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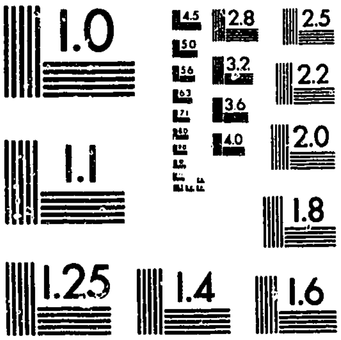

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THE ROLE OF INORGANIC COLLOIDAL PARTICLES IN TRANSPORT OF CONTAMINANTS THROUGH POROUS MEDIA

BY

MBANGISENI PATRICK NEPFUMBADA

A THESIS SUBMITTED TO

THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL

FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE

IN

SOIL PHYSICS

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA, CANADA

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The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled: **THE ROLE OF INORGANIC COLLOIDAL PARTICLES IN TRANSPORT OF CONTAMINANTS THROUGH POROUS MEDIA** submitted by Mbangiseni Patrick Nepfumbada in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE** in **SOIL SCIENCE**.

Y. S. Feng (Supervisor)

M. J. Dudas

C. A. Mendoza

DATE: Jan 26. 95

DEDICATION

This thesis is dedicated
to my parents,
Mukondeleli Pauline and Johannes Mafeladzulo Nepfumbada,
and all those who fought for the emancipation of the people of South Africa.

You have taught me that
the struggle for land is the struggle for emancipation,
and that
the best investment of all is in respecting and protecting the land,
for it is the source of our livelihood.
With this you have instilled in me the desire to learn more about this treasure - the land!!
For that I will forever be grateful.
Ndi a livhuha!

"...without the thin mentle we call soil, the Earth would be almost as lifeless as the other planets are. A people who do not prize and appreciate this gift from nature risk both an impoverishment of their culture and an impoverishment of their soils."

W. R. Gardener, 1992

ABSTRACT

A conceptual model was developed to describe the transport and fate of the contaminant (represented by Pb) and carrier material (represented by montmorillonite) in a porous medium. The problem is represented by a three-phase model with two solid phases; colloids and stationary solid matrix and an aqueous phase. Sorption and migration processes of the contaminant and colloids were formulated using convection-dispersion and mass balance equations of respective phases and sorption relations. The interaction of colloids with the contaminant and porous matrix were included in the model by assuming local equilibrium for colloids/matrix-contaminant mass partitioning. Numerical solutions were obtained to provide estimations of colloid and contaminant concentrations. A significant sensitivity to the model parameters, particularly the contaminant equilibrium distribution coefficients with mobile and immobile colloids, was obtained. This conclusion has practical implications in low permeability material where flow rate is slower than sorption rate. Lead, tracer (NaBr) and colloid column transport experiments were also conducted to evaluate the validity of the model. Results indicated that the presence of colloids is more significant when the porous media is adsorbing. The contaminant would be expected to migrate faster in the presence of mobile colloids than in colloid-free environment.

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I have had have surely helped me understand the perils of the world we leave in. Indeed the world has become a *village* and each one of us should cherish this gift from nature!!

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CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1. INTRODUCTION

Contaminants originating from human activities enter the subsurface environment through agricultural and land use practices such as irrigation and fertilization, waste disposal, spillage and land application of sewage sludge and animal wastes (McCarthy and Wobber, 1988a, b; Younus and Smolen, 1983). The establishment of effective disposal and isolation procedures for chemical wastes, the protection of public health and amelioration of subsurface contamination rely on the ability to predict the rate at which contaminants move through the vadose and saturated zones. However, attempts to describe and predict contaminant transport cannot succeed if major pathways and mechanisms for transport are not accounted for (McCarthy and Zachara, 1989).

Traditionally, organic and inorganic contaminants that migrate through the vadose and saturated zones have been simulated assuming a two-phase system in which contaminants are partitioned between a mobile aqueous phase and the immobile solid phase (rock or soil constituents) (McCarthy and Degueldre, 1983). For some subsurface environments, however, components of the solid phase have been found to exist as colloids suspended in and transported with the subsurface water. This constitutes a third phase (mobile solid phase) which may account for a significant fraction of contaminant migration especially in groundwater where high colloid concentrations have been reported.

Concentrations of 10^{10} colloid particles/l in granitic rock fragments (Degueldre *et al.*, 1989) and greater than 10^{12} colloid particles/l in sandy aquifers (Gschwend and Reynolds, 1987) have been reported. Other estimates of colloidal concentrations in ground water range as high as 20-63 mg/l (Puls, 1990). Gschwend *et al.*,(1990) observed 10-100 mg/l silicate colloids in ground water receiving recharge from evaporation ponds and fly ash basin. If contaminants do associate with this additional mobile solid phase (colloids), the net rate of migration of chemicals could be significantly enhanced. Conversely, deposition of the colloidal particles may reduce the permeability of a formation and thereby decrease transport (McCarthy and Zachara, 1989; McDowell-Boyer *et al.*, 1986). Fundamental understanding of the potential role of colloidal particles in enhancing or diminishing contaminant transport in the subsurface is required for accurate assessment of current contamination problems, engineering and safety assessment of containment and disposal options, and development of cost-effective remediation strategies (McCarthy and Degueldre, 1993).

The overall objective of this chapter is to provide a review of colloid migration and associated contaminant transport in the subsurface environment. In addition, an overview of the overall objectives and scope of the study will be provided.

1.2. REVIEW

1.2.1 Origin and behavior of colloids

Colloids are generally regarded as particles having diameters less than 10μm (Stumm, 1977), which tend to remain suspended in water. Colloids in subsurface water can originate from several sources and can be removed or stabilized by a number of hydrogeochemical mechanisms (McCarthy and Degueldre, 1993). Colloids may be detrital, or formed *in situ* as a result of geochemical alteration of thermodynamically unstable primary mineral phases or formed by generation of inorganic solid phases. Depending on the depositional environment and mineral composition of the geological deposit the nature of the detrital colloidal material can include a variety of layer silicates as well as iron- and aluminum-oxides.

Mechanisms postulated for the generation of colloids include: dispersion due to changes in ground water chemistry such as decreases in ionic strength or changes from Ca^{2+} to Na^{+} dominated chemistry; decementation of mineral phases cementing the colloids to each other and to the larger mineral grains; geochemical alteration of primary minerals; homogeneous nucleation/precipitation of inorganic solids due to changes in ground water chemistry; and stabilization of inorganic suspensions due to association with natural organic matter (McCarthy and Degueldre, 1993). Other sources include: translocation of inorganic and organic substances from the vadose or recharge zone; detachment of particles from immobile soil and mineral matrices (e.g., clay platelets and silicate particles); viruses and small bacteria; emulsions or microemulsions of fine droplets (e.g., a colloidal size benzene-water emulsion); macromolecules that agglomerate to form micelles or hemimicelles (e.g., agglomerated humic acid molecules) when present at high concentrations; and colloids directly introduced by aerial sources such as in landfill leachate (Mills *et al.*, 1991).

Mechanisms of colloid transport are poorly understood (Toran and Palumbo, 1992). Like solutes, colloids are subjected to advection, dispersion and both reversible and irreversible adsorption. Additional factors that influence movement of colloids include; sieving (physical retention), fast flow along preferential paths, size exclusion from small pore spaces resulting in enhanced flow compared to ground water velocity (Puls, 1990) and forces such as Brownian motion and gravity.

When particles are much smaller than the size of the grains of the media, the retaining force is provided by adhesion rather than sieving (Yao *et al.*, 1971; McDowell-Boyer *et al.*, 1986). Surface chemistry of the particles and the media control the electrostatic and van der Waals forces leading to adhesion (Toran and Palumbo, 1992). Conditions favorable for colloid-colloid attachment or colloid-solid matrix attachment result when the attractive force (van der Waals force) is large relative to the repulsive force (typically electrical, although other forces might be operative). Quantitative relationships between electrical repulsion and van der Waals attraction have been developed based on the theory of Derjaguin, Landau, Verwey and Overbeek (the DLVO theory). The theory combines van der Waals attractive forces for different geometrical shapes with electrical double layer repulsive forces. Repulsive forces become important when, for example, Na-Montmorillonite clays or in solutions of low ionic strengths, repulsive forces will be expected to be dominant. In addition, if concentration of colloids is low in solution (i.e., lower than the critical coagulation concentration) then one would expect more repulsion between colloidal particles.

The relative importance of these forces depend on the distance between colloidal particles. For instance, repulsive forces become important when the distance of closest approach is less than 600 Å but greater than 20 Å. When interparticle distance is less than 20 Å the van der Waals forces become dominant, and may facilitate flocculation. Experiments have shown that predictions based on DLVO theory do not match the observed data when electrochemical repulsive forces become important (Mills *et al.*, 1991). Therefore, data for electrochemical forces needed to predict retention rates are not easily estimated (McDowell-Boyer, 1986, 1989; Germann and Douglas, 1987). The present lack of understanding in this area is a major reason why predictive capabilities of colloid transport are so limited. In addition, attachment depends in part on physical processes leading to particle capture: Brownian motion, interception and gravity. Particle diameter, velocity and ionic strength have been demonstrated to be important in attachment.

