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A comprehensive mathematical model developed describes the colloid-associated contaminant transport in groundwater flows based on equilbrium adsorption of contaminants, hydrodynamic release, migration, and capture of colloidal fines in groundwater flows. This model is more realistic than the existing models in that the physics of migration of colloidal fines is adequately incorporated. It also accounts for the entrapment and plugging of fine particles and, therefore, predicts both facilitation and retardation of the transport of contaminants depending on the flow and other conditions. The conditions leading to inhibition/retardation of contaminant transport due to plugging are: high release coefficient, low initial porosity, high inlet fines concentration, and high initial permeability. The mobilization and migration of colloidal fines, kaolin and their role on plugging, as well as on Ni2+ contaminant transport through kaolin-sand packed beds, were studied, and the model was tested with published experimental measurements, as well as with our laboratory column results. The plugging-based retardation of contaminant transport can be used to develop a new containment technique.

Introduction

Transport modeling can be considered to be an integral part of characterization and remedial design of any contaminated sites, especially sites with groundwater contamination. Several models have been developed to describe the transport of inorganic contaminants in subsurface systems. These models have traditionally been based on a two-phase approach: the mobile fluid phase and the immobile solid phase. However, when colloidal particles are present in the subsurface system, it should be modified as a three-phase porous medium with two solid phases, that is, mobile colloidal particles and stationary solid matrix.

The release of fines from a pore surface is the first step in the phenomenon of migration of fines in porous media, which has been experimentally observed (Sen, 2001). In general, two major types of forces are responsible for the release of fines: colloidal forces and hydrodynamic forces. It has also been observed that the release of fines is a threshold process, that is, a minimum perturbation is required to detach the fines from the pore surface (Khilar and Fogler, 1998). This could be in terms of a critical hydrodynamic stress (Arulanand et al., 1975) or a critical salt concentration (Khilar and Fogler, 1984). The released colloidal fines while flowing with the liquid phase can either re-adhere to the pore surface, flow without capture, or get entrapped at the pore constrictions.

Many researchers have carried out studies concerning the development of mathematical models to describe the colloid-facilitated transport of contaminants during the past ten years (Magee et al., 1991; Enfield and Bengtsson, 1988; Mills et al., 1991; Abdel-Salam and Chryskopoulos, 1995; Sayers and Hornberger, 1996; Smith and Degueldre, 1993; Corapcioglu and Jiang, 1993; Roy and Dzombak, 1998). Most of these studies have assumed equilibrium interactions between the colloidal particles and the contaminant in the dissolved phase (Magee et al., 1991; Enfield and Bengtsson, 1988; Mills et al., 1991; Abdel-Salam and Chryskopoulos, 1995). These models predict a reduction of the effective retardation arising out of sorption onto the solid matrix depending on the concentration of the colloidal fines and the...
partition coefficient for contaminant sorption on the colloidal fines.

Corapcioglu and Jiang (1993) have proposed a mathematical model based on equilibrium adsorption to describe the facilitated contaminant transport. The model consists of mass balance equations for fine particles, as well as for the contaminants. Since the contaminant species reside in four different sites (mobile fines, captured fines, liquid and solid phase), mass balance equations are written for each site. These equations with appropriate boundary conditions and initial conditions are numerically solved for a system of finite length and where the fine particles, contaminant species, and fluid are fed at a constant rate to the system. They have carried out simulations describing the variations in total mobile concentration of the contaminant as a function of time and axial length for various values of the system parameters. They have observed that the total mobile concentration, in general, is higher when compared with the concentration which does not have migration of fines. Their simulations also showed that a higher rate of sorption of contaminant species, as well as a higher rate of release, significantly facilitate the transport of contaminants. On the other hand, higher rates of sorption and capture of fine particles weakly facilitate the transport.

Smith and Deguelde (1993) modeled the transport of a radioactive material in the presence of colloids in a single fracture with the assumption of constant colloid concentration, that is, rate of colloid deposition and release were assumed to be equal. Saiters and Hornerber (1996) developed a three-phase model, analogous to the model developed by Corapcioglu and Jiang (1993), which can successfully explain the transport behavior of $^{137}$Cs in the absence and presence of kaolin colloids through a sand packed column. Their model is based on independently determined parameters for first-order colloidal fines deposition kinetics, $^{137}$Cs sorption equilibrium and sorption kinetics on kaolin and quartz sand, and hydrodynamic solute dispersion in the porous medium.

