

# Colloid-Associated Contaminant Transport in Porous Media: 1. Experimental Studies

Tushar Kanti Sen, S. P. Mahajan, and Kartic C. Khilar

Dept. of Chemical Engineering, Indian Institute of Technology, Bombay, Powai, Mumbai 400076, India

*Many studies have identified colloid-associated transport of contaminants as an important mechanism of contaminant migration through groundwater. It is a complex phenomenon in porous media involving several basic processes such as adsorption of contaminants, release and migration of colloidal fines, and entrapment of fines at the pore constrictions. The effects of these basic processes on the contaminant transport are studied. Column experiments are conducted to study the effects of the mobilization and migration of colloidal fines, kaolin on the transport of contaminant, and  $\text{Ni}^{2+}$  metal ion through the sand beds containing kaolin particles under both nonplugging and plugging conditions. As reported in literature, colloidal fines can facilitate the contaminant transport when they migrate with the flow. In the absence of migration, kaolin-sand beds retard  $\text{Ni}^{2+}$  transport in comparison to sand beds due to their higher adsorption capacity, but the sand-kaolin composite bed acts like an inefficient adsorption column with percentage saturation (which is in general below 25%). It is interesting to note that under plugging conditions, which can be induced by using a lower bead size to particle-size ratio, the breakthrough curves are more flattened and delayed at a higher kaolin content of the bed.*

## Introduction

The migration of colloidal particles that are present in natural porous media such as rock and soil mass or in unconsolidated porous media, such as packed beds, is an engineering concern in processes, such as oil production, soil erosion, and groundwater pollution, and in the operation of filter beds. These colloidal fines are mainly composed of clay minerals, oxides of iron and aluminum, silica, and/or natural organic matter. Also, they generally possess the colloidal characteristics such as surface electric charge.

Many types of contaminants, which are released from a variety of sources, reach subground systems. These contaminants are transported along with the groundwater flows, thereby causing soil and groundwater pollution. Significantly, some recent evidence suggests that, under certain conditions, existing mobile colloidal particles can provide a potentially relevant transport pathway for strongly sorbing contaminants (Honeyman, 1999; Kersting et al., 1999; Roy and Dzombak,

1997,1998; Saiers and Hornberger, 1996). The colloidal particles act as highly mobile contaminant carriers and thereby can enhance the spreading of sorbing pollutants in subsurface systems. This contaminant transport has been known as "colloid-facilitated contaminant transport" in literature (McCarthy and Zachara, 1989; Penrose et al., 1990; Puls and Powell, 1992; Kaplan et al., 1993; Corpacioglu and Jiang, 1993; Abdel-Salam and Chrysikopoulos, 1995; Grolimund et al., 1996; Ryan and Elimelech, 1996; Saiers and Hornberger, 1996; Roy and Dzombak, 1997, 1998; Smith and Degueldre, 1993; Kretzschmar et al., 1999; Kersting et al., 1999). The present study is focused comprehensively on the role of colloidal fines present on the transport of contaminants in porous media. We shall term this phenomenon as "colloid-associated contaminant transport," to incorporate aspects other than facilitation.

Previous studies are either based on model systems or on natural aquifer systems. Puls and Powell (1992) performed experiments on the transport of arsenate in the presence of ferric oxide particles and showed that the colloid associated arsenate transport is 21 times faster than that of the dis-

Correspondence concerning this article should be addressed to K. C. Khilar. Current address of T. K. Sen: Dept. of Chemical Engineering, National Institute of Technology, Rourkela-769008, Orissa, India.

solved arsenate. Magee et al. (1991) have found that water-soluble soil organic matter (DOM) can be an effective carrier, enhancing the transport of a hydrophobic compound through a sand column. Sojitra et al. (1995) investigated the influence of sulfate latex colloids on pyrene and phenanthrene transport through columns packed with precleaned glass beads or quartz sand. Grolimund et al. (1996) have demonstrated that colloid-facilitated transport can become a dominant transport pathway for a strongly sorbing contaminant. Their observation is deduced from laboratory column experiments with a noncalcareous soil and leaching solutions containing  $\text{Na}^+$  and  $\text{Ca}^{2+}$  as major cations and  $\text{Pb}^{2+}$  as a contaminant in the presence of *in-situ* mobilized colloid particles from the porous matrix. Roy and Dzombak (1996, 1997) have studied the *in-situ* colloid mobilization, as well as colloid enhanced transport of  $\text{Ni}^{2+}$  contaminant through two natural porous media (sands) and one model system (glass beads with deposited latex colloids) under changes in solution chemistry of the groundwater. Significant enhancement of transport by colloidal fines was observed. Without colloidal fines,  $\text{Ni}^{2+}$  concentration approached the inlet concentration after about 15-pore volumes whereas with colloidal fines it reached only after 3-pore volumes.

A number of studies have been conducted to investigate the migration and transport of radionuclides from the former nuclear test sites (Champ et al., 1982; Saltelli et al., 1984; Buddemeir and Hunt, 1988). Faure et al. (1996) conducted packed column experiments with sand and 5% bentonite clay to study the transport of colloidal fines and radio nuclide induced by a salinity gradient. Saiers and Hornberger (1996) studied the influence of kaolin particles on the transport of  $^{137}\text{Cs}$  in the presence of different concentrations of particles in the influent, and it was found that the average travel time for the main  $^{137}\text{Cs}$  breakthrough peak was decreased by about a factor of 2 as the concentration of colloidal particles in the influent was increased from zero to 200 mg/L.

All these studies have not considered the possibility of the occurrence of plugging of colloidal fine particles. Plugging can occur when the size of colloidal fine particles is not very small compared to the pore size or grain size of porous medium. Migration of fine particles in porous media is a reasonably well-understood topic. It is found that under certain conditions, entrapment of the migrating colloidal fines can occur which could eventually lead to the plugging of the porous media (Khilar and Fogler, 1998; Ramachandran and Fogler, 1999). The plugging results in drastic reduction in flow rates and, therefore, there exists a possibility of retardation of contaminant transport and subsequent containment under a constant pressure gradient flow as it occurs in groundwater flows.

The major objective of this experimental study is to investigate the colloid-associated contaminant transport under a wide range of conditions that includes both plugging and nonplugging circumstances. In particular the objective is to evaluate the effectiveness of the retention of contaminants by adsorption both onto solid matrix and onto colloidal fines present in the porous media. In addition, the objective is to investigate the possibility of retardation of transport of contaminant under plugging condition.

A major obstacle to develop the knowledge on the possible occurrence of plugging-based retarded contaminant transport is the absence of experimental data coupled with a lack of

any existing model for describing such phenomenon. Therefore, an attempt has been made in this work to understand the effects of the release, migration, and entrapment of colloidal fines on the transport of contaminants in seepage flow. The work is presented in two parts: experimental studies and modeling studies.