1.2.2 Association of colloids with contaminants

Despite the uncertainties about quantification, there is extensive evidence that colloid transport occurs (Toran and Palumbo, 1992), and may facilitate the transport of contaminants in some systems (Puls, 1990). Two types of evidence suggest that colloids may influence the transport of subsurface contaminants; (1) laboratory column studies demonstrating cotransport of contaminants sorbed on mobile colloids and (2) field studies demonstrating the association of contaminants with natural ground water colloids (McCarthy and Degueldre, 1993). For example, Vinten *et al.*, (1983, 1985) showed that pesticides such as DDT and paraquat can be cotransported with montmorillonite through soil under saturated conditions. Champ *et al.*, (1982) demonstrated the rapid transport of plutonnium (Pu) in undisturbed aquifer cores eluted with ground water for 8 months. Half the eluted Pu was particulate. Newman (1990) introduced a pulse input of metals (Pb, Cr, Cu and Ni) on a column of aquifer sediments and found that metals were adsorbed to the surface of the turbidity-causing colloids.

Several field studies have also shown the association of contaminants such as transition metals (Mn and Co) and radionuclides of Co, Zr, Ru, Cs, Ce and Eu with inorganic colloids recovered from ground water inside a nuclear detonation cavity and from contaminant plumes (Penrose *et al.*, 1990; Buddemeier and Hunt, 1988). In a few instances, contaminants associated with colloidal particles have been recovered from monitoring wells much further from the input source than models and laboratory sorption experiments predicted (e.g., Walton and Merritt, 1980). Unfortunately there is no clear demonstration that the contaminants migrate by attaching to mobile colloids. Sorption experiments have demonstrated that colloids are capable of associating with many metals, radionuclides and hydrophobic organic contaminants (Penrose *et al.*, 1990; Vilks and Degueldre, 1991; Puls and Powell, 1992). However, simulations of colloid-facilitated transport (Mills *et al.*, 1991) suggest that information on the affinity, kinetics and reversibility of that association is critical to evaluating the significance of transport. This information is largely unavailable for ground water particles.

Mills *et al.*, (1991) illustrated the general complexity of metal-colloid interactions in a ground water system where both organic and inorganic colloids are likely to be present (Figure 1.1). Generally, there appears to be a consensus among researchers that the same types of processes are operative between metal-colloids and metal-immobile solids (Stumm, 1977; James and Parks, 1982). Dissolved metal species (shown within the dashed lines in Figure 1.1) can interact with either dissolved or colloidal materials to produce both mobile and immobile complexes. Five types of colloids are shown to interact with metals, namely; clay colloids, oxides and hydroxides of iron and other elements, other mineral colloids, organic colloids and precipitated colloids that form when a supersaturated aqueous phase exists. For the latter, metals can both be occluded within the colloid as it grows (coprecipitate), or participate in surface reactions.

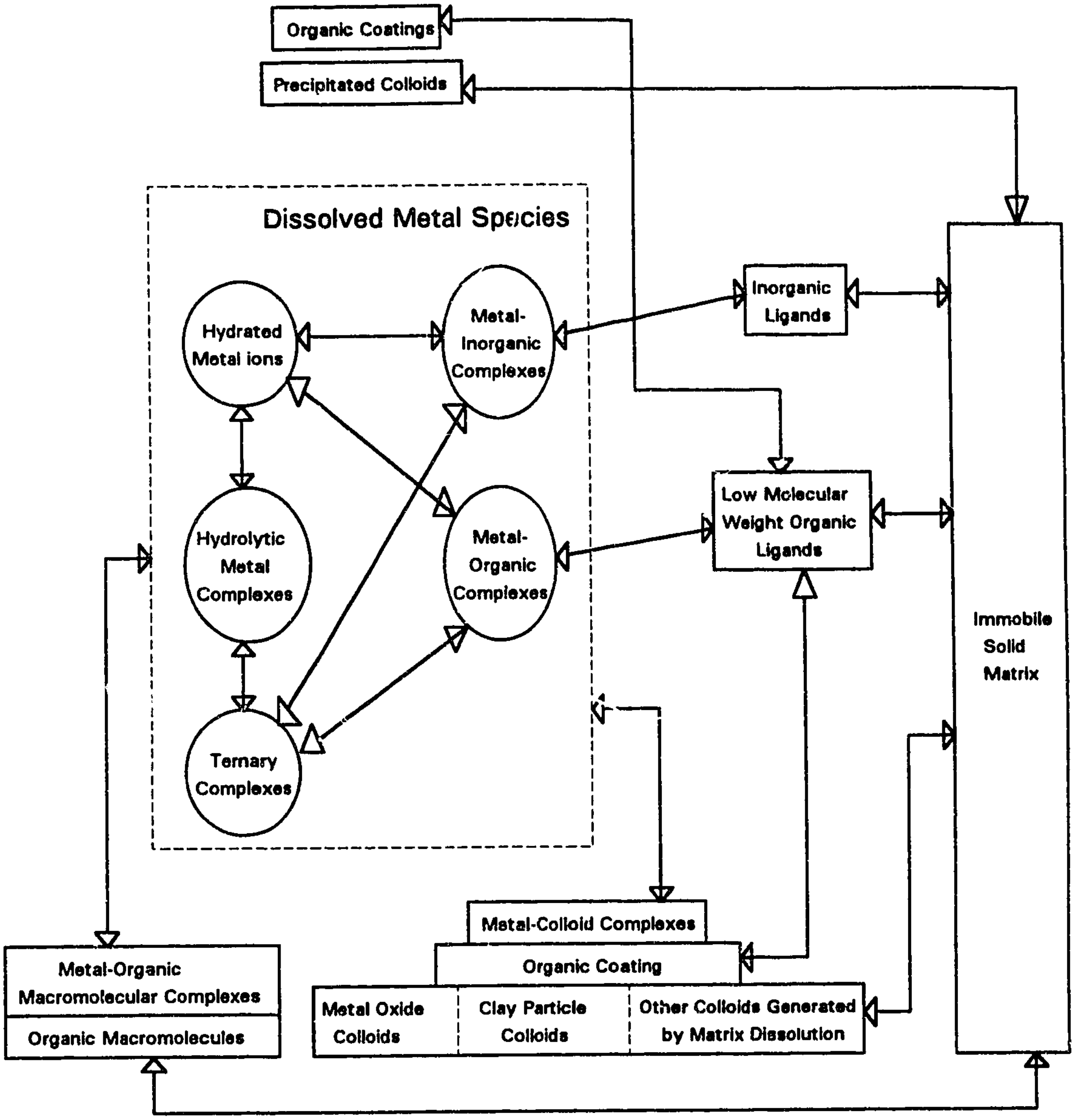

Figure 1.1 Metal speciation in subsurface environment, with consideration of colloids interaction (after Mills *et al.*, 1991)

1.2.3 Colloid stability

As already established, colloids are mobile in some subsurface environments. This mobility is controlled by the stability of the colloids in ground water and the chemical interactions between colloids and immobile matrix surfaces, as by hydrological factors that control flow rates and flow paths of ground water (McCarthy and Degueldre, 1993). To be mobile, over significant distances, a colloidal particle must be in suspension, and must avoid filtration (i.e., physical entrapment by the immobile aquifer media). The stability of colloids in ground water depends on colloid-colloid and colloid-media interaction energy (McDowell-Boyer, 1986; Lyklema, 1978; O'Melia, 1990). Whether particles will be stable, aggregated, filtered or settle in ground water depends on a complex combination of density, size, surface chemistry, water chemistry and water flow rates. The complicated interdependence of these factors makes it difficult to predict particle behavior. General concepts for qualitative assessment of these interactions, however are well established (McCarthy and Zachara, 1989).

Colloidal particles and immobile material in aquifers often possess surface charges controlled by ionizable surface groups such as hydroxyl and/or carboxyl groups. Changes in aqueous chemistry may cause aggregation of colloidal particles or favor the attachment to the aquifer media. Destabilization due to compression of the double layer surrounding particles can occur by increased counterion concentrations (Khilar and Fogler, 1984; Cerda, 1987, Newman, 1990), by pH-induced changes in surface charge (Kia *et al.*, 1987), or by the presence of strongly binding ions that decrease the net surface charge (James and Healy, 1972). Conversely, transport of colloids through porous media columns is enhanced by conditions promoting the colloidal stability of particles. For example, low ionic strength of the eluting solution increases the mobility of latex microspheres (McDowell-Boyer, 1989; Tobiason and O'Melia, 1988; Toran and Palumbo, 1992), montmorillonite (Vinten and Nye, 1985), hematite (Puls and Powell, 1992) and natural soil colloids (Newman, 1990). Likewise increased pH (above pH_{zpc} of colloid), or the presence of sorbing ions such as arsenates and phosphates at lower pH's can electrostatically stabilize colloids and promote their transport through negatively charged porous media (Newman, 1990; McDowell-Boyer, 1989; Puls and Powell, 1992; Liang and Morgan 1990; Champlin and Eichholz, 1976).

