

Subsurface colloids in groundwater contamination: a mathematical model

Tushar Kanti Sen^{a,*}, Sachin Shanbhag^b, Kartic C. Khilar^b

^a Department of Chemical Engineering, National Institute of Technology, Rourkela 769008, Orissa, India

^b Department of Chemical Engineering, Indian Institute of Technology, Powai, Mumbai 400076, India

Abstract

In this paper, a new role of subsurface colloidal fines on the transport of contaminants in groundwater flows has been presented. Here, an equilibrium three-phase model based on colloidal induced release, migration and finally capture of these colloidal fines at pore constrictions has been developed. This model is more realistic than the existing models in that the physics of release, migration and finally capture at pore constrictions leading to plugging phenomenon has been adequately incorporated. Presence of colloids can either facilitate or inhibit the spreading of contaminants depending on the values of the parameters, such as the inlet colloid concentration, the release coefficient and more significantly on the sensitivity of the permeability to the concentration of captured fines at the pore constrictions. For a range of conditions, plugging of the porous media occurs resulting in retardation of contaminant transport. The plugging-based retardation of contaminant transport can be used to develop a new containment technique.

Keywords: Colloidal fines; Contaminants; Plugging/entrapment; Groundwater

1. Introduction

The contamination of groundwater and soil due to mobilization and transport of organic, inorganic and biological pollutants from many sources such as spillage, land application and waste disposal practices is a well recognized problem. The presence and transport of contaminants constitute a potential threat to human health and ecosystems. Natural colloids, which are ubiquitous in groundwater system, are composed of inorganic and organic molecular constituents or microorganisms. Colloids are commonly defined as mean particles or macromolecules smaller than 1 μm in diameter but larger than 1 nm [1,2]. These colloidal particles having surface charge and are typically smaller than intergranular pores and fractures in rock and can migrate long distance with the groundwater. When these colloidal fines are transported over large distances, they can act as a carrier for contaminant, which are adsorbed on their surface and thereby enhance the spreading of pollutants in subsurface system. This contaminant transport has been known as “colloid-facilitated contaminant transport” in literature.

Experimentally as well as theoretically, it has been found that mobile colloidal fines can often carry contaminants such as radionuclides, transition metals and hydrophobic organic compounds adsorbed onto their surface and can, thus, significantly accelerate the transport of contaminants through porous media [1,3–19]. Kretzschmar et al. [1] mentioned in their review article that only a few field studies provide evidence for colloid-facilitated transport of contaminants.

Previous studies concerning contaminant transport in subsurface environment have considered soil or groundwater as essentially a two-phase system where the contaminants could partition between the mobile aqueous phase and the immobile solid phase. Based on this concept, it has been predicted that many contaminants would be relatively immobile, as they are generally sparingly soluble and hence get adsorbed on the solid phase. But unexpected appearance of low solubility contaminants some distance away from known source or sooner than would be expected from their solubility, led to examination of the possible involvement of nonaqueous, mobile colloids in contaminant transport. Invoking colloids to explain such observations gave rise to the three-phase model of species transport, i.e. mobile liquid phase, mobile colloidal phase and the immobile solid phase. Few three-phase models describing coupled colloid and contaminant transport have been reported so far

* Corresponding author. Tel.: +91-661-2476838.

E-mail addresses: tksen@nitr.ren.nic.in, sentushar@rediffmail.com (T.K. Sen), kartic@che.iitb.ac.in (K.C. Khilar).

Nomenclature

C_c	aqueous contaminant concentration (kg/m ³)
C_{c0}	aqueous contaminant concentration at the inlet (kg/m ³)
C_f	concentration of suspended fines of (kg/m ³)
C_{f0}	concentration suspended fines at the inlet (kg/m ³)
D	dispersion coefficient of colloids (m ² /s)
D_c	dispersion coefficient of contaminant (m ² /s)
k	permeability (m ²)
K_f	partition constant between fines-aqueous phases (m ³ /kg)
K_m	partition constant between matrix-aqueous phases (m ³ /kg)
L	length (m)
q	flow rate (m/s)
r_c	rate of colloidal capture (kg/(m ³ s))
r_r	rate of colloidal release (kg/(m ³ s))
t	time (s)
x	distance (m)
X_f	mass fraction of contaminant on the fines (kg/kg)
X_m	mass fraction of the contaminant on the solid matrix (kg/kg)

Greek letters

α	colloid release rate constant (s ⁻¹)
β	colloid capture rate constant (s ⁻¹)
ϕ	porosity of the matrix
μ	viscosity of aqueous phase (Pa s)
ρ_f	density of fines (kg/m ³)
ρ_m	density of solid matrix (kg/m ³)
σ_1	concentration of fines on release sites (kg/m ³)
σ_2	concentration of fines on capture sites (kg/m ³)
σ_{10}	initial concentration of fines on release sites (kg/m ³)
σ_{max}	parameter defining the sensitivity of velocity changes (kg/m ³)

[8,10,11,13–15]. Most of these studies have assumed equilibrium interactions between the colloidal particles and the contaminant in the dissolved phase [10,13–15]. These models predict a reduction of the effective retardation arising out of sorption on to the solid matrix depending on the concentration of the colloidal fines and the partition coefficient for contaminant sorption on the colloidal fines.