In Part 1 of this study the results of column experiments are presented concerning the mobilization and migration of colloidal fines, kaolin, and the fate of contaminant  $\text{Ni}^{2+}$  metal ion through sand beds containing kaolin particles under non-plugging and plugging conditions. A heavy metal ion, nickel (presented as  $\text{Ni}^{2+}$ ) was chosen as a model contaminant because of its strong sorption to natural materials, that is, to mineral surfaces, and it is one of the strong contaminants in the subsurface whose transport is likely to be affected by the presence of natural colloidal fines, kaolin. The kaolin-sand bed acts as a natural porous media. The sand bed has been used as a standard porous medium in many earlier studies relating to transport of contaminant in porous media.

## Experimental Setup and Procedure

### Materials used

All chemicals used were of analytical grade. Salts used in the preparation of synthetic contaminant bearing solution is  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , obtained from Merck, India. Kaolin was obtained from Thomas Baker (chemicals) Ltd, Mumbai, India and was used as such after drying. Sodium dithionate, hydrogen peroxide, and 12N HCl, used for the cleaning of sand, obtained from Thomas Baker (Chemicals) Ltd, Mumbai, India and S. D. fine chemicals Ltd, Mumbai, India, respectively. The Ennore sand used in these experiments, obtained from Tamil Nadu Minerals Ltd, India, was quartz of a light gray or whitish variety and was free from silt. There were two types of sand used: one "coarse" sand, which was retained by a 0.693 mm sieve and passed through a 0.853 mm sieve, and another "fine" sand, which passed through a 0.178 mm sieve and was retained by a 0.105 mm sieve. The sauter mean size of the kaolin powder was  $2.8 \mu\text{m}$ . The size distribution data are given elsewhere (Sen, 2001). All plastic sample bottles and glass ware were cleaned, then rinsed with double distilled water and dried at  $60^\circ\text{C}$  in a temperature controlled oven prior to each experiment.

### Sand cleaning

The sand was thoroughly cleaned prior to use by using a procedure given elsewhere (Johnson et al., 1996). Sand was immersed in sodium dithionate solution ( $0.1\text{M Na}_2\text{S}_2\text{O}_3$ ) for 2 h to remove surfacial metallic compounds such as iron oxide and manganese oxide, if any. Then, organic impurities, if present, were removed by soaking the sand in hydrogen peroxide ( $5\% \text{H}_2\text{O}_2$ ) for 3 h, followed by a wash with double distilled water and subsequent overnight soaking in 12 N HCl. The sand was then washed thoroughly with distilled water until the conductivity remained fairly constant in the decanted wash water and it was oven dried at  $105^\circ\text{C}$  for 24 h.

### Experimental measurements

All quantitative determinations of samples of  $\text{Ni}^{2+}$  were conducted (before and after experiments) using a GBC dou-

ble beam flame atomic absorption spectrophotometer, GBC Scientific Equipment Pvt. Ltd, Australia. The turbidity of the solution was measured by a Systronics digital nephelo-turbidity meter 132, Ahmedabad, India, and the conductivity was measured by a Autoranging conductivity meter, model no. EQ.667, Equip-tronics, Mumbai, India. Kaolin sizes are determined by MasterSizer X Ver.1.2, Malvern Instruments Ltd, U.K. The measurements are described in detail elsewhere (Sen, 2001).

### Experimental setup and transport experiments

Contaminant transport experiments were conducted in an experimental setup consisting of a 0.305 m long, 25 mm inner dia. and 30 mm outside dia. acrylic column. Both ends of column are connected with circular threaded caps. The column was fitted with a 60  $\mu$ m wire mesh supported on a perforated distributor at both ends.

The input solution (either distilled water or 20.5 ppm,  $\text{Ni}^{2+}$  solution) was injected into the column at a fixed flow rate by a variable speed peristaltic pump (Electrolab, Mumbai, India, range 0.5–120 mL/min), which was placed at the bottom of the vertical column. The column orientation can be changed by a clamp arrangement. Experiments were conducted with two different bead-size/particle-size ratios, which is defined by Eq. 1

Bead size to particle size ratio (SR)

$$= \frac{\text{Sauter mean size of sand used}}{\text{Sauter mean size of kaolin particles used}} \quad (1)$$

For each set of experiments, a fresh column was packed to a height of 0.279 m by pouring clean and dried sand of particle density 2,666  $\text{kg/m}^3$  or sand containing different weight percentage of kaolin. Wet-packing method was used to eliminate air from the column. Dilute aqueous solution of  $\text{Ni}^{2+}$  was sent through the bed at constant flow rate in all experimental runs. The effluent from the column was collected at fixed time intervals for measuring  $\text{Ni}^{2+}$  concentration, as well as for measuring kaolin particle concentration. Some experiments were repeated to test the reproducibility of the measurements. It is found that, in general, the measurements are reproducible within  $\pm 10\%$ .

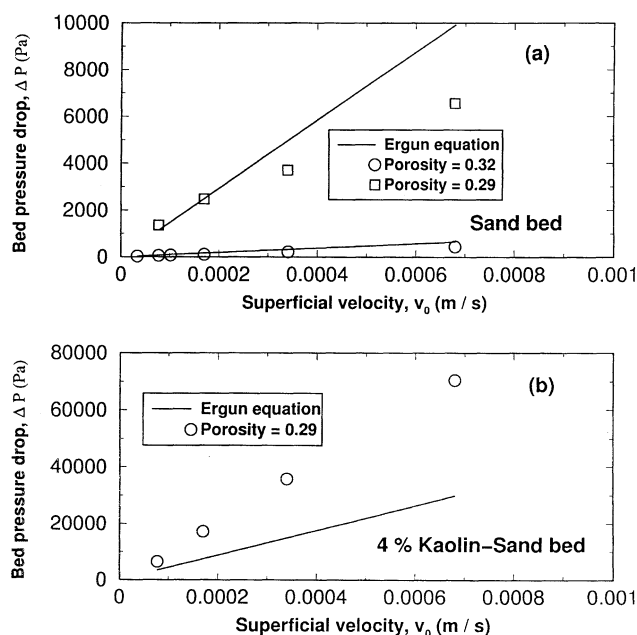
### Hydrodynamic and Fines Migration Studies

#### Pressure drop measurements and calculations

Pressure drop across different packed beds (0%, 2%, & 4%) at various superficial velocities were measured. Pressure drop ( $\Delta P$ ) across the bed of length  $L$  and porosity  $\epsilon$ , at low particle Reynolds number  $N_{Rep}$  can be determined by a simplified Ergun equation which can be rearranged as given below

$$\frac{\Delta P}{L} = \frac{150\mu v_0(1-\epsilon)^2}{D_p^2\phi_s^2\epsilon^3} \quad (2)$$

Where  $v_0$  is the superficial velocity and  $\phi_s$  is sphericity of particles.



