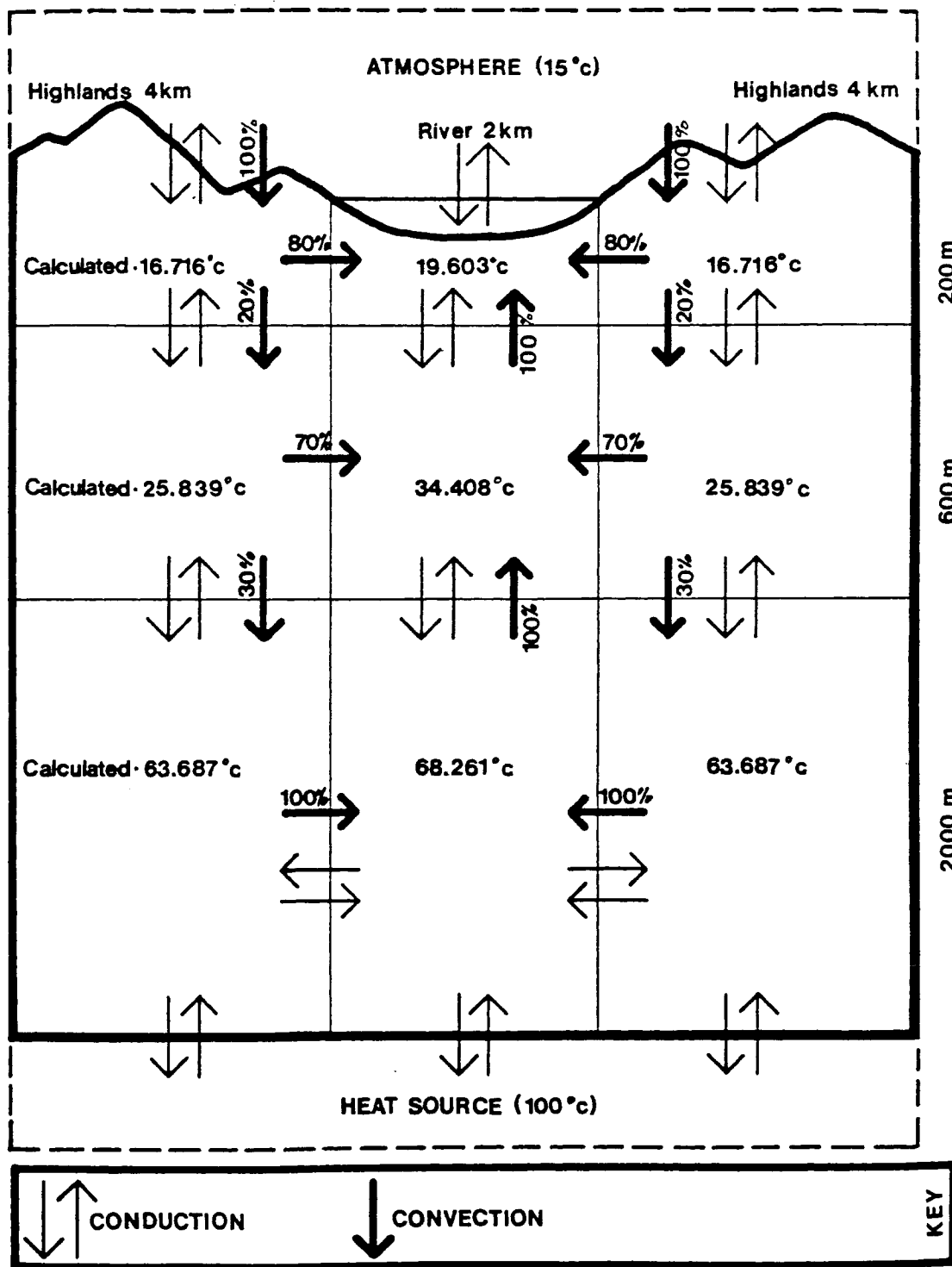


Figure 5-5: Heat flow in a hypothetical aquifer including conduction and convection

CHAPTER 6

CONCLUSIONS

The production of high-level radioactive wastes (HLRW) has required the assessment of various strategies for the safe disposal of those wastes. Various transport processes have been identified which could cause the movement of HLRW from the containment structure into the biosphere. The processes include advection, mechanical dispersion and diffusion. Diffusion through the rock matrix, termed matrix diffusion, along with sorption of the escaped radionuclides onto the rock matrix, may retard the migration of the HLRW. Radioactive decay of the HLRW also accounts for a reduction in the concentration of hypothetical contaminants. Heat production from the decay of the HLRW could also contaminate the biosphere.