Changes in aqueous chemistry can also disperse and remobilize trapped particles. For example, McDowell-Boyer (1989, 1992) found that lowering ionic strength of water solutions promoted the mobilization of latex microspheres previously deposited on a column. In an artificial recharge site studied in California, clay colloids were dispersed from surface soil during recharge by an aqueous solution of low ionic strength. However, addition of gypsum at the recharge area to increase the ionic strength of the recharge water prevented the release of clays from aggregates (Nightingale and Bianchi, 1977).

When particle-particle and/or particle-media attachment are energetically favorable, deposited particles will accumulate on media surfaces, decreasing porosity and thereby causing a decrease in media permeability. This results in a decrease in the mean ground water flow rate. Large changes in permeability of aquifers have been observed when the electrolyte concentration of pore water was altered (Goldenberg *et al.*, 1983, 1984; Hardcastle and Mitchell, 1974). This coupling between particle deposition and associated permeability reduction is important to the transport of both colloid-associated and dissolved contaminants.

As McCarthy and Zachara (1989) pointed out, the destabilization of suspended colloids in ground water due to increase in ionic strength or equivalent fraction of Ca^{2+} over Na^{+}, or through strong ion adsorption, does not necessarily mean that they will be rendered immediately immobile. Coagulation kinetics is complex, and electrostatic interactions that occur during particle collations are not well understood (O'Melia, 1990). These interactions are a function of many variables, including particle size, and particle size distribution, all of which can influence the extent of particle-particle collisions in the ground water. Moreover, destabilized colloids in ground water still may be transported as aggregates if the aggregates are sufficiently small compared to the pore diameters.

1.3 PARTICLE MIGRATION STUDIES

Models developed for sand filters can be used successfully to describe the dynamics of subsurface particle migration (Yao *et al.*, 1971), provided that certain restrictions, such as homogeneity of porous media, are imposed (McDowell-Boyer, 1989). Parameter values representative of natural the environment rather than filtration conditions need to be specified.

The filtration theory may be useful in studies involving sandy aquifers of relatively well sorted porous material but its use in other aquifers may not be appropriate especially in media of unevenly distributed macropore space. In fact there is considerable field data suggesting that transport of colloids can occur very rapidly and over long distances in at least some locations (McCarthy and Degueldre, 1993). The mechanism of transport in these cases may involve travel through highly transmissive zones of preferred flow paths such as fractures, solution channels, or soil macropores that can greatly enhance transport and reduce retention of particles. Pilgrim and Huff (1983) attributed the rapid movement of layer silicates and organic matter through the vadose zone during storm events in the field to transport through macropores. Toran and Palumbo (1992) examined the role of fractures on particle transport and simulated fractures by inserting small (0.2- or 1 mm-diameter) tubes into a sand column. The "fractures" significantly increased the transport (i.e., decreased retention) of latex microspheres and bacteria.

While there is ample evidence that ground water colloids are able to bind contaminants and may be mobile in aquifers, much of the information specific to ground water colloids is more anecdotal than systematic. Thus, it is insufficient to reliably evaluate the significance of colloids as vectors or to develop predictive capability. For colloid-contaminant-interaction involving a rapid and reversible linear association, the transport of the contaminant could only be slightly faster in the presence of colloids. As the advancing front of colloids arrives at "clean" portions of the aquifer, the contaminant would be stripped from the mobile colloids due to desorption and rapid reequilibration with sorption sites on the aquifer matrix (McCarthy and Degueldre, 1993). Continued migration of the "stripped" colloids has little effect on the contaminant mobility (Mills *et al.*, 1991). However, for a more complex model incorporating rapid but irreversible association, mobile colloids could significantly accelerate contaminant migration; the transport of the contaminant would then be strongly dependent on the extent of colloid-aquifer media interaction.

1.4 OVERALL OBJECTIVES AND SCOPE OF WORK

Current scientific understanding is not adequate to allow accurate prediction of the effects of mobile colloids on contaminant transport. There is a need to develop an understanding of processes controlling the extent and especially the kinetics of association and dissociation of different types of colloids with metals, radionuclide and organic contaminants, at a fundamental level, before the combined influence of ground water chemistry, porous media lithology, and hydrology on colloid occurrence and behavior can be generalized to a predictive level. As McDowell-Boyer (1989) indicated, predictability of a process ultimately lies in the understanding of fundamental mechanisms. Furthermore, the effect of temporal or spatial changes in aqueous chemistry and aquifer surface properties along a flow path on the transport of contaminants needs to be assessed.

In view of the above literature and findings we set out to investigate and develop an understanding of the enhanced transport of contaminants as a result of sorption and cotransport on mobile colloids (i.e., to examine the potential role of colloids in migration of highly adsorbed contaminants). The study involved investigating the role of the mobile inorganic colloids in transport through porous media under controlled laboratory conditions. Colloid transport was compared with solute transport and a simple model was developed to the significance of colloid-facilitated contaminant transport in a controlled environment.

Factors that are likely to influence colloidal transport include, ionic strength, electrolyte composition, flow rate, quantity, nature and size of suspended colloids, geologic composition and structure, and ground water chemistry. Because of the complexity of these factors in influencing colloidal transport, experimentation requires isolation of factors by allowing variation of only one or two parameters between experiments; those parameters being the ones identified as critical to the mechanism of interest. Previous studies have shown that ionic strength and flow rate are important factors in colloid transport. In addition the extent of colloid-facilitated contaminant transport will also be determined by the type and concentration of the colloids.

Therefore, the scope of this study was limited to examining the effect of sorption on the transport of inorganic contaminants. The purpose was to establish the basis for the significance of colloids in contaminant transport and carry out a preliminary development of a transport model that can be extended in future studies. The influence of other factors such as ionic strength, electrolyte composition and colloid concentration on the transport of contaminants by colloids, have not been directly examined. No test for suitability of extending filtration theory to colloid transport was done as this has been studied elsewhere (e.g., McDowell-Boyer, 1989).

1.5 HYPOTHESIS

Colloids enhance transport of contaminants through coarse aquifer material. Therefore, inclusion of colloidal transport in describing contaminant transport through porous media is important.

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CHAPTER TWO

MODEL FOR COLLOID FACILITATED TRANSPORT IN SAND PACKED COLUMNS

2.1 INTRODUCTION

The fate of many pollutants in the subsurface environments may be influenced by the particulate matter with which they are associated. Association of contaminants with mobile colloidal particles may enhance the transport of strongly sorbing pollutants. Furthermore, mobile metals and radionuclides may themselves form mobile colloidal-sized precipitates. Current approaches to monitoring and predicting solute transport generally ignore colloid-facilitated transport mechanisms because of lack of enough information on the abundance and distribution of colloidal particles in ground water, their affinity to bind contaminants and their mobility in subsurface systems (McCarthy and Wobber, 1988).

Approaches to modeling colloid-facilitated transport have been based on the filtration models. These models are based on particle removal rather than mobilization, and consider a 'clean' bed or medium. In modeling colloid facilitated transport, particle mobilization is important. The effect of mobile colloids on contaminant migration cannot be predicted accurately if mobilization is not considered, as it is affected by changes in pore water chemistry.

As McCarthy and Zachara (1989) indicated, empirically, the colloid interaction may be integrated into a distribution coefficient (based on solute transport) between the mobile and immobile phase, thus decreasing the retardation factor. This approach is believed to be applicable in hydrophobic contaminants that show linear adsorption. McCarthy and Zachara (1989) have suggested that this approach is not appropriate for most inorganic solutes because they exhibit nonlinear sorption. It can be argued however, that inasmuch as solute transport based models can be used to predict nonlinear adsorption, so can the colloids' contribution be accounted for from these models. Nevertheless, in this study, linear adsorption approach was used to develop the basis for the significance of colloidal particles in transport of contaminants.

In this Chapter, the objective is to develop a simple conceptual model for describing contaminant and colloid transport. The model combines theories that describe transport of solutes and colloids, and is used to illustrate the effects of colloids on solute transport. The solution of the model will be presented and evaluated in Chapter 4.

2.2 MODEL DEVELOPMENT

2.2.1 Colloid transport

Suspended colloidal particles are carried along as water moves in porous media. As suspended colloids move through the porous media, they may collide with the surface of the solid phase and subsequently be retained by the solid matrix. They may also break away and become resuspended, or mobilized (Amirtharajah, 1988; McDowell-Boyer, 1989; 1992)

Most studies of colloid transport have been based on filtration theory. Filtration generally involves two processes, viz., transport of particles to the solid-liquid interface and attachment of the particles to the surface. Filtration studies emphasize particle removal from solution. They have not addressed mechanisms for particle remobilization back into the solution. Remobilization can be important in natural subsurface media due to aqueous chemistry changes. For example, remobilization has been observed in the unsaturated zone due to rainfall (Mills and Liu, 1989).