**Figure 1. Bed pressure drops: Ergun prediction eq. (—) vs. experimental measurement (○, □) at different superficial velocity during upward flow through packed beds.**

(a) Sand bed; (b) 4% Kaolin-Sand bed.

All the parameters present on the righthand side of Eq. 2 have been measured and, therefore,  $\Delta P$  across the bed can be calculated. As expected, the pressure drop across the bed increases with an increase in superficial velocities and with a decrease in porosity, with other parameters remaining the same. The pressure drop also significantly increases with the amount of kaolin present in the beds at a fixed superficial velocity.

Predictions of pressure drop using the Ergun equation agree well with the measurements for the sand bed. However, for the composite kaolin-sand packed-beds, deviations are significantly increased with the amount of kaolin present in the beds, particularly under plugging conditions. These comparisons are presented in Figure 1. Overall, it is found that a composite kaolin-sand bed gives poor agreement with pressure drops calculated using the Ergun equation and accounting for the presence of kaolin particles in the calculation of mass average particle size. Disagreements are larger for a higher amount of kaolin present in the bed. As one observes from Figure 1b, the increase of pressure drop due to the presence of kaolin in the bed is over 100%. This can be attributed to the migration and entrapment of kaolin particles in the bed, causing local spots of very low porosity in the bed which is not accounted for in the Ergun equation.

#### Measurements of migration of fines particles

Table 1 presents the conditions, as well as the amounts of kaolin particles migrated out from different composite packed beds under both nonplugging and plugging conditions. From this Table 1, we observe that the percentage of kaolin parti-

**Table 1. Amounts of Kaolin Washed Out from Different Composite Beds during Stabilization Period**

Kaolin-Sand Bed	Size Ratio (SR)	% Migrated Out
0.5%	277	2.3
1.0%	Nonplugging	5.45
2.0%		1.5
4.0%		0.60
6.0%		0.47
2.0%	50	0.20
4.0%	Plugging	0.24
6.0%		0.29

$L = 28 \text{ cm}$ ,  $v_0 = 7.74 \times 10^{-5} \text{ m/s}$  for (SR) = 277, and  $v_0 = 3.39 \times 10^{-4} \text{ m/s}$  for SR = 50.

cles migrated under nonplugging condition is more than the percentage of kaolin particles migrated under plugging conditions. Actually, these amounts of kaolin particles were washed out during the initial stage of flow possibly from the last few layers of bead particles comprising about a few percentage of the bed length at the outlet of bed. This indicates that, for this relatively large size of colloidal fine particles, the average length of migration in the sand bed is only a small fraction of the bed length. Under plugging conditions, the amount of particles migrating out of the bed decreases indicating a further decrease in the migration length.

### Contaminant Transport Measurements under Nonplugging Conditions: Results and Discussions

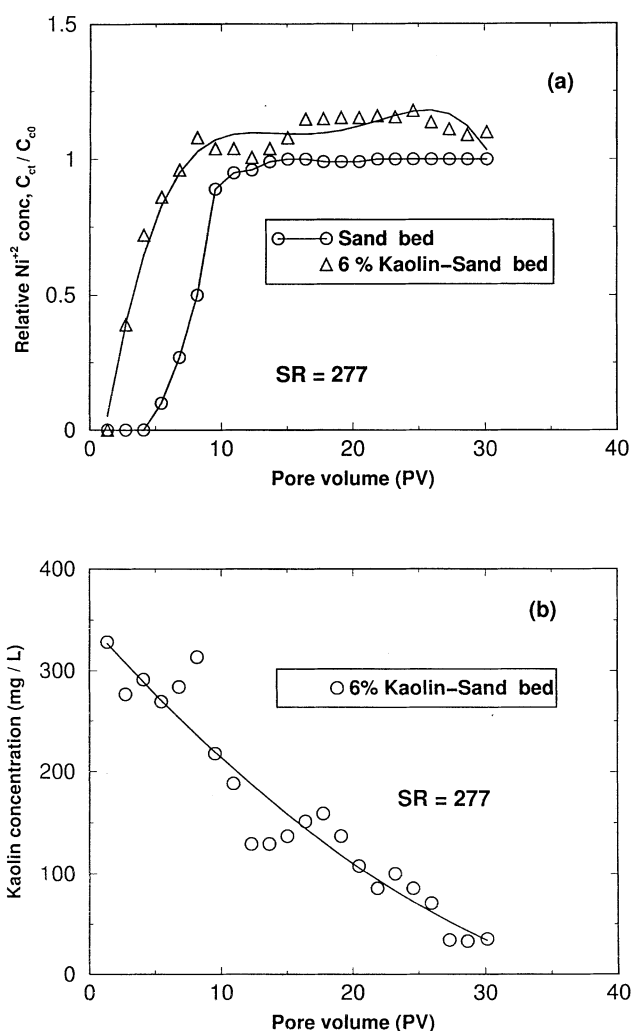
The experimental procedure has been discussed in a preceding section. An aqueous solution of 11.0 ppm  $\text{Ni}^{2+}$  was injected continuously upwards through the sand and kaolin-sand beds under nonplugging conditions. Coarse sand was used in these experiments with bead-size to particle-size ratio (SR) as 277. It needs to be mentioned here that the concentration of  $\text{Ni}^{2+}$  at the outlet  $C_{ct}$  is calculated by accounting for the contribution from both the aqueous phase, as well as the mobile colloid phase, which is presented in Eq. 3.

$$C_{ct} = C_c + X_f C_f \quad (3)$$

where  $C_c$  is the concentration of  $\text{Ni}^{2+}$  ions in the aqueous phase and  $X_f$  is the mass fraction of the contaminants adsorbed onto the colloidal fines, and kaolin and  $C_f$  is the effluent kaolin concentration. In these calculations, linear equilibrium adsorption relation has been taken, that is,  $X_f = K_f C_c$ , where  $K_f$  is the partition coefficient for the colloidal fines and is determined from batch experiments (0.00172 L/mg). The volumetric flow rate was kept constant at  $2 \times 10^{-5} \text{ m}^3/\text{min}$ .