Roy and Dzombak (1997) studied colloid-facilitated transport of phenanthrene through columns packed with natural sands. These experimental data were modeled under considerations of release and deposition colloidal fines, as well as equilibrium and non-equilibrium sorption and desorption of phenanthrene on colloidal particles and matrix grains (Roy and Dzombak, 1998). Model calculations show that slow desorption kinetics of the contaminant from the colloidal particles is an essential prerequisite in order for colloid-facilitated transport to become significant. If the contaminant would desorb rapidly, it would be transferred to binding sites on immobile matrix surfaces as the colloidal particles move into an uncontaminated zone of the porous medium. All these models do not incorporate the effects of entrapment of particles which can occur as shown in Part I of this study when ratio of bead or pore size to particle size is not high.

In this work a comprehensive mathematical model is developed based on the equilibrium adsorption of a contaminant, hydrodynamic release, migration, and capture of colloidal fines in groundwater flows. This model is more realistic than the existing models in that the physics of migration of colloidal fines is adequately incorporated. Finally, the model has been tested with published experimental measurements, as well as with our laboratory column results (Sen et al., 2002).

Formulation of a Comprehensive Model

This model has been formulated in a manner analogous to that of existing models such as the model developed by Corapcioglu and Jiang (1993). Additional equations relating to release and the variations in permeability, as well as porosity due to entrapment/plugging, have been incorporated. The model has been developed based on the following assumptions and considerations:

- A single species of contaminant is considered.
- Contaminant is partitioning among the three phases, namely solid matrix, mobile colloidal fines, and aqueous phase.
- The variation in concentrations and other quantities are significant only in the major flow direction, that is, axial direction in this case.
- The release of fines occurs due to hydrodynamic forces.
- The effect of capture of fines is negligibly small until the concentration of fines reaches the critical particle concentration (CPC). Beyond CPC, the porous medium gets plugged due to convective jamming and the flow stops.

The last two considerations are the new features and are not accounted in any of the existing models in the literature.

An unsteady-state mass balance on colloidal fines in the aqueous phase gives

$$\frac{\partial C_f}{\partial t} = D \frac{\partial}{\partial x} \left( \frac{\partial C_f}{\partial x} \right) - \nu_0 \frac{\partial C_f}{\partial x} + r_c e$$

where $C_f$ is the concentration of fines in aqueous phase, $e$ is the porosity of the medium, $\nu_0$ is the superficial velocity, $D$ is the dispersion coefficient, and $r_c$ is the rate of release of the fines from the solid matrix.

The temporal variation of porosity can be obtained by writing an unsteady-state mass balance for fines in the solid phase and is given by

$$\frac{d e}{dt} = \frac{r_c e}{\rho_f}$$

where $\rho_f$ is the material density of the fines.

The rate of release is given by (Arulanandan et al., 1975)

$$r_c = \alpha_s A_p (\tau_c - \tau_w) \text{ for } \tau_w > \tau_c$$

$$= 0 \text{ for } \tau_w < \tau_c$$

where $\alpha_s$ is the release coefficient, $A_p$ is the pore surface area per unit pore volume, $\tau_w$ is the wall shear stress, and $\tau_c$ is the critical shear stress.

It should be noted that we have only considered here the release due to hydrodynamic forces. For a colloidally induced release, the rate of Eq. 3 will change and the salt concentration becomes an important parameter for release and, hence, it needs to be determined in the model, through an additional salt balance equation (Khilar et al., 1983).

To account for the change in porosity and permeability due to erosion, we need a model for the pore structure. In this work, we have adopted a simple capillary model for the pore structure. This model has been used successfully to describe the soil erosion (Khilar et al., 1985).
Using a capillary model consisting of capillaries of diameter $\delta$, we get

$$A_s = \frac{4}{\delta}$$  \hspace{1cm} (4)

$$\epsilon = \epsilon_0 \left( \frac{\delta}{\delta_0} \right)^2$$  \hspace{1cm} (5)

$$\delta^2 = \frac{32K}{\epsilon}$$  \hspace{1cm} (6)

$$\tau_w = \left( \frac{8\mu}{\epsilon \delta} \right) v_0$$  \hspace{1cm} (7)

where $\delta$ is the diameter of the pore and $K$ is the permeability of the medium. The subscript 0 refers to the initial condition.