The potential transport mechanisms are described as diffusion, sedimentation, interception, inertia, and advection (Ives, 1970). It is generally accepted that for particles less than one micron in size, under the conditions of filtration, the dominant mechanism in colloid transport is diffusion, which is transport resulting from random Brownian motion by bombardment of the particles by water molecules (Amirtharajah, 1988). For particles greater than one micron, diffusion, sedimentation and interception are dominant.

Based on Amirtharajah (1988), a mass balance equation for particles moving in a column, and for particles attached to immobile bed, can be represented by the following equation

$$\frac{\partial \sigma}{\partial t}+\frac{\partial\left[C_c(\theta-\sigma/\rho_s)\right]}{\partial t}=-\frac{\partial J_c}{\partial x} \qquad (2.1)^1$$

Where σ is mass of particles deposited per total volume, t is time, θ is porosity or water content when the porous media is saturated, ρ_s is particle density J_C is colloid flux, C_C is colloid concentration and x is the distance in flow direction.

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[1] For explanation on notation see end of the Chapter

Assuming, that $\frac{\sigma}{\rho_s} << \theta$, and that in saturated media θ is constant so that $\frac{\partial\theta}{\partial t} = 0$, then Equation (2.1) becomes

$$\frac{\partial\sigma}{\partial t} + \theta\frac{\partial C_c}{\partial t} = -\frac{\partial J_c}{\partial x} \tag{2.2}$$

But the colloid flux can be represented by

$$J_c = -D_c\frac{\partial C_c}{\partial x} + qC_c \tag{2.3}$$

where q is specific discharge and D_c is colloid dispersion coefficient.

The hydrodynamic dispersion term $(-D_c\frac{\partial C_c}{\partial x})$ in Equation (2.3) has often been neglected in filtration studies on the basis that the diffusion coefficient of the suspended particles are negligibly small. However, D_c describes the combined effect of particle diffusion and mechanical dispersion. Although the diffusion coefficient of colloidal particles may be small, the magnitude of mechanical dispersion may still be significant. D_c is mainly a function of bed characteristics and flow dynamics. Assuming that colloids will experience the same hydrodynamic forces as the solute and based on Dullien (1979)'s suggestion the dispersion coefficient, D_c, can be estimated from

$$D_c = \mu D_0 + \frac{\varepsilon d_m}{1 + \gamma D_0 / d_m v} v \tag{2.4}$$

where D_0 is molecular diffusion coefficient of solute in water, d_m is effective average particle diameter of bed, v is average pore water velocity (or Darcy velocity) and μ, ε and γ are dimensionless coefficients depending on the pore geometry of the porous medium packing and flow dynamics. $\mu = 1/\tau$ where τ = tortuosity, and is always greater than 1. For colloidal particles, $D_0 \cong 0$ since colloids do not behave like solutes, so that $D_c = \varepsilon d_m v$ where εd is often called the dispersivity of the porous media. The average values reported for μ , ε and γ are 0.7, 1 and 10, respectively. The values of μ , ε and γ (longitudinal) reported for irregular packing are 2.5 and 8.8 respectively.

Substituting Equation (2.3) into (2.2) yields

$$\frac{\partial \sigma}{\partial t} + \theta \frac{\partial C_c}{\partial t} = D_c \frac{\partial^2 C_c}{\partial x^2} - q \frac{\partial C_c}{\partial x} \tag{2.5}$$

In Equation (2.5), the first term can be represented as

$$\frac{\partial \sigma}{\partial t} = K\sigma H - \lambda C_c v \tag{2.6}$$

where K is an empirical coefficient representing mobilization rate coefficient, H is the hydraulic gradient (*q/Knocked*) and λ is the filtration coefficient. Equation (2.6) is an expression that accounts for both attachment and detachment. The first term in Equation (2.6) represents retention rate and the second term mobilization rate of particles. The rate of mobilization of particles can be represented by (Amirtharajah, 1988),

$$g = K\sigma H \tag{2.7}$$

The retention of colloidal particles by the solid phase of the porous media has been treated extensively in filtration studies (Herzig *et al.*, 1970; Younos and Smolen, 1983; McDowell-Boyer *et al.*, 1986; Tobiason and O'Melia, 1988). The retention of suspended particles is generally described by

$$f = -\lambda C_c v \tag{2.8}$$

The substitution of Equation (2.6) into (2.5) yields

$$\theta \frac{\partial C_c}{\partial t} = D_c \frac{\partial^2 C_c}{\partial x^2} - q \frac{\partial C_c}{\partial x} - K \sigma H + \lambda C_c v \tag{2.9}$$

The filtration coefficient, λ, represents the probability that a colloidal particle will be attached to the surface of the porous matrix per unit time. Attachment of colloidal particles to the solid matrix is a function of specific surface area of the porous media and interactions between colloids and solid surfaces. Factors that determine particle-surface interactions include particle size, density and surface charge.

Yao *et al.*, (1971) derived an expression for the filtration coefficient in porous media,

$$\lambda = \frac{3}{4} \alpha \eta \frac{(1-\theta)}{a} \tag{2.10}$$

where a is the grain radius, α is attachment coefficient and η is the hitting probability.

The terms α and η describe the kinetics of the deposition of suspended particles. The attachment coefficient, or sticking probability, α is the rate at which particles attach to the collector surface divided by the rate at which particles strike the collector surface. $(1-\theta)/a$ is directly related to specific surface area of the bed. The collectors are the matrix particles.

The hitting probability or single collector efficiency, η, is defined as the total rate at which particles strike a single collector (particles per time) divided by rate at which particles approach the collector per projected area (particles per time). η is a function of Brownian motion, interception and gravitational settling or sedimentation. Mills and Liu (1989) calculated typical values for conditions that correspond to ground water flow through a sandy aquifer, and these are shown in Table 2.1.

Table 2.1 Collector efficiencies through a packed bed for conditions simulating ground water flow through a sandy aquifer (adapted from Mills and Liu, 1989).

Particle Diameter		*Collector Efficiencies (η)
µm	**cm**	
0.001	**10^{-7}**	**3.00**
0.01	**10^{-6}**	**0.64**
0.1	**10^{-5}**	**0.14**
1.0	**10^{-4}**	**0.33**

*** Calculations were based on interstitial velocity of 0.091 cm/min. (100m/yr., particle density of 2.65 g/cm^3 and a temperature of 15 °C)**

Equation (2.9) was developed for σ that accounts for mobilization or detachment. However, most researchers do not consider detachment mechanisms, but instead consider only deposition because they are involved with clean bed studies. In this study, mobilization and retention of particles are concidered.

2.2.2 Solute Transport

Two mechanisms for solute movement are used in modeling solute transport through porous media: mass flow (or advective flow) and diffusion. The movement of water through the pore space carries dissolved solutes with it. This mechanism is called mass flow or advection. The dispersion or migration through pore water of a dissolved substance from areas of high concentration to areas of low concentration is called diffusion.

As already discussed in Chapter 1, solute transport studies consider contaminant transport as a two phase system, the mobile aqueous phase and the immobile solid phase. The contaminant may be adsorbed by the matrix and thus assumed to be retarded relative to flow rate of the pore water. Adsorption onto moving colloids is not accounted for in solute transport models.

In the absence of mobile colloids, dissolved solute flux is given by

$$J_{s,d} = -D_s \frac{\partial C_s}{\partial x} + q C_s \tag{2.11}$$

where, $J_{s,d}$ is dissolved solute flux, C_s is solution-phase solute concentration, D_s is solute diffusion-dispersion coefficient.

For steady state water flow conditions, the general one-dimensional convective-dispersive transport equation, considering mass balance of solute in a representative elementary volume, is given by

$$\theta \frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} - q \frac{\partial C_s}{\partial x} - \frac{\partial S}{\partial t} \tag{2.12}$$

where, S is sorbed phase solute concentration. D_s is described by an equation similar to Equation (2.4) with $D_0 > 0$.

2.2.3 Co-transport (colloid-facilitated transport) of contaminants

When colloidal particles are stable, they do not deposit on collector (matrix) surfaces, they migrate in the aqueous phase and carry colloid-surface reactive contaminants on them (Jiang and Corapcioglu, 1993). However, when they are unstable, they deposit and attach to solid surfaces. Co-transport of contaminants refers to enhanced transport of contaminants by adsorbing onto moving colloids. The proposed model shown in Figure 2.1 is adapted from the kinetic framework for a transport model that accounts for colloid-facilitated transport developed by Mills et al. (1991).

