CONF-791112--47

PRELIMINARY RATE EXPRESSIONS FOR ANALYSIS OF RADIONUCLIDE MIGRATION RESULTING FROM FLUID FLOW THROUGH JOINTED MEDIA*

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ABSTRACT

A theoretical and experimental basis is being developed for analysis of radionuclide transport in jointed geologic media. Batch equilibration and rate experiments involving samples of Eleana argillite and tertiary silicic tuffs in contact with solutions containing Cs, Sr, or Pm indicated that most radionuclide sorption was associated with the surfaces of very small intergranular regions and that the rate of sorption was controlled by diffusion of the nuclides into such regions. Based on these experimental results, the continuity equations for radionuclides in the mobile and immobile phases were reduced to a model analogous to Rosen's equations for packed beds and were solved similarly. Using the model and experimental data, limited radionuclide transport analyses were made which indicated that important parameters controlling transport include the intergranular porosity and nuclide penetration depth, fracture plate spacing and length, fluid velocity, and sorption distribution coefficient. Many of these parameters represent physical quantities or processes which can be quantified in the laboratory. However, fluid velocities and fracture plate spacings and lengths must be obtained from the field, and methods must be developed to establish reliable bounds for such field-determined parameters.

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*This work supported by the United States Department of Energy (DOE), under Contract DE-AC04-76-DP00789.
**A DOE facility.

INTRODUCTION

Current literature regarding analysis of radionuclide transport in jointed geologic media is very limited. This situation has probably partly resulted because finite rates of mass transfer between phases must be considered. This paper summarizes initial work conducted to develop theoretical and experimental approaches which adequately account for finite mass transfer rates between phases and which will provide a basis for analyzing radionuclide transport in jointed geologic media. In the following discussion, the theoretical and experimental approaches are illustrated and then used to develop a transport model for relatively simple systems. The model and experimental data are used for limited transport analyses which identify important parameters and some possible deficiencies in current methods of parameter evaluation.

THEORETICAL APPROACH

For purposes of discussion, the solution phase which is subject to bulk motion has been referred to as the mobile phase, and the solid phase, which includes voids containing stagnant solution, has been referred to as the immobile phase and was idealized as consisting of distinct permeable and impermeable regions. The permeable regions were defined as the fractures, pores, and intergranular regions containing stagnant solution, and the impermeable regions were defined as the crystal grains.

Assuming that the mobile phase is an aqueous solution in laminar flow, the material balance for a dissolved component is

$$\frac{\partial C}{\partial t} = -\vec{\nabla}\cdot\vec{v}C - \vec{\nabla}\cdot\vec{J} + \sum R_j \qquad (1)$$

where C is the component's concentration; J is the component's flux relative to the solution's mass average velocity v; R_j are terms representing rates of production and/or depletion due to homogeneous chemical reactions and/or nuclear decay, and t is time. The initial condition assumed for the mobile phase is that $C(X_1,X_2,X_3,0)$ is a known function of the general coordinates X_i. Two commonly used boundary conditions are sorption equilibrium at the interface between phases and continuity of the radionuclide flux across the interface.

For the permeable regions of the immobile phase, the material balance is

$$\frac{\partial \hat{C}}{\partial t} = -\vec{\nabla}\cdot\vec{\hat{J}} + \sum \hat{R}_j \qquad (2)$$

where $\hat{C}$ is the local concentration; $\hat{J}$ is the diffusional flux, and $\hat{R}_J$ are terms representing rates of production an/or depletion due to homogeneous chemical reaction and/or nuclear decay. Similar initial and boundary conditions as given for Eq. 1 also apply to Eq. 2. Furthermore, at the interface between permeable and impermeable regions, the conditions of sorption equilibrium and continuity of the radionuclide flux also apply.

EXPERIMENTAL APPROACH

The objective of the experimental program is to identify the important sorption mechanisms and the important homogeneous and heterogeneous chemical reactions and to obtain sufficient data so that these phenomena can be described quantitatively using appropriate mathematical expressions. A basic approach for achieving this objective is illustrated in the following discussion of experimental results.

Initial batch equilibration and rate experiments have been conducted using samples of Tertiary silicic tuffs which were contacted with simulant groundwater solutions containing cesium, strontium, and promethium and also using samples of Eleana argillite contacted with solutions containing cesium.[1] The argillite experiments have been most amenable to analysis, and the results from those experiments are summarized below, so that the development of rate expressions can be illustrated in the next section.