The relationship between the permeability and the porosity according to the capillary model is taken as

$$K = K_0 \left( \frac{\epsilon}{\epsilon_0} \right)^2$$  \hspace{1cm} (8)

where $K_0$ is the initial permeability and $\epsilon_0$ is the initial porosity of the medium.

The CPC is expected to increase with an increase in porosity. Very little knowledge is available on CPC, let alone its variations with relevant parameters. A recent study has shown that CPC varies with the ratio of bead to particle diameters (Pandya et al., 1998). Without any knowledge on its variations with porosity, we have assumed a constant value for the CPC.

Darcy’s law gives the velocity of flow in the porous medium

$$v_0 = \frac{K}{\mu} \left( -\frac{\Delta P}{L} \right)$$  \hspace{1cm} (9)

where $\mu$ is the viscosity of the suspension, and $\Delta P / L$ is the pressure gradient across the medium.

An unsteady-state mass balance on the contaminants in the aqueous phase and the solid matrix together is given as

$$\frac{\partial \rho_m X_m}{\partial t} + \frac{\partial \epsilon C_c}{\partial t} + Q_{sf} = D_c \frac{\partial}{\partial x} \left( \epsilon \frac{\partial C_c}{\partial x} \right) - v_0 \left( \frac{\partial C_c}{\partial x} \right)$$  \hspace{1cm} (10)

where $\rho_m$ is the bulk density of the matrix, $X_m$ is the mass fraction of the contaminants on the matrix, $C_c$ is the concentration of the contaminants in the aqueous phase, $D_c$ is the dispersion coefficient for the dissolve contaminants, and $Q_{sf}$ is the net rate of transfer of contaminants from the aqueous phase onto the colloidal fines.

A balance on contaminants adhering to the colloidal fines is given as

$$\frac{\partial \epsilon X_f C_f}{\partial t} = \tau_r X_f \epsilon + D \frac{\partial}{\partial x} \left( \epsilon \frac{\partial X_f C_f}{\partial x} \right) - v_0 \left( \frac{\partial X_f C_f}{\partial x} \right) + Q_{sf}$$  \hspace{1cm} (11)

where $X_f$ is the mass fraction of the contaminants adsorbed onto the colloidal fines. The low contaminant concentrations generally encountered in groundwater permit us to assume linear adsorption isotherm

$$X_m = K_m C_c$$  \hspace{1cm} (12)

$$X_f = K_f C_c$$  \hspace{1cm} (13)

where $K_m$ and $K_f$ are the partition coefficients for the matrix and the colloidal fines, respectively. It is shown later that the adsorption process can be assumed to be at the equilibrium. Otherwise, equations describing the rate of adsorption are required.

The rate of adsorption of contaminant onto surface of the fines is given as follows

$$Q_{sf} = k_a C_c - k_d X_f$$  \hspace{1cm} (14)

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

$$C_f(x,0) = 0$$  \hspace{1cm} (15)

$$X_f(x,0) = 0$$  \hspace{1cm} (16)

$$X_f(0,t) = 0$$  \hspace{1cm} (17)

$$v_0 C_c \bigg|_{x=0} = v_0 C_c - D \frac{\partial C_c}{\partial x} \bigg|_{x=0}$$  \hspace{1cm} (18)

$$\epsilon(x,0) = \epsilon_0$$  \hspace{1cm} (19)

$$\frac{\partial C_c}{\partial x} \bigg|_{x=L} = 0$$  \hspace{1cm} (20)

$$C_c(x,0) = 0$$  \hspace{1cm} (21)

$$v_0 C_c \bigg|_{x=L} = v_0 C_c - D \frac{\partial C_c}{\partial x} \bigg|_{x=L}$$  \hspace{1cm} (22)

$$\frac{\partial C_c}{\partial x} \bigg|_{x=L} = 0$$  \hspace{1cm} (23)

Equations 1 to 23 provide a mathematical framework to determine various relevant quantities.

**Comparisons of Model Predictions with Measurements**

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 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.

