Analytic Studies of Colloid Transport
in Fractured Porous Media

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1. Introduction

We analyze the interactive migration of radioactive colloids and solute in fractured rock. Two possible interactions between radionuclides as colloids and as solute are considered: (1) solute sorption on nonradioactive colloids to form pseudocolloids, and (2) dissolution of radioactive colloids.

Previous studies[1,2] have discussed the formation and transport of colloids in porous media, including removal of colloids by filtration and sedimentation. Colloids can migrate faster than solute because of weaker sorption on stationary solids and because of hydrochromatography of colloid particles in flow channels. However, the migration of colloids and pseudocolloids can be retarded by the interaction of colloids with solute, and the migration of solute in local equilibrium with colloids can be more rapid than if colloids were not present. Here we present a new quantative analysis to predict the interactive migration of colloids and solute in porous and fractured media.

2. Pseudo-colloid migration

Consider a radioactive solute at concentration $C_2(x,t)$ in water in the fracture of fractured porous rock. Also present in the fracture are natural colloids, on which solute can sorb to concentration $C_1(x,t)$ on the colloids to form pseudocolloids. We assume the one-dimensional convective-diffusive transport within the fracture, and assume that colloids are too large to diffuse into the rock matrix. Neglecting possible colloid filtration within the fracture, the equation governing the transport of solute as pseudocolloids is:

$$\epsilon_1\xi_1\frac{\partial C_1(x,t)}{\partial t}+\epsilon_1\xi_1 v_1\frac{\partial C_1(x,t)}{\partial x}+\epsilon_1 S_1(x,t)+\epsilon_1 S_2(x,t)-\epsilon_1\xi_1 D_1\frac{\partial^2 C_1(x,t)}{\partial x^2}+\epsilon_1\xi_1\lambda C_1 = 0, \quad x>0, t>0 \quad (1)$$

where $C_1(x,t)$ is the amount of species sorbed on the colloid per unit volume of solid colloid, v_1 is the colloid pore velocity, D_1 is the colloid dispersion coefficient, λ is the decay constant, ϵ_1 is the porosity within the fracture, ξ_1 is the constant volume fraction of colloids in fracture liquid, $\epsilon_1 S_1(x,t)$ is the rate of sorption to stationary solid, and $\epsilon_1 S_2(x,t)$ is the rate of desorption from the pseudocolloid.

For the same species as solute in liquid in the fracture

$$\epsilon_1\frac{\partial C_2(x,t)}{\partial t}+\epsilon_1 v_2\frac{\partial C_2(x,t)}{\partial x}-\epsilon_1 S_2(x,t)+\epsilon_1 S_3(x,t)-\epsilon_1 D_2\frac{\partial^2 C_2(x,t)}{\partial x^2}+\epsilon_1\lambda C_2+\frac{q(x,t)}{b} = 0, \quad x>0, \ t>0 \quad (2)$$

where $C_2(x,t)$ is the solute concentration in the fracture liquid, v_2 is the solute pore velocity, $\epsilon_1 S_3(x,t)$ is the rate of solute sorption on stationary fracture solids, b is the fracture half-width, and $q(x,t)$ is the diffusive solute flux into the rock matrix, given by

$$q(x,t) = -\epsilon_p D_p\frac{\partial N(x,y,t)}{\partial y}\bigg|_{y=b}, \qquad x>0, \quad t>0 \qquad (3)$$

ϵ_p is the rock porosity, D_p is the solute diffusion coefficient in water in porous rock, and $N(x,y,t)$ is the solute concentration in pore water in the rock.

For solute species sorbed on stationary fracture solids

$$(1-\epsilon_1)\frac{\partial C_3(x,t)}{\partial t} - \epsilon_1 S_3(x,t) + (1-\epsilon_1)\lambda C_3(x,t) = 0, \qquad x>0, \qquad t>0 \qquad (4)$$

where $C_3(x,t)$ is the concentration of sorbed solute species..

For species sorbed as pseudocolloids on the stationary fracture solids

$$(1 - \epsilon_1)\xi_2\frac{\partial C_1(x,t)}{\partial t} - \epsilon_1 S_1(x,t) + (1 - \epsilon_1)\xi_2\lambda C_1(x,t) = 0, \qquad x > 0, \qquad t > 0 \tag{5}$$

where ξ_2 is the constant volume fraction of the sorbed colloid per unit volume of the stationary fracture solid.

