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ANALYSIS OF COLLOID TRANSPORT

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ABSTRACT

The population balance methodology is described and applied to the transport and capture of polydispersed colloids in packed columns. The transient model includes particle growth, capture, convective transport, and dispersion. We also follow the dynamic accumulation of captured colloids on the solids. The multidimensional parabolic partial differential equation was solved by a recently enhanced method of characteristics technique. This computational technique minimized numerical dispersion and is computationally very fast. The FORTRAN 77 code ran on a VAX-780 in less than a minute and also runs on an IBM-AT using the Professional FORTRAN compiler. The code was extensively tested against various simplified cases and against analytical models.

The packed column experiments by Saltelli et al. were re-analysed incorporating the experimentally reported size distribution of the colloid feed material. Colloid capture was modeled using a linear size dependent filtration function. The effects of a colloid size dependent filtration factor and various initial colloid size distributions on colloid migration and capture were investigated. Also, we followed the changing colloid size distribution as a function of position in the column.

Some simple arguments are made to assess the likelihood of colloid migration at a potential NTS Yucca Mountain waste disposal site.

INTRODUCTION

To date both laboratory (Saltelli et al. 1984; Freid et al. 1976) and site studies (Champ et al. 1982; Travis and Nuttall 1985) have demonstrated the existence and in some cases the accelerated transport of colloids. Nuttall, Hart, and Travis (1985) developed a theory for colloid transport using the population balance concept. Travis and Nuttall (1985) applied the population balance theory and the TRACR3D computer code to study the hydrology and transport of radiocolloids at a Los Alamos waste disposal site. Saltelli et al. (1984) derived and tested a one-dimensional filtration model and applied it to transient column profile data obtained by injecting ^{241}Am contaminated waste-glass colloids into a 26 mm by 180 mm sand packed column. They measured the size distribution of feed colloids and attempted to model the effects of the polydispersed colloids on the capture profile by assuming a distribution for the filtration factor. This approach did not yield a fundamental understanding of the effect of colloid size, but they did show that one must consider the size distribution in treating the experimental data.

In the following analysis of colloid transport, we used the multidimensional form of the population balance equation to analyze directly the effects of polydispersed colloids. The theory is developed for the transport of polydispersed colloids through a one-dimensional porous region. Conversion from a weight distribution to the corresponding number density function and back to a weight distribution after solution of the population balance equation is treated. We used the model to investigate the effect of two size distributions and to compare the effect of a constant versus size dependent filtration type colloid capture model.

THEORY

Randolph (1962) derived the general form of the population balance model in 1962. The population balance theory was derived at about the same time by Hulburt and Katz (1964). The population balance is a number continuity equation which has been applied successfully to crystallization, aerosols, and biological processes. Recently Travis and Nuttall (1985) applied this methodology to the problem of colloid transport. In this study, we apply the dynamic microscopic form of the population balance model with convective transport in one spatial dimension and particle growth along a colloid size axis to the problem of radiocolloid transport in nuclear waste disposal.

The colloid population density function, $P(t,s,L)$, is dependent on time, space and the colloid characteristic size which we assume to be the colloid diameter. $P(t,s,L)$ is the number of colloids of a particular size L at a point s in space and time t per unit volume of solution. When P is integrated over the colloid size range we have the total number of colloids per unit volume. In general, colloid charge or any other useful colloidal properties could be modeled by simply adding the appropriate property axes. The population balance also includes a birth/death term $f(P,t,s,L)$ which again accounts for the birth of new colloids as well as the adsorption and release of colloids by the rock matrix. The adsorption and release function treats colloids of arbitrary size. In this study we do not treat the adsorption of radionuclides on the colloids nor are we investigating the growth of colloids. To model colloids of the same size but with differing amounts of radionuclides would require an additional property axis for concentration.