A simulation is carried out and the obtained results are presented graphically. The model parameters used in the simulation have been obtained from the published works and are summarized in Table 1.
Table 1. Base Values of the Model Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{f0}$</td>
<td>0.05 kg/m³</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>2.500 kg/m³</td>
</tr>
<tr>
<td>$\alpha_h$</td>
<td>$1.4 \times 10^{-8}$ kg/N·s</td>
</tr>
<tr>
<td>$\tau_e$</td>
<td>0.3 Pa</td>
</tr>
<tr>
<td>$K_m$</td>
<td>$1.6 \times 10^{-14}$ m²</td>
</tr>
<tr>
<td>$\phi_f$</td>
<td>0.3</td>
</tr>
<tr>
<td>$\mu$</td>
<td>0.001 Pa·s</td>
</tr>
<tr>
<td>$\Delta P/L$</td>
<td>$10^6$ Pa/m $= 10^4$ Pa/m</td>
</tr>
<tr>
<td>$\rho_m$</td>
<td>1.500 kg/m³</td>
</tr>
<tr>
<td>$C_{e0}$</td>
<td>0.001 kg/m³</td>
</tr>
<tr>
<td>$K_f$</td>
<td>0.007 m²/kg</td>
</tr>
<tr>
<td>CPC</td>
<td>2.0 m²/kg</td>
</tr>
<tr>
<td>L</td>
<td>5.0 kg/m³</td>
</tr>
<tr>
<td>K</td>
<td>0.1 m</td>
</tr>
<tr>
<td>K_a</td>
<td>0.06 s⁻¹</td>
</tr>
<tr>
<td>K_d</td>
<td>0.15 kg/m³·s</td>
</tr>
</tbody>
</table>

*From Abdel-Salam and Chrysikopoulos, 1995; Corapcioglu and Jiang, 1993; Khilar and Fogler, 1998; Puls and Powell, 1992; Roy and Dzombak, 1998; Saisers and Hornberger, 1996.*

Influent solutions of colloidal fines and contaminants are continuously fed at a constant pressure drop across a porous cylinder. Breakthrough curves are presented as plots of $C_{ct}/C_{ct0}$ against time, where $C_{ct}$ is the total mobile contaminant concentration ($C_{ct} = C_c + X_f/C_f$). $C_{ct0}$ 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 adsorption of contaminants on colloidal fines generally exhibits fast kinetics. In seepage flow situations such as the present case, the residence time ($L/e_{i}/v_0$) is much greater than the characteristic time of adsorption ($1/k_a$) assuming a first-order rate equation for adsorption. From our calculations, it can be inferred that for high values of $k_a$ and typically for ($k_a L/e_{i}/v_0$) > 2,000, the kinetic effects can be neglected. Also, for all practical purposes, the adsorption of the contaminants on colloids can be assumed to be adequately represented by equilibrium isotherms. Therefore, henceforth, we shall analyze the results obtained from only considering equilibrium adsorption isotherm.

In order to validate our model, we have compared the predictions of our comprehensive model with experimental measurements conducted with, as well as without, release of colloidal fines under a wide range of conditions. The results of these comparisons are presented next for the case of no-release of colloidal fines.

**Contaminant transport with release of colloidal fines**

Figure 1 compares the simulation results with those obtained from the experiments performed by Saisers and Hornberger (1996). The experimental setup consisted of a sand packed column of length 52 m, inner diameter of 25 mm, and a porosity of 0.30. Discharge rate was 0.0368 mL/h. The contaminant species was Cesium and colloidal fines were kaolin particles. The experimental values of parameters $K_m$ and $K_f$ obtained for this system are 0.007 m²/kg and 3.00 m²/kg, respectively. In this case colloidal fines were injected in the form of a pulse for 8.2 h. There was no release of fines from the solid matrix. The results obtained from the model simulations showed slightly higher values of effluent $C_{ct}$ than the experimental results. The breakthrough time and the overall nature of the plots are, however, in considerable agreement.

**Contaminant transport with release of colloidal fines**

Phenanthrene sorption/mobilization experiments were performed by Roy and Dzombak (1997) with Lincoln sand. The colloids are comprised of silica, clay minerals and iron oxides. A solution of 1 mg/L phenanthrene with 0.1 M NaCl was injected at a flow rate of 26 mL/h for 61 pore volumes. The influent after this was changed to 0.001 M NaCl solution with no phenanthrene. This ionic strength reduction resulted in the release of colloids. The results obtained from this experiment are plotted in Figure 2.

