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ABSTRACT

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The ultimate goal of this work is to quantify through basic chemistry and physics the role of radiocolloids as a mechanism in the release of radioactive material from the proposed waste repository site at Yucca Mountain, Nevada. Colloids are very fine particles that can carry large amounts of radioactive material and have been shown to migrate in groundwater through porous media over hundreds of meters. Colloids migrate at rates greater than the average groundwater velocity and at rates much greater than reactive dissolved radionuclides because they remain in the large fractures or paths because of size exclusion from the small pores and fissures. The chemical and physical behavior of colloid migration in geological media is markedly different from that of dissolved species. The role of colloids in geological systems is not well established since these submicroscopic particles have only recently become detectable through laser optics. Hence one goal of this ongoing colloid study is to experimentally and theoretically develop a fundamental mathematical model to predict the transport of radiocolloids in groundwater.

The purpose of this study is to analyze and compare the dissolved species and colloid breakthrough curves obtained from a series of laboratory-scale single-fracture tracer experiments. Experiments were performed with a block of fractured tuff collected from the surface outcropping of the Topopah Spring Member of the Paintbrush Tuff at Yucca Mountain, Nevada. The sample was selected for its network of natural fractures. Carbonate cements within the fractures were removed before the tracer tests by leaching with dilute HCl solution. The experiments were part of the Dynamic Transport Task of geochemical investigations for the Yucca Mountain Project, sponsored by the U.S. Department of Energy.

I. INTRODUCTION

The Yucca Mountain Project (YMP) is a U.S. Department of Energy (DOE) effort to determine whether a nuclear waste repository constructed in unsaturated tuff beneath Yucca Mountain, Nevada, will meet the U. S. Nuclear Regulatory Commission (NRC) criteria for licensing. The NRC 10CR60 Regulation sets limits on the cumulative release of many radionuclides from the repository to the accessible environment for 10 000 years after disposal (U.S. NRC, 1983). Estimates of the transport and retardation of radionuclides are necessary to assess the expected postclosure performance of a potential repository. Laboratory experiments and computer-based modeling studies are being performed to obtain reliable estimates of

radionuclide transport in the Yucca Mountain tuffs. In addition, an Exploratory Shaft Facility will be constructed that provides access to the target rock formations of the planned repository. In situ experiments will be conducted from the shaft as part of site evaluation.

In their comments on the Final Environmental Assessment, Yucca Mountain Site (U.S. NRC, 1983), NRC raised several concerns regarding the colloid transport of radionuclides. Among these questions is the effect of colloid size on transport through pores and fractures. To resolve those questions, the effects of colloid birth and death processes that can modify the affinity of colloids for attachment or repulsion by matrix materials must be understood, and the dynamics of colloid size distributions must be modeled. Further, mechanisms of charge effects that can modify the affinity of colloids for attachment or repulsion by matrix materials must be understood to model radiocolloid transport. Figure 1 is a schematic diagram illustrating the major processes that may occur during migration of colloids in a saturated porous/fractured medium. Assessing the total system performance of the repository will require incorporating these colloid effects into the performance models.

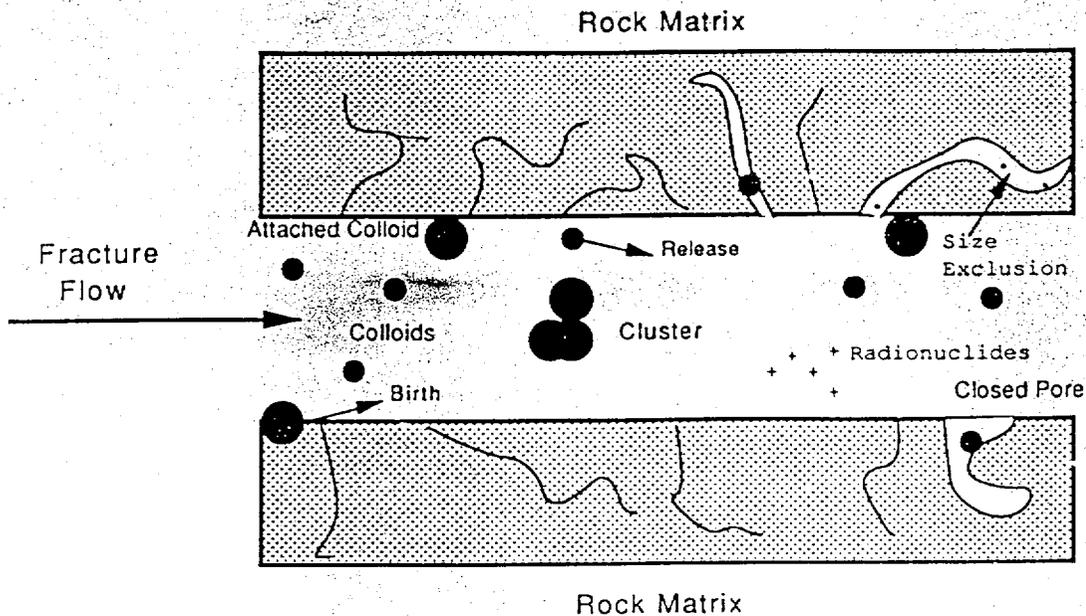


Fig. 1. Colloid transport processes.

This report includes a synopsis of Los Alamos National Laboratory's (LANL's) recent colloid migration studies. An overview of modeling and experimental studies, presented in Fig. 2, shows how colloid research at LANL is being integrated to predict the behavior of radiocolloids at the Yucca Mountain repository. A comprehensive colloid migration study is required because colloid migration in groundwater is a new area of investigation and is poorly understood. The existence of groundwater colloids and their potential importance to nuclear waste disposal is of concern to the NRC, DOE, and numerous foreign countries that are developing waste disposal strategies and sites.

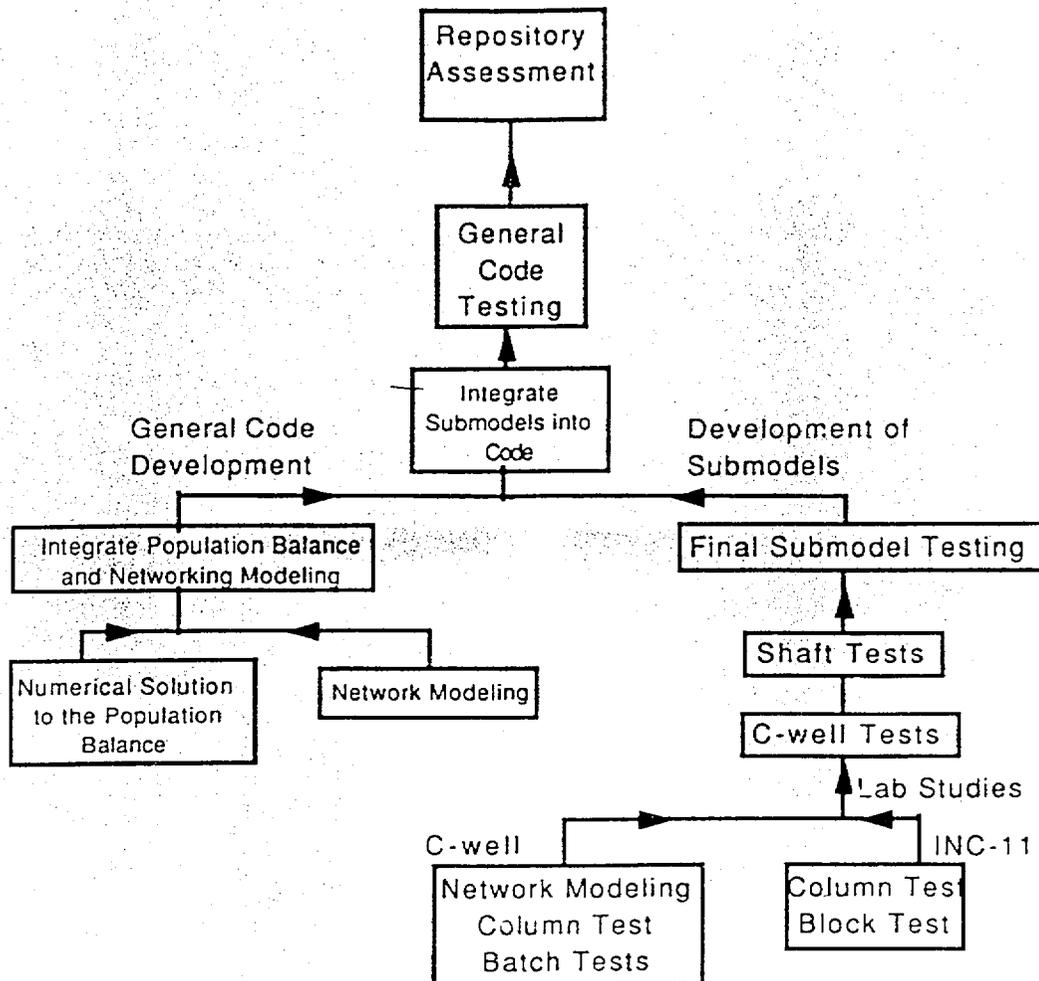


Fig. 2. Colloid study plan.