### Role of mobilizing colloidal fines, kaolin in the transport of $\text{Ni}^{2+}$ ions

Figure 2a presents the dimensionless concentration of nickel ions as a function of cumulative pore volumes of solution sent through the core. These plots are commonly known as “breakthrough curves” (BTC). BTCs are presented for two



**Figure 2. Role of mobilizing kaolin particles on the facilitation of Ni metal ions transport during flow through kaolin-sand bed under nonplugging condition.**

(a) Comparisons of experimental BTCs for Ni-metal ions during upward flow through the sand bed and the 6% kaolin-sand bed; (b) condition of effluent kaolin concentrations during flow through same bed. Initial Ni metal ion concentration = 11.0 ppm,  $L = 0.28 \text{ m}$ ,  $\epsilon = 0.32$ , superficial velocity =  $6.69 \times 10^{-4} \text{ m/s}$ .

beds: a sand bed and 6% kaolin-sand bed. All other conditions were kept the same for the two beds. Let us first consider the BTC for the sand bed. One observes from this curve that the outlet dimensionless concentration of  $\text{Ni}^{2+}$  levels off at the value of 1.0 implying that the sand bed has got saturated with  $\text{Ni}^{2+}$  ions after about 13 pore volumes of solution have passed through the bed. This breakthrough after 13 pore volumes (corresponds to 30 min) does not compare well with the batch equilibrium time of about 1 h. The amount of  $\text{Ni}^{2+}$  ions retained in the bed was calculated as 1.732 mg. The amount that would have been retained if the bed was completely saturated is 7.0 mg based on the batch adsorption data. Therefore, the bed saturation was only 24.7% at the breakthrough. Such a low value of saturation implies that the bed is not efficient in retaining contaminants through adsorption

and the entire bed is not utilized in adsorbing the contaminants at such low pressure drop.

Let us now focus on the breakthrough curve (BTC) of the kaolin-sand bed. One finds some significant differences as compared to those for the BTC with the sand bed. First, the breakthrough has occurred earlier at around 6 pore volumes. Secondly, the dimensionless outlet of  $\text{Ni}^{2+}$  concentration has increased beyond 1.0 implying that colloidal kaolin particles with  $\text{Ni}^{2+}$  ions adsorbed on their surface have migrated out of the bed. Both these observed effects clearly show that the presence of colloidal kaolin particles in the bed has facilitated the  $\text{Ni}^{2+}$  transport process. The fact that colloidal kaolin particles were migrating out of the bed can be confirmed by the measurements shown in Figure 2b. One observes from the figure that particles migrated out of the bed for about 25 pore volumes during which period, the dimensionless  $\text{Ni}^{2+}$  concentration was above 1.0. Such measurements in our study clearly document the well-established phenomenon of colloid-facilitated contaminant transport. Furthermore, it documents that the facilitation occurs as long as the fine particles migrate out.

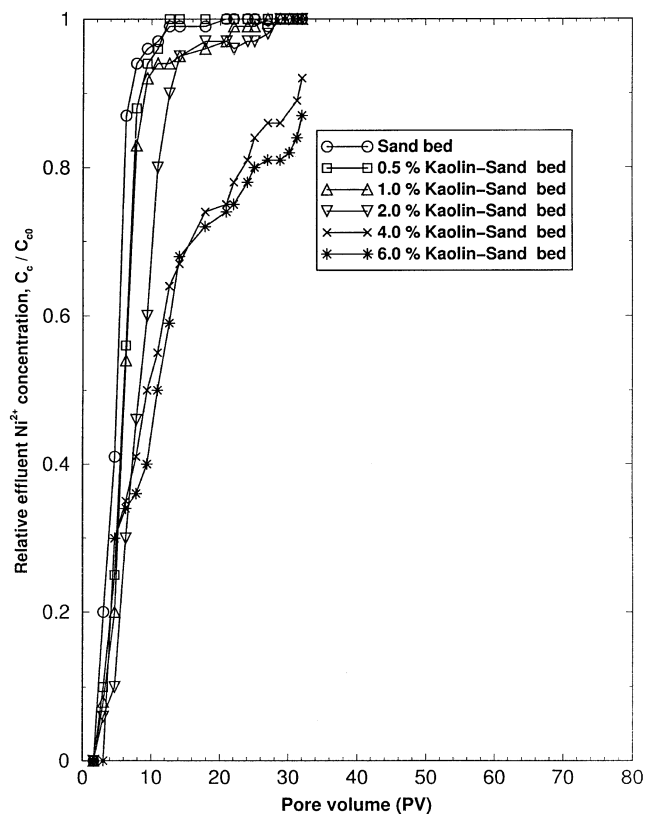
#### *$\text{Ni}^{2+}$ transport in kaolin-sand bed without migration of kaolin particles*

To study the effects of some pertinent parameters without the clay particles migrating out of the bed, a sufficient amount of water was sent through these beds so that most, if not all, mobilizing kaolin particles got out of the bed. Hence, these beds were essentially washed-off beds where fines migration out of the bed was absent.

Using these beds, the effects of two important parameters, the amount of kaolin present in the bed and the flow rate through the bed on the transport of  $\text{Ni}^{2+}$ , were studied.

#### *Effects of amount of kaolin present in the bed*

Figure 3 presents the measured breakthrough curves (BTCs) for different packed beds. In these measurements, only the composition of the bed, that is, the initial weight percent of kaolin in the bed, was different (0%, 0.5%, 1.0%, 2.0%, 4% and 6%); everything else remained the same for all bed flow experiments, that is, superficial velocity was  $7.74 \times 10^{-5}$  m/s, initial  $\text{Ni}^{2+}$  concentration was 20.5 ppm, and the bed porosity was 0.32. BTCs are presented as plots of  $C_c/C_{c0}$  against pore volumes,  $PV$  where  $C_c$  is the aqueous phase effluent  $\text{Ni}^{2+}$  concentration (no colloidal fines in the effluent), and  $C_{c0}$  is the influent  $\text{Ni}^{2+}$  concentration. One observes from these BTCs that the breakthrough is delayed as expected as the content of kaolin in the bed is increased.  $\text{Ni}^{2+}$  is eluted more slowly in the presence of colloidal kaolin than in its absence. For instance, the time required for reduced  $\text{Ni}^{2+}$  concentrations ( $C_c/C_{c0}$ ) to reach a level of 0.8 occurred approximately after passing 6.5 pore volumes for a 0.5% bed, 7 pore volumes for a 1% bed, 11 pore volumes for a 2% bed, 24 pore volumes for a 4% bed, and 25 pore volumes for a 6% bed, respectively, whereas only 5 pore volumes are required for the sand bed only. As the kaolin content of the bed is increased, the total adsorption capacity of the bed increases. Therefore, the breakthrough of  $\text{Ni}^{2+}$  is expected to be delayed. More prominent is, however, the slow