The release of colloidal fines from a pore surface is the first step in the phenomenon of migration of fines in subsurface zone. In general, two major types of forces are responsible for the release of these colloidal fines: colloidal

and hydrodynamic. The released colloidal fines while flowing with the liquid phase, can either readhere to the pore surface or flow without capture or get entrapped at the pore constrictions. The later two occurrences are more common as the colloidal and hydrodynamical conditions that bring about their release are not likely to allow these particles to readhere back to the pore surface in the same conditions. It has been observed that the release of fines is threshold process that is, a minimum perturbation is required to detach the fines from the pore surface. This could be in terms of a critical hydrodynamics stress [20] or a critical salt concentration [2]. The release fines may get entrapped or plugged at the pore constrictions. Entrapment can occur in three forms, namely size exclusion, multiparticle bridging and surface deposition. Whether the particles get entrapped or not depends on the factors such as pore structure, relative sizes of fines and pore constrictions and concentration of fines [2,12]. Recently, it has been found experimentally that colloidal fines, kaolin retarded Ni²⁺ transport at constant flow under plugging condition [12]. The existing reported models, however, do not adequately incorporate this phenomenon and therefore may fail to describe the process completely, i.e. for a wide range of conditions.

Moreover, the reported modeling studies, thus far, are based on the convective diffusion equations for the contaminant and for the colloidal fines, and the rate equations for the process of adsorption of contaminant. The mobilization/hydrodynamic release of indigenous colloidal fines and their possible capture at constriction sites are only considered in the reported model developed by Sen et al. [13].

In this paper, we presented a comprehensive mathematical model based on equilibrium adsorption of contaminants and on the colloidal induced release, migration and finally capture of colloidal fines at pore constrictions leading to plugging phenomenon. This model can be used to predict both facilitation and retardation of the transport of contaminants in presence of colloidal fines in underground flow depending on the flow and other conditions. Results of model simulations performed to investigate the impact of the model parameters on the spatial and temporal variations of contaminant concentrations and fluxes are discussed. It is shown that under a range of conditions, entrapment/plugging phenomenon can occur which leads to the retardation of contaminant transport. Based on this finding, a containment technology can be developed to check the spreading of groundwater and soil pollution as well as for an effective treatment and remediation.

2. Model development

This model has been formulated in a manner analogous to that of existing model such as the model developed by Sen et al. [13] and by Corapcioglu and Jiang [15]. Additional equations relating to colloid induced release and the

variations in flow rate due to plugging/entrapment has been incorporated.

A cylindrical porous medium of length L in the direction of flow and of unit cross sectional area, having porosity ϕ and initial permeability K_0 is considered. A set of unsteady state mass balance equations are derived based on the following assumptions:

- A single species of contaminant is considered.
- Contaminant is partitioning among the three phases, namely solid matrix, mobile colloidal fines and aqueous phase.
- The release of fines due to only colloidal forces, which is dependent on underground solution chemistry.
- The porosity remains virtually unaltered during plugging/entrapment phenomenon.
- The variation in concentrations and other quantities are significantly only in the major flow direction that is axial direction in this case.
- The release and capture sites are different.

An unsteady state mass balance equation for the colloidal fine particles in suspension can be written as

$$\phi \frac{\partial C_f}{\partial t} = D\phi \frac{\partial^2 C_f}{\partial x^2} - q \frac{\partial C_f}{\partial x} + r_r - r_c \quad (1)$$

where C_f is the concentration of colloidal fines in suspension (kg/m^3), D the hydrodynamic dispersion coefficient (m^2/s), q the superficial flow flux (m/s), r_r the rate of colloidal induced release of fines ($\text{kg}/(\text{m}^3 \text{ s})$), r_c the rate of capture of colloidal fines ($\text{kg}/(\text{m}^3 \text{ s})$), ϕ the porosity of the solid matrix, x the distance along flow (m), and t is time (s).

The particles are released from the surface of the body while they are entrapped at the constriction sites. The permeability reduces due to the entrapment at the pore constrictions. The rate equations for the release and capture of particles are given as follows:

For release:

$$\frac{\partial \sigma_1}{\partial t} = -\alpha \sigma_1 \quad (2)$$

For capture:

$$\frac{\partial \sigma_2}{\partial t} = \beta C_f \quad (3)$$

where σ_1 is the concentration of fines at release sites (kg/m^3) and σ_2 is the concentration of fines at capture sites (kg/m^3). We assume a first ordered form for the rate equations

$$r_r = \alpha \sigma_1 \quad (4)$$

$$r_c = \beta C_f \quad (5)$$

where α is the release coefficient (s^{-1}) and β is the colloid capture coefficient (s^{-1}). It is pointed out that the equation for the rate of release of fines as given above would hold true as long as the salt concentration is smaller than the critical salt concentration [2]. Similarly, the equation for the capture

of the fines would be applicable contingent on the fines concentration exceeding the critical particle concentration. However, in this simulation, these effects are not considered.

An overall contaminant balance on all the sites namely, the solid matrix, aqueous phase, captured colloids and free colloids yields

$$\begin{aligned} & \frac{\partial \rho_m X_m}{\partial t} + \phi \frac{\partial C_c}{\partial t} + \phi \frac{\partial X_f C_f}{\partial t} + \frac{\partial \sigma_1 X_f}{\partial t} + \frac{\partial \sigma_2 X_f}{\partial t} \\ & = \phi D_c \frac{\partial^2 C_c}{\partial x^2} - q \frac{\partial C_c}{\partial x} + \phi D \frac{\partial^2 X_f C_f}{\partial x^2} - q \frac{\partial X_f C_f}{\partial x} \end{aligned} \quad (6)$$

where ρ_m is the bulk density of the solid matrix, X_m the mass fraction of contaminant on solid matrix, X_f the mass fraction of contaminant on colloids, C_c the contaminant concentration in aqueous phase (kg/m^3) and D_c is the dispersion coefficient for dissolved contaminant (m^2/s).