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A. Project Overview

The work presented in this report is in harmony with the colloid study plan presented in Fig. 2. The purpose of this work is to quantify the role of radiocolloids as a mechanism in the release of radioactive material from the proposed Yucca Mountain waste repository site. The colloid study plan is to develop a particulate transport model using basic chemistry and physics and to verify this model through laboratory and field experiments. The model development is based on the Population Balance equation, which is a basic transport equation capable of describing in great detail the migration of colloids through geological media [Randolph and Larson 1988]. Development of this model requires both a generalized numerical solution to the Population Balance equation and the mathematical representation of the physical and chemical processes that affect colloid migration and the ultimate transport of radionuclides [Nuttall 1986; Nuttall 1989]. This report concentrates on the INC-11 Block Tests, as illustrated in Fig. 2.

In this report Robert Rundberg's [Rundberg et al. 1988] single-fracture data are modeled and the results are analyzed. A model and computer code were developed from the work by Tang et al. [1981] (See Appendix D for additional modeling references.) With this code, the dissolved species breakthrough curves and colloid breakthrough curves from Rundberg's fractured tuff experiment were analyzed and the results were presented. Next is a description of the ongoing general code development, followed by a summary of the submodel development studies.

B. General Code

The general numerical solution to the Population Balance equation is being developed by the method of lines (MOL) technique. This method, which is described in this report, has several advantages. First, it is able to solve high-dimensional partial differential equations. The Population Balance, in addition to two or three spatial dimensions, has a dimension for particle size and one for the concentration of each radionuclide that adsorbs to the colloids [Randolph and Larson 1988]. Second, the method was developed at LANL by Hyman [1979] and has been tested in the public domain for over 12 years.

The following steps will be taken.

1. Implement quality assurance (QA) software procedures and plans.
2. Become familiar with computer access procedures.
3. Write a FORTRAN code using the open CRAY computers to reproduce the GAS REACTION test case results presented by Hyman in his MOL1D documentation manual [Hyman 1979].

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4. Move and convert Hyman's MOL1D subroutines and test case from the Cray computer to the ESS-5 Sun computer system. Use the Sun VMS-compatible FORTRAN compiler to repeat the GAS REACTION test case.
5. Write a report detailing and summarizing accomplishments in Tasks 1-3.

C. Development of Submodels

This subtask requires both theoretical efforts and close interactions with the ongoing experimental programs at LANL and throughout the world. Since colloid migration in porous media is poorly understood, we are having to develop and test many of the submodels. In general, the submodels are mathematical descriptions of the following physical and chemical phenomena:

- Birth (heterogeneous and homogeneous nucleation) rate
- Release rate of colloids from the rock matrix
- Death rate
- Growth rate
- Agglomeration rate
- Deagglomeration rate
- Adsorption/desorption of radionuclides
- Decay of nuclei in or on a colloid

The development of each submodel is tied to the colloid study plan presented in Fig. 2. The birth of colloids in the far field is caused by the formation and release of clay particles from rock. The birth rate of new particles will be determined from field water sample studies to be performed as part of the shaft tests. The birth rate or release of previously captured particles will be determined from both the current Rundberg experiments and future column tests. The death or capture rate of particles was determined from the Rundberg et al. [1988] experiments, with the results presented in this report. It is anticipated that further colloid capture data will be available from future laboratory column and field experiments. Studies to date have indicated that colloid adsorption and desorption can be modeled by considering electrokinetic and molecular forces [Barouch et al. 1987; Israelachvili 1985; Kally and Matijevic 1981; Nelligan et al. 1982; Matijevic and Kallay 1982; Spielman and Friedlander 1974]. (See Appendix D for additional references.)

Colloid growth rates are considered unimportant in the far field since the main source of colloids in this region is believed to be from clay present either in the groundwater or released from rock. Clay particles do not grow in solution.

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Agglomeration can be modeled by adding electrokinetic forces to the Smoluchowski theory [Levich, 1962; Nuttall, 1989]. The agglomeration caused by the presence of bacteria is being studied by Hersman [1988]; it appears to be caused by polymer bridging resulting from excretions from the bacteria that coat the clay and cause rapid coagulation. Further investigation and studies of this phenomenon are planned by Hersman and are currently underway. Deagglomeration is not believed to be a major factor in the far field but further studies will be required to verify this assumption.

Adsorption/desorption studies of species on clay are being planned by both HSE-12 and INC-11 groups at LANL. This rate and capacity information should be adequate to model the phenomena. Finally, decay of nuclei is well known from the published half-lives of various species.

II. TREATMENT OF RUNDBERG'S DATA

The purpose of this task is to analyze and compare the dissolved species and colloid breakthrough curves obtained from a series of laboratory-scale single-fracture tracer experiments. Experiments were performed with a block of fractured tuff collected from the surface outcropping of the Topopah Spring Member of the Paintbrush Tuff at Yucca Mountain in Nevada. The sample was selected for its network of natural fractures. Carbonate cements within the fractures were removed before the tracer tests by leaching with diluted HCl solution. The experiments were part of the Dynamic Transport Task of geochemical investigations for the Yucca Mountain Project.

A. Experiment and Data

The block of fractured tuff used in these experiments was collected from surface outcropping of the Topopah Spring Member of the Paintbrush Tuff. This sample is composed of devitrified ash-flow tuff, and its mineralogy is similar to that of other Topopah Spring samples used for previous fracture flow experiments [Rundberg et al. 1986]. This sample was selected for its network of natural fractures. When the block was collected, fractures in the block were filled with carbonate minerals. Such fracture cements are common constituents of surface samples but are absent in deeper drill core samples. After the block was partially encapsulated, the fracture carbonate cements were removed by leaching with a diluted HCl solution. Accessible matrix porosity and fracture network volume have been determined to be 149 cm^3 ($21.3 \text{ cm}^3/\text{kg}$ dry weight), from measurements of block dry weight and total saturated weight.

The block of tuff was encased in a LEXAN box and sealed with SILACIC. This design is not capable of simulating natural lithostatic or hydrostatic loads but was designed to eliminate leakage of solutions around the seals.

Tracer-loaded solutions were injected through the fracture network sample with SAGE syringe pump using 60-cm³ syringes. The syringe pump was chosen because it could provide a steady flow at low to high rates for the large volumes and time periods necessary to obtain data for these experiments. Pressure drops across the fracture were measured by placing Kistler 4053A1 piezoresistive transducers at the enclosure inlet and outlet ports.

B. Model

In this section, the model used to analyze Rundberg's data is derived from the general form of the population balances, and the filtration type submodel for particle capture is developed. The general Population Balance Model [Nuttall 1989; Nuttall 1986] can be reduced to a model that has been solved analytically by Tang et al. [1981]. We begin with the general form of the population balance:

$$\frac{\partial \psi_k}{\partial t} + \nabla \cdot (\bar{v} \psi_k) - D_b \nabla^2 \psi_k + \sum_{j=1}^m \frac{\partial (v_j \psi_k)}{\partial \xi_j} + L_k - B_k = 0. \quad (1)$$

Here,

D_k represents the rate of particle number disappearance from a particular particle size category per unit solution volume. Death is caused by colloid capture on the rock matrix, by agglomeration, and by dissolution.