The Eleana argillite primarily consisted of quartz and layered silicate minerals, kaolinite, pyrophyllite, and mixed layer "illite." Samples of the argillite generally contained some macroscopic fractures, and scanning electron micrographs indicated that the surface of the samples contained intergranular regions having thin, approximately rectangular cross sections and wall spacings on the order of 0.1 microns and less. The porosity associated with these regions appeared to be between one and ten percent. For 30 to 60 mesh particles, surface areas determined by the BET method were about 9 m^2/gm.

Based on the solution chemistry of cesium and of the constituents of the groundwater solutions, it was felt that if the surface of the immobile phase remained unaltered, no homogeneous and no heterogeneous chemical reactions other than sorption should be involved. The sorption equilibrium isotherm at room temperature determined from batch equilibration experiments using 30 to 60 mesh particles, was found to be represented by

$$\bar{\bar{C}} \doteq (0.05\ C\ \text{cm})/(1 + (5 \times 10^4\ \text{cm}^3/\text{mmole})C) \qquad (3)$$

for values of C between 10^{-2} and 10^{-10} M. The term $\bar{\bar{C}}$ represents the nuclide concentration associated with the surfaces of the impermeable regions, and it has been assumed that at the interface between phases, $C = \hat{C}$. The distribution K is defined as $\bar{\bar{C}}/C$.

Sorption rate data were obtained from independent batch experiments using argillite tablets which were approximately 1/4 inch thick by 2-3/8 inch in diameter and were contacted with well-mixed cesium solutions. At the conclusion of these experiments, the tablets were examined using autoradiography. Based on autoradiographs from intact and cleaved tablets, it appeared that most sorption occurred in intergranular regions having effective lengths of 0.01 cm or less, which was consistent with the surface area measurements and estimated intergranular porosities.

RADIONUCLIDE TRANSPORT MODEL

Analysis of Rate Data

Based on the literature concerning ion-exchange kinetics,[2] the rate of cesium sorption should have been limited by diffusion rather than by the intrinsic rate of a "sorption reaction." For the batch rate experiments, the boundary layer thickness in the mobile phase should have been on the order of 10^{-2} to 10^{-3} cm, and for the tablets, it appeared reasonable to expect that diffusion into the relatively long, narrow intergranular regions would primarily dominate the rate of mass transfer across the interface between mobile and immobile phases.

Referring to Fig. 1, equations describing mass transfer in the intergranular regions were developed[3] by assuming local sorption equilibrium between the bulk stagnant solution and impermeable surface, constant-valued parameters, continuous physical and chemical properties, by assuming that solution-phase nuclide concentrations were sufficiently dilute so that Fick's law was valid, that diffusion was essentially one-dimensional, and that there was no surface diffusion. The resulting flux expression describing mass transfer across the interface between phases was

$$\vec{n} \cdot \vec{J} = \vec{n} \cdot \vec{\hat{J}} = -(D/a_t)(\partial \hat{C}/\partial X_1) = -(\bar{D}/a_t)(\partial \bar{C}/\partial X_1) \qquad (4)$$

where a_t is a tortuosity factor; D is the diffusion coefficient for the nuclide in the solution; $\bar{C} = \bar{K}C$; $\bar{D} = D/\bar{K}$; $\bar{K} = 1 + a_c hK$; h is the ratio of the perimeter length to the area of a simple characteristic cross section for the intergranular regions, and a_c is a roughness factor. The material balance for the bulk of the intergranular regions is

$$\partial \bar{C}/\partial t = (\bar{D}/a_t^2)\,\partial^2 \bar{C}/\partial X_1^2 \qquad (5)$$

with $C(X_1,0) = 0$, and $\partial \underline{C}(H,t)/\partial X_1 = 0$. The $\hat{R}_j$ terms in Eq. 2 have been assumed negligible, and $\bar{H}$ is a characteristic depth to which the intergranular regions penetrate the immobile phase.