These results were compared with the results obtained from simulations. Simulating the situation as described in the above experiment, $C_{ct0}$ was set to 1 mg/L and no release of colloids were taken ($\alpha_h = 0$ kg/N·s) until 61 pore volumes. After that, influent contaminant concentration was set to 0 mg/L and the value of $\alpha_h$ was set to $1.6 \times 10^{-8}$ kg/N·s. As the release of colloid takes place, a peak is observed in the total contaminant concentration, which matches with the experimental results. The overall trend of the results shows a good deal of agreement.

The experimental breakthrough curves (BTCs) are presented in the previous experimental part under two broad
categories: nonplugging and plugging conditions. In this section the predictions of the model are compared with these measurements. The values of the measured parameters used in this model are $C_{e0} = 0.0205$ kg/m$^3$, $r_0 = 0.32$ (nonplugging) and 0.29 (plugging), $v_0 = 7.74 \times 10^{-5}$ m/s (nonplugging) and $3.39 \times 10^{-4}$ m/s (plugging), and $L = 0.28$ m. All other parameters remain the same as given in Table 1.

**Nonplugging condition without fine particles migrating out of the bed**

Figure 3 presents the comparisons between the model predictions using the batch adsorption parameters values and the measurements. Three different beds are taken to typically represent this comparison. The batch adsorption coefficient values for composite beds are calculated from the equation

$$K_m = K_s(1 - F) + FK_f$$

where $K_s$ and $K_m$ are the partition coefficients of sand and kaolin, respectively, and $F$ is the weight fraction of kaolin present in the bed.

One observes from this figure that there are some disagreements between model calculations and the measurements. The disagreements between the model calculations and the measurements increase with an increase in kaolin content of the bed. The calculated BTCs using batch adsorption parameter values for kaolin-sand beds appear later in comparison to measured BTCs. Such a delay in breakthrough indicates that the amount of adsorption in the bed is substantially lower than that predicted using batch adsorption measurements. Such disagreements are also indicated by the low percentage saturation calculated in Part 1 of this article. Interestingly, the BTC for the sand bed appears earlier than the measurements. This may indicate that the influence of external mass transfer in the adsorption process. In order to fit the model predictions $K_s$ was taken as an adjustable parameter. First, the BTC for the sand bed was fitted using the model and the value of $K_s$ was determined. This value of $K_s$ was then used for fitting the BTCs of other composite beds. Figures 4 to 5 show this comparison. One observes from these figures that the data can be reasonably fitted with this equilibrium model.

Table 2 presents the value $K_m$ as used in the model and the values as measured in our batch study. As one observes from this table, there is reasonable agreement for beds 0%, 0.5%, and 1.0%, however, in the case of 2%, 4%, and 6% bed, the measured values are substantially higher. Experimental data show nonlinear behavior, as well as to indicate the presence of a kinetically controlled regime. The model has been developed based on linear equilibrium adsorption isotherms only. Therefore, some deviations between the model predictions and the measurements are expected. Besides, as mentioned in Part 1, the mobilization of particles may continually provide new sites for adsorption which in turn will bring in an equivalent rate process for adsorption similar to a kinetic controlled fixed-bed adsorption.
Plugging condition without fine particles migrating out of the bed

Using the same approach as used in the fitting of the nonplugging BTCs, the BTCs in the case of beds where plugging had occurred are fitted. These comparisons are shown in Figure 5. One observes from these figures that model predictions compare well with the measurements.

Table 3 presents the fitted values of $K_m$ in case of plugging with the measured values. The comparisons are similar as in Table 2. For low kaolin content beds, there is reasonable agreement. The agreement is not satisfactory for 4% and 6% kaolin beds. The values of adsorption coefficients in the case of plugging are higher than those in the case of nonplugging situations. This can be partly attributed to the expected better flow distribution and sweeping in the bed at higher-pressure gradients. In addition, the continued mobilization as mentioned earlier also occurs in these cases.