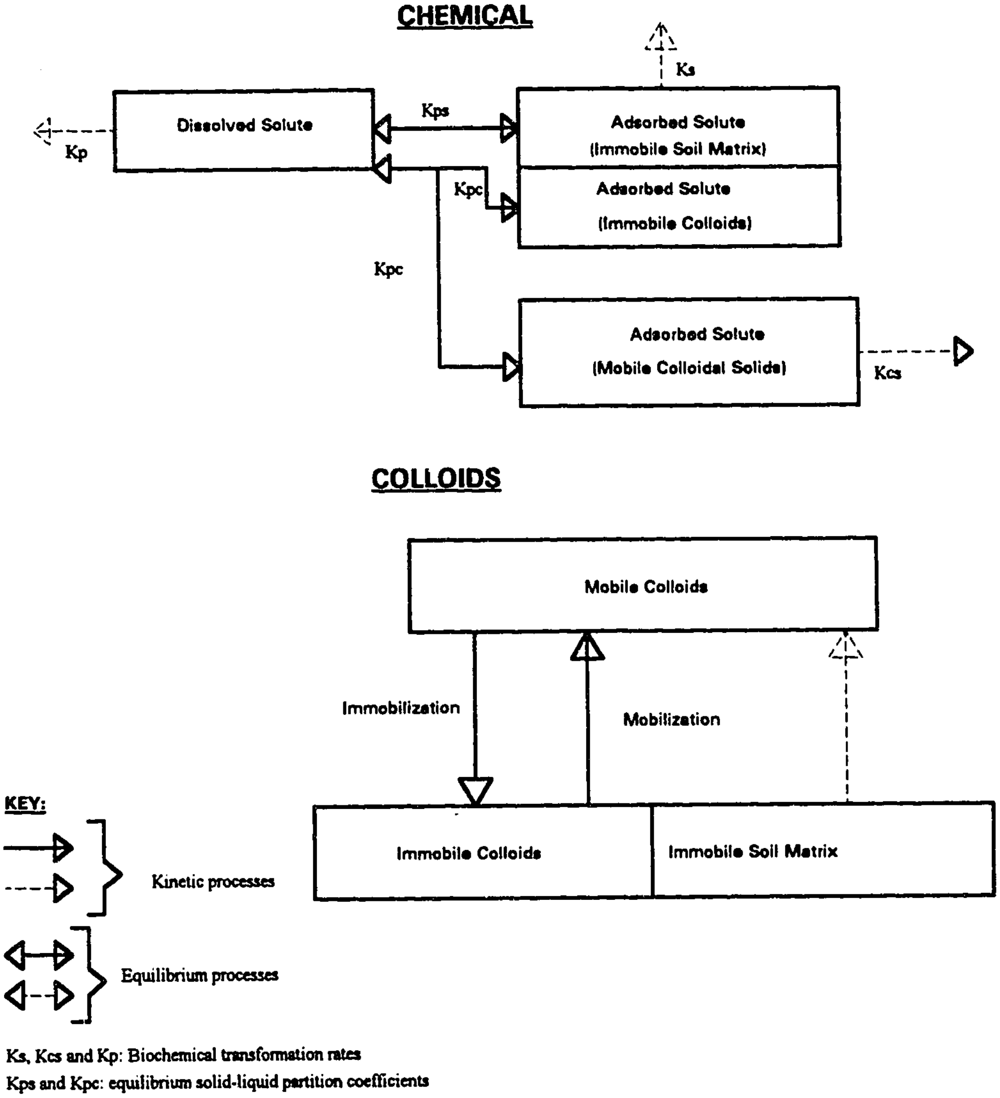

Figure 2.1. Kinetic framework for transport models that account for colloid-facilitated transport (adapted from Mills *et al.*, 1991)

From Figure 2.1 it can be seen that the colloid migration model is based on a conceptualization of the problem as a three-phase medium. Mobile and immobile colloids interactions are included with the porous solid matrix in a three-phase co-transport model. The contaminant can be present in any (or all) phase(s), namely, the dissolved phase, solid matrix phase and colloidal particles, both mobile and immobile. The major assumptions used in developing the model include: (a) that there is equilibrium adsorption between the dissolved and colloidal phases, (b) colloids occupy the same pore volumes as dissolved species, and (c) colloid velocity may differ from dissolved solute velocity.

Assuming a linear adsorption isotherm, the total solute mass in a given volume of the medium can be given by

$$m_s = \theta\, C_s + K_{p_c}(\theta\, C_c + \sigma)C_s + K_{p_s}\,\rho_b C_s. \tag{2.13}$$

The first term on the right hand side of Equation (2.13) represents the dissolved solute, the second term represents adsorption by the suspended colloids and retained colloids and the last term shows the adsorption by the matrix. Rearranging (2.13) we get

$$m_s = \theta C_s + K_{p_c}(\theta C_c + \beta)C_s \tag{2.14}$$

where $\beta = \sigma + \dfrac{K_{p_s}}{K_{p_c}}\rho_b$

Differentiating Equation (2.14),

$$\frac{\partial m_s}{\partial t} = \theta\frac{\partial C_s}{\partial t} + K_{p_c}(\theta C_c + \beta)\frac{\partial C_s}{\partial t} + K_{p_c} C_s \frac{\partial(\theta C_c + \beta)}{\partial t}$$

$$= \left\{\theta + K_{p_c}(\theta C_c + \beta)\right\}\frac{\partial C_s}{\partial t} + K_{p_c} C_s \frac{\partial(\theta C_c + \beta)}{\partial t} \tag{2.15}$$

By mass balance, the total solute mass can be given by

$$\frac{\partial m_s}{\partial t} = -\frac{\partial J_{s,d}}{\partial x} - \frac{\partial J_{s,c}}{\partial x} \tag{2.16}$$

where the dissolved solute flux, $J_{s,d}$, is given by Equation (2.11), and the solute flux carried by colloids by

$$J_{s,c} = K_{p_c} C_s J_c , \tag{2.17}$$

where the colloid flux, J_c, is given by Equation (2.3)

Differentiating Equations (2.11) and (2.17) gives

$$-\frac{\partial J_{s,d}}{\partial x} = D_s \frac{\partial^2 C_s}{\partial x^2} - q\frac{\partial C_s}{\partial x} \tag{2.18}$$

$$-\frac{\partial J_{s,c}}{\partial x} = -J_c \frac{\partial C_s}{\partial x} K_{p_c} - C_s \frac{\partial J_c}{\partial x} K_{p_c} \tag{2.19}$$

From Equation (2.2)

$$-\frac{\partial J_c}{\partial x} = \frac{\partial(\theta C_c + \sigma)}{\partial t} \tag{2.20}$$

Therefore, from Equations (2.19) and (2.20),

$$-\frac{\partial J_{s,c}}{\partial x} = -J_c \frac{\partial C_s}{\partial x} K_{p_c} - C_s \frac{\partial(\theta C_c + \sigma)}{\partial t} K_{p_c} \tag{2.21}$$

Combining Equations (2.15), (2.16), (2.18) and (2.21) leads to

$$\left\{\theta + K_{P_c}\left(\theta C_c + \beta\right)\right\}\frac{\partial C_s}{\partial t} + K_{P_c} C_s \frac{\partial\left(\theta C_c + \beta\right)}{\partial t}$$

$$= D_s \frac{\partial^2 C_s}{\partial x^2} - q\frac{\partial C_s}{\partial x} - J_c K_{P_c}\frac{\partial C_s}{\partial x} + C_s K_{P_c}\frac{\partial\left(\theta C_c + \sigma\right)}{\partial t} \tag{2.22}$$

Simplifying Equation (2.22) and noting that

$$\beta - \sigma = \frac{K_{P_s}}{K_{P_c}}\rho_b \tag{2.23}$$

does not change with time, i.e. $\frac{\partial(\beta - \sigma)}{\partial t} = 0$, Equation 2.22 yields

$$\left\{\theta + K_{P_c}\left(\theta C_c + \beta\right)\right\}\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} - \left(q + J_c K_{P_c}\right)\frac{\partial C_s}{\partial x} \tag{2.24}$$

Division by θ gives

$$\left\{1 + K_{P_c}\left(C_c + \frac{\beta}{\theta}\right)\right\}\frac{\partial C_s}{\partial t} = D_e \frac{\partial^2 C_s}{\partial x^2} - \left(v + v_c C_c K_{P_c}\right)\frac{\partial C_s}{\partial x} \tag{2.25}$$

where, D_e is the effective dispersion (D_s/θ), the colloid velocity, $v_c = J_c / C_c\theta$ and Darcy velocity $v = q/\theta$. The retardation factor that accounts for colloids is given by

$$R_c = 1 + K_{P_c}\left(C_c + \frac{\beta}{\theta}\right) = 1 + \frac{K_{P_c}\sigma + K_{P_s}\rho_b}{\theta} + \frac{K_{P_c} C_c}{\theta} \tag{2.26}$$[2]

In the absence of colloids Equation (2.26) becomes

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[2] For explanation on notation see end of the Chapter

$$R = 1 + \frac{K_{p_s} \rho_b}{\theta} \tag{2.27}$$

Since Equation (2.9) is independent of Equation (2.12), it can be solved independently to obtain C_c. Then Equation (2.25) can be solved to obtain C_s.

The effective velocity, v_e, of the contaminant is represented by

$$v_e = \frac{v + v_c K_{p_c} C_c}{R_c + K_{p_c} C_c} \tag{2.28}$$

In Equation (2.28) when $C_c = 0$, R_c becomes R. The effective velocity is neither the velocity of dissolved phase nor the velocity of the colloids. The equation can be evaluated to compare the effective contaminant transport velocity with and without the influence of colloids.