B_k represents the rate of appearance of particles into a size category per unit solution volume. Births result from nucleation, agglomeration, and release of captured or new colloids from the rock matrix.

v_j is the growth rate or dissolution rate on a molecular scale for colloids. This term accounts for the gradual increase or decrease of particle size caused by mass addition or subtraction from colloids.

$$\sum_{j=1}^m \frac{\partial (v_j \psi_k)}{\partial \xi_j}$$

is the rate of population density change along a property axis, for example, colloid growth along the particle size axis. Also, it represents and accounts for the concentration of radionuclides on the colloids.

$$\frac{\partial \psi_k}{\partial t} + \nabla \cdot (\bar{v} \psi_k) - D_b \nabla^2 \psi_k$$

These three terms represent respectively, the accumulation in the number of colloids of a particular size per unit solution volume, the convective transport of particles, and the dispersive transport of particles in the fluid stream.

In summary, the submodels needed to treat radiocolloid transport are

- Birth (heterogeneous and homogeneous nucleation) rate
- Release rate of colloids from the rock matrix
- Death rate
- Growth rate
- Agglomeration rate
- Deagglomeration rate
- Adsorption/Desorption of radionuclides
- Decay of Nuclei within or on a colloid

Parameters within the submodels can, in some cases, be determined from theory; others require experimental evaluation. Many investigators in numerous fields have used the Population Balance Model, and their modeling results can aid in developing and evaluating the necessary submodels.

The model and analytical solution by Tang et al. [1981] for transport through a single fracture was used in this report to model dissolved species data presented in the report by Janecky et al. [1987]. Rundberg [1988] used the same basic model, but with a filtration capture submodel to describe the colloid transport data. The Tang model follows directly from the the general Population Balance Eq. (1). The simplifying assumptions that reduce Eq. (1) to Tang's model are

1. One spatial dimension
2. One particle size (monodispersed particles)
3. No birth term (particles are introduced as an initial condition)
4. Particles disappear by three mechanisms:
 - a. radioactive decay (this term will represent removal by filtration, as will be explained later)
 - b. Adsorption/desorption on the fracture surface
 - c. Diffusion into the rock matrix with adsorption/desorption

The reduced equation [See Tang et al. (1981) Eq.(1)] becomes

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial z} - D \frac{\partial^2 c}{\partial z^2} + \text{Death Model} = 0, \quad (2)$$

where death terms in Tang's model are: $\lambda c + \left(\frac{\lambda}{b} s \right) + \frac{q}{b}$

1. radioactive decay or filtration (λc or vfc)
2. fracture surface adsorption $\left(\frac{\lambda}{b}\right)s$
3. diffusion into the rock matrix $\left(\frac{q}{b}\right)$

Other terms used here or in the equations below are

- a = dispersivity in the fracture, L
 $2b$ = fracture width, L
 c = colloid concentration in solution, $c(t, z)$, M/L^3
 D' = diffusion coefficient in the matrix, ($D' = \tau D^*$), L^2/T
 D = hydrodynamic dispersion coefficient, $(\alpha_L v + D^*)$, L^2/T
 D^* = molecular diffusion coefficient in water, L^2/T
 g = decay constant, $(\ln 2/t)$, $1/T$
 f = filtration coefficient, $1/L$
 K = distribution coefficient, s/c
 R' = matrix retardation coefficient, dimensionless, $(1 + K)$
 s = mass of solute adsorbed per unit length of fracture surface, $s(z, t)$, M/L^2
 t = time, T
 q = diffusive flux perpendicular to the fracture axis, M/L^3T
 v = groundwater velocity in the fracture, L/T
 z = coordinate along the fracture axis, L
 r = bulk density of the matrix, M/L^3
 τ = rock matrix Tortuosity

Tang et al. [1981] define a surface distribution coefficient K (s/c) and corresponding retardation coefficient $R = 1 + \frac{Kf}{b}$. Substituting these into Eq. (2) gives

$$\frac{\partial c}{\partial t} + \frac{v \partial c}{R \partial z} - \frac{D \partial^2 c}{R \partial z^2} + \lambda c + \frac{q}{bR} = 0 \quad (3)$$

In this study of colloid migration and capture in a fracture, the radioactive decay term in Eq. (3) was replaced by the particle filtration expression, vfc (velocity \times filtration coefficient \times concentration). The classic filtration model represented by vfc was first developed by Iwasaki [1937]. The substitution of vfc for the radioactive decay λ was derived by Tien and Payatakes [1979] under the assumptions of uniform velocity and no axial dispersion. Tien and Payatakes [1979] note that the Iwasaki filtration model is tantamount to first-order kinetics. In this study, filtration is basically treated as first-order kinetics of adsorption as also derived for this type of problem by Rajagopalan and Chu [1982]. The concept of a first order-kinetic adsorption/desorption process is further developed in

Sec. III. ELECTROKINETIC MODEL FOR ADSORPTION/DESORPTION. The basic filtration model has been extensively investigated in numerous studies as discussed by Tien and Payatakes, [1979]. Problems with the filtration model are that it is empirical in the treatment of electrokinetic forces and that it does not treat the very important phenomenon of colloid desorption. In fact, the results of this current study show the inadequacy of the filtration model for treating colloid migration through natural media.

In further development of Tang's model, the analytical solution in dimensionless form of Eq. (3) is

$$\frac{c}{c_0} = \frac{\exp(vz)}{\sqrt{\pi}} \int_1 \exp \left[-\xi^2 - \frac{\eta^2 z^2}{4\xi^2} \right] \exp(-\eta z^2) \left\{ \exp[-\sqrt{\lambda}Y] \operatorname{erfc} \left[\frac{Y}{2T} - \sqrt{\lambda}T \right] + \exp[\sqrt{\lambda}Y] \operatorname{erfc} \left[\frac{Y}{2T} + \sqrt{\lambda}T \right] \right\} d\xi \quad (4)$$

where the groups are

$$1 = \frac{z}{2} \sqrt{\frac{R}{Dt}}$$

$$Y = \frac{v^2 \beta^2 z^2}{4A\xi^2}$$

$$v = \frac{V}{2D}$$

$$\beta^2 = \frac{4RD}{v^2}$$

$$T = \sqrt{t - \frac{Rz^2}{4D\xi^2}}$$

$$\eta = \frac{\lambda R}{4D\xi^2} \text{ or } \frac{v\lambda R}{4D\xi^2}$$

$$A = \frac{bR}{\theta V R' D'}$$

Eq. (4) represents mathematically the migration of a species through a single fracture in a porous media, as illustrated in Fig. 3. Figure 3 was assumed to schematically represent the experimental setup used by Janeky et al. [1987] in their study to consolidate dissolved specie

tracers, and to schematically represent the experimental setup used by Rundberg et al. [1988] for his study of colloid migration through fractured tuff.

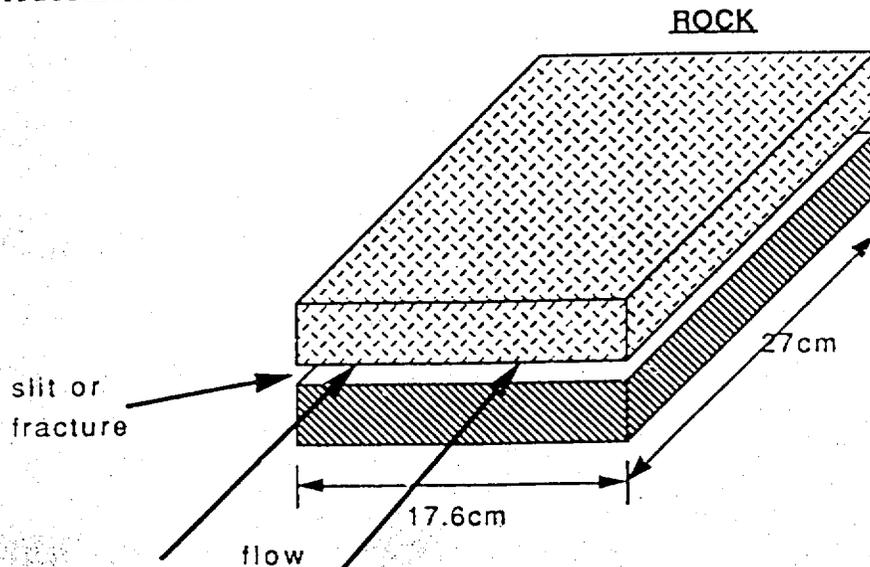


Fig. 3. Model representation of Rundberg's experimental system [Rundberg et al. 1988]

C. Results

To interpret the experimental data, Eq. (4) was solved by use of a numerical computer code (Appendix A). This code was first verified by comparing code results with a published problem present by Tang et al. [1981]. Test problem conditions are given in Table I, and the comparison of the calculated and published concentration profiles is shown in Fig. 4. The code showed very good agreement with the published results.