Overall, it appears that the equilibrium model may not be able to describe the data very well, since external mass trans-

Table 2. Values of $K_m$ for: Model Calculations vs. Those Measured Based on Batch Experiment under Nonplugging Condition

<table>
<thead>
<tr>
<th>Kaolin-Sand Bed</th>
<th>$K_m$ for Model Calc. (m$^3$/kg)</th>
<th>$K_m$ Meas. by Batch Exp. (m$^3$/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%</td>
<td>0.020</td>
<td>0.01</td>
</tr>
<tr>
<td>0.5%</td>
<td>0.024</td>
<td>0.018</td>
</tr>
<tr>
<td>1.0%</td>
<td>0.028</td>
<td>0.026</td>
</tr>
<tr>
<td>2.0%</td>
<td>0.036</td>
<td>0.044</td>
</tr>
<tr>
<td>4.0%</td>
<td>0.050</td>
<td>0.078</td>
</tr>
<tr>
<td>6.0%</td>
<td>0.054</td>
<td>0.112</td>
</tr>
</tbody>
</table>
fer and an equivalent rate attribute arising out of continued exposure of the new adsorption site appear to have significant effects. Therefore, future models should incorporate these effects, particularly the continual exposure to new adsorption sites due to mobilization and better sweeping at higher pressure drops for a more accurate description of contaminant transport in porous media in the presence of colloidal fine particles.

Nevertheless, we can conclude that the present model based on a number of coupled basic processes seems to capture the important features of the phenomena.

**Role of effective adsorption coefficient (K_m) on the transport of contaminants through kaolin-sand packed column**

This model has been applied to find out the effective adsorption coefficient K_m for different composite kaolin-sand beds during column flow experiments under plugging and nonplugging situation. Figure 6 presents the plots of K_m vs. F for different conditions. As expected, K_m calculated from the batch adsorption data increases linearly with F, whereas, in actual column flow situations, K_m as obtained by fitting the model under plugging and nonplugging conditions, is significantly less indicating that a lesser amount adsorption takes place in actual column flow experiments. One observes from this figure that K_m under a plugging condition is higher due to the higher mobilization of clay particles and better sweeping of flow.

**Model Predictions and Discussions**

In this section, the equilibrium model has been applied to gain some new insights and findings related to the contaminant transport in underground flows. Influences of different system parameters on colloid-associated contaminant transport in porous media have been simulated and the model has been applied to predict some new consequences.

**Influence of partition coefficient K_f on contaminant transport**

As mentioned in Part 1 of this article, contaminant sorption onto fines is critical for facilitated transport, and the greater the degree of association, the greater is the enhancement in contaminant transport. Figure 7 depicts the case of enhancement of contaminant transport due to the adsorption

<table>
<thead>
<tr>
<th>Wt. % of Kaolin</th>
<th>K_m for Model Calc. (m²/kg)</th>
<th>K_m Measured by Batch Expt. (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.020</td>
<td>0.010</td>
</tr>
<tr>
<td>1.0%</td>
<td>0.025</td>
<td>0.026</td>
</tr>
<tr>
<td>2.0%</td>
<td>0.035</td>
<td>0.044</td>
</tr>
<tr>
<td>4.0%</td>
<td>0.066</td>
<td>0.078</td>
</tr>
<tr>
<td>6.0%</td>
<td>0.078</td>
<td>0.112</td>
</tr>
</tbody>
</table>

Figure 6. Model-based adsorption coefficient vs. batch-based value with the amount of kaolin present in the bed.

Figure 7. Model predictions of enhancements in contaminant transport due to release and migration of colloidal fines.
of contaminants on the colloidal fines. The value of the partition coefficient $K_f$ seems to have a significant influence on the extent of enhancement. A low value of $K_f$ implies that the association between the contaminants and the colloidal fines is weak. A lesser amount of contaminants gets sorbed onto the colloidal fines and, hence, lesser total contaminant concentration is observed in the effluent. Further, as shown in this figure, the release of colloidal fines from the pore surface enhances the transport of contaminants to even greater extent.

**Influence of release coefficient $\alpha_h$ on contaminant transport**

The dependency on the value of release coefficient $\alpha_h$ is shown in Figure 8. One observes from this figure that the total contaminant concentration in the effluent is significantly higher than the inlet concentration due to colloid facilitation of transport. For high values of $\alpha_h$, more colloidal fines get released resulting in higher effluent colloidal fine concentration. With the increase in concentration fines, $C_f$, the total contaminant concentration ($C_e = C_e + C_fX_f$), increases. The extent of increase is higher at a faster rate of release of fine particles.