The low contaminant concentration generally encountered in groundwater permits us to assume linear partitioning between any of the solid phases and aqueous phase [21,22].

$$X_m = K_m C_c \quad (7)$$

$$X_f = K_f C_c \quad (8)$$

where K_m and K_f are the partition coefficients for the matrix and colloidal phases, respectively. Literatures [22–24] reveal that K_f is ordinarily several times larger than the corresponding values of K_m . To model the variation of velocity in the porous media with changing concentration of the captured colloid, we use Darcy's law for horizontal flow as follows:

$$q = \frac{K}{\mu} \left(-\frac{\Delta P}{L} \right) \quad (9)$$

where K is the permeability of the medium (m^2), μ the viscosity of the fluid (Pa s) and ΔP is the pressure difference across the medium.

To determine the decrease in permeability with entrapment, a relationship is required. No theoretical correlation has been reported between the permeability (K) and the amount of entrapment (σ_2). An empirical expression [2], which has been used in our model, is as follows:

$$K = K_0 \exp \left(-\frac{\sigma_2}{\sigma_{\max}} \right) \quad (10)$$

where K_0 is the initial permeability and σ_{\max} is an adjustable parameter that characterizes the effectiveness of entrapment in reducing the permeability.

The overall permeability, K is computed by

$$\frac{L}{K} = \int_0^L \frac{dx}{K(x)} \quad (11)$$

The following initial and boundary conditions can be written for this geometry are

For colloids:

$$qC_f|_{0^-} = qC_f|_{0^+} - D \left. \frac{\partial C_f}{\partial x} \right|_{0^+} \quad (12)$$

$$C_f(x, 0) = 0 \quad (13)$$

$$\left. \frac{\partial C_f}{\partial x} \right|_{x=L} = 0 \quad (14)$$

$$\sigma_1(x, 0) = \sigma_{10} \quad (15)$$

$$\sigma_2(x, 0) = 0 \quad (16)$$

For contaminants:

$$qC_c|_{0^-} = qC_c|_{0^+} - D_c \left. \frac{\partial C_c}{\partial x} \right|_{0^+} \quad (17)$$

$$C_c(x, 0) = 0 \quad (18)$$

$$\left. \frac{\partial C_c}{\partial x} \right|_{x=L} = 0 \quad (19)$$

Eqs. (1)–(19) provides a mathematical framework to determine various relevant quantities.

3. Results and discussion

For our simulations we consider a porous cylinder, across which a constant pressure difference ΔP is applied. Through one end of the cylinder, colloids of concentration C_{f0} and contaminant of concentration C_{c0} are injected. The temporal variation of the concentration of the colloids and the contaminant at the exit of the cylinder is monitored. Numerical solution to the set of partial differential equations has been obtained using a finite difference method. A fully implicit scheme employing a two-point forward difference approximation for time and space derivatives is used. In this method, the entire region of interest is divided into a grid of uniform

Table 1

Base values of porous medium properties used in simulation [2,8–15]

Parameter	Value
C_{f0} (g/m ³)	50.0
C_{c0} (mg/m ³)	1.0
D (m ² /s)	4×10^{-9}
D_c (m ² /s)	4×10^{-7}
α (s ⁻¹)	1.0×10^{-4}
β (s ⁻¹)	1.0×10^{-7}
L (m)	0.1
σ_{10} (kg/m ³)	1.5
σ_{\max} (kg/m ³)	0.0015
K_f (m ³ /kg)	5.0
K_m (m ³ m/kg)	1.0
ϕ	0.4
ρ_m (kg/m ³)	2000
ρ_f (kg/m ³)	1500

resolution in each of the dimensions. The implicit formulations of partial differential equations along with boundary conditions led finally to a set of linear algebraic equations with a tridiagonal matrix, which was then solved by Gauss elimination solution algorithm at each time step.

Breakthrough curves are presented as plots of C_{ct} against time, where C_{ct} is the total mobile contaminant concentration ($C_{ct} = C_c + X_f C_f$). C_{ct} is chosen as the ordinate because it accounts not only for the contaminants in the aqueous phase, but also accounts for the contaminants on the mobile colloid phase. The model parameters used in the simulations have been obtained from the published works and are summarized in Table 1.

Simulations have been conducted in a variety of cases. Due to deficiency of constant pressure plugging-based

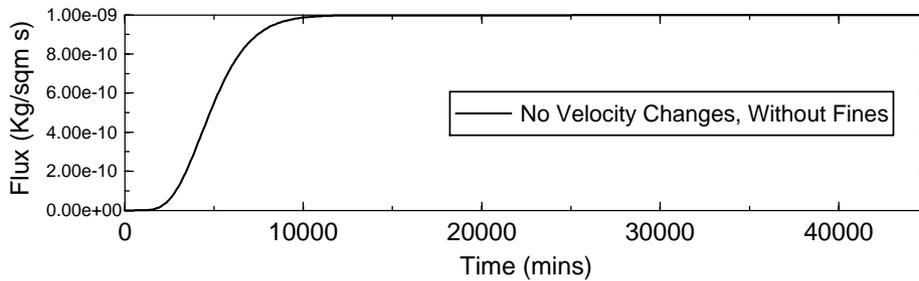


Fig. 1. Contaminant flux vs. time plot for the case of without fines and no velocity change.