TABLE I. MODEL PARAMETERS FOR CODE VERIFICATION

Parameters	Definition
100 μm	fracture width
$5.78 \times 10^{-4} \text{ cm}^2/\text{s}$	dispersion coefficient in the fracture
50 cm	dispersivity
$1.6 \times 10^{-6} \text{ cm}^2/\text{s}$	diffusion in the rock matrix used in simulation
$1.78 \times 10^{-9} \text{ s}^{-1}$	decay constant
$1.16 \times 10^{-5} \text{ cm/s}$	fluid velocity

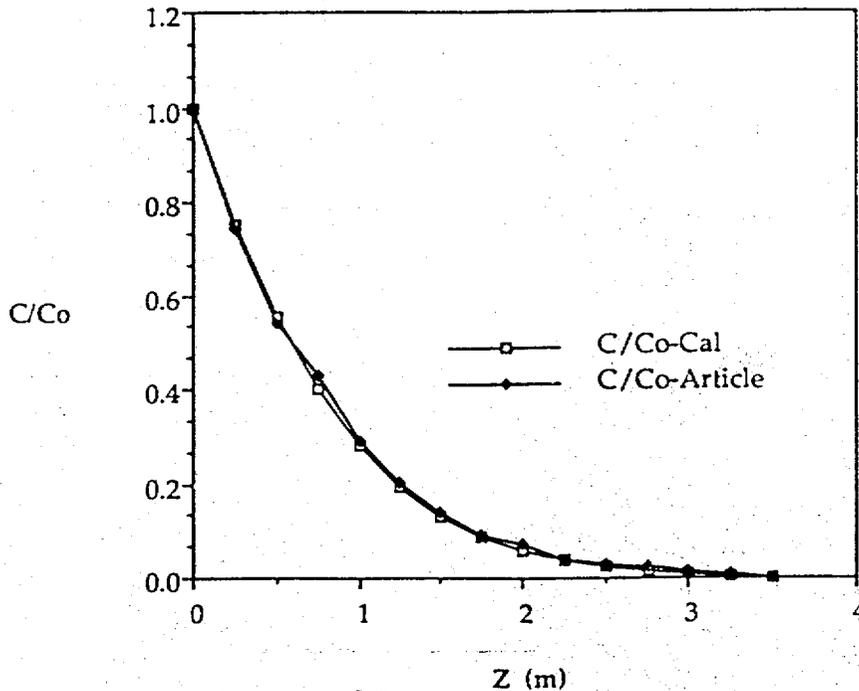


Fig. 4. Comparison of code values and published values from Tang et al. [1981].

Next the percent recoveries were calculated for the three sizes of colloids (10 μm , 0.91 μm , and 0.1 μm) and for two dissolved species (^{131}I and TcO_4^-) (Fig. 5). The TcO_4^- recovery data were not analyzed but were presented to show that conservative tracers other than ^{131}I are also retained in the tuff. Recovery of ^{131}I and the 0.91- μm colloid were about the same at 27% and 25% respectively. The major effect was the low recovery of the 0.1- μm and the 10- μm colloids at 5% and 0.01% respectively. This indicates that for the large particles, additional capture mechanisms are present such as straining, inertial capture, and gravitational effects. I believe that the low recovery of the smaller 0.1- μm colloids is due to migration of these particles into microfractures and dead pores, whereas the large 0.91- μm colloids were excluded from those smaller pores. The effects of size exclusion appears to be real and were also seen in the field data of Harvey et al. [1988] although the experiments by Harvey et al. were in a sandy aquifer. Their data indicate that 1.0- μm colloids traveled on the

average much faster than the smaller 0.1- μm colloids. This effect of particle size exclusion is illustrated graphically in Fig. 10.

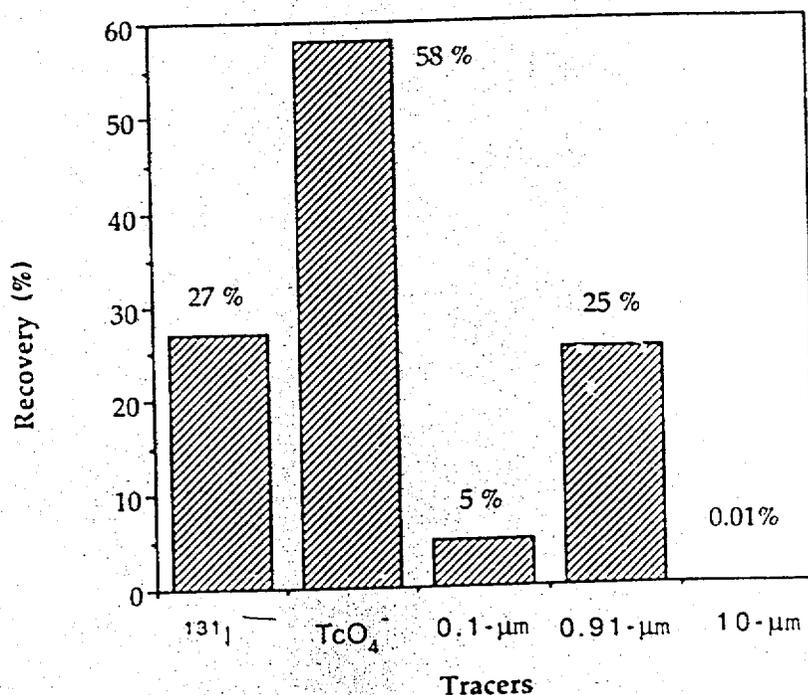


Fig. 5. Recovery of tracers used in fracture flow experiments. (The numbers refer to colloids of various sizes. The ^{131}I and TcO_4^- are conservative tracers.)

The Tang code shown in Appendix A was used to simulate the ^{131}I tracer tests. The detailed information about these dissolved species tracer tests is given by Janecky et al. [1987]. The purpose in modeling this dissolved species data was to test Tang's model and determine the effective dispersion coefficient for the fracture network. (The rock sample was the same for both the dissolved tracer and the colloid tracer experiments.) Neretnieks et al. [1982] studied the movement of tracers in a single fracture and used a mathematical model similar to Tang's for interpreting the results. Recently Moreno et al. [1985] also used Tang's model to analyze their single-fracture experiments. Their results were in good agreement with Tang's model. Table II provides a list of modeling parameters used to calculate the breakthrough curve presented in Fig. 6.

Tang's analytical solution fits the dissolved species data very well, as illustrated by the comparison of breakthrough curves in Fig. 6. The diffusivity used in the model to represent loss of ^{131}I into the rock matrix was about $2.2 \times 10^{-5} \text{ cm}^2/\text{s}$, whereas the measured diffusivity of ^{131}I in water was $2.44 \times 10^{-5} \text{ cm}^2/\text{s}$, or within about 11%. However, the measured diffusivity of ^{131}I in tuff was much lower.¹ The rock in both the fracture experiment and the diffusion experiment were from the Topopah Spring Member of the Paintbrush Tuff. This result indicates that the effective rock diffusion in a fracture experiment may be controlled by micron-size fractures as opposed to rock pores, thus leading to higher diffusivities within the rock.

Next, Tang's model was used to simulated the 0.91- μm colloid breakthrough curve data. Table III gives the run parameters. A filtration-type capture model described the removal of colloids and no pore diffusion was permitted. It was necessary to increase the fracture width to fit the leading edge of the curve versus that which was used for the ^{131}I simulations. The reasons for increased fracture size and, consequently, lower water velocity in the colloid simulation is not fully understood but may in part be explained by the inadequacy of the filtration model in describing colloid capture. Future work should reinvestigate the data through use of the electrokinetic adsorption/desorption submodel, as described later.

TABLE II. SIMULATION AND RUN CONDITIONS FOR ^{131}I EXPERIMENTS.