**New role of colloidal fines: retardation by plugging**

The phenomenon of plugging occurs when the concentration of colloidal fines reaches the CPC provided the ratio of pore size to particle size is not very high. It has been found that, at any given time, the concentration of colloidal fines is maximum at the outlet (Sen, 2001). As the waterfront traverses the porous medium, it collects the fines released from the solid matrix. As a result, the concentration of colloidal fines in the aqueous phase is found to be maximum at the outlet. Hence, plugging may take place near the outlet. It is, thus, sufficient to monitor the effluent colloidal fines concentration to examine the conditions that lead to plugging.

As shown in Figure 9, initially, there is a rapid buildup of the colloidal fines concentration. After that, the concentration increases slowly. Initially, the concentration gradient along the length of the porous medium is negative. As a result, the convective rate of input becomes greater than the convective rate of output in the mass balance equation and leads to a rapid buildup of colloidal fines concentration. Afterwards, the concentration gradient becomes positive and, thereby, the concentration of colloidal fines increases slowly with the release of particles as the source.

CPC should increase with the increase in porosity. Without the knowledge on this dependency, CPC has been assumed constant in this study. The value of CPC is taken from the measurements of Pandya et al. (1998). It is implicitly assumed that the ratio of pore size to particle size is not very high and, therefore, plugging can occur. The slope of the graph after the initial buildup increases with an increase in $\alpha_h$. Higher $\alpha_h$ implies a higher rate of release and, hence, a higher rate of increase of the fines concentration. For $\alpha_h = 2.50 \times 10^{-8}$ kg/N·s at $t = 1,238$ min, the effluent fines concentration reaches CPC and, hence, plugging occurs. At this situation,
the flow of the solution more or less stops completely, and the spreading of contaminant is prevented. This is the case of inhibition of contaminant transport due to plugging. The time required for plugging to occur decreases with an increase in $\alpha_p$, which is also shown in Figure 9.

The effects of pore structure on the transport of colloidal fines and contaminants are studied using two parameters: initial permeability $K_0$ and initial porosity $\phi_0$. It is found that the initial rise in concentration increases with an increase in $K_0$. Higher initial permeability implies higher flow velocity and, hence, a higher rate of release of fines. As the rate of release increases, the effluent fines concentration increases and reaches CPC and, hence, plugging takes place.

Naturally occurring porous media generally have porosity between 0.25 and 0.35. It is found that the initial rise in concentration of fines increases with a decrease in initial porosity. Therefore, plugging is more likely in porous media having low porosity.

Figure 10 shown the dependence on the concentration of the inlet fines. With an increase in the value of $C_{in}$, the effluent fines concentration also increases. At $C_{in} = 0.8 \text{ kg/m}^3$, plugging takes place and the flow stops. Thus, increasing the inlet concentration of fines can actually lead to inhibition rather than facilitation of contaminant transport.

**Demarcation of plugging and nonplugging zones**

At any particular value of $\alpha_p$, the presented model predicts that there exists a range of values of $K_0$ for which the plugging phenomenon occurs, keeping other parameters constant. We assume here that CPC is constant at its initial value of 5 kg/m$^3$ which is based on measurements conducted by Pandya et al. (1998). As one observes from Figure 10, it can be noted that the concentration of fines could reach CPC in two ways. One way is that, first, there is an initial buildup of a concentration of fines and then the concentration gradually increases to the value of CPC. This occurs in the range depicted in Figure 11. The lower limit for $K_0$ ($1.4 \times 10^{-14} \text{ m}^2$) is set by the fact that a minimum velocity to generate critical hydrodynamic stress is required for the release of fines. Below this value of $K_0$, the fines do not get released from the walls of the solid matrix. The second way is that the initial buildup itself becomes so high that the concentration of fines reaches CPC. The range for this is depicted in Figure 12.