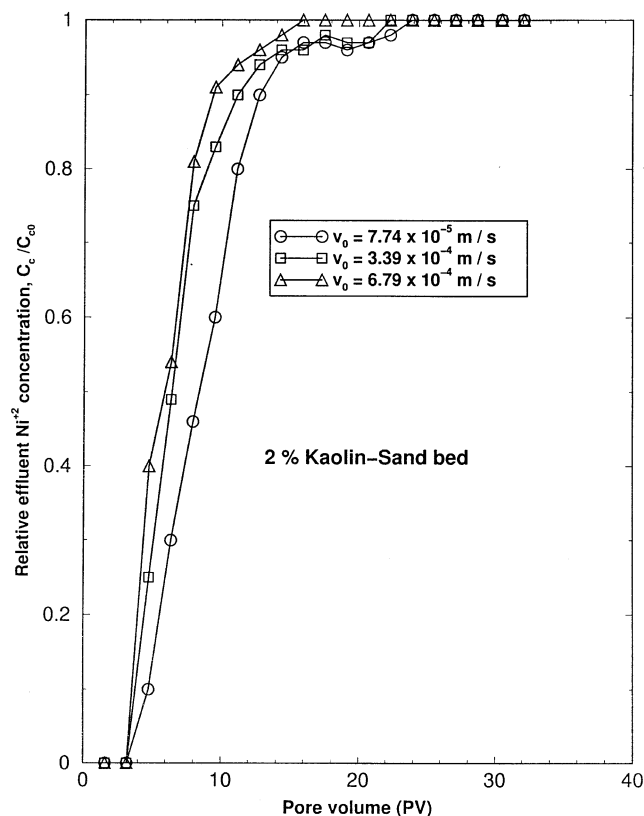
**Figure 3. Experimental BTCs for Ni metal ions during upward flow through different composite kaolin-sand beds under nonplugging condition.**

Initial Ni metal ion concentration = 20.5 ppm,  $L = 0.28$  m,  $\epsilon = 0.32$ , superficial velocity =  $7.74 \times 10^{-5}$  m/s.

elution of the bed, as the concentration of kaolin is increased. With a higher concentration of kaolin in the bed, the pressure drop across the bed is higher which in turn increases the sweep efficiency. As a result, more fine particles are exposed to flow and there is an increase in the amount of adsorption. Further discussions on this important experimental observation are presented in Part 2 of this article, along with comparisons with model predictions. In all cases, the percentage saturation was calculated and was found to be below 25%, implying that the beds were not efficient in adsorbing the contaminants,  $\text{Ni}^{2+}$ .

#### *Effects of flow velocity*

Figures 4 and 5 show the effects of flow velocity on the breakthrough curves (BTCs) for 2% and 6% kaolin bed at a size ratio, and as SR of 277 with same inlet  $\text{Ni}^{2+}$  concentration of 20.5 ppm. From these BTCs, it can be observed that  $\text{Ni}^{2+}$  eluted more rapidly as the velocity is increased. It can be further observed that, from both the figures, the influence of velocity is reduced showing a level-off tendency as the velocity increases to a higher value. The above two pieces of observations indicate that the external mass transfer may be controlling the rate of adsorption. As the velocity increases,



**Figure 4. Effect of flow velocity on BTCs for Ni metal ions during upward flow through 2% kaolin-sand bed.**

Initial Ni metal ion concentration = 20.5 ppm,  $L = 0.28$  m, and  $\epsilon = 0.32$ .

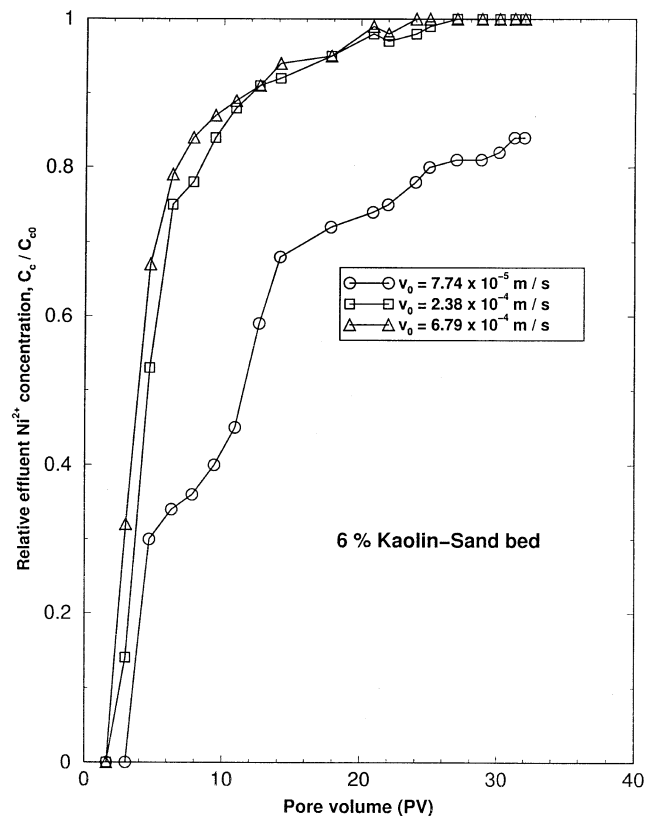
the rates of mass transfer increase thereby enhancing the rate of adsorption. As a result, breakthrough occurs at lower pore volumes.

### Contaminant Transport Measurements under Plugging Conditions: Results and Discussions

The primary objective in this part of the experimental studies was to investigate the transport of  $\text{Ni}^{2+}$  ions through the bed under a condition of migration and entrapment of kaolin particles. Plugging was induced in the bed following the work of Pandya et al. (1998). It is shown that, when the ratio of bead size to particle size (SR) is approximately below 75, there exists a critical particle concentration above which plugging occurs due to multiparticle jamming at pore constrictions. Accordingly, the SR value was taken as 50 by taking finer size sand particles. Experiments were conducted to study the phenomenon of bed plugging first and then the contaminant transport.

#### Effects of bead/particle ratio on plugging

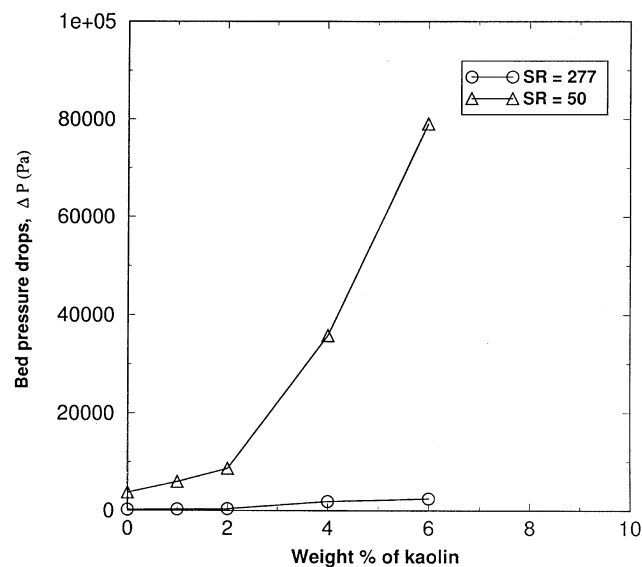
Figure 6 indicates that the ratio of bead/particle size (SR) has a strong effect on plugging. Here, the extent of plugging by straining or convective jamming is decreased as the bead/particle ratio (SR) is increased for a fixed flow condi-