Parameters	Definition
59 μm	fracture width
0.0011 cm^2/s	dispersion coefficient in the fracture
0.461 cm	dispersivity
$2.2 \times 10^{-5} \text{ cm}^2/\text{s}$	diffusion in the rock matrix used in simulation
$2.44 \times 10^{-5} \text{ cm}^2/\text{s}$	measured diffusivity of ^{131}I in water
$1.83 \times 10^{-6} \text{ cm}^2/\text{s}$	measured diffusivity of ^{131}I in rock
$2.4 \times 10^{-3} \text{ cm/s}$	fluid velocity in the fracture estimated for simulation
52.1 ml	feed pulse width
$2.5 \times 10^{-4} \text{ ml/s}$	flow rate of water

¹ Information provided by Robert Rundberg, Los Alamos National Laboratory, INC-11, November 1988.

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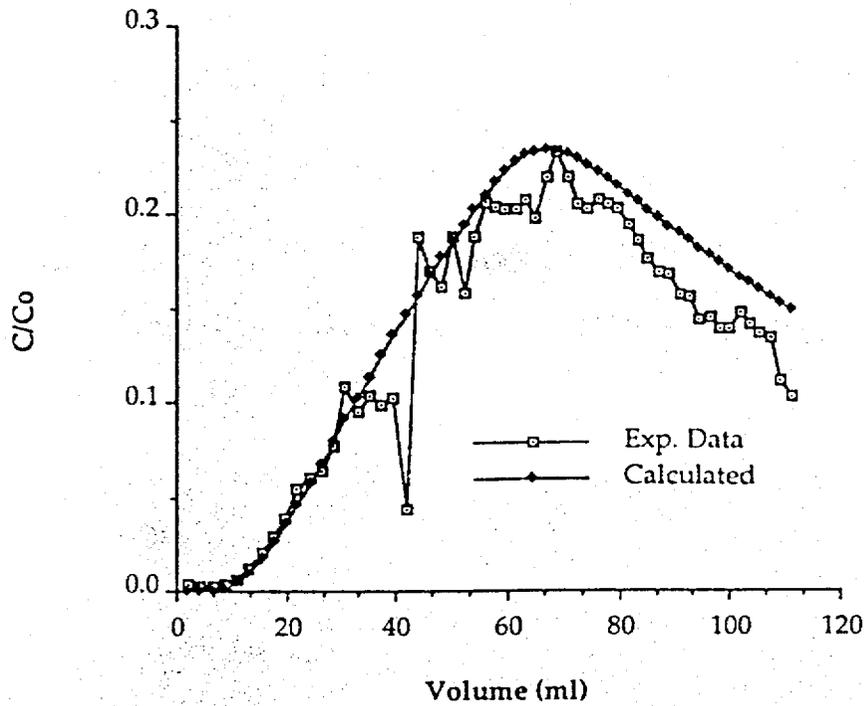


Fig. 6. Breakthrough curves for ^{131}I . Comparison of experimental and calculated. (Data listed in Appendix B.)

As shown by the calculated versus experimental curve in Fig. 7, the model did not adequately describe the colloid breakthrough curve. The reason for the lack of fit at the higher volumes or longer times may be that the filtration capture model is incorrect since it doesn't treat the problem of colloid desorption, which is strongly evident by the long tail on the experimental colloid breakthrough curve. Figure 8 more clearly illustrates the desorption or long tail associated with the experimental colloid breakthrough curve.

TABLE III. SIMULATION AND RUN CONDITIONS FOR COLLOID EXPERIMENTS.

Parameters	Definition
590 μm	fracture width
0.178 cm^{-1}	filtration coefficient
0.0011 cm^2/s	dispersion coefficient in the fracture
68.75 cm	dispersivity
0.0 cm^2/s	diffusion in the rock matrix used in simulation
1.6×10^{-4} cm/s	fluid velocity in the fracture estimated for simulation
0.5 ml	feed pulse width
1.66×10^{-4} ml/s	flow rate of water
500 ppm	feed concentration

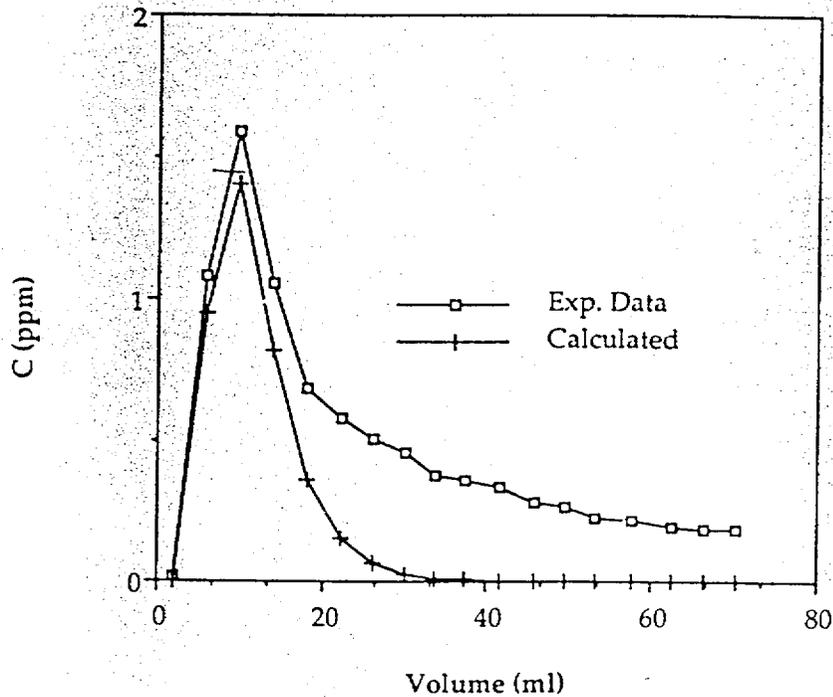


Fig. 7. Breakthrough curves for the 0.91- μm colloids. Comparison of experimental and calculated. (Data listed in Appendix C.)

The breakthrough curve shown in Fig. 8 is from Rundberg's fracture experiments and is an extension in volumes of the curve and data shown in Fig. 7. The curve shows experimental volumes out to 948 ml or 66 days. Note that colloids are still being released from the rock matrix. Hence the capture of colloids is a reversible process that cannot be described by a filtration-type capture model. The concept of adsorption/desorption is discussed further in Section IV.

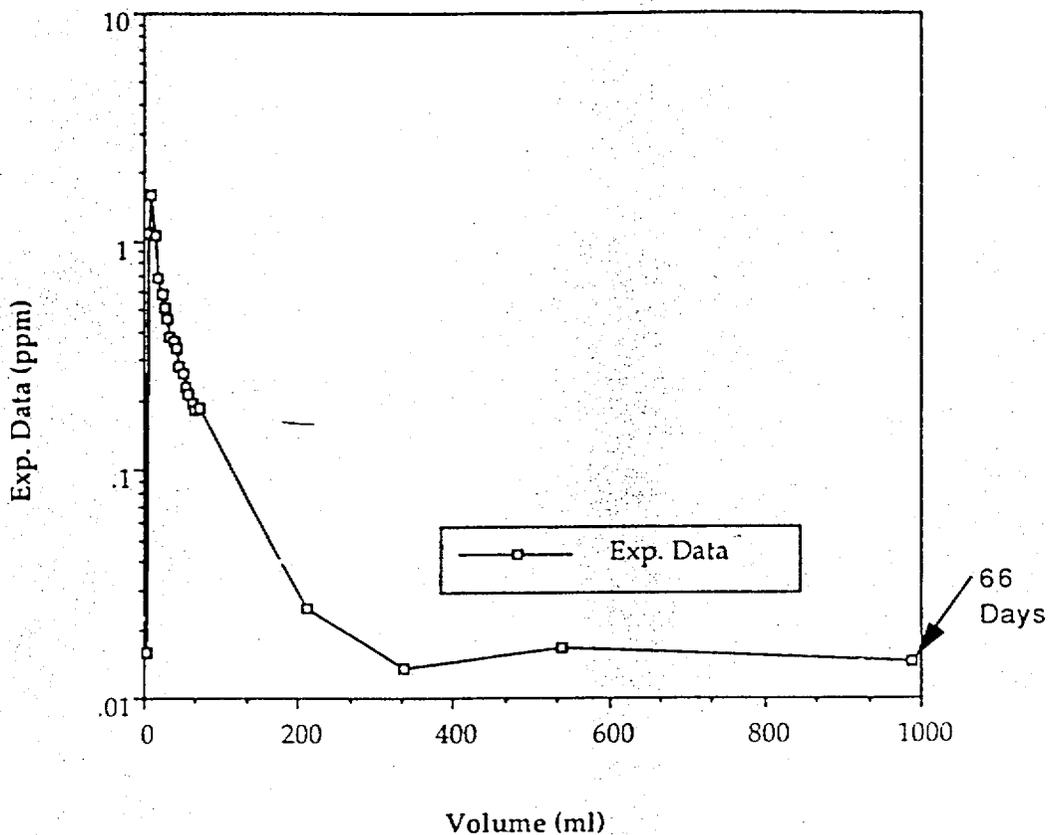


Fig. 8. Experimental colloid breakthrough curve (0.91 μm).