**Conclusions**

- A comprehensive mathematical model is developed based on equilibrium adsorption of a contaminant species and on the release, migration, and capture of colloidal fines. The model can be used to predict the transport of a contaminant in the presence of colloidal fines in underground flows for a wide range of flow conditions. The model agrees well with measurements as reported in the literature, as well as the measurements presented in Part 1 of this article. Parameter values based on batch adsorption studies, in general, overpredict the extent of adsorption in column flow studies. However, when plugging of fine particles occurs in the bed, the model predictions do agree well with the measurements.
- The developed model predicts both facilitation and retardation of the transport of contaminants depending on the
flow and other conditions as observed experimentally (Sen et al., 2001). The key parameters for determining whether facilitation or retardation would occur are the ratio of grain size to particle size, initial permeability, the release coefficient and the initial colloidal fines concentration. A new containment technique can be developed based on this plugging-based retardation of transport of contaminants.

**Acknowledgment**

One of the authors, TKS, thanks National Institute of Technology, Rourkela-8 (Orissa), India, for allowing him the study leave for his doctoral work under the Quality Improvement Programme (QIP) Scheme. The authors thank one of reviewers for giving many good suggestions.

**Notation**

\[ A_s = \text{pore surface area per unit pore volume, m}^2/\text{m}^3 \]
\[ C_f = \text{concentration of free colloid in aqueous phase, kg/m}^3 \]
\[ C_c = \text{concentration of contaminant in the aqueous phase, kg/m}^3 \]
\[ C_{cm} = \text{total mobile contaminant concentration in the aqueous phase, kg/m}^3 \]
\[ C_{in} = \text{initial concentration of contaminant in the aqueous phase, kg/m}^3 \]
\[ C_{inf} = \text{inlet concentration of colloidal fines in the aqueous phase, kg/m}^3 \]
\[ D = \text{dispersion coefficient of colloids, m}^2/\text{s} \]
\[ D_s = \text{dispersion coefficient for the dissolved contaminants, m}^2/\text{s} \]
\[ F = \text{weight fraction of kaolin present in the bed} \]
\[ K_p = \text{permeability of porous medium, m}^2 \]
\[ K_i = \text{initial permeability, m}^2 \]
\[ k_a = \text{rate constant for adsorption, s}^{-1} \]
\[ k_d = \text{rate constant for desorption, s}^{-1} \]
\[ K_f = \text{partition coefficient for the colloidal fines, m}^2/\text{kg} \]
\[ K = \text{partition coefficient for the kaolin-sand bed, m}^3/\text{kg} \]
\[ K = \text{partition coefficient for sand material, m}^3/\text{kg} \]
\[ L = \text{length of packed column, m} \]
\[ Q_{cr} = \text{net rate of transfer of contaminants from the aqueous phase on the fines} \]
\[ Q = \text{volumetric flow rate, m}^3/\text{s} \]
\[ t = \text{duration of time, s} \]
\[ u_0 = \text{superficial velocity, m/s} \]
\[ w = \text{weight of packing material, kg} \]
\[ r = \text{rate of release of fines from the solid matrix, kg/m}^2 \cdot \text{s} \]
\[ \Delta P/L = \text{pressure gradient across the medium, Pa/m} \]
\[ \Delta P = \text{pressure drop across the composite bed, Pa/m} \]
\[ \Delta P_0 = \text{pressure drop across 0% bed, Pa} \]
\[ X_f = \text{mass fraction of contaminant on captured colloids, kg/kg} \]
\[ X_f = \text{mass fraction of contaminant adsorbed onto the colloids, kg/kg} \]
\[ X_m = \text{mass fraction of contaminant on the matrix, kg/kg} \]

**Greek letters**

\[ \alpha_s = \text{release coefficient, kg/N} \cdot \text{s} \]
\[ \delta = \text{diameter of pores, m} \]
\[ \epsilon = \text{porosity of the medium} \]
\[ \epsilon_0 = \text{initial porosity} \]
\[ \mu = \text{viscosity of the suspension, Pa} \cdot \text{s} \]
\[ \rho_f = \text{bulk density of fines, kg/m}^3 \]
\[ \rho_m = \text{bulk density of matrix, kg/m}^3 \]
\[ \tau_c = \text{critical shear stress, Pa} \]
\[ \tau_s = \text{wall shear stress, Pa} \]
\[ \phi_s = \text{sphericity of material} \]

**Literature Cited**