In addition to the effective velocity, Equation (2.25) can be used to determine the fraction of total chemical that is mobile:

$$m_f = \frac{1 + K_{p_c} C_c}{R_c + K_{p_c} C_c} \tag{2.29}$$

where m_f is the fraction of mobile chemical. Equation (2.29) can be compared to the situation where $C_c = 0$ to determine whether the presence of colloids influence the total mobile phase concentration. The equations outlined above can be modified to include multiple colloidal, immobile and dissolved phases.

The presence of colloids should reduces the retardation factor and increase the effective velocity. The amount of contaminant depends on K_{ps}, K_{pc} and C_c.

2.3 CONCLUSIONS

Suspended colloidal particles may be important component in describing contaminant migration. Association of colloids with contaminants could enhance the migration of chemicals. The presence of colloids reduces the retardation factor and increases the effective velocity. Therefore, neglecting colloidal mobility in predictive contaminant transport models may underestimate both transport rate and mass flux (Puls and Powell, 1992) of contaminants.

Having established the development of the model, the following Chapter covers the results of experiments to determine the effects of colloids on contaminant transport. The solution of the model is covered in Chapter 4.

2.4 NOTATION

a = grain radius of bed/matrix(L)

α = attachment coefficient or sticking probability

$\beta = \sigma + \frac{K_{p_s}}{K_{p_c}} \rho_b$

η = collector efficiency

λ = filter coefficient

σ = mass of particles deposited/total volume (M/L^3)

θ = porosity or water content in saturated condition (fraction)

ρ_b = bulk density (mass of solids/total vol.) (M/L^3)

ρ_s = density of colloidal particles, mass of solids / volume of solids

C_c = colloid concentration. (M/L^3)

C_s = solution-phase solute concentration (M/L^3)

d_m = effective average particle diameter (L)

D_c = dispersion coefficient for colloids (L^2/T)

D_e = effective diffusion-dispersion coefficient (L^2/T)

D_s = diffusion-dispersion coefficient (L^2/T)

D_o = molecular diffusion coefficient of solute in water (L^2/T)

f = retention rate of colloids

g = mobilization rate of colloids

H = hydraulic gradient ($= q/K_{cond}$)

J_c = colloid flux per unit area per unit time

$J_{s,c}$ = Solute flux carried by colloids per unit area per unit time

$J_{s,d}$ = Dissolved solute flux per unit area per unit time

K_{cond} = hydraulic conductivity (L/T)

K = mobilization rate coefficient

μ, ε, γ = empirical coefficients

K_{ps}, K_{pc} = concentration dependent partition or distribution coefficients for immobile and mobile solid phases, respectively (L^3/M)

m_f = mobile fraction of the total

q = specific discharge or Darcy flux (L/T)

R_c = retardation factor with colloids

R = retardation factor without colloids

S = sorbed phase solute concentration (M/M)

t = time (T)

v = average pore water velocity or Darcy velocity [$v = q/\theta$] (= velocity of dissolved component) (L/T)

v_c = velocity of colloid components(L/T)

v_e = effective velocity(L/T).

x = distance in flow direction (L)

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CHAPTER THREE

THE EFFECT OF COLLOIDS ON CONTAMINANT TRANSPORT IN SAND PACKED COLUMNS

3.1 INTRODUCTION

As described in the previous Chapter, the two-phase system of describing contaminant transport may be inadequate due to the presence of a third phase (the mobile solid phase), colloid-facilitated transport which may account for a substantial amount of contaminant transport through aquifer material. This mechanism of contaminant transport has not been studied as extensively as the solute transport, and yet some studies have shown that it does play an important role in the transport of contaminants (Puls and Powell, 1992; Chung and Lee, 1992; Mills *et al.*, 1991; Vinten *et al.*, 1983). Industrial wastes are an issue of concern to the public due to the high levels of toxic heavy metals that they contain. One such heavy metal is lead (Pb) which is found in higher concentrations in sewage sludge treated soils (McBride, 1994) than in most natural soils. The health concern with Pb polluted soils arises mostly from the intake of soil by humans and grazing animals. It is possible that Pb may find its way into the groundwater supplies. Understanding transport of Pb through the subsurface is therefore, important in risk assessment.

In the light of the above, and given the complexity associated with colloid transport determinations, we set out to investigate the role of colloidal particles in transport of Pb using column and batch experiments. In order to estimate the concentration of lead (Pb) in the column transport experiments, it was necessary to conduct batch sorption experiments. This was done to ensure that Pb concentration remains measurable after sorption onto montmorillonite, and also to get some estimate of adsorption coefficients. The experiments were also used to determine the effect of ionic strength (or electrolyte concentration) on Pb sorption by montmorillonite. The effect of electrolyte concentration on colloid transport was not determined because of time factors.

3.2 MATERIALS AND METHODS

3.2.1 Experimental set - up

Figure 3.1 illustrates the overall scheme of the experimental set-up. Particle suspension, deionized water, lead or bromide were fed to the system via 20L carboys. These solutions were fed to the sand columns via a peristaltic pump (Spectra/Chrom™ microflow pump from Spectrum).

Tubing used in all lines from the carboys to about 30 cm just before the sand column was 3.2 mm (1/8 in) inside diameter (ID) Nalgene tubing (from Fisher Scientific). This type of tubing was chosen for its translucence and flexibility. The tubing immediately upstream and downstream of the sand column was 1.6 mm (1/16 in) ID tubing supplied with the columns. The glass columns were Kontes Chromaflex® from Fisher Scientific. Column assembly and end-fittings are shown in Figure 3.1.

The tubing before the pump was branched leading to solution/suspension carboy and water carboy for washing and saturating the column. Clamps were used to control which solution from the carboys was to flow toward the column from upstream. A fraction collector was used in the timed mode to collect fractions at two minutes intervals.

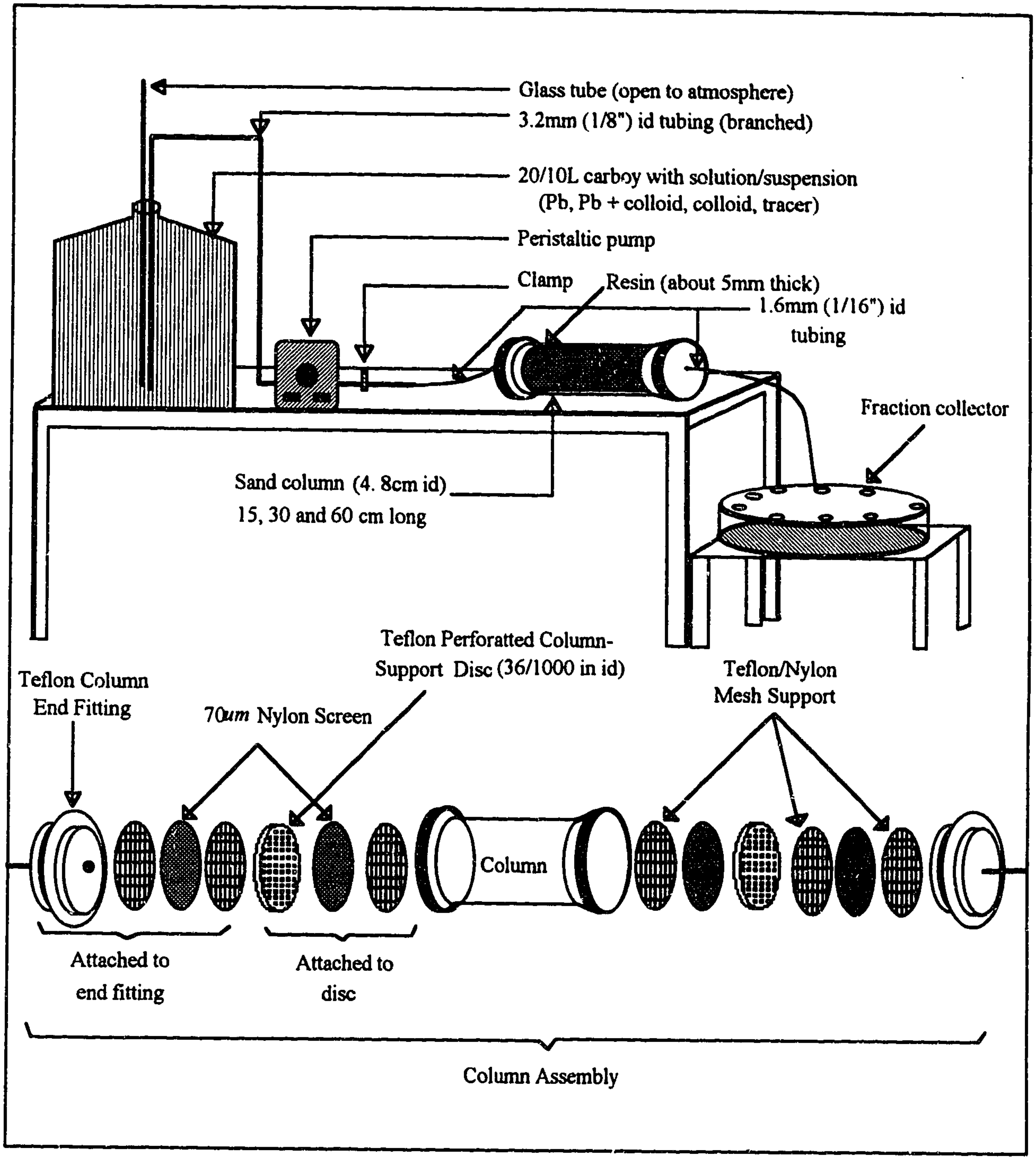

Figure 3.1 Overall scheme of the experimental set up

3.2.2 Materials

3.2.2.1 Solutions and particle suspension

Colloidal particles used were Wyoming bentonite (montomorillonite). Montmorillonite was chosen because of its high sorptivity, and it has been identified as a component of particles that is likely to be obtained in aquifers. The fraction of montmorillonite <1μm in size was prepared by allowing larger particles to settle down in the clay suspension, as calculated from Stoke's law, and then decanting the <1μm particles remaining in suspension. The Na-montmorillonite was prepared by saturating the colloidal fraction with 0.5M NaCl. This treatment was repeated three times. The clay was then washed with deionized water and separated in a high speed centrifuge until the equilibrium solution was free of chloride. Chloride was presumed to be absent when the supernatant liquid tested negative with $AgNO_3$. The treated fraction was then freeze-dried, ground and stored.