The filtration coefficient determined by trial and error of 0.178 cm^{-1} was about an order of magnitude larger than the 0.024 cm^{-1} value obtained experimentally by Ives and Gregory [1966] for pvc microspheres ($1.3 \mu\text{m}$ diam) passing through a column of $460\text{-}\mu\text{m}$ -diam glass spheres. Ives and Gregory [1966] also showed that the filtration coefficient increased with increased ionic strength of the feed solution and with decreasing zeta potential of both the pvc microspheres and the glass sphere packing. The larger filtration coefficient obtained in this work is reasonable since the matrix was a block with small fractures opposed to a column of uniform spheres. Figure 9 shows the dramatic increase in the filtration coefficient with decreasing colloid zeta potential.

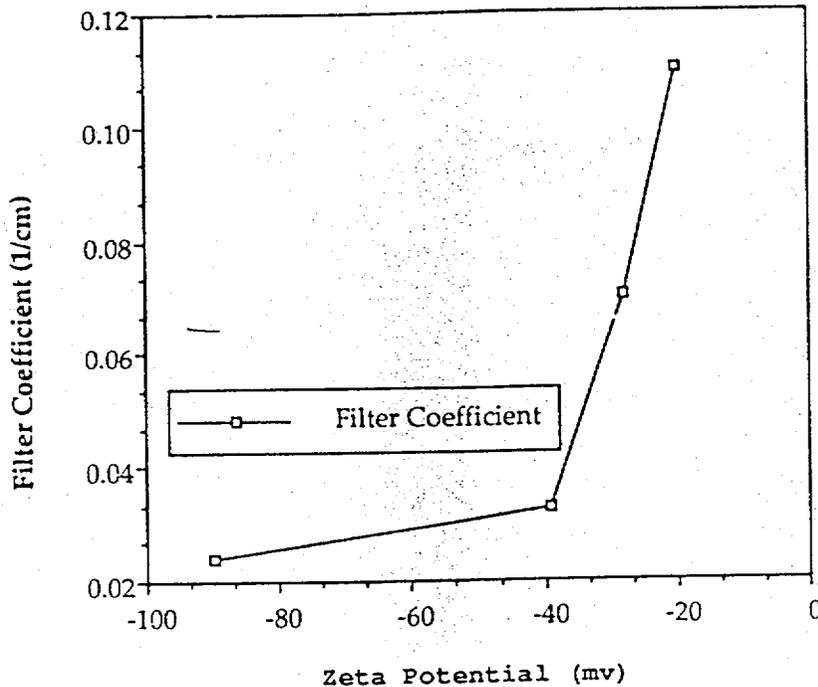


Fig. 9. Effect of colloid zeta potential on filtration coefficient [Ives and Gregory 1966].

III. ELECTROKINETIC MODEL FOR ADSORPTION/DESORPTION

Spielman and Friedlander [1974] developed a model for the rate of colloid adsorption where electrokinetic forces are repulsive and thus retard colloid capture (i.e., adsorption onto the rock matrix). The

authors account for the double-layer repulsive force and the van der Waal attraction force. They assume ordinary convective diffusion in the bulk fluid with a first-order reaction occurring at the collector surface (rock matrix). An expression for the surface reaction coefficient is derived in terms of the interaction energy potential. Using the derivation of Spielman and Friedlander [1974], the death term of Eq. (1) is expressed as a diffusion term plus diffusion caused by an electrokinetic force:

$$\text{Death} = \nabla \cdot \left(D \nabla \psi - \frac{D\psi}{kT} K \right). \quad (5)$$

From the theory of diffusion of Brownian particles with electrical double layers, K , the external force acting on the particles can be derived from a potential so that

$$K = -\nabla \phi. \quad (6)$$

Here, ϕ = the sum of the double layer repulsion energy and the van der Waal attraction. Israelachvili [1985] describes the calculation of ϕ under various ion concentrations for various materials.

Spielman and Friedlander [1974] showed that the flux of particles moving toward the rock is equal to

$$J(z) = -D_y \left(\frac{\partial \psi}{\partial y} + \frac{\psi}{kT} \frac{\partial \phi}{\partial y} \right) \quad (7)$$

and can be approximated by the first order rate expression

$$J(z) = -k' \psi, \quad (8)$$

where

$$k' = \frac{D_y}{\int_0^{\infty} \left(e^{-\frac{\phi(y')}{kT}} + 1 \right) dy'} \quad (9)$$

Therefore, the death rate of charged colloids migrating to the rock surface is

$$\text{Death} = -k' a_s \psi, \quad (10)$$

where

- a_s = surface area per unit volume of fluid,
- $J(z)$ = particle flux in the x direction,

- k' = surface adsorption rate constant,
 D_y = particle diffusion in the y direction,
 K = external force acting on particles,
 k = Boltzmann's constant,
 y = direction normal to flow,
 $\phi(y)$ = sum of the double layer repulsion energy and van der Waal energy of attraction,
 ψ = colloid concentration.

Rajagopalan and Chu [1982] investigated the dynamics of colloid adsorption/desorption in packed beds. They suggested a simple rate equation of the type

$$\frac{\partial C_s}{\partial t} = k_f C - k_r C_s, \quad (11)$$

where k_f (cm/s) and k_r (s^{-1}) are the adsorption and desorption rate coefficients specified as functions of Hamaker's constant, surface potential collision diameter, particle radius, and ionic strength. The mass balance equation for the flow of particles through a bed is

$$\frac{\partial C}{\partial t} + u_i \frac{\partial C}{\partial x} + \frac{\rho_g a_s (1 - \epsilon)}{\epsilon} \frac{\partial C_s}{\partial t} = 0, \quad (12)$$

where

- $u_i = u_s / \epsilon$, the interstitial velocity in the bed (u_s is the superficial velocity obtained by dividing the volumetric flow rate by the overall cross-sectional area of the bed);
 a_s = the specific surface area--area (available for adsorption) per unit mass of the grains of the bed;
 C = concentration of the particles/colloids in the liquid--number per unit volume of suspension;
 C_s = concentration of the captured particles on the grains--number per unit area of the grain; and
 ρ_g = grain density.

In Eq. (11), k_f is the same term as the k' used by Spielman and Friedlander [1974] and may be evaluated by Eq. (9). Ruckenstein and Prieve [1976] show that the desorption rate coefficient, k_r , is equal to k_f / I_2 , where

$$I_2 = \int_0^{\delta_2} \exp[-\phi(h)/kT] dh, \quad (13)$$

and δ_2 is the largest h in the interval near the collector for which a Boltzmann distribution of particles may be assumed.

Finally, the diffusivity of colloids, D_y , toward the rock/surface is calculated with the Stokes-Einstein equation [Bird et al. 1960], $D_{AB} = \frac{kT}{6\pi R_A \mu}$. Evaluating this equation for 1- μ m colloids at 25°C in water gives a diffusivity of 4.3×10^{-9} cm²/s. This value of diffusivity for colloids is very small as compared with molecular diffusion of species under these conditions, which is between 10^{-5} - 10^{-6} cm²/s.