Inside the rock matrix

$$R_p\frac{\partial N(x,t)}{\partial t} - D_p\frac{\partial^2 N(x,t)}{\partial y^2} + R_p\lambda N(x,t) = 0, \qquad x > 0, \quad t > 0, \quad y > 0 \tag{6}$$

where R_p is the solute retardation coefficient in the rock matrix.

We assume linear sorption equilibrium between the solute species in the fracture liquid and the same species sorbed on the colloid. Both the solute species and the colloids in the fracture liquid are assumed to undergo linear sorption equilibrium with the fracture solids

$$K_{d_1} = \frac{\xi_2}{\xi_1}, \qquad K_{d_2} = \frac{C_3(x,t)}{C_2(x,t)}, \qquad K_{d_3} = \frac{C_1(x,t)}{C_2(x,t)} \tag{7}$$

Adding eq. (1)-(5) with equation (7), we can obtain the equation for C_1 in terms of the effective retardation factor R, dispersion coefficient D, and velocity v.

$$R\frac{\partial C_1(x,t)}{\partial t} + v\frac{\partial C_1(x,t)}{\partial x} - D\frac{\partial^2 C_1(x,t)}{\partial x^2} + R\lambda C_1(x,t) + \frac{q(x,t)}{\epsilon_1 b} = 0, \qquad x > 0, \quad t > 0 \tag{8}$$

where

$$R = \left[\xi_1(1 + \frac{1 - \epsilon_1}{\epsilon_1}K_{d_1})\right] + \left[1 + \frac{1 - \epsilon_1}{\epsilon_1}K_{d_2}\right]\frac{1}{K_{d_3}} \tag{9}$$

$$v = v_1\left(\xi_1 + \frac{v_2}{K_{d_3}v_1}\right) \tag{10}$$

$$D = D_1\left(\xi_1 + \frac{D_2}{D_1 K_{d_3}}\right) \tag{11}$$

Then the solute and pseudocolloid apparent migration speed is

$$\frac{v}{R} = \frac{v_1\left(\xi_1 + \frac{v_2}{K_{d_3}v_1}\right)}{\left[\xi_1(1 + \frac{1-\epsilon_1}{\epsilon_1}K_{d_1})\right] + \left[1 + \frac{1-\epsilon_1}{\epsilon_1}K_{d_2}\right]\frac{1}{K_{d_3}}} \tag{12}$$

Depending on parameters, the apparent speed can be greater or less than the apparent speed of solute without colloid-solute sorption interaction.

The initial and boundary conditions are

$$N(x,\infty,t) = 0, \qquad x > 0, \quad t > 0 \tag{13}$$

$$N(x,b,t) = \frac{1}{K_{d_3}}C_1(x,t), \qquad x > 0, \quad t > 0 \tag{14}$$

$$N(x,y,0) = 0, \qquad x > 0, \quad y > 0 \tag{15}$$

$$C_1(0,t) = K_{d_3}C_o, \qquad t > 0 \tag{16}$$

$$C_1(\infty,t) = 0, \qquad t > 0 \tag{17}$$

$$C_1(x,0) = 0, \qquad x > 0 \tag{18}$$

where C_o is the inlet solute concentration.

The solution is

$$C_1 = \frac{2K_{d_3}C_o}{\sqrt{\pi}} \int_{\frac{x}{2}\sqrt{R/Dt}}^{\infty} \exp\left\{-\frac{\sqrt{v^2 + 4R\lambda D} - v}{2D}x\right\} \text{erfc}\left[\frac{x^2\epsilon_p\sqrt{D_p}R_p}{8Db\epsilon_1\eta^2\sqrt{t - \frac{Rx^2}{4D\eta^2}}}\right] \exp\left[-\left(\eta - \frac{xv}{4D\eta}\right)^2\right] d\eta$$

$$x \geq 0, t \geq 0 \qquad (19)$$

Figure 2 illustrates the predicted concentrations of solute and pseudocolloids as a function of distance from the fracture inlet, assuming a step-function source of pseudocolloids and solute at the relative concentrations shown at the fracture inlet. In figure 3 the solute concentration is shown as a function of distance from the fracture inlet for various R in the equation (9) where R has the distribution coefficients between solute and colloid, etc. Here the solute-colloid distribution coefficient is held constant. As we expect the front migrates faster for smaller R.