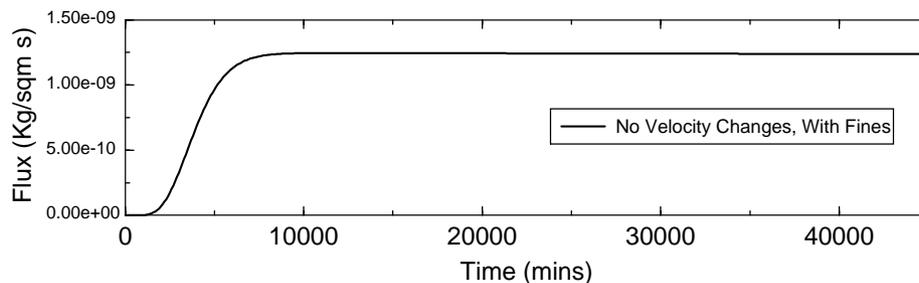


Fig. 2. Contaminant flux vs. time plot for the case of with fines but no velocity change (colloid-facilitated contaminant transport).

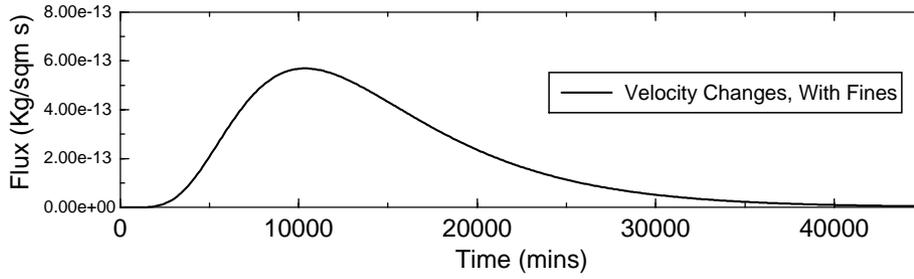


Fig. 3. Contaminant flux vs. time plot for the case of with fines and with velocity changes (colloid-retarded contaminant transport).

contaminant transport experimental data, we have first compared our simulation results with the results of earlier modeling studies. With negligible decrease in flow rate due to plugging/entrapment, it is found that colloid-facilitated spreading of contaminants increases with increasing inlet colloid concentrations and increasing partition coefficient of the contaminant between the colloids and aqueous phase. It decreases with increasing capture coefficient. These results are in good agreement with earlier studies [8,14,15] and are not presented here.

We shall present some typical results focused on the new role of the colloidal fines that is the retardation in the rate of contaminant transport. This retardation is a consequence of the reduction in velocity of flow, which in turn depends on the permeability reduction resulting from capture of fines at constriction sites.

3.1. Role of colloidal fines on contaminant transport

Figs. 1–3 present the temporal variation of the total contaminant flux issuing from the exit for three different cases. Fig. 1 represents the case in which no fines are present. A

part of the contaminant sorbs on the solid matrix and the rest flows with the fluid. Fig. 2 indicates the effect of the presence of fines with variations in flow rate neglected. The parameter σ_{\max} is used to define the sensitivity in velocity changes to the concentration of the fines at capture sites. A value of $\sigma_{\max} = 1.5 \text{ kg/m}^3$ is found to be large enough to adequately represent the case of no flow rate change. An increase in the steady state throughput is observed when compared to the case in which no fines were present. This represents the well documented case of colloid-facilitated transport of contaminants. Fig. 3 presents the effect of colloids coupled with the effect of velocity changes due to entrapped fines. Here, a smaller value of σ_{\max} (0.0015 kg/m^3) is chosen to incorporate the velocity effects. It is observed that the magnitude of the flux goes through a maximum after which there is a significant decrease in total contaminant flux is obtained. Release of fine particles increases the concentration of particles thereby enhancing the rate of capture of particles. As a result, the permeability decreases causing rapid reduction in flow rate and decrease in total contaminant flux. This can be called as colloid-retardation of contaminant transport. Therefore, depending on the values of the system

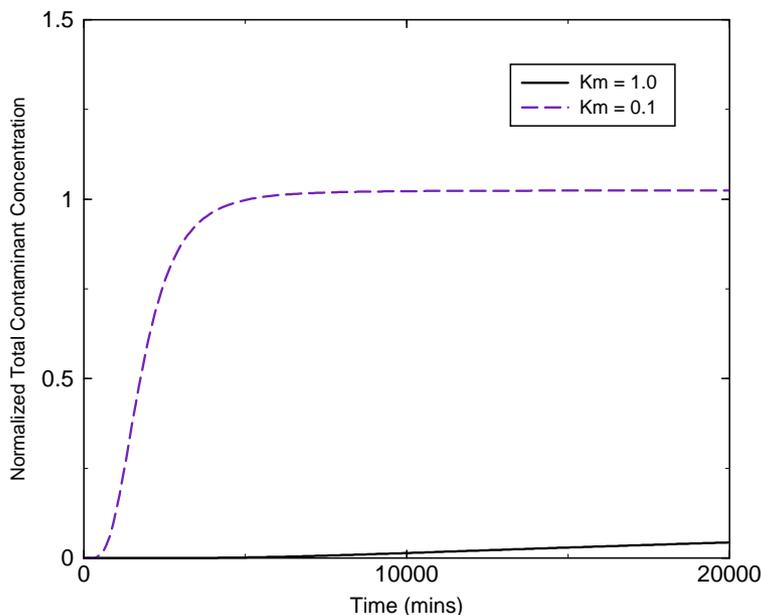


Fig. 4. Breakthrough curves for total contaminant concentration with partition coefficient as parameter.