NaBr was used for tracer experiments and $(PbNO_3)_2$ was used as Pb source. $(PbNO_3)_2$ was chosen as Pb source for its availability and relatively high solubility (337.65g/100 cm^3).

3.2.2.2 Sand columns

The matrix used in all experiments was Ottawa sand, composed mainly of quartz and feldspars. In order to reduce the heterogeneity in size distribution, the sand was allowed to pass through a 420*μm* but retained on a 210*μm* sieve (i.e. it was 70-40 mesh). In order to enhance sorptivity of the matrix, a cation exchange resin (Amberlite® IR-50, 16-50 mesh) from Supelco - Chromatography products was added to the column, as indicated in Figure 3.1. The resin was added at the inflow point to minimize the effect on physical properties of the columns. The adsorbing medium was necessary to simulate conditions where the matrix retards or adsorbs the contaminants.

Preparation of the sand surface involved washing with deionized water by swirling approximately 1000g sand in a glass beaker (or flask), decanting the water and refilling with fresh water (MacDowell-Boyer, 1989). The procedure was repeated eight times or until conductivity remained fairly constant in the wash water. After cleaning, sand was poured into a tray and dried at 105°C for at least 24 hours. It was then stored in glass jars for at least two weeks before used being in the experiments.

A more rigorous cleaning of sand surface to remove organic coatings was not utilized to avoid altering the sand by dissolving more vulnerable minerals (MacDowell-Boyer, 1989).

Packing the column with sand required assembling one end of the column, stabilizing it vertically while sand was being poured in. The method was adapted from MacDowell-Boyer (1989). Initially an estimate of sand needed to pack a column of a given size was made based on the following equations:

$$\rho_b = (1-n)\rho_s, \tag{3.1}$$

and

$$\rho_b = M/V \tag{3.2}$$

where ρ_b is bulk density, n is porosity, ρ_s particle density, M is mass and V is volume of sand. A porosity of 0.40 is suggested as a reasonably stable pack for experimental purposes (Lade, 1972). Assuming a ρ_s of 2.645 g.cm^{-3} for the sand (Blake and Hartge, 1986), the desired bulk density obtained from Equation 3.1 was 1.59 g.cm^{-3}.

Packing of sand columns was done by pouring the entire estimated amount of dry sand from a constant height of 60 cm in one continuous stream with tapping at 10 cm intervals marked on the column. This required moving the beaker from which the sand was poured at a constant rate upward to ensure that the fall velocity of all sand grains was approximately the same through the column. This was accomplished by taping a 60 cm glass capillary tube to the bottom of a funnel, and keeping the bottom end of the tubing at the sand surface in the column as sand was poured through the funnel. For the last centimeter or so of the column, to avoid spilling over, sand was carefully poured and mounded, and the top screen was used to compress sand onto the column. The resultant packed column was connected to the tubing as shown in Figure 3.1 with minimum observable disturbance. The column was then saturated by feeding deionized water in a vertical position from bottom upwards to avoid bubbles. The resin was added by carefully removing about 5 mm depth from the inflow end of the column and fill with resin. Packing in this manner resulted in consistency. The bulk density ranged from 1.53 g.cm^{-3} to 1.63 g.cm^{-3} and porosity from 0.47 to 0.38. The slight increase in bulk density and decrease in porosity with column length could be attributed to increase in height of the column which resulted in some compaction.

3.2.3 Procedures

3.2.3.1 Sorption experiments

In sorption studies 5 ml aliquots of the clay suspension were adjusted to three electrolyte concentrations by adding NaCl (0.00, 0.004 and 0.01M NaCl). Appropriate volumes of distilled deionized water and $(PbNO_3)_2$ solution (0 to 50 ppm) were then added to give a final volume of 50 ml. The final colloid concentration was 90 mg/l. The solutions, contained in centrifuge tubes, were mixed for over 24h using a shaker.

After mixing, the tubes were centrifuged and filtered using Whatman paper #42 for Pb determination with Atomic Absorption Spectrophotometer (AAS). Measurements were made using an air-acetylene flame and appropriate resonance lines (217.0 nm for Pb). The amount of Pb adsorbed by the clay was calculated from the change in solution concentration. The loss of Pb from the change in solution was reported as amount adsorbed per unit mass of clay. It is assumed that the amount of Pb lost has been adsorbed, even though it may have been lost through other processes such as precipitation.

3.2.3.1 Column Transport experiments

Column transport experiments involved feeding Pb with or without montmorillonite suspension to the prepared sand columns under saturated conditions, and measuring the effluent particle and/or Pb concentration. Saturation of sand was attained by feeding the columns with deionized water from bottom up with the columns standing vertically to ensure that no bubbles occur in the column. The columns were then put horizontally during the experiments. Particle suspension and Pb solution continued to enter the system until about three pore volumes were introduced. For each experimental run, clamps were used to control the solution/suspension entering the system at time equal to zero.

Pb concentration was measured using an Atomic Absorption Spectrophotometer (IL - 751 AAS). Particle concentration was determined using a UV Spectrophotometer (SP1800 UV Spectrophotometer) with wavelength, slit and band width set to 250 nm, 02 mm and 0.6 nm respectively. Preliminary experiments were done to establish the wavelength at which maximum sensitivity occurs. This was established by first "scanning" all the wavelengths to obtain one at which maximum absorption occurs at various montmorillonite concentrations and matrix. The standards were then prepared in various matrix solutions representing conditions in which the experiments were going to be conducted. An example of the standards prepared is shown in Figure 3.2 Standards based on various colloid concentrations and solution matrix were tested to determine the reliability of the method.

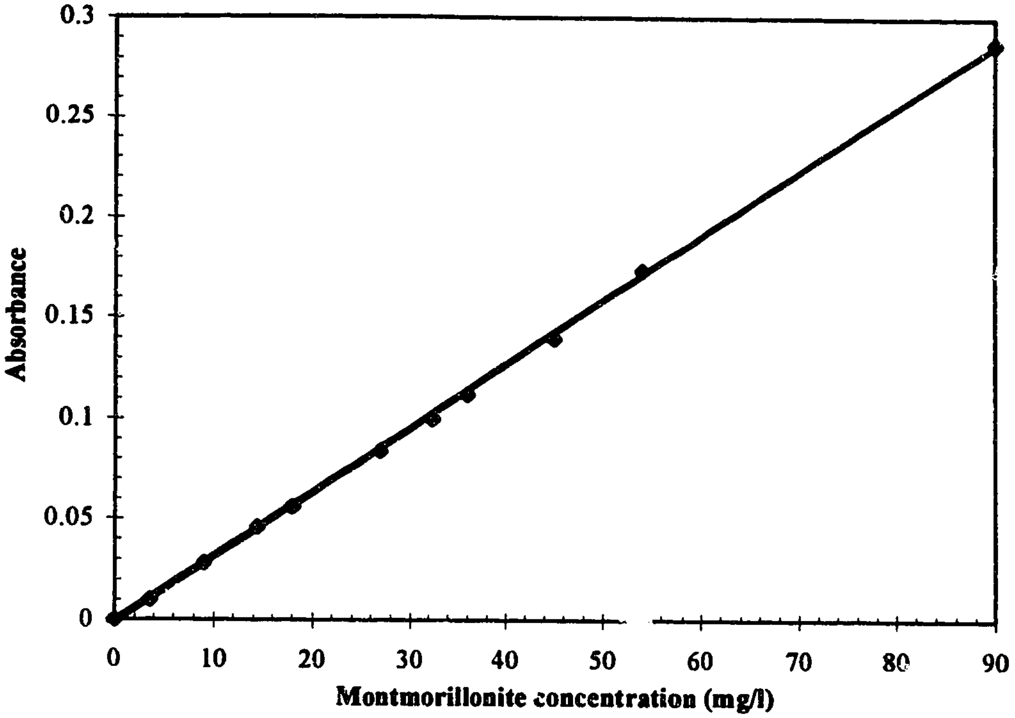

Figure 3.2 An example of determination of colloid concentration using a UV Spectrophotometer.