3. True colloid migration

Consider a radioactive solute and colloids of the same species in fracture of fractured porous rock. We assume one-dimensional advective transport of colloids and solute in the fracture. Here we assume that the rock surrounding the fracture is impermeable against solute and colloids. Therefore, the equations will also apply to a porous medium. Considering colloid filtration within the fracture, the colloid transport governing equation is:

$$\epsilon_1\frac{\partial C_1(x,t)}{\partial t} + \epsilon_1 v_1\frac{\partial C_1(x,t)}{\partial x} + \epsilon_1 S_1(x,t) + \epsilon_1 S_2(x,t) = 0,$$
$$x > 0, \qquad t > 0 \qquad (20)$$

where $C_1(x,t)$ is the true colloid concentration in liquid and v_1 is the true colloid pore velocity, and the other terms are the same as defined in equation (1).

Similar to equation (2) for the solute in the liquid

$$\epsilon_1\frac{\partial C_2(x,t)}{\partial t} + \epsilon_1 v_2\frac{\partial C_2(x,t)}{\partial x} + \epsilon_1 S_2(x,t) + \epsilon_1 S_3(x,t) = 0, \qquad x > 0, \qquad t > 0 \qquad (21)$$

For solute sorbed on the rock

$$(1 - \epsilon_1)\frac{\partial C_3(x,t)}{\partial t} - \epsilon_1 S_3(x,t) + (1 - \epsilon_1)\lambda C_3(x,t) = 0, \qquad x > 0, \qquad t > 0 \qquad (22)$$

where $C_3(x,t)$ is the concentration of sorbed solute on the rock

For colloids sorbed on the rock

$$(1 - \epsilon_1)\frac{\partial C_4(x,t)}{\partial t} - \epsilon_1 S_1(x,t) = 0, \qquad x > 0, \qquad t > 0 \qquad (23)$$

where $C_4(x,t)$ is the sorbed colloid concentration per unit solid volume

Assuming linear sorption equilibrium between the species in the liquid and on stationary solid the retardation coefficients are

$$R_1 = 1 + \frac{1 - \epsilon_1}{\epsilon_1}\frac{C_4(x,t)}{C_1(x,t)} \qquad (24)$$

$$R_2 = 1 + \frac{1 - \epsilon_1}{\epsilon_1}\frac{C_3(x,t)}{C_2(x,t)} \qquad (25)$$

Using the linear sorption assumption, we have

$$R_1\frac{\partial C_1(x,t)}{\partial t} + v_1\frac{\partial C_1(x,t)}{\partial x} + S_2(x,t) = 0, \qquad x > 0, \qquad t > 0 \qquad (26)$$

$$R_2\frac{\partial C_2(x,t)}{\partial t} + v_2\frac{\partial C_2(x,t)}{\partial x} - S_2(x,t) = 0, \qquad x > 0, \qquad t > 0 \tag{27}$$

We now have the three unknowns $C_1(x,t)$, $C_2(x,t)$, and $S_2(x,t)$ but only two equations.

Where colloids are present, we expect that the solute will be at saturation concentration. This suggests the assumption

$$C_2(x,t) = C_s U(t - \frac{\alpha x}{v_2}), \qquad x \geq 0, \qquad t \geq 0 \tag{28}$$

where C_s is the solute solubility limit and $\frac{v_2}{\alpha}$ is the effective migration velocity controlled by colloid dissolution, with α yet to be determined.

Adding equation (26) to (27), substituting equation (28) and neglecting decay.

$$R_1\frac{\partial C_1(x,t)}{\partial t} + v_1\frac{\partial C_1(x,t)}{\partial x} + (R_2 - \alpha)C_s\delta(t - \frac{\alpha x}{v_2}) = 0, \qquad x > 0, \qquad t > 0 \tag{30}$$

We solve the above equation using the method of characteristic or of extended Laplace transform applicable to a generalized function with the following side conditions

$$C_1(x,0) = 0, \qquad\qquad\qquad t > 0 \tag{31}$$

$$C_1(0,t) = C_0, \qquad\qquad\qquad x > 0 \tag{32}$$

where C_0 is the inlet colloid concentration. Then the solution is

$$C_1(x,t) = C_0 U(t - \frac{xR_1}{v_1}) + \frac{(R_2 - \alpha)v_2}{\alpha v_1 - R_1 v_2}C_s[U(t - \frac{\alpha x}{v_2}) - U(t - \frac{R_1 x}{v_1})], \qquad x \geq 0, \qquad t \geq 0 \tag{33}$$

To specify the yet-unknown quantity α, assume the colloid and the solute migration fronts move at the same velocity $\frac{v_2}{\alpha}$ in the fracture.