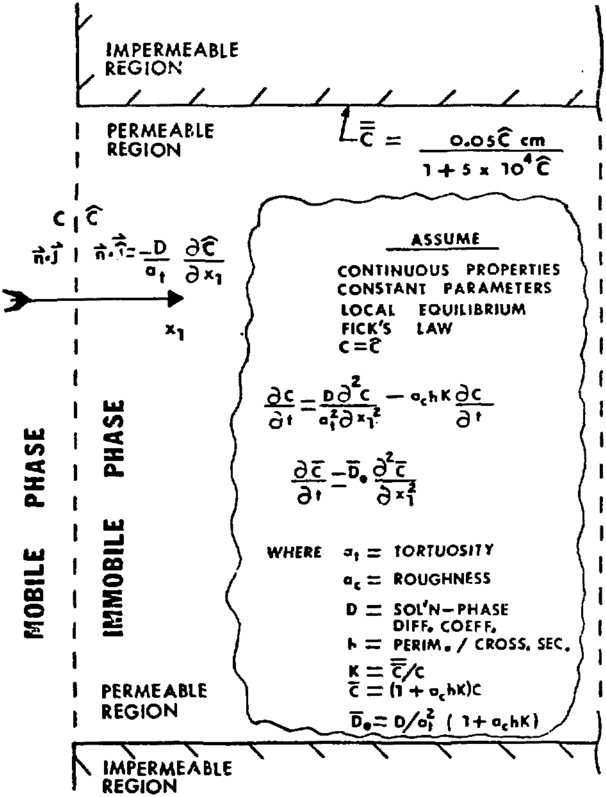


Fig. 1. Schematic Representation of Mass Transfer in Intergranular Regions.

To describe a batch rate experiment, Eq. 5 is solved simultaneously with Eq. 6 below

$$(V/apAa_t\bar{K})(\partial C/\partial t) = (\bar{D}/a_t^2)(\partial \bar{C}/\partial X_1) \qquad (6)$$

where $C(0) = C_o$ = a constant; A is the gross geometrical surface area of the tablet; a is a roughness factor for the tablet's surface; p is the interfacial intergranular porosity, and V is the volume of the mobile phase. The solution to Eqs. 5 and 6 can be obtained from Crank.[4] Some typical data from batch rate experiments with argillite tablets and cesium solutions are shown in Fig. 2. Analogous data calculated using the given parameter values are shown by the solid line. The agreement between calculated and experimental data is not entirely quantitative. However, when inhomogeneities in and variations between rock samples are considered, as well as the purely representative nature of some of the parameters, and when initial effects due to diffusion through the boundary layer in the mobile phase are also considered, the agreement between calculated and experimental results appears sufficiently good to support the validity of Eqs. 5 and 6 and the parameter values used.

Model Development and Solution of Equations

Based on the preceding analyses, a fundamental transport model for cesium solutions in laminar, one-dimensional flow through linear fractures in Eleana argillite was obtained by: assuming constant, uniform dimensions and constant, continuous properties for the fractures, replacing the parabolic velocity profile by an appropriate average, assuming that the fracture wall spacing H is sufficiently small so that diffusion in the X_1-direction in the mobile phase can be approximated as a quasi-steady-state process, neglecting terms due to nuclear decay, and assuming constant-valued parameters. The result is

$$\partial C/\partial t + v(\partial C/\partial Z) = -(1/M)(\partial Q/\partial t) \qquad (7)$$

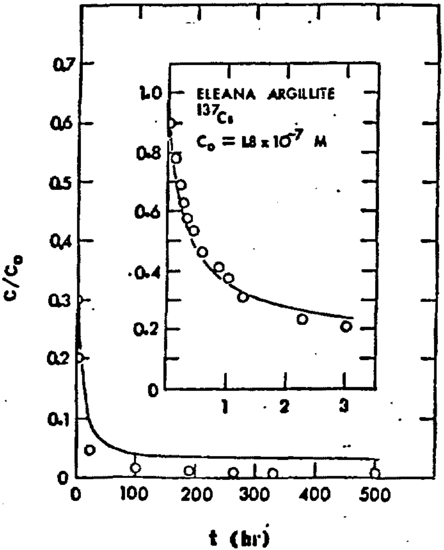
where $Q = \int_0^{\bar{H}} \bar{C}(X_1,Z,t)dX_1$; $C(0,t)/C_o = 1$; $C(Z,0) = 0$, and $Q(Z,0) = 0$.