Under these assumptions the population balance is:

$$\frac{\partial P}{\partial t} + v\frac{\partial P}{\partial z} - D\frac{\partial P^2}{\partial z^2} + u\frac{\partial P}{\partial L} = -f \qquad (1)$$

The filtration term is

$$f = \lambda(L)\, v\, P(t,z,L) \quad . \qquad (2)$$

It is sometimes desirable to work with a dimensionless form of the population balance. Carrying out the transformation of Eq. (1) using the dimensionless variables defined in the notation section leads to:

$$\frac{\partial \psi}{\partial \tau} + \phi\frac{\partial \psi}{\partial \beta} - \frac{D}{\bar{z}\,\bar{v}}\frac{\partial^2 \psi}{\partial \beta^2} + v\frac{\partial \psi}{\partial \rho} = \frac{\bar{z}}{P_i \bar{v}} f(\psi,\tau,\beta,\rho) \qquad (3)$$

Adsorption of colloids onto the surrounding matrix is assumed to follow the filtration model where the rate of mass accumulation is proportional to the concentration of colloids in the solution. In our model the colloids concentration in solution must be expressed in terms of the population distribution function. The mass concentration c(t,z) of colloids in the fluid is

$$c = \int_0^{\infty} c(L)dL \qquad (4)$$

where

$$c(L) = \rho K_v P(t,z,L) L^3 \quad , \qquad (5)$$

and K_v = volumetric shape factor, $\pi/6$ for a sphere.

The rate of mass build up on the matrix at a point in space for each colloid size is

$$\frac{d\sigma_i}{dt} = \varepsilon\, \lambda(L)\, v\, c(L) \qquad (6)$$

The total rate of mass accumulation for all colloid sizes is equal to the integral of Eq. (6) over the colloid size range.

$$\frac{d\sigma}{dt} = \varepsilon\, \rho\, v\, k_v \int_0^{L_m} \lambda(L)\, P(t,z,L)\, L^3\, dL \qquad (7)$$

In the general case $\lambda(L)$ will be some function of colloid size. However, if $\lambda(L)$ is size independent then the filtration follows the conventional form showing a straight line profile for the concentration of colloids captured on the sand packing when plotted on semilog paper.

To treat experimental data, it is often necessary to convert between weight distributions and number distributions. In terms of the number density function the distributed weight function is (Randolph and Larson 1971):

$$w(L) = \rho K_v L^3 P(L)/M_T \qquad (8)$$

The population balance, Eq. 3, was solved numerically by an improved method of characteristics technique presented by Douglas and Russell (1982). The buildup of colloids on the porous matrix is described by Eq. 7 which was coupled to the population balance and solved as a series of ODEs using the 4th order Runge-Kutta method. Note that σ is a function of column position, z, and time.

In our studies we tested both a gamma and a log-normal distribution to model the initial weight distribution of radiocolloids. The log-normal distribution gave a better fit to the measured feed distribution. The cumulative and distributed forms for the log-normal distribution are respectively: (Randolph and Larson 1971, p. 32)

$$W(L) = 0.5 + 0.5\ \mathrm{erf}(z) \qquad (9)$$

$$z = [\ln(L/\bar{L}')]/2^{1/2} \ln \sigma'$$

where $\bar{L}'$ = geometric mean size, μm; σ' = width parameter, (geometric STD), μm and the distributed form of the log-normal function is

$$w(L) = \frac{1}{(2\pi)^{1/2} \ln \sigma'} \exp\left[\frac{-\ln^2(L/\bar{L}')}{2\ln^2 \sigma'}\right] \qquad (10)$$

CASE STUDIES

Packed Column Simulations

Saltelli, et at. (1984) investigated the migration of polydispersed ^{241}Am colloids through a packed column of glauconitic sand. Colloidal ^{241}Am, leached from a simulated waste glass, was injected into a column. Three experiments of 28, 80, and 170 day duration were run. At the end of each test the column was dismantled, sectioned, and the ^{241}Am profile analysed. These authors analysed their data using the filtration capture model and found that the column profiles could not be matched using the conventional constant parameter filtration model. To fit the profile curves they assumed that the colloid feed exhibited a distribution of filtration coefficients. In this way they hoped to approximate size dependent filtration and by adjusting the filtration distribution parameters they did fit the shape profile curves. Their model also included a Langmuir isotherm model to treat the observed early adsorption of ^{241}Am which occurred throughout the length of the column. This rapid adsorption of ^{241}Am on the porous matrix was at a very low concentration level and the mechanism for this phenomenon has not been directly investigated; therefore, we did not choose to include this mechanism in our model. To match the experimental data we simply assumed an initial adsorbed ^{241}Am concentration of 10^{-10} moles/liter.