In this investigation, a Discrete-State Compartment (DSC) model has been applied to the problem of simulating the processes mentioned above. The DSC has previously been converted to a computer code by M.E. Campana (1975). The parameters required by the DSC models were related to various aquifer characteristics, including the coefficients of molecular diffusion and hydro-mechanical dispersion, the specific heat conductivity and the heat capacity of the aquifer, as well as to the thermodynamic equilibrium coefficient.

The computer code was shown to accurately reproduce the effects of advection through a simple fracture system when compared to the analytic solution. It was also shown to accurately model matrix

diffusion in a direction normal to the fracture orientation.

The DSC model was shown to reproduce the analytic solution corresponding to a one-dimensional system in which the dispersive component dominates the advective component (a Peclet number less than 1.0). In addition, the computer code was shown to be capable of accurately modeling the case of pure advection within the one-dimensional system. The only cases that the model were unable to reproduce were when both advection and diffusion occur within the one-dimensional system. The source of the failure was shown to be attributable to an error in the computer code and not to an error in the conceptual model.

An application of the DSC model to heat transport was also made. The results indicate that the model can accurately reproduce conductive heat transport from a heat source located at a great depth.

In addition, it was shown that the sorption and desorption processes can be modeled by the use of a new dispersion coefficient in steady-state conditions. During transient conditions, it was shown that the DSC model can consider the time-dependent nature of the sorption-desorption process if a first-order coefficient is utilized.

Finally, the use of a retardation factor was shown to affect the steady-state concentration of an unstable radionuclide. A previous author (Van Genuchten, 1981) had reached the opposite conclusion. His conclusion was shown to be in error.

APPENDIX A

DEPENDENCE OF STEADY STATE SOLUTION ON RETARDATION FACTOR

The general form of the advection-dispersion (AD) equation is:

$$\frac{\partial}{\partial x} (\Omega D \frac{\partial C}{\partial x} - vC) - \frac{\partial}{\partial t} (\Omega C + \rho S) = \alpha \Omega C + \beta \rho S - \lambda \Omega \quad (A-1)$$

- where
- C - solution concentration (M/L³)
 - S - adsorbed concentration (M^o)
 - Ω - porosity (L^o)
 - D - dispersion coefficient (L²/T)
 - v - fluid flux density (L/T)
 - ρ - porous medium bulk density (M/L³)
 - α - first-order liquid phase decay constant (1/T)
 - β - first-order solid phase decay constant (1/T)
 - λ - zero-order liquid phase source term (M/L³/T)

An equilibrium constant, K_d (L³/M), can be defined such that;

$$S = K_d C \quad (A-2)$$

a retardation factor can be defined such that;

$$R = 1 + \rho/\Omega K_d \quad (A-3)$$

and a decay factor would be;

$$\mu = \alpha + \beta \rho/\Omega K_d \quad (A-4)$$

Equation A-1 can be reduced to;

$$\frac{\partial}{\partial x} (\Omega D \frac{\partial C}{\partial x} - vC) - \frac{\partial}{\partial t} (\Omega RC) = \Omega \mu C - \lambda \Omega \quad (\text{A-5})$$

For boundary conditions:

$$\frac{\partial C}{\partial x}(\infty) = 0 \quad (\text{A-6})$$

$$(-D \frac{\partial C}{\partial x} + vC) = vC_0 \quad \text{at } x = 0 \quad (\text{A-7})$$

Assuming constant D, the governing equation would be:

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \mu C + \lambda = 0 \quad (\text{A-8})$$

and the steady-state solution would be (Van Genuchten, 1981):

$$C(x) = \frac{\lambda}{\mu} + (C_0 - \frac{\lambda}{\mu}) \left(\frac{2v}{v+u} \right) \exp \left[\left(\frac{v-u}{2D} \right) x \right] \quad (\text{A-9})$$

$$\text{where; } u = v \left(1 + 4 \mu D / v^2 \right)^{1/2} \quad (\text{A-10})$$

Van Genuchten (1981) states that this solution is not affected by the retardation factor, R, which does not appear in the equation.

Equations A-4 and A-5, however, relate R to μ in the following manner:

$$R - 1 = \rho / \Omega K_d \quad (\text{A-11})$$

$$\mu = \alpha + \beta(R - 1) \quad (\text{A-12})$$

when $\alpha = \beta$, then $\mu = \alpha R$ indicating that the decay factor is directly related to R, to the contrary of the observation made by Van Genuchten.