$$\partial\bar{C}/\partial t = \bar{D}_e\, \partial^2\bar{C}/\partial X_1^2 \qquad (8)$$

with $\bar{C}(X_1,Z,0) = 0$, and $\partial\bar{C}(\bar{H},Z,0)/\partial X_1 = 0$.

$$\partial Q/\partial t = (1/R_M)(C - \bar{C}_s/\bar{K}) \qquad (9)$$

The term C is now the average concentration for the cross section; C_o is the constant mobile phase concentration entering the fracture; $\bar{C}_s$ is the value of $\bar{C}$ at the interface between mobile and immobile phases; $D_e = D/a_t^2$; $M = H/2ap\bar{H}$; $R_M = H\bar{H}/4D$, and Z is the spatial coordinate parallel to the direction of bulk fluid motion. Eqs. 7,8 and 9 can be



PARAMETER	VALUE USED	ESTIMATED RANGE
a	1	1 - 2
a_c	√2	~1 - 4
ξ^2	1	~1 - 4
D	2×10^{-5} cm^2/sec	—
$\bar{H}$	5×10^{-3} cm	10^{-3} - 10^{-2} cm
h	6×10^{6} cm^{-1}	*
K	5×10^{-2} cm	—
K^*	4×10^{5}	—
ρ	3×10^{-2}	10^{-2} - 10^{-1}

* CALCULATED SO AS TO BE CONSISTENT WITH SURFACE AREA MEASUREMENTS AND VALUES USED FOR a_c, a_ξ, $\bar{H}$, AND ρ

Fig. 2. Comparison of Experimental (circles) and Calculated (solid line) Rate Data Using the Parameter Values Given.

solved analogously to Rosen's[5] development for packed beds. The result is identical in form to Rosen's solution. The numerical differences which exist are small and should be masked by the inherent uncertainties associated with the parameter values, and for purposes of making preliminary calculations, the results given by Rosen[6] should be applicable. For values of $2\,apDZ/H\bar{H}v$ on the order of 50 and greater, the solution approaches the following asymptotic expression

$$U(\bar{Z},\bar{t}) = 1/2 + (1/2)\mathrm{erf}((2Y/\bar{X}) - 1)/2((1 + 3g)/3\bar{X}))^{1/2} \qquad (10)$$

where $U = C/C_0$; $\bar{t} = t - Z/v$; $\bar{Z} = Z/Mv$; $\bar{X} = 2\,apDZ/H\bar{H}v$; $Y = (D/2\bar{H}^2\,a\xi^2 K)(t - Z/v$ and $g = H/4\bar{H}$.

Discussion

If $t_{0.01}$ is defined as the elapsed time required for U to reach a value of 0.01 for a given value of Z, and if $t_{0.5}$, $v_{0.01}$, and $v_{0.5}$ are defined analogously, then from Eq. 10 and appropriate values of the error function it can be shown that as Z/v becomes sufficiently large,[7]

$$v_{0.5} = vM/(M + \bar{K}) \doteq v_{0.01} \qquad (11a)$$

$$t_{0.5} = (1 + \bar{K}/M)Z/v \doteq t_{0.01} \qquad (11b)$$

conversely, as Z/v becomes small, $V_{0.5}$ and $v_{0.01}$ approach v. Referring to Rosen's numerical results, if g/X is much less than 0.2 and $\bar{X}$ is greater than 50, Eq. 11a applies. For Eq. 11b to apply, $\bar{X}$ must be much greater than 50, say on the order of 500. This leads to the following criteria for application of Eq. 11b

$$Z/v > 250H\bar{H}/ap\bar{D}_e\bar{K} \qquad (11c)$$

As also shown by Rosen, for t = Z/v, the value of $\bar{t}$ is zero, and

$$U(\bar{Z}, 0) = \exp(-Z/vMR_M) \qquad (13)$$

which leads to the following criteria for when the value of $t_{0.01}$ can be greater than Z/v

$$Z/v > 2.\bar{3}H^2/4apD \qquad (14)$$

RADIONUCLIDE TRANSPORT ANALYSIS

Model Evaluation

Some initial experiments have been conducted in which stable cesium solutions ($C_0 \doteq 10^{-3}$ M) have been pumped through artificially prepared fractures in argillite samples. These experiments were primarily designed to develop sample preparation techniques, and quantitative analysis of the data has been complicated by the nonlinear nature of the sorption isotherm. However qualitative analysis of the data has been encouraging.