Sharma and Yortsos [1987], in their study of particle transport through porous media, use first-order kinetic expressions for the rates of particle release and deposition, as was shown above. They also refer to the paper by Ruckenstein and Prieve [1976] for evaluating the rate constants where electrokinetic forces are important. Their resulting integrated expression for the rate constants are

$$k_f = D(H_{max}) \left(\frac{v_{max}}{2\pi kT} \right)^{1/2} \exp\left(-\frac{V_{Tmax}}{kT}\right) \quad (14)$$

and

$$k_r = D(H_{max}) \left(\frac{v_{max} v_{mir}}{2\pi kT} \right)^{1/2} \exp\left(-\frac{V_{Tmax} - V_{Tmir}}{kT}\right), \quad (15)$$

where v_{max} and v_{mir} denote $\frac{\partial^2 V_T}{\partial H^2}$ evaluated at H_{max} and H_{min} respectively,

and the other terms are

- H = separation distance between particle and flat plate,
- K = Boltzmann constant,
- T = temperature, and
- V_T = total potential energy of interaction.

In summary, the adsorption/desorption of colloids where electrokinetic forces are present may be modeled by a simple forward and reverse reaction. This model can be applied directly to the general form of the population balance and thus be used to describe the adsorption/desorption of radiocolloids in a porous medium. The physical parameters that affect the rate coefficients are (1) ionic strength of the solution; (2) colloid radius, collision diameter; (3) surface potential; and (4) the Hamaker constant. Experimental studies [Matijevic and Kallay 1982; Kallay and Matijevic 1981;

Nelligan et al. 1982; Barouch et al. 1987] for the specific system of hematite colloids adsorbing/desorbing on steel show the validity of this type of forward/reverse kinetic model. Finally, the text by Israelachvili [1985] is very useful in understanding electrokinetic phenomena.

IV. SIZE EXCLUSION EFFECTS

As illustrated in Fig. 10, small particles have more paths available to them for migration through typical porous media, or, stated another way, the large particles are excluded from many of the smaller paths. This effect appears to explain the field data of Harvey et al. [1988]. In two well tests, their data showed that the larger particles (1.35 μm) traveled on the average faster through the porous media than did the smaller colloids (0.23 μm). They simultaneously injected three different size latex particles. This may be an important effect that will need to be considered in the Yucca Mountain colloid test plan. Planned column tests by Rundberg will include size exclusion effect studies and direct investigation into the location of trapped colloids within the columns.

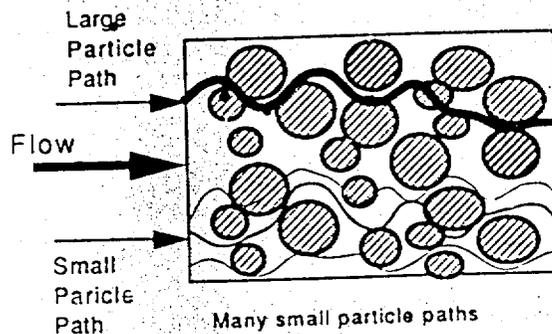


Fig. 10. Particle size exclusion phenomenon.

V. PLANNED WORK

Two colloid study topics will be addressed. Topics to be investigated are numerical solution of the general population balance and development of an electrokinetic submodel..

1. General Code Development

This task is the focal point of the colloid modeling. A general numerical solution to the population balance is being developed using the Method of Lines (MOL) numerical technique. The nature of the population balance and justification for using this approach was discussed by Nuttall [1989]. The Colloid transport Code-Nuclear (CTCN) will be based on Hyman's [1979] partial differential equation solver which is a collection of Fortran subroutines that implements the Method of Lines numerical technique. A stepwise approach was adopted for code development. The 1-D version of MOL with test problems is currently being tested on the LANL Cray computers. Next, the multidimensional version of MOL will be tested against sample problems. When the Cray version of the MOL routines operate satisfactory, they will be transported to the ESS-5 Sun computer system and retested. Following completion these steps, the MOL routines will be used to develop the CTCN code

2. Electrokinetic Submodel

Recent investigations of colloid capture and release indicate that a K_d -type model may represent the actual physics of colloid adsorption/desorption better than a simple filtration model does. This idea will be developed and tested against Rundberg's [Rundberg et al. 1988] experimental data.

VI. SUMMARY

Significant progress was made in understanding the transport of colloids in tuff and in developing a general numerical solution to the population balance equation. The classical filtration model was shown to greatly overpredict the capture rate of latex colloids passing through fractures in a block of tuff and, therefore, is not an appropriate model to use in estimating colloid capture. Model results presented in this report and recent literature suggest an adsorption/desorption process for the migration of colloids. It appears from literature studies that colloid adsorption/desorption is controlled by a combination of electrokinetic forces, Brownian motion, van der Waals forces, Born repulsion, and solvation forces.

In summary, the key points are

1. Colloid migration/capture in tuff is likely to be controlled by electrokinetic forces.
2. Charged colloids in a weak ionic strength groundwater tend to migrate as conservative tracers.
3. The effective diffusivity of ^{131}I into tuff was substantially greater in the fractured block experiment than predicted by batch experiments.
4. Electrokinetic models found in the literature should be

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adequate for describing colloid capture in porous/fractured
tuff.

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Appendix A

Numerical Code for Modeling Colloid Transport

program tang

c

c TANG'S FRACTURE TRANSPORT MODEL-VAX VERSION

c FORTRAN F77

c

c This code is designed to evaluate Tang's solution to
c the single fracture problem. The code contains subroutines for
c both the general solution (no integration routines yet) and the
c special case with no longitudinal diffusion.

c

c Reference: Tang, D. H., E. O. Frind, and E. A. Sudicky,
c "Contaminant Transport in Fractured Porous Media:
c Analytical Solution for a Single Fracture,"
c Water Resources Research, Vol. 17, No. 3, p. 555-
c 564, June, 1981.

c

c Modified 8/16/88
c Corrected Version
c Modified 8/27/88 to match tested version (ttangd.for @unmb)
c Treatment of Rundberg's colloid data

c

c Evaluates discharge only in this version of the code
c But uses the full solution with axial dispersion
c Evaluates Equation 35 of the Tang, Frind, and Sudicky model
c This version runs on the VAX system and uses IMSL integration
c routine, qdagi to numerically integrate the semi infinite
c analytical solution.

c

c The complete integrand is coded in function "fnct"

c

c

c This version is specifically designed to simulate the
c single fracture data generated by Dr. Rundberg

c

c This code uses the mk system with time in years

c

c definition of terms

c

c a = special group ()

c b = half width of the fracture, m

c bg = special group

c ci = initial concentration or source concentration, kg/ cu m

c cf = concentration in the fracture

c cp = concentration in the porous matrix

c db = bulk density of the porous matrix, kg/cu m

c dp = diffusivity in the porous matrix, sq m/yr

c df = diffusivity in the fracture, sq m/yr

c fi = feed flow rate, cu m/yr

c kf = equilibrium distribution, fracture, m

c km = equilibrium distribution, porous matrix, cu m/kg

c ld = lambda

c por = porosity, dimensionless

c rf = retardation in the fracture

c rp = retardation the porous matrix

c stime = starting time for discharge calculation, yr

c t = time, yr

c td = dimensionless time

c tstep= time increment for discharge calculation, yr

c v = special velocity

c vol = experimentally measured fluid volumes, cu m

c vw = velocity of water in the fracture, m/yr

c x = distance coordinate normal to fracture, m

c xi = integration variable

c y = special group

c z = length parameter (distance from source to discharge), m

c

c

external fncf

real ld

real km, kf

common a,b,b1,b2,df,ld,rf,rp,t,v,vw,x,yp,z

dimension alist(100),blist(100),rlist(100)

dimension elist(100),iord(100)

dimension vol(100)

parameter (limit=100)

parameter (pi=3.14159)

```

c open output files (*.dat and *.plt)
open (unit=2,file='output.dat',status='new')
open (unit=1,file='output.plt',status='new')
c open input file of experimental fluid volumes
open (unit=10,file='cvol.dat',status='old')
c input parameters
c data ci,db,km/0.001,2300.,2.0/
c data kf,dp,vw/0.0,1.0e-9,3.2e-6/
c data por/0.3/
c
c .....input section.....
c
c do 5 i=1,22
c read(10,*) vol(i)
c convert from ml to cu m
c vol(i)=vol(i)/1.0e6
5 continue
c b= 2.95e-4
c df=3.5
c Let the pore diffusion be zero and assume all capture is by
c filtration
c
c dp=1.0e-10
c por=0.047
c z=0.27
c kf=0.0
c db=2300.0
c km=0.0
c ld=900.0
c ci=1.0
c Volumetric flow rate, fi= (0.6 ml/hr = 5.26 E -3 cu m /yr)
c fi=5.26e-3
c Holdup volume, cu m
c hvol=2.0*b*(0.176)*(0.27)
c Calculate the water velocity vw from the fracture apperture width
c fi = cu m/yr and the denominator is the cross-sectional area of the
c fracture in sq m.
c vw= (fi)/(2.0*b*(0.176))
c stime=hvol/fi
c t=stime