Therefore,

$$C_0 - \frac{(R_2 - \alpha)v_2}{\alpha v_1 - R_1 v_2}C_s = 0 \tag{34}$$

Therefore, the colloid concentration is

$$C_1(x,t) = C_0 U(t - \frac{\alpha x}{v_2}), \qquad x \geq 0, \qquad t \geq 0 \tag{35}$$

where

$$\alpha = \frac{(R_1 C_0 + R_2 C_s)v_2}{C_0 v_1 + C_s v_2} \tag{36}$$

Physically the colloid and solute migration front with dissolution is between the colloid migration front and the solute migration front without dissolution. Therefore, α satisfies

$$\frac{v_1}{R_1} < \frac{v_2}{\alpha} < \frac{v_2}{R_1}$$

Figure 3 presents profiles of colloid and solute concentrations for the specified data set. Without colloid dissolution, at a thousand years since radionuclides are released into the fracture inlet, the colloid migration front locates 100 meters from the inlet and the solute migration front is 20 meters from the inlet. But with colloid dissolution into solute, the colloid front is at 800 meters away from the inlet and the solute front also advances to the same 800 meters. Therefore, the dissolution mechanism is important to the solute migration in the fracture, especially when the inlet colloid concentration is much greater than that of the solute. This can happen when oxidized actinides suddenly meet a redox front, precipitate, and form colloids.

Then the solute concentration will be controlled by the reduced solubility limit, but a colloidal aggregate of the precipitated solute can be at much higher concentration.

This analysis is a tool to investigate the assumption of colloid dissolution. Experimentally v_1, v_2, R_1, and R_2 are measurable, and based on the colloid dissolution assumption, $\frac{v_2}{\alpha}$ is also measurable. Agreement of the measured α with the theoretical value from equation (35) would validate the colloid dissolution assumption.

4. Conclusions

The migration of colloids and solute in fractured medium with two types of colloid-solute interaction has been studied. When the colloid-solute interaction is by dissolution, solute that normally has greater retardation than colloids is accelerated by colloid dissolutions. For sorption interaction, the apparent migration speed of pseudocolloids can be greater or less than the solute migration speed without interaction, depending on the chice of parameters. Further studies of the interactive migration of colloids and solute with dissolution equilibria are under way.

References

1. A. Avogadro and G. De Marsily, "The Role of Colloids in Nuclear Waste Disposal ," Material Research Society, *vol 26*, pp 495-505, 1984