General Analyses

The equations and discussion of the preceding section are summarized in Fig. 3, which represents the superposition of independent plots of Eq. 11c and Eq. 14. For values of $4apD/H^2$ and Z/v in regions 3 and 4, the breakthrough time t_B at which the value of U equal to 0.01 or greater appears at distance Z is equal to Z/v. For values of $4apD/H^2$ and Z/v in regions 1 and 6 and values of $apD_eK/H\bar{H}$ and Z/v in regions 1, 2 and 3, t_B is given by

$$t_B \doteq (1 + 2ap\overline{HK}/H)Z/v \qquad (15)$$

For other combinations of parameter values the time t_B is between Z/v and that given by Eq. 15.

The above conditions for the applicability of Eq. 15 essentially define the parameter values required to apply the local equilibrium assumption to transport models for jointed media. Furthermore, many of

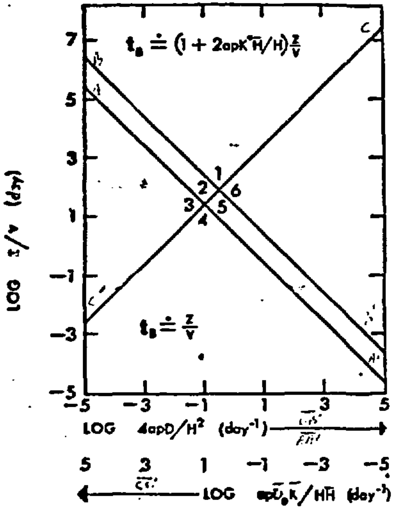


Fig. 3. Effect of Parameter Values on t_B.

the required parameters represent physical quantities or processes which can be quantified in the laboratory. However parameters such as v and H must be determined from field measurements. Current measurement techniques are crude and introduce large uncertainties into the parameter values. The importance of these uncertainties can be illustrated by choosing a typical hydraulic gradient $\Delta P/Z$ and then calculating the maximum value of H which will allow some minimum value of t_B at selected distances L from a radionuclide source. For purposes of illustration, parameter values are taken from Fig. 1; t_B is taken as 10^5 years, and $\Delta P/Z$ as about 10 feet of water per mile. The largest maximum values of H will occur when Eq. 15 is valid, and if the value of $2ap\overline{HK}/H$ is much greater than unity,

$$H_{max} = (2ap\overline{H}\overline{K} / t_{0.01} \times 10^4 \text{ m cm}^{-2} \text{ day}^{-1})^{1/3} L^{1/3} .$$

For axial distances of 30 and 10^4 meters, the resulting values of H_{max} are about 10^{-3} and 10^{-2} cm, respectively, and are on the same order as some values estimated for actual joint widths. Therefore, the uncertainties in such estimates must be reliably determined.

CONCLUSIONS

The initial work conducted to develop a theoretical and experimental approach for analysis of radionuclide transport in jointed geologic media has been encouraging. The transport model developed for relatively simple systems indicated that important parameters controlling radionuclide transport include the intergranular porosity p and penetration depth $\bar{H}$, the fracture plate spacing H and length Z, the fluid velocity v, and the sorption distribution coefficient $\bar{K}$. Values determined for these parameters can be used to determine when the assumption of local equilibrium between bulk phases can be applied to radionuclide transport in jointed geologic media. Furthermore, many of the parameters represent physical quantities or processes which can be characterized in the laboratory. However, parameters such as joint widths H and fluid velocities v must be obtained from the field, and methods must be developed to establish reliable bounds on the uncertainties in the values of such field-determined parameters.

REFERENCES

1. K. L. Erickson, to be published.
2. F. Helfferich, Ion Exchange, McGraw-Hill, New York (1962).
3. K. L. Erickson, to be published.
4. J. Crank, The Mathematics of Diffusion, Clerendon Press, London (1975).
5. J. Rosen, "Kinetics of a Fixed-Bed System for Solid Diffusion into Spherical Particles," J. Chem. Phys., 37:387 (1952).
6. J. Rosen, "General Numerical Solution for Solid Diffusion in Fixed Beds," Ind. Eng. Chem., 46:1590 (1954).
7. T. Sherwood, R. Pigford, C. Wilke, Mass Transfer, McGraw-Hill, New York (1975).