**Figure 5. Effect of flow velocity on experimental BTCs for Ni metal ions during upward flow through 6% kaolin-sand bed.**

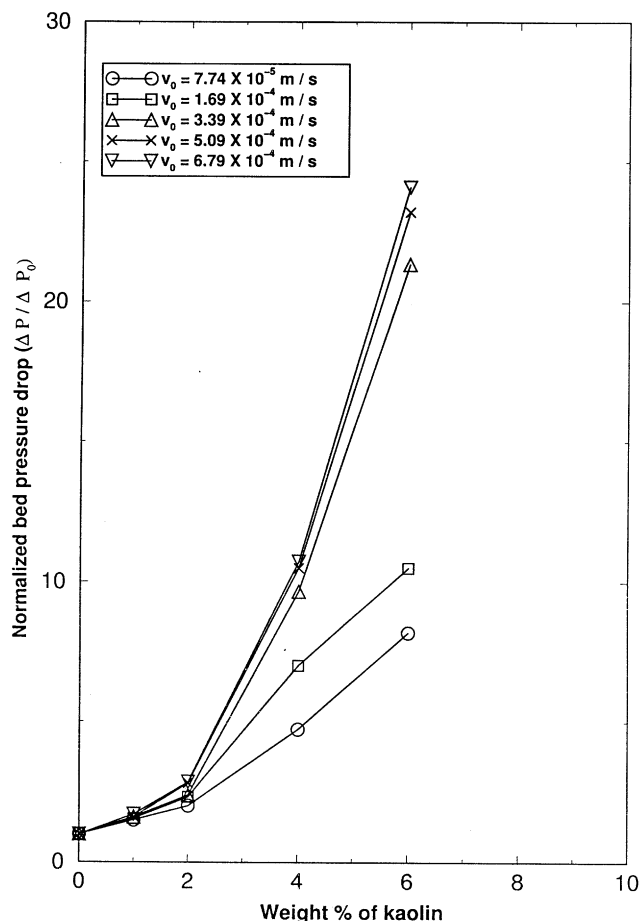
Initial Ni metal ion concentration = 20.5 ppm,  $L = 0.28$  m, and  $\epsilon = 0.32$ .

tion. Similar results have been found by Pandya et al. (1998). Multiparticle bridging or jamming appears to be the likely process leading to plugging (Khilar and Fogler, 1998).



**Figure 6. Effect of bead size to particle size (SR) on plugging phenomenon.**

$L = 0.28$  m,  $\epsilon = 0.29$ , superficial velocity =  $3.39 \times 10^{-4}$  m/s.



**Figure 7. Effect of flow velocity on plugging phenomenon.**

$L = 0.28$  m,  $SR = 50$ , and  $\epsilon = 0.29$ .

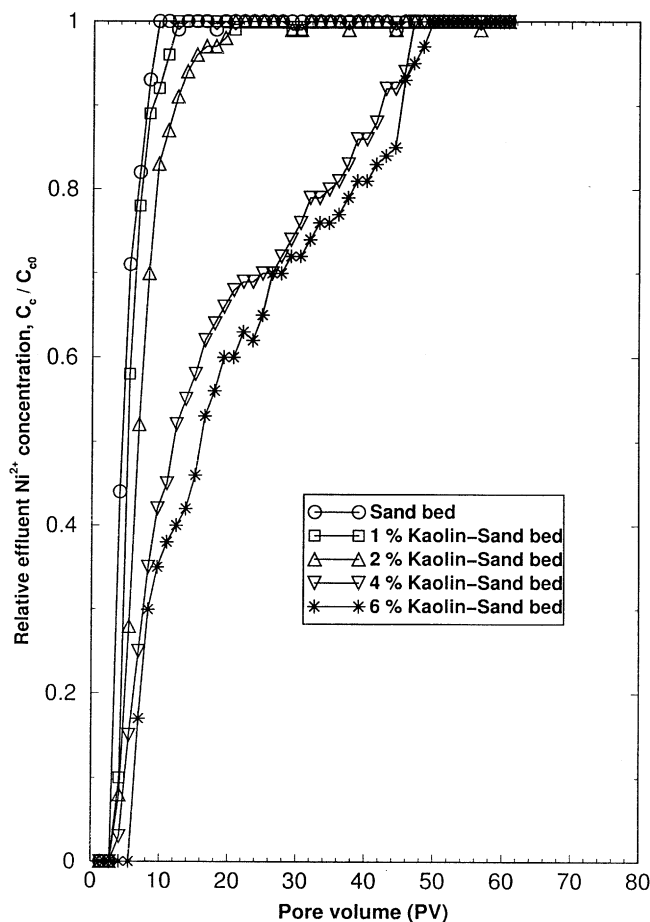
#### Effects of flow velocity on plugging

The effects of flow rates on the plugging of different composite packed beds are shown in Figure 7. The plots show the steady-state normalized pressure drop across the bed as a function of the amount of kaolin present in the beds for a ratio of bead size to particle size ( $SR$ ) of 50 for different flow rates. The normalized pressure drop is the ratio of pressure drop across the composite beds during water/ $Ni^{+2}$  solution flow to that of flow through a sand bed at the same flow rate. One can observe from this figure that, at superficial velocities of  $7.74 \times 10^{-5}$  m/s and of  $1.69 \times 10^{-4}$  m/s, there is a slow rise in normalized pressure drop with different weight percentage of kaolin present in the bed. However, there is a rapid rise in steady-state normalized pressure drop with superficial velocities of  $3.39 \times 10^{-4}$  m/s,  $5.09 \times 10^{-4}$  m/s, and  $6.79 \times 10^{-4}$  m/s respectively. This observation is consistent with the observation of the existence of a critical flow rate in the phenomenon of convective jamming (Ramachandran and Fogler, 1999). Such a steep rise indicates that plugging has occurred in the bed. It should be mentioned here that by increasing the kaolin content, there is a small change in the sauter mean size and in the porosity of the bed. Hence, the observed increase of pressure drop is due to particle entrapment and the consequent plugging of the bed.

These results show that both flow rates, as well as the amount of kaolin present in the bed, are influencing parameters for the plugging phenomenon. The amount of kaolin present in the bed determines the concentration of kaolin in the pore liquid. The concentration in-turn influences the plugging phenomenon and the nature of the influence is in the form of a threshold process, that is, plugging occurs when concentration goes beyond a critical concentration. Hence, at a higher amount of kaolin present, the concentration goes beyond the critical concentration and plugging occurs. The flow rate affects the process of multiparticle bridging leading to plugging at the pore constrictions and thereby influences it (Ramachandran and Fogler, 1999). In addition, a higher flow rate is expected to release a larger amount of kaolin particles resulting in an increase in the concentration of kaolin in the pore liquid. Therefore, as observed, flow rate is a strong parameter in the phenomenon of plugging.