The presence of Pb or salts (NaCl, $CaCl_2$) did not affect the results. Of importance, however, is that solution matrix of the sample is the same as that of standards. This method of measurement was found to be reliable for 1*μm* montmorillonite particles to concentrations as low as 3 ppm. The highest concentration for colloids that was examined was up to 90 ppm.

Prior to the Pb/suspension experiments, tracer experiments using NaBr were conducted to determine the column properties and estimation of travel and residence time through the column.

3.3 RESULTS AND DISCUSSION

3.31 Sorption experiments

The amount of Pb taken up by the clay suspensions (90 mg/l) as a function of electrolyte concentration is shown in Figure 3.3. At low electrolyte concentration, Pb adsorption is higher than at higher electrolyte concentration. This could be attributed to the fact that at higher electrolyte concentration, Pb ions compete with Na^+ for exchange sites. (Griffin and Shimp, 1976).

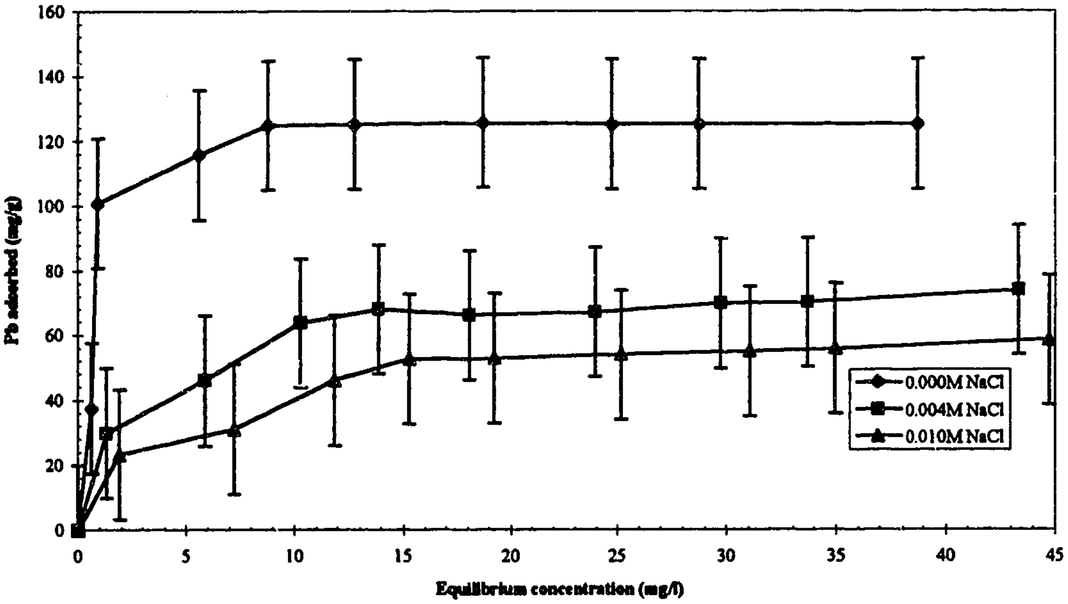

Figure 3. 3. Lead adsorption by montmorillonite from $(PbNO_3)_2$ solutions and 0.00, 0.004 and 0.01M NaCl.

The linear forms of Langmuir-type adsorption isotherms for Pb are shown in Figure 3.4. The isotherms were plotted according to the Langmuir adsorption equation (Griffin and Shimp, 1976; Griffin and Au, 1977),

$$\frac{C_s}{x/m} = \frac{1}{kb} + \frac{C_s}{b} \tag{3.3}$$

where C_s is equilibrium concentration of Pb, *x/m* is the amount adsorbed per unit mass of clay, *b* is the adsorption maximum and *k* is a term relating to the energy of adsorption.

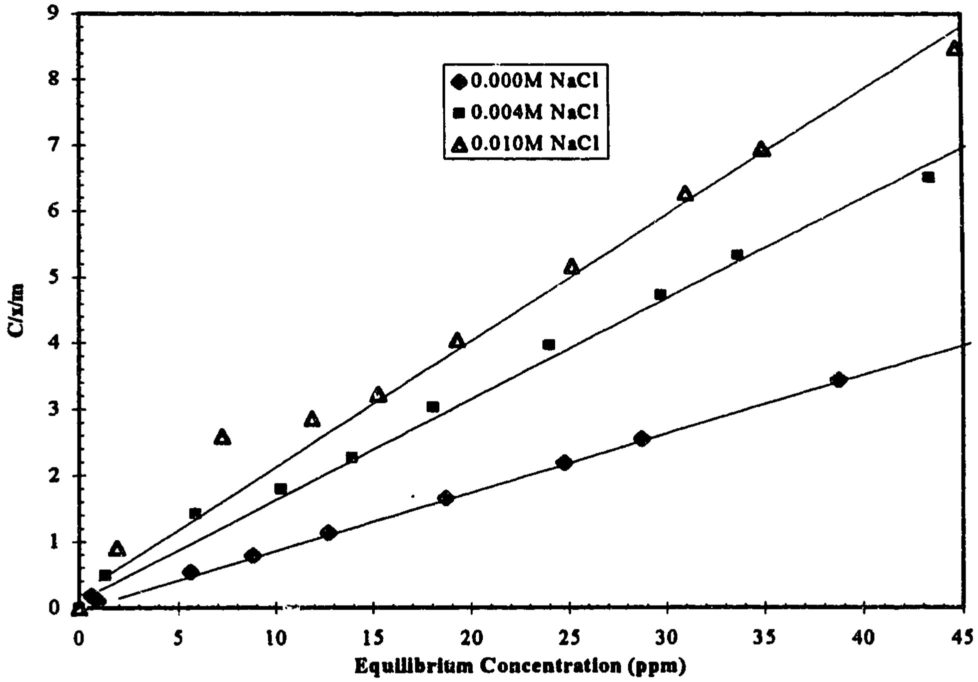

Figure 3.4 **Adsorption of lead by montmorillonite from $(PbNO_3)_2$ solutions and 0.00, 0.004 and 0.01M NaCl plotted according to the Langmuir adsorption equation.**

The adsorption maxima computed from the sorption curves for $(PbNO_3)_2$ solutions by Na-saturated montmorillonite were, 120.7, 75.1 and 53.6 meq/100g clay, corresponding to electrolyte (NaCl) concentrations of 0.00, 0.004 and 0.01M. These values are compared with the cation exchange capacity (CEC) value of montmorillonite which ranges between 80 to 120 meq/100g clay (Bohn, McNeal and O'Connor, 1985). The CEC value is close to the Pb adsorption maximum computed from the Langmuir equation, i.e. Pb adsorption could be viewed as another way of estimating CEC of clay. Griffin and Shimp (1976) reported similar results. The maximum amount adsorbed was used to estimate concentration range that could be used in the colloid transport.

3.3.2 Tracer experiments

Tracer experiments were conducted by continuously introducing a tracer (NaBr) of concentration, C_{so}, into the column when it was initially saturated with deionized water. The results of these experiments are plotted in Figure 3.5. The data are plotted as C_s/C_{so} versus displaced pore volume of the solution, were C_s and C_{so} represent effluent and influent tracer concentrations for the experimental system respectively. The non-dimensional time in terms of pore volumes was determined as follows:

Normalized Pore volume, $$P_v = \frac{tQ}{\theta V_t} = \frac{vt}{L} = t_R \tag{3.4}$$

where, t = time, Q = discharge, θ = porosity, V_t = total volume of column (Cross sectional Area x Length) and t_R = dimensionless time. The purpose of tracer experiments was to characterize the dispersive properties of the system thereby determining diffusion/dispersion, Pe an estimate residence time through the columns. As Brusseau (1993) indicated the general accepted procedure for performing a set of miscible displacement experiments involves performing tracer experiments with a nonsorbing, nonreactive solute such as ^3H_2O or chloride, in this case NaBr. The results obtained from tracer experiments are then analyzed with selected transport model, usually the well-known advective-dispersive equation. This analysis includes solving the inverse problem to obtain a value for the dispersion-related parameter. This value is thereafter used in the analysis of experimental results obtained for all solutes with the system.

A major assumption inherent to the approach described above is that dispersive flux will be the same for all solutes, irrespective of solute characteristics such as size, shape, and chemical reactivity. A corollary to the assumption that dispersion is solute invariant is that hydrodynamic dispersion is the only mechanism contributing to the dispersive flux. The assumption that hydrodynamic dispersion constitutes total dispersion measured in a column experiment is one of the most widely held in the field of solute transport (Brusseau, 1993).

From Equation 3.3 the number of pore volume is equivalent to a dimensionless time, t_R. With this equivalency the solution of the one-dimensional advection-dispersion equation can be used to estimate dispersion parameters (Fetter, 1993). Sauty (1980) gave the Ogata-Banks (1961) solution for a one dimensional advective-dispersive equation (