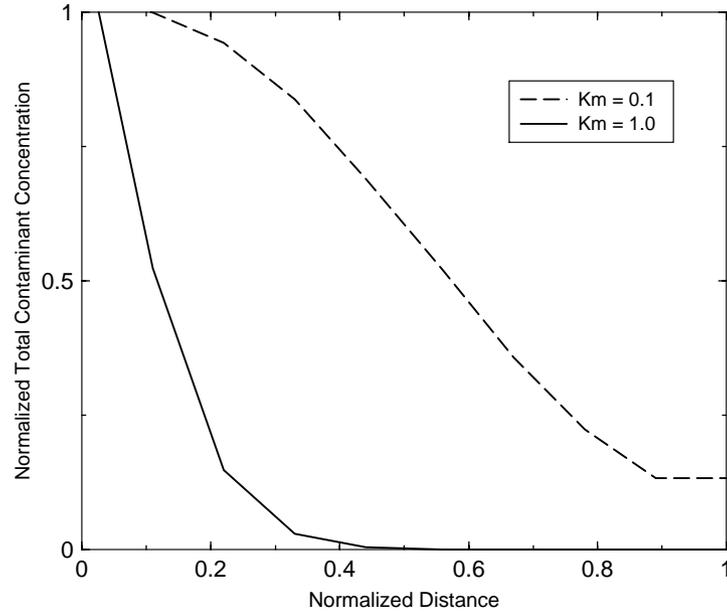


Fig. 5. Spatial total contaminant concentration profiles at 100 min with K_m as parameter.

parameters C_{f0} , σ_{max} , σ_{10} and α , one can have either of colloid facilitation or retardation of contaminant transport.

3.2. Effect of partition coefficient on contaminant transport

An increase in the value of K_m renders the aqueous phase relatively leaner with respect to the contaminant concentration, thus retarding the motion of the contaminant concentration front, which gives a delayed breakthrough as observed in Fig. 4. At small values of K_m the association between

the contaminant and the solid matrix is weak and the contaminant front travels almost independently of the colloid concentration. In such a case, the contaminant breakthrough curves are relatively unaffected by changes in α and β , since most of the contaminant is transported through the aqueous phase.

Fig. 5 portrays the spatial total contaminant concentration profiles with K_m as a parameter. At the inlet, the aqueous concentration of fines is maximum, once the temporary concentration effect of colloids from release sites wears out. Also the aqueous concentration of the contaminant is

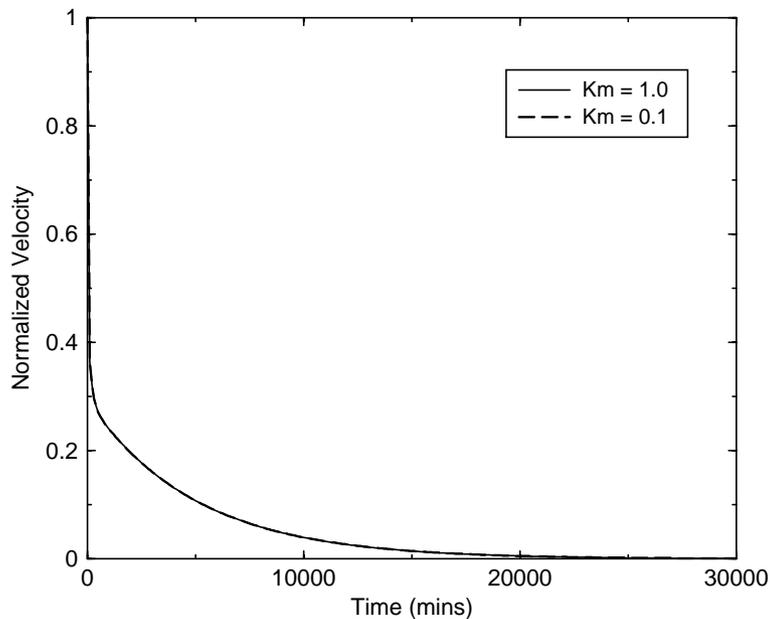


Fig. 6. Temporal variation of velocity change with K_m as parameter.