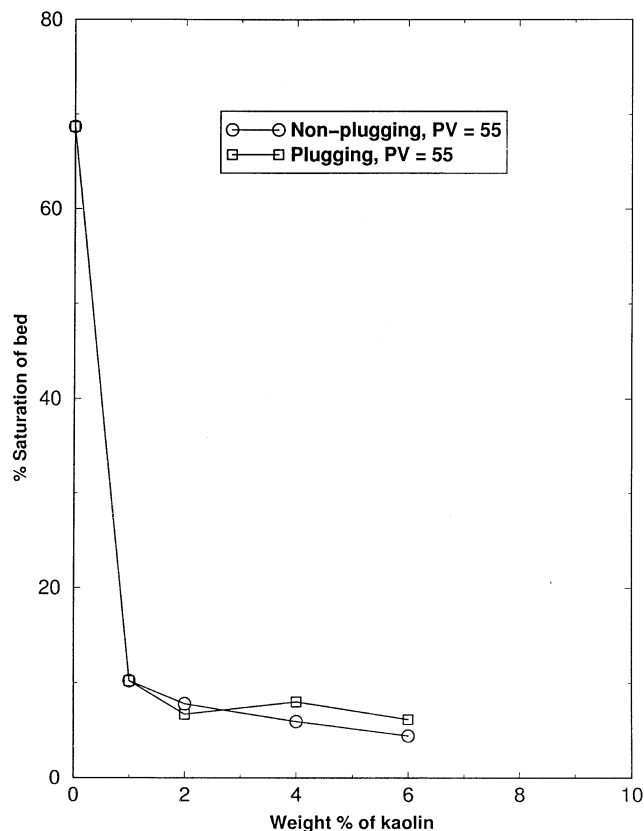
#### BTCs with migration and plugging in the bed

Figure 8 presents the measured BTCs for different packed beds. One can observe from these BTCs that the  $Ni^{2+}$



**Figure 8. Experimental BTCs for  $Ni$  metal ions during upward flow through different composite kaolin-sand beds under plugging condition.**

Initial  $Ni$  metal ion concentration = 20.5 ppm,  $L = 0.28$  m,  $SR = 50$ ,  $\epsilon = 0.29$ , and superficial velocity =  $3.39 \times 10^{-4}$  m/s.



**Figure 9. Percentage saturation of different composite kaolin-sand beds during Ni metal ion flow under plugging and nonplugging conditions.**

breakthrough gets delayed as the content of kaolin in the bed is increased. One further observes that the dimensionless effluent  $\text{Ni}^{2+}$  concentration becomes close to unity after passing approximately 12 pore volumes in the case of 1%, and 18 pore volumes in the case of 2% kaolin bed where little plugging occurs. Plugging, however, occurs for beds containing 4% and 6% kaolin. For plugging conditions, the dimensionless effluent  $\text{Ni}^{2+}$  concentration is below 0.65 after passing 18 pore volumes through the beds. In this situation, the dimensionless effluent  $\text{Ni}^{2+}$  concentration is almost one after passing approximately 44 pore volumes for 4% bed and 54 pore volumes for 6% bed. The BTCs, particularly in the plugging cases, exhibited a long, slow increase in effluent  $\text{Ni}^{2+}$  concentration with variations in the slope of the curves. Such a nature indicates that the rates of sorption of  $\text{Ni}^{2+}$  may involve a fast and a slow kinetic component. It also indicates that there may be a continuous generation of new accessible sites for adsorption particularly offered by colloidal fines due to mobilization. Furthermore, as the pressure drop increases due to plugging, the sweeping efficiency increases and, hence, new sites are available for adsorption in solid matrix.

The percentage saturation of the bed was also calculated under a plugging and a nonplugging condition at a pore volume of 55. It was calculated as the area of the breakthrough curve (BTC) of  $(1 - C/C_0)$  vs. PV divided by the bed capacity for a particular bed. Bed capacity was calculated based on

batch adsorption data. The results are given in Figure 9. One observes from this figure that the percentage saturation is higher in case of plugging. In the plugging situation, the pressure drop is higher which in turn makes sweeping of the flow better. High sweeping makes otherwise inaccessible adsorption sites available for adsorption and thereby increases the amount of adsorption. The kaolin-sand composite beds, however, act like a poor adsorber column with the percentage saturation, in general, below 25%. It should be noted that, if the contaminant transport experiments under plugging conditions were to be carried out at a constant pressure gradient rather than at a constant flow rate, then the flow rate will decrease. This will be so much so that in most cases the flow rate may become virtually zero, resulting in no transport of contaminants.

## Conclusions

The following conclusions have emerged from this experimental study:

- Only a small fraction of colloidal kaolin present in the bed migrates out of the bed particularly when the particle size is about a few microns.
- The transport of a contaminant species through a bed gets facilitated when the colloidal kaolin present in the bed migrates out of the bed. This migration occurs for a short period and as does the facilitation of contaminant transport, when there are no fines entering the bed.
- Without migration and plugging of kaolin particles, the kaolin-sand bed acts like a poor adsorption column for adsorbing the  $\text{Ni}^{2+}$  ions. The percentage of saturation is found to be below 25%. Hence, the retardation of transport of contaminants due to adsorption is not very significant in kaolin-sand bed.
- When migration and plugging of kaolin particles occur, the retardation in transport due to adsorption increases. Such an increase can be attributed to the increase in accessibility to adsorption sites arising out of more mobilization and higher sweeping at higher pressure drops and at higher concentrations of kaolin.