```

```

c
c evaluate special groups
c
  rp=1.0+db*km/por
  rf=1.0+kf/b
  a=b*rf/(por*sqrt(rp*dp))
  b1=sqrt(rp/df)
  v=vw/(2.0*df)
  b2=sqrt(4.0*rf*df/vw**2)
c
c   output all input parameters
c
  write(2,200) a,b,b1,b2,ci
200 format(/' TANG'S FULL MODEL',//,' a=',g10.3,' special group',
  1 /,' b=',g10.3,' fracture half width, m',/,
  2 ' b1=',g10.3,' special group',/, ' b2=',g10.3 ' spacial group',/,
  3 ' ci=',g10.3,' initial concentration, kg/cu m')
  write(2,205) db,df,dp,rf,rp
205 format(' db=',g10.3,' bulk density of porous matrix, kg/cu m',/,
  1 ' df=',g10.3,' diffusivity in the fracture, sq m/yr',/,
  + ' dp=',g10.3,' diffusivity in the porous matrix, sq m/yr',/,
  2 ' rf=',g10.3,' retardation on the fracture surface',/,
  3 ' rp=',g10.3,' retardation in the porous matrix')
  write(2,210) ci, kf, km, ld, vw
210 format(' ci=',g10.3,' initial concentration, kg/cu m',/,
  1 ' kf=',g10.3,' equilibrium distribution on fracture surface, m',/,
  2 ' km=',g10.3,' equilibrium distribution in matrix, cu m/kg',/,
  3 ' ld=',g10.3,' decay constant, 1/yr',/,
  4 ' vw=',g10.3,' fluid velocity in the fracture, m/yr')

c
c DISCHARGE CALCULATION SECTION
c
c   output section
c
c   Print volume versus normalized concentration
c
  write(2,10)
10  format(/,' Vol., ml           C, ppm ',/)
  do 20 i=1,22

```

```

c Modified to treat Rundberg's data
c Full solution with axial dispersion
c
c
c Define integration parameters
  inf = 1
  epsabs = 1.0e-3
  epsrel = 1.0e-3
c
c Treat finite step input using supper position
c Solution = s1(t)-s2(t+tspike)
c First Solution
c First Solution at time = t
  t=vol(i)/fi
c Calculate lower bound
  bound1 = (z/2.0)*sqrt(rf/(df*t))
c Calculate time from measured volumes and flow rate
  t=(vol(i)/fi)
c The integration routine qdagi is available on IMSL
  call qdagi(fncf,bound1,inf,epsabs,epsrel,s1,errest)
c
c Second Solution at time = t - delta t
c
  tspike=9.5e-5
  s2=0.0
  t=t-tspike
  bound2 = (z/2.0)*sqrt(rf/(df*t))
c print*, ' bound2=',bound2,' t2=',t
c print*, ' z2=',z,' rf2=',rf,'df2=',df
  call qdagi(fncf,bound2,inf,epsabs,epsrel,s2,errest)
  t=t+tspike
c Conversion from time to volume (ml) = flow rate (ml/h)
c x (8,760.00) x time (y)
c For a flow rate of 0.6 ml/h the conversion is
c (5.256 x E+3) time
c vol=volume passed through the column in ml.
c Initial concentration is 500 ppm and the pulse volume is 0.5 ml.
c Solution is in ppm when s1-s2 is multiplied by the inlet
  write(2,15) vol(i)*1.0e6, 500.0*(s1-s2)
  write(1,17) 500.0*(s1-s2)

```

```

15  format(g10.4,5x,g10.4)
17  format(g10.4)
20  continue
c
  end
c
function fncf(xi)
c
  common a,b,b1,b2,df,ld,rf,rp,t,v,vw,x,yp,z
  real ld,n
c
c
c function for fracture concentration
c
  n=ld*rf/(4.0*df*xi*xi)
  y=((v*b2*z)**2)/(4.0*a*xi*xi)
  td=sqrt(t-rf*z*z/(4.0*df*xi*xi))
  t1=1.0*(exp(v*z)/sqrt(3.14159))
  t2=exp(-xi*xi-(v*z/(2.*xi))**2)*exp(-n*(z**2))
c The if else statements prevent the erfc functions from overflowing
  arg=y/(2.0*td)+sqrt(ld)*td
  if(arg .lt. 9.0) then
    t3=exp(-sqrt(ld)*y)*erfc(y/(2.0*td)-sqrt(ld)*td)
    t4=exp(sqrt(ld)*y)*erfc(y/(2.0*td)+sqrt(ld)*td)
  else
    t3=0.0
    t4=0.0
  endif
  fncf=t1*t2*(t3+t4)
  return
end

```

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Appendix B

Calculation versus Measured ^{131}I Breakthrough Curves

Volume, ml	Experimental, C/Co	Calculated, C/Co
2.2	0.004	0.0000000005267
4.4	0.003	0.000009873
6.6	0.003	0.0002948
8.8	0.004	0.001674
11	0.006	0.004877
13.2	0.012	0.01009
15.4	0.02	0.01714
17.6	0.029	0.02567
19.8	0.039	0.03532
22.	0.054	0.04577
24.2	0.06	0.05675
26.4	0.064	0.06805
28.6	0.077	0.0795
30.8	0.109	0.09099
33.	0.095	0.1024
35.2	0.104	0.1137
37.4	0.099	0.1249
39.6	0.103	0.1358
41.8	0.043	0.1465
44.	0.188	0.1569
46.2	0.17	0.1671
48.4	0.162	0.1771
50.2	0.188	0.185
52.4	0.158	0.1945
54.23	0.188	0.2021
56.06	0.206	0.2096
57.9	0.204	0.2167
59.73	0.202	0.2229
61.56	0.202	0.2278
63.39	0.207	0.2311
65.22	0.198	0.2329
67.06	0.219	0.2333
68.89	0.232	0.2325
70.72	0.219	0.2309
72.55	0.205	0.2284
74.38	0.202	0.2255
76.22	0.207	0.222
78.05	0.205	0.2183
79.88	0.202	0.2143
81.71	0.194	0.2102
83.54	0.185	0.206
85.38	0.176	0.2018
87.21	0.169	0.1975
89.04	0.168	0.1933
90.87	0.157	0.1891

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92.7	0.155	0.185
94.53	0.143	0.181
96.36	0.144	0.177
98.2	0.138	0.1731
100.03	0.139	0.1693
101.86	0.147	0.1656
103.69	0.141	0.1621
105.52	0.136	0.1586
107.36	0.134	0.1552
109.19	0.111	0.1519
111.02	0.103	0.1487

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Appendix C

Calculated versus Measured Colloid Breakthrough Curves

Volume, m	Experimental, ppm	Calculated, ppm
2.	0.015783	0.0003949
5.9	1.078313	0.9488
9.75	1.587349	1.405
14.	1.054216	0.8205
18.3	0.686746	0.3617
22.4	0.581325	0.1515
26.3	0.509036	0.06402
30.1	0.454819	0.02728
33.8	0.376506	0.01182
37.5	0.361445	0.005119
41.6	0.337349	0.002021
45.8	0.28012	0.0007786
49.6	0.263554	0.0003297
53.2	0.227108	0.000149
57.6	0.215963	0.00005774
62.4	0.195783	0.00002049
66.3	0.183433	0.000009313
70.1	0.187048	0.000001863

Appendix D

Selected References by Topic

Experimental Studies and Colloid Modeling

- R. Byron Bird, Warren E. Stewart, and Edwin N. Lightfoot, *Transport Phenomena* (John Wiley & Sons, Inc., 1960)
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