An alternate way of approaching this problem would be to use residence time theory (Himmelblau and Bischoff, 1968; Newton, 1959) where the distribution coefficient can be related to mean residence times. In theory, the ionic species can be described as spending a specific length of time sorbed onto the rock matrix as well as in the dissolved state in the free pore or fissure water. At equilibrium, the rate of sorption would equal the rate of desorption;

$$\Omega \frac{C_W}{t_W} = \rho \frac{C_S}{t_S} \quad (A-13)$$

where ΩC_W - number of ions in solution per unit bulk volume
 ρC_S - number of ions on solid per unit bulk volume
 t_W - mean residence time of ion in water
 t_S - mean residence time of ion on solid

rearranging yields:

$$t_S / t_W = \rho / \Omega K_d = R - 1 \quad (A-14)$$

The total life of a radioactive ion, t_t , would be equal to the time spent in the water plus the time spent sorbed onto a solid.

$$t_t = t_S + t_W \quad (A-15)$$

The distance that the ion travels, Δx , while in a mobile state would be:

$$\Delta x = t_W v_W \quad (A-16)$$

Substituting the value of t_W obtained from Equation A-15 into Equation

A-16 yields:

$$\Delta x = v_w (t_t - t_s) \quad (\text{A-17})$$

Let t_t' equal the half-life of the radioactive tracer. The distance traveled in one half-life, $\Delta x'$, would be:

$$\Delta x' = v_w (t_t' - t_s) \quad (\text{A-18})$$

Because t_t' and v_w are constants, it is clearly indicated by Equation A-18 that the magnitude of $\Delta x'$ depends on the magnitude of t_s .

APPENDIX B

DERIVATION OF TRANSIENT STATE EQUATION FOR SORPTION-DESORPTION EQUILIBRIA

It is the purpose of this appendix to obtain the solution to the first-order linear differential equation which was previously presented as Equation 4-20. The equation was presented as an approximation for the time dependent sorption of a dissolved tracer onto a rock substrate. Equation 4-20 is of the form:

$$\frac{dC_W}{dt} = -\frac{1}{K_+} (C_W - C_S / K_d) \quad \text{for } C_S < K_d C_W \quad (\text{B-1})$$

where C_W - number of ions in solution/volume of solution (M/L^3)
 C_S - number of ions on solid/gram of solid (M°)
 K_d - thermodynamic equilibrium coefficient (L^3/M)
 K_+ - Sorption rate coefficient (T)

The total concentration, C_t , can be obtained by adding the sorbed concentration of the tracer to the dissolved concentration. This can be expressed by:

$$\rho/\Omega C_S + C_W = C_t \quad (\text{B-2})$$

where ρ - bulk density of the medium, dry mass (M/L^3)
 Ω - porosity of the medium (L°)

At equilibrium, the concentration of tracer in the water can be related to the concentration sorbed onto the matrix by the relation:

$$C_w = C_s / K_d \quad (B-3)$$

Substituting Equation B-3 into B-2 yields:

$$(\rho/\Omega K_d + 1) C_s / K_d = C_t \quad (B-4)$$

or;

$$C_s / K_d = C_t / R \quad (B-5)$$

where;

$$R = 1 + \rho/\Omega K_d \quad (B-6)$$

Substituting Equation B-6 into B-1 yields the expression:

$$\frac{dC_w}{dt} = -\frac{1}{K_+} (C_w - C_t / R) \quad \text{for } C_s < K_d C_w \quad (B-7)$$

Separating variables yields:

$$\frac{dC_w}{dt} + \frac{C_w}{K_+} = \frac{C_t}{K_+ R} \quad (B-8)$$

Applying an integrating factor results in:

$$\frac{d (C_w e^{t/K_+})}{dt} = e^{t/K_+} [C_t / (K_+ R)] \quad (B-9)$$

Integrating both sides of Equation B-9 yields:

$$C_w e^{t/K_+} = e^{t/K_+} (C_t / R) + \text{constant} \quad (B-10)$$

Multiplying by the reciprocal of the integrating factor leaves:

$$C_w = C_t / R + \text{constant } e^{-t/K_+} \quad (B-11)$$

Solving for the boundary conditions:

$$C_w = C_t \quad \text{for } t = 0 \quad (\text{B-12})$$

$$\text{constant} = C_t (R - 1) / R \quad (\text{B-13})$$

or;

$$\text{constant} = C_t (\rho/\Omega K_d) / R \quad (\text{B-14})$$

The solution can thus be written as:

$$\frac{C_w}{C_t} = F / R \quad (\text{B-15})$$

where;

$$F = 1 + \rho/\Omega K_d e^{-t/K_+} \quad (\text{B-16})$$

Equations B-15 and B-16 are presented in the text as Equations 4-22 and 4-23.

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