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## Notation

- $A$  = cross-sectional area of column,  $\text{m}^2$   
 $C_c$  = concentration of contaminant in the aqueous phase,  $\text{kg}/\text{m}^3$   
 $C_{ct}$  = total mobile contaminant concentration in the aqueous phase,  $\text{kg}/\text{m}^3$   
 $C_{c0}$  = inlet concentration of contaminant in the aqueous phase,  $\text{kg}/\text{m}^3$   
 $C_f$  = concentration of colloids in aqueous phase,  $\text{kg}/\text{m}^3$   
 $D_m$  = mass average particle diameter, m  
 $D_p$  = particle diameter, m  
 $K_f$  = partition coefficient for the colloidal fines,  $\text{m}^3/\text{kg}$   
 $L$  = length of packed column, m  
 $N_{\text{Rep}}$  = Reynolds number

$v_0$  = superficial velocity, m/s  
 $\Delta P/L$  = pressure gradient across the medium, Pa/m  
 $\Delta P$  = pressure drop across the composite bed, Pa  
 $\Delta P_0$  = pressure drop across sand bed, Pa  
 $X$  = adsorption density, mg/g  
 $X_f$  = mass fraction of contaminant adsorbed on to the colloids, kg/kg

### Greek letters

$\epsilon$  = porosity of the bed  
 $\epsilon_0$  = initial porosity  
 $\rho$  = fluid density, kg/m<sup>3</sup>  
 $\mu$  = viscosity of the suspension, Pa·s  
 $\phi_s$  = sphericity of material

### Literature Cited

- Abdel-Salam, A., and C. V. Chrysikopoulos, "Analysis of a Model for Contaminant Transport in Fracture Media in the Presence of Colloid," *J. Hydrology*, **165**, 261 (1995).
- Buddemeier, R. W., and J. R. Hunt, "Transport of Colloidal Contaminants in Groundwater: Radionuclide Migration at the Nevada Test Site," *Appl. Geochem.*, **3**, 535 (1988).
- Champ, D. R., W. F. Merritt, and J. L. Young, *Potential for the Rapid Transport of Plutonium in Groundwater as Demonstrated by Core Column Studies. Scientific Basis for Radioactive Waste Management*, W. Luze, ed., V. Elsevier, Amsterdam, p. 745 (1982).
- Corapcioglu, M. Y., and S. Jiang, "Colloid-Facilitated Ground Water Contaminant Transport," *Water. Resour. Res.*, **29**, 2215 (1993).
- Faure, M. H., M. Sarden, and P. Vitorge, "Transport of Clay Particles and Radio Elements in a Salinity Gradient: Experiments and Simulations," *J. Contam. Hydrol.*, **21**, 255 (1996).
- Grolimund, D., M. Borkovec, K. Barmettler, and H. Sticher, "Colloid-Facilitated Transport of Strongly Sorbing Contaminants in Natural Porous Media: A Laboratory Column Study," *Environ. Sci. Technol.*, **30**, 3118 (1996).
- Honeyman, B. D., "Colloidal Culprits in Contamination," *Nature*, **397**, 23 (1999).
- Johnson, P. R., N. Sun, and M. Elimelech, "Colloid Transport in Geochemically Heterogeneous Porous Media: Modeling and Measurements," *Environ. Sci. Technol.*, **30**, 3284 (1996).
- Kaplan, D. L., P. M. Betsch, D. C. Adriano, and W. P. Million, "Soil Borne Mobile Colloids as Influenced by Water Flow and Organic Carbon," *Environ. Sci. Technol.*, **27**, 1193 (1993).
- Kersting, A. B., D. W. Efurud, D. L. Finnegan, D. J. Rokop, D. K. Smith, and J. L. Thomson, "Migration of Plutonium in Groundwater at the Nevada Test Sites," *Nature*, **397**, 57 (1999).
- Khilar, K. C., and H. S. Fogler, *Migration of Fines in Porous Media*, Chapter 1 and Chapter 4, Kluwer Academic Publishers, Dordrecht, Boston and London (1998).
- Kretschmar, R., M. Borkovec, D. Grolimund, and M. Elimelech, "Mobile Subsurface Colloids and their Role in Contaminant Transport," *Advances in Agronomy*, **66**, 121 (1999).
- Magee, B. R., L. W. Leon, and A. T. Lemley, "Transport of Dissolved Organic Macromolecule and Their Effect on the Transport of Phenanthrene in Porous Media," *Environ. Sci. Technol.*, **25**, 323 (1991).
- McCarthy, J., and J. Zachara, "Subsurface Transport of Contaminants," *Environ. Sci. Technol.*, **23**, 496 (1989).
- Pandya, V. B., S. Bhuniya, and K. C. Khilar, "Existence of a Critical Particle Concentration in Plugging of a Packed Bed," *AIChE J.*, **44**, 978 (1998).
- Penrose, W. R., W. L. Polzer, E. H. Essington, D. M. Nelson, and K. A. Orlandini, "Mobility of Plutonium and Americium Through Shallow Aquifer in a Solid," *Environ. Sci. Technol.*, **24**(2), 228 (1990).
- Puls, W. R., and R. M. Powell, "Transport of Inorganic Colloids Through Natural Aquifer Media: Implications of Contaminant Transport," *Environ. Sci. Technol.*, **26**, 614 (1992).
- Ramachandran, V., and H. S. Fogler, "Plugging by Hydrodynamic Bridging During Flow of Stable Colloidal Particles within Cylindrical Pores," *J. Fluid. Mech.*, **385**, 12 (1999).
- Roy, S. B., and D. A. Dzombak, "Colloid Release and Transport Processes in Natural and Model Porous Media," *Colloids and Surfaces A*, **107**, 245 (1996).
- Roy, S. B., and D. A. Dzombak, "Chemical Factors Influencing Colloid-Facilitated Transport of Contaminants in Porous Media," *Environ. Sci. Technol.*, **31**, 656 (1997).
- Roy, S. B., and D. A. Dzombak, "Sorption Nonequilibrium Effects on Colloid-Enhanced Transport of Hydrophobic Organic Compounds in Porous Media," *J. Cont. Hydrol.*, **30**, 179 (1998).
- Ryan, J. N., and M. Elimelech, "Colloid Mobilization and Transport in Ground Water," *Colloids and Surfaces A*, **107**, 1 (1996).
- Saier, J. E., and G. M. Hornberger, "The Role of Kaolinite on the Transport of Contaminant in Porous Media," *Water. Resour. Res.*, **32**, 33 (1996).
- Saltelli, A., A. Avogadro, and G. Bidoglio, "Americium Filtration in Glauconite Sand Column," *Nucl. Technol.*, **67**, 245 (1984).
- Sen, T. K., "Studies on Colloidal Fines-Associated Contaminant Transport in Porous Media," PhD Thesis, Dept. of Chemical Engineering, Indian Institute of Technology, Bombay, Mumbai, India (2001).
- Smith, P. A., and C. Degueldre, "Colloid-Facilitated Transport of Radionuclides through Fractured Media," *J. Cont. Hydrol.*, **13**, 143 (1993).
- Sojitra, L., K. T. Valsaraj, D. D. Reible, and L. J. Thibodeaux, "Transport of Hydrophobic Organics by Colloids Through Porous Media: 1. Experimental Results," *Colloids and Surfaces A*, **94**, 197 (1995).
- Sojitra, L., K. T. Valsaraj, D. D. Reible, and L. J. Thibodeaux, "Transport of Hydrophobic Organics by Colloids through Porous Media: 2. Commercial Humic Acid Macromolecules and Polyaromatic Hydrocarbons," *Colloid Surfaces A*, **110**, 141 (1996).

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