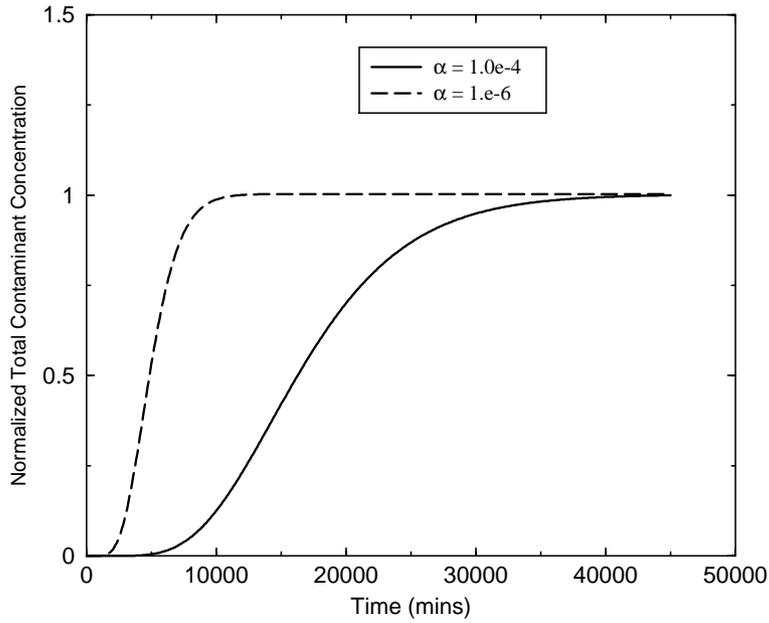


Fig. 7. Breakthrough curves for total contaminant concentration with release coefficient as parameter at $C_{f0} = 500 \text{ mg/m}^3$.

maximum at the inlet. Therefore, the total contaminant concentration is maximum here. At high values of K_m , however, C_{ct} depends on the relative rates of fines deposition and release. A considerably larger amount of contaminant sorbs onto the solid matrix and captured fines and thus gets trapped. It must also be noted that if the capture coefficient, β , were small then increased K_m would significantly facilitate contaminant transport. Fig. 6 presents that the spatial distribution of velocity at different values of K_m coincide. This is in tune with expected behavior of the system, since velocity changes are governed by the release, capture and

sensitivity of the system to the concentration of entrapped fines.

3.3. Effect of rate of release of fines on contaminant transport

It can be inferred from Fig. 7 that the release rate, α , affects the kinetics of the breakthrough without altering the steady state values attained. As α is increased the release of fines from release sites becomes faster. When the fines concentration front has not advanced far enough, the aqueous

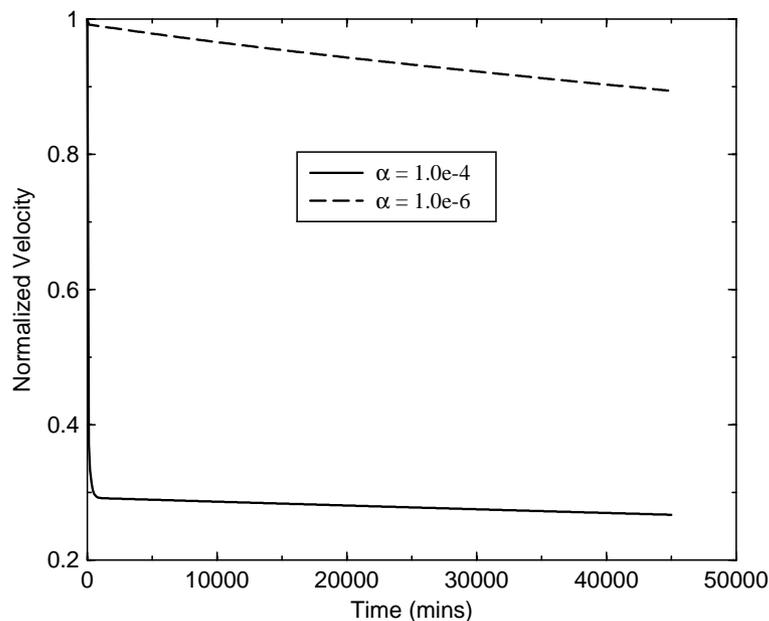


Fig. 8. Temporal variation of velocity with release coefficient as parameter at $C_{f0} = 500 \text{ mg/m}^3$.

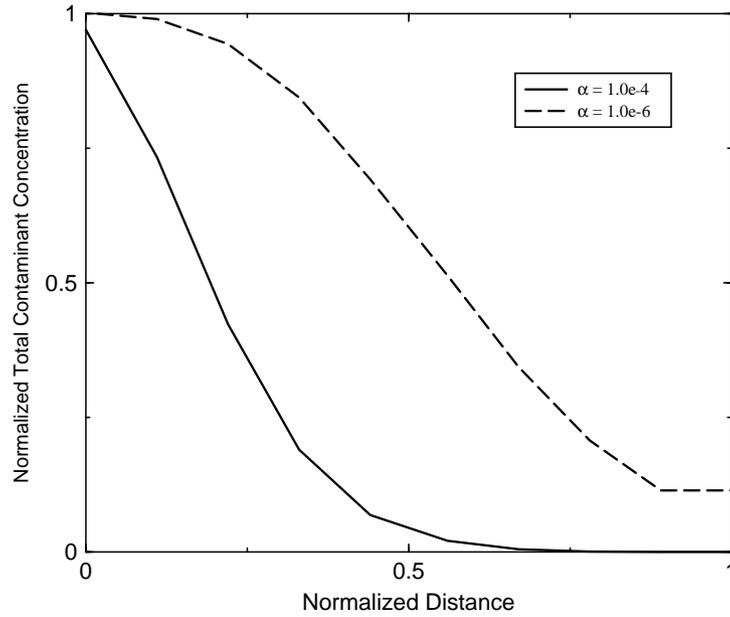


Fig. 9. Spatial variation of the total contaminant concentration at 3000 min, for $C_{f0} = 500 \text{ mg/m}^3$ with α as parameter.