2. B.J. Travis and H.E. Nuttall, "A Transport Code for Radiocolloid Migration: With an Assessment of an Actual Low-Level Waste Site," Material Research Society, *vol 44*, pp 969-976, 1985.
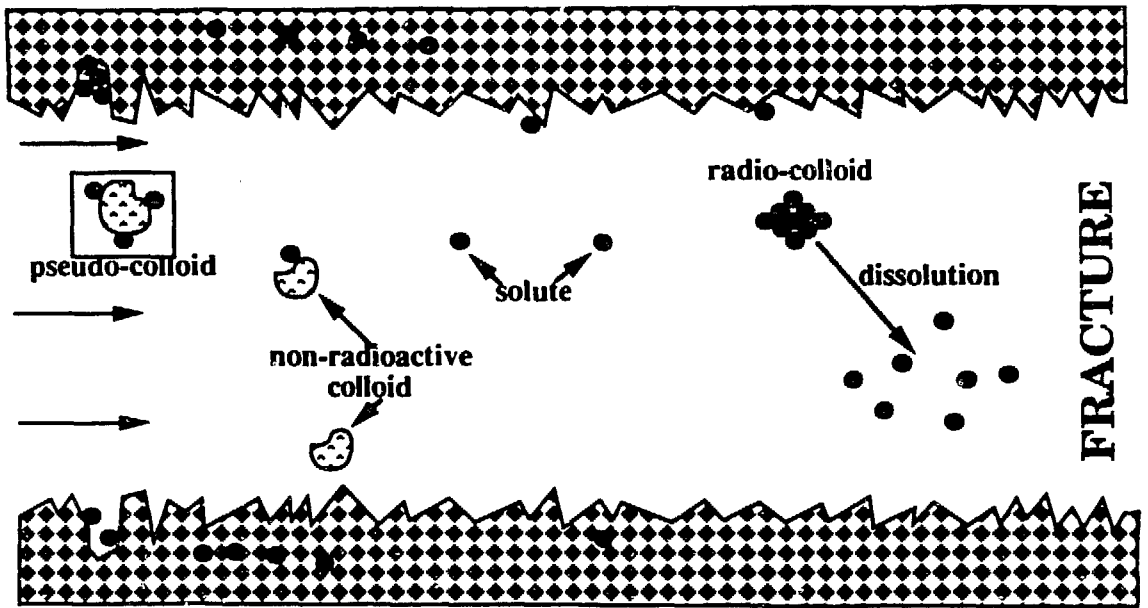
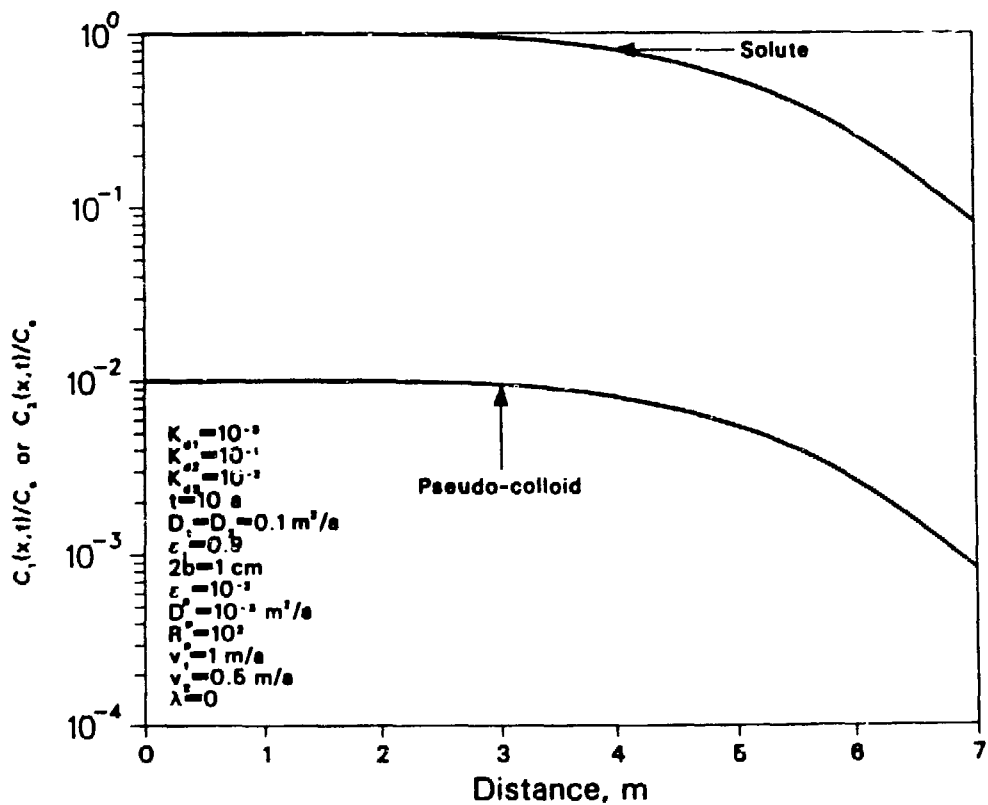## Figure 1. Colloid Migration in a Fracture

Figure 2. Relative Concentration of Pseudocolloid and Solute
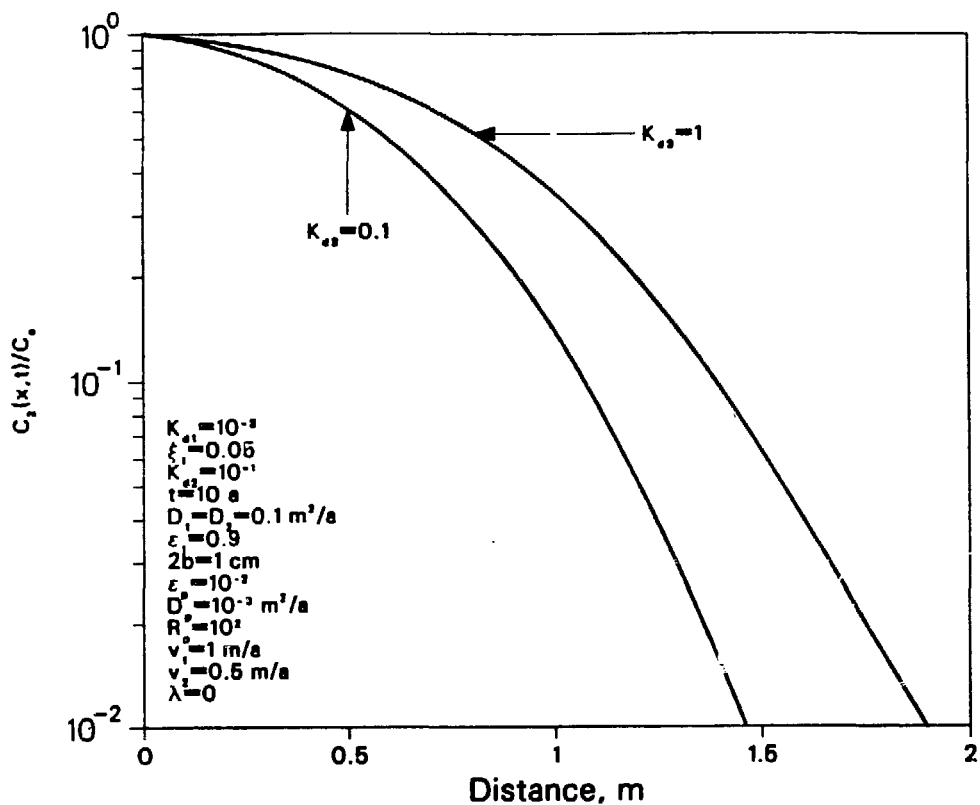with Fracture Flow and Matrix Diffusion of Solute

Figure 3. Relative Concentration of Solute for Different K_{d3} with Fracture Flow and Solute Matrix Diffusion
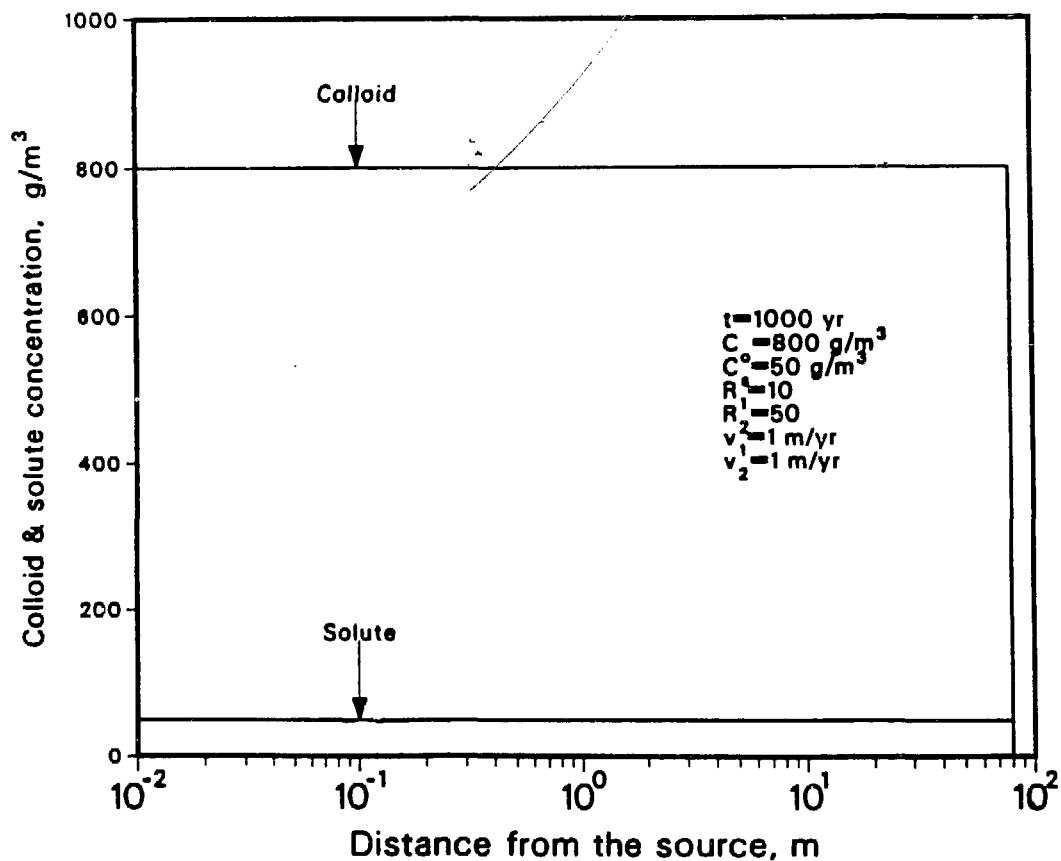

Figure 4. Concentration of Colloid and Solute in the Fracture with Colloid Dissolution to Solute