The size distribution of the colloid feed was measured by filtration and represented in our analysis by a log-normal distribution. The measured ^{241}Am colloid distribution along with our curve-fitted distributed and cumulative log-normal distributions are illustrated in Fig. 1. The measured range of the feed colloids was from approximately .05 μm to a maximum of 10 μm. Our

curve-fit parameters for the log-normal distribution were $\bar{L}$ = 0.45 μm and σ = 7.39 μm.

The upper colloid size was experimentally controlled by passing the feed solution through a 10 μm filter prior to entering the column. The experimental conditions are give in Table I.

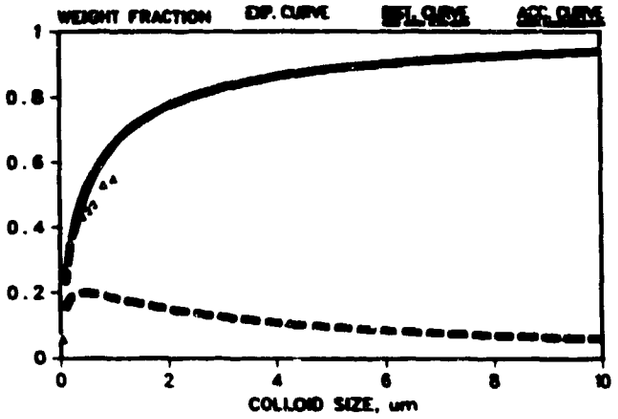

Figure 1. Colloid feed size distribution.

TABLE I - Experimental Parameters

Column Dimensions:	18 cm X 2.6 cm
Porosity:	0.38
Dispersion Coefficient:	62.6 cm^2/d
Darcy Velocity:	20.9 cm/d
Inlet Concentration:	3.8×10^{-10} M
Exit Concentration:	$3.5\text{-}6.5 \times 10^{-13}$ M
Feed Concentration Correction at 170 d:	0.242
Column Packing:	Sand with 20% clay

We solved the population balance model for the above conditions and used the log-normal distribution to represent the colloid feed. We also found that a size dependent λ was required. In our analysis, however, λ represents the actual capture mechanism whereas in Saltelli et al. (1984), λ represented capture mechanism and size distribution effects together. The resulting concentration profile for ^{241}Am on the porous matrix is compared with the experimentally measured profile after 170 days of continuous column operation and shown in Fig. 2 . The strong curvature in the calculated profile is created by the linear size dependent filtration function, $\lambda = 2L$. The asymptotic level of concentration at 10^{-10} shown on the far right of the curve was modeled by arbitrarily setting this level of concentration as an initial condition in the column. The mechanism for this early low level of concentration is still speculative and can be modelled in several ways; however, the true physical mechanism has not been identified.

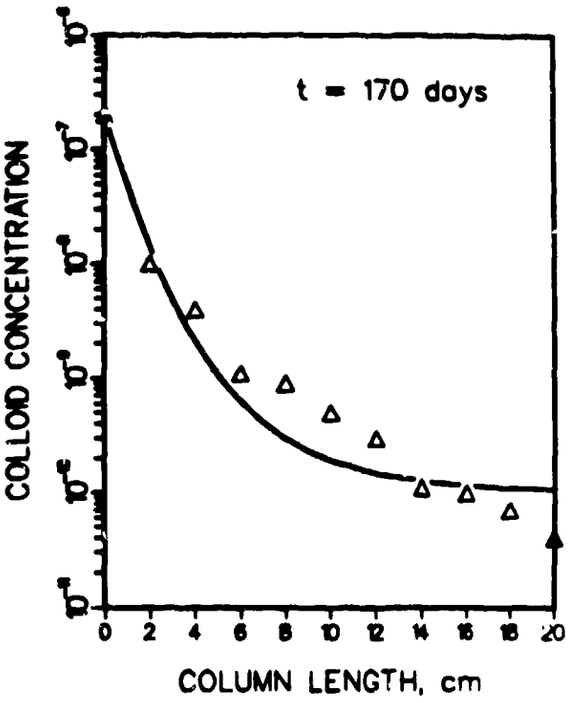

Figure 2. Measured and calculated solid concentration profile for ^{241}Am. (concentration, moles/liter of column.)

The numerical solution of the population balance also provides some interesting information on the change in the fluid phase colloid size distribution as a function of position down the vertical column. Fig. 3 illustrates in three dimensions the position varying colloid weight distribution in the liquid. The surface shows both the rapid decrease in the mass of colloids in solution and the shift in the mode of the distribution to small sizes. Because of the size dependent filtration coefficient the larger colloids are preferentially removed early at the top of the column leaving the smaller particles to transport downward through the porous medium. In the case of a constant filtration factor, λ, the nature of the colloid size distribution has no effect on the solid concentration profile since then each particle has the same capture probability independent of size.

The calculated ^{241}Am concentration profile in Fig. 2 follows the trend of the experimental data but does not agree equally well at every point. A major cause of this is the uncertainty in the true form of the filtration function λ(L). An alternative approach to analysing this experiment is to consider it an inverse problem for λ(L). That is, instead of estimating λ(L) and then calculating colloid transport, we could solve Eqs. (1) and (7) directly for λ(L). That is, we could solve the minimization problem

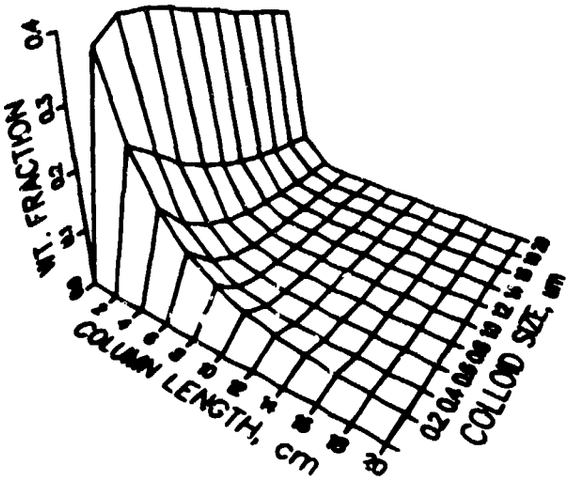

Figure 3. Liquid phase colloid weight distribution versus position along column.

$$\min \sum_i \sum_j (\sigma_o(t_i,z_j) - \sigma_m(t_i,z_j))^2 \qquad (11)$$

subject to

$$\frac{d\sigma_m}{dt} = \varepsilon \rho v K_v \int_0^{L_m} \lambda(L)\, P(t,z,L)\, L^3\, dL \qquad (12)$$

and

$$\frac{\partial P}{\partial t} + v\frac{\partial P}{\partial z} - D\frac{\partial^2 P}{\partial z^2} = -v\,\lambda(L)\,P, \qquad (13)$$

$$P(t,o,L) = g(L),\ P(o,z,L) = 0 \qquad (14)$$

where $\sigma_o(t_i,z_j)$ is the observed mass accumulation at time t_i and location z_j and σ_m is the calculated value. The solution can be obtained by nonlinear optimization techniques, such as the adjoint method. The solution will be the most likely form for $\lambda(L)$. We plan in fact to solve the equation set (11) to (14) in the near future. This analysis points out a problem frequently encountered--incomplete data. In this case, a set of experiments, each using a different but uniform colloid size, would allow independent determination of $\lambda(L)$.

NTS YUCCA MOUNTAIN SITE

Colloids may originate in a waste repository from several sources: by the corrosion of waste glass and canisters, by degradation of the engineered backfills, and by erosion from naturally occurring clays. Hence, there is a reasonable likelihood that colloids will exist; however, the important consideration is whether the geological medium is conducive to colloid transport or whether colloid migration and capture will retard their transport. Colloid transport depends on at least four factors: filtration, pH of the solution, water velocity, and diffusion.

At Yucca Mountain filtration will be an effective barrier in the tuff matrix. Pore size is an important element in filtration. Pseudocolloids will obviously not flow through pores that are smaller than the pseudocolloids themselves. Pore size distributions have been measured for several Yucca Mountain tuff samples. Mercury porosimetry data, measured by Quantachrome Co., on a sample of Topopah Spring tuff showed that most of the pores are less than 1 µm and approximately 50% are smaller than 0.1 µm. Even though a small percentage of pores are larger than 1.0 µm these large pores will not transport colloids because they will be dry. In the Topopah Spring formation at NTS, the saturation is less than 90% and large pores are the last to become saturated. In another NTS site formation, Calico Hills, approximately 50% of the pores are smaller than 0.06 µm. Hence colloids must be on the order of 0.1 µm in diameter or less to pass through the NTS tuff.

Pore water velocities, assuming matrix flow, are estimated at less than 2.0 cm/yr. These low velocities are on the order of molecular diffusion rates thus greatly limiting the migration of colloids within the tuff matrix. Transport of colloids through fractures is possible; however, for the measured fracture apertures of 50 to 250 µm in Topopah Spring tuff the water flow rate would only be about 2 m/yr or still not much greater than molecular diffusion transfer rates. If fracture flow were episodic, corresponding to a few intense rainfalls per year, flow rates in fractures might be much larger but for only very short times.

Colloids greater than 0.1 µm in diameter will likely be removed by gravitational settling (Apps, et al. 1983). The transporting ability of very small colloids may be diminished by diffusion of radionuclides out of the particles and subsequent adsorption of the nuclides onto the tuff matrix. Diffusivities for some nuclides in some clays have been measured at 10^{-13} to 10^{-16} cm^2/s. Characteristic diffusion times for 0.1 µm particles are consequently only a few days. Migration of small colloids may be possible in a fracture flow regime. Work is continuing to understand the migration mechanisms of the very small colloids.

SUMMARY

The population balance methodology which operates on a number continuity approach is well suited for describing the complex phenomena of colloid transport. In the present study the problem of polydispersed colloid transport in a porous medium was successfully modeled and agreement was found between model results and data. The advantages of this methodology are that it provides a comprehensive and fundamental tool for analysing the complex mechanisms of colloid migration. The approach requires conversion back and forth between the weight and number distributions; however, this conversion is a straight forward process. In this study, the colloid size distribution had a significant effect on the migration and capture process when a size dependent filtration capture model was

used. In the case of size dependent filtration, the larger colloids were rapidly captured while the smaller ones migrate much further through the porous medium. Both a constant and a linear size dependent filtration type capture model were tested. The size dependent model was required to match the measured column profile data. The experimental data was modeled successfully with only one adjustable parameter, s, the slope of the filtration coefficient function. If λ, the filtration factor, is constant then the colloid size distribution has no effect on transport or capture.

A limited study of parameter sensitivity showed that the width of the colloid feed distribution influenced the curvature on a semilog plot of the solid phase concentration profile with narrowing of the distribution converging to the monodispersed model and producing a linear concentration profile on a semilog plot.

In light of our findings, we made a preliminary review of some colloid transport characteristics for a potential NTS nuclear waste disposal site. We found geological factors favorable for retarding colloid migration. However, the potential for very small colloids to migrate in fractures with episodic flow characteristics may be significant and therefore requires further study and analysis.

NOTATION

c	Colloid Concentration in fluid	gm/cm^3
n	Hydrodynamic Dispersion Coefficient	cm^2/d
f	Birth/Death Rate Function	$\#/cm^3\mu m d$
L	Colloid Size Dimension	μm
M_T	Initial Mass Concentration of Colloids	gm/cm^3
P	Population Density Function	$\#/cm^3\mu m_{-1}$
s	Slope of Filtration Function	$cm^{-1}\mu m^{-1}$
t	Time	d
u	Growth Rate Along the Size Axis	$\mu m/d$
v	Darcy Water Velocity	cm/d
w	Weight Distribution Function	$gm/cm^3\mu m$
W	Cumulative Weight Dictribution	gm/cm^3
z	Space Dimension	cm

Greek Symbols

ϕ	Population Density Function (P/P_o)	dimensionless
ϕ	Velocity $(v/\bar{v})$	dimensionless
ν	Growth Rate $(u\bar{z}/\bar{v}\bar{L})$	dimensionless
β	Space $(z/\bar{z})$	dimensionless
ρ	Colloid Size $(L/\bar{L})$	dimensionless
λ	Filtration Coefficient	cm^{-1}
σ	Mass Concentration of Colloids on the Matrix	gm/cm^3
σ_i	Mass Concentration of Colloids at Size L on the Matrix	$gm/cm^3\mu m$
τ	Time $(t\bar{v}/\bar{z})$	dimensionless
-	Average Properties or Limiting Properties	
ϵ	Porosity	

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