concentration of fines downstream is primarily due to fines issuing from release sites. This local and temporary enhancement in the aqueous fines concentration results in greater amounts of fines being entrapped and thus a greater initial reduction in velocity (Fig. 8). After this significant initial fall in velocity most of the fines originating from the release sites inventory are flushed out and the small decrease in velocity can be attributed to the fines being fed at the inlet. The velocity decrease at smaller α is slower, because of the ab-

sence of pockets of fines downstream. It has also been found that the effect of fines originating from the release sites inventory is smeared over a larger time interval, resulting in a larger slope compared to the case of larger α . This influence of α on the spatial profiles of the total contaminant concentration are shown in Fig. 9. In the case of high α , the stock of fines at the release sites is exhausted before the contaminants can get sorbed thereby depriving the system of any colloid facilitation due to fines at release sites.

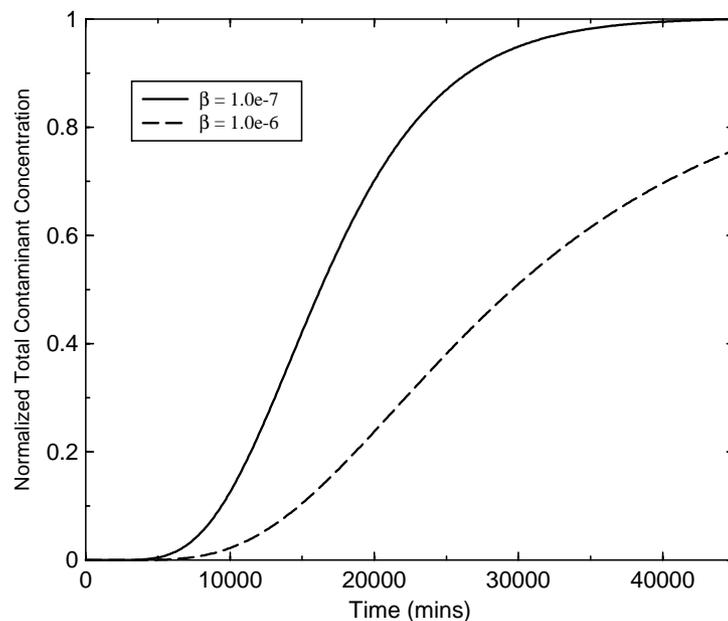


Fig. 10. Breakthrough curves for total contaminant concentration with β as parameter at $C_{f0} = 500 \text{ mg/m}^3$.

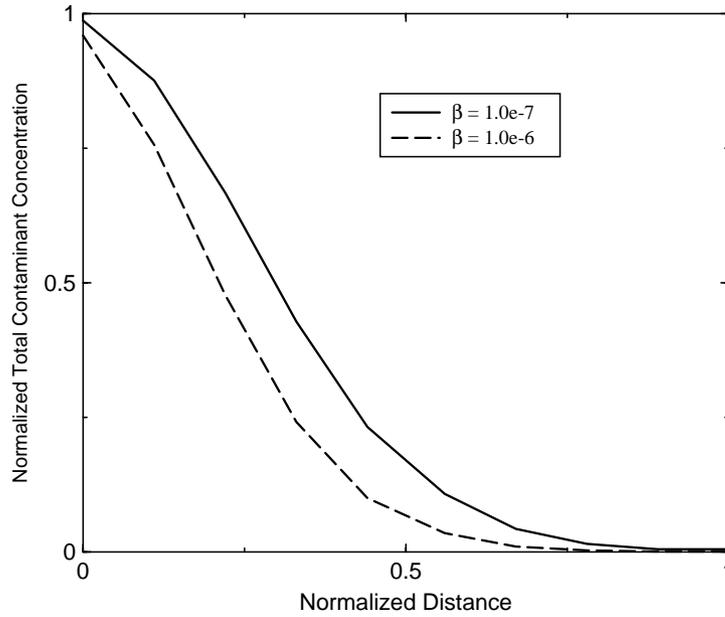


Fig. 11. Spatial variation of the total contaminant concentration at 5000 min with β as parameter, for $C_{T0} = 500 \text{ mg/m}^3$.

3.4. Effect of capture coefficient on contaminant transport

When the value of the capture coefficient, β , decreases, the amount of colloids captured decreases. Here, the presence of colloids in the system facilitates the transport of the contaminant (Fig. 10). When the value of β is small or when the changes in velocity are negligible, it is found that the breakthrough of the fines concentration front occurs much faster compared to the breakthrough of the contaminant concentration front, for the choice of parameter

made. They thus serve as a device to transport the contaminant at much faster rates. The spatial total contaminant concentration profiles depicted in Fig. 11 indicate that at smaller capture rates, the amount of colloids with contaminant adsorbed on their surface deposited at the capture sites is smaller, thereby increasing the total contaminant concentration.

Fig. 12 portrays the effect of β on the hydraulic conductivity. At larger values of β , the amount of colloids accumulated at the capture sites is larger when exposed to the same aqueous fines concentration, causing a commensurate

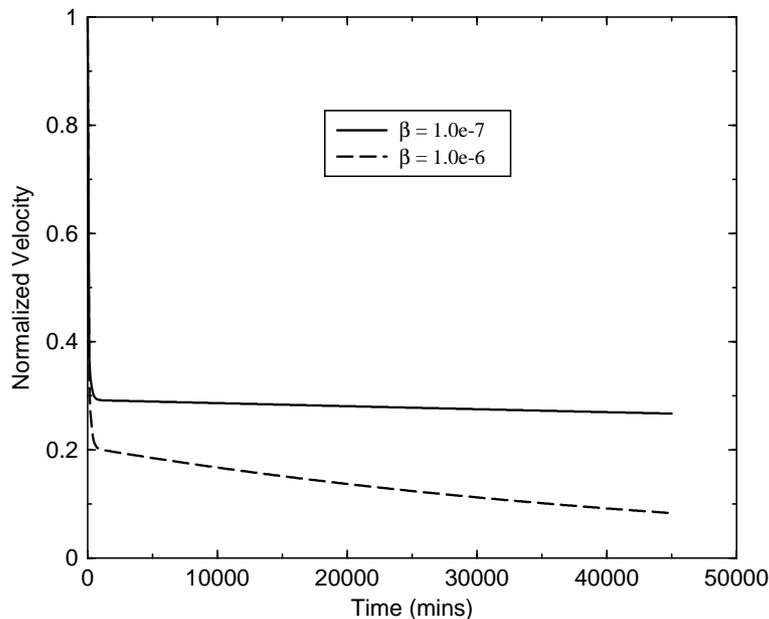


Fig. 12. Temporal variation of velocity with β as parameter at $C_{T0} = 500 \text{ mg/m}^3$.

reduction in velocity. The unequal slopes of the two curves reaffirm the above conclusion.

4. Conclusions

- A one-dimensional three-phase transport model has been developed based on equilibrium adsorption of a contaminant species and on colloidal induced release, migration and capture of colloidal fines at pore constrictions. Therefore, this model offers a better description of the physics of this colloid-associated contaminant transport phenomenon.
- Presence of colloids has been shown to enhance or retard the extent of contamination depending crucially on the system parameters such as C_{f0} , σ_{max} , σ_{10} , and α , particularly the sensitivity of the hydraulic conductivity to the concentration of captured fines.
- For a range of conditions, plugging of the porous media occurs resulting in retardation of contaminant transport in groundwater flows.
- To develop a containment technology utilizing this plugging phenomenon, more constant pressure experimental studies on colloid-associated contaminant transport are required.

References

- [1] R. Kretzschmar, M. Borkovec, D. Grolimund, M. Elimelech, *Adv. Agron.* 66 (1999) 121.
- [2] K.C. Khilar, H.S. Fogler, *Migration of Fines in Porous Media*, Kluwer Academic Publishers, Dordrecht, 1998.
- [3] B.D. Honeyman, *Nature* 397 (1999) 23.
- [4] A.B. Kersting, D.W. Efur, D.L. Finnegan, D.J. Rokop, D.K. Smith, J.L. Thomson, *Nature* 397 (1999) 57.
- [5] J. McCarthy, J. Zachara, *Environ. Sci. Technol.* 23 (1989) 496.
- [6] W.R. Puls, R.M. Powell, *Environ. Sci. Technol.* 26 (1992) 614.
- [7] J.N. Ryan, M. Elimelech, *Colloids Surf. A* 107 (1996) 1.
- [8] S.B. Roy, D.A. Dzombak, *J. Contam. Hydrol.* 30 (1998) 179.
- [9] S.B. Roy, D.A. Dzombak, *Environ. Sci. Technol.* 31 (1997) 656.
- [10] J.E. Saiers, G.M. Hornberger, *Water Resources Res.* 32 (1996) 33.
- [11] H. van de Weerd, A. Leijnse, *J. Contam. Hydrol.* 26 (1997) 245.
- [12] T.K. Sen, S.P. Mahajan, K.C. Khilar, *AIChE J.* 48 (2002) 2366.
- [13] T.K. Sen, N. Nalwaya, K.C. Khilar, *AIChE J.* 48 (2002) 2375.
- [14] A. Abdel-Salam, C.V. Chrysikopoulos, *J. Hydrol.* 165 (1995) 261.
- [15] M.Y. Corapcioglu, S. Jiang, *Water Resources Res.* 29 (1993) 2215.
- [16] S. Tanaka, S. Nagasaki, *Nucl. Technol.* 118 (1) (1997) 58.
- [17] T.K. Sen, *Studies on Colloidal Fines-associated Contaminant Transport in Porous Media*, Ph.D. Thesis, IIT Powai, Mumbai 76, India, 2001.
- [18] J.E. Saiers, G.M. Hornberger, *Water Resources Res.* 35 (1999) 1713.
- [19] D. Grolimund, M. Borkovec, *Water Resources Res.* 37 (2001) 559.
- [20] K. Arulanandan, P. Longanathan, R.B. Krone, *J. Geotech. Eng. Div. ASCE* 101 (1975) 51.
- [21] S.W. Karickhoff, D.D. Brown, T.A. Scott, *Water Res.* 13 (1979) 241.
- [22] T.K. Sen, S.P. Mahajan, K.C. Khilar, *Colloids Surf. A* 211 (2002) 91.
- [23] C.T. Voice, C.P. Rice, W.J. Weber, *Environ. Sci. Technol.* 17 (1983) 513.
- [24] W.J. Weber, T.C. Voice, M. Pirbazari, G.E. Hunt, D.M. Ulanoff, *Water Res.* 17 (1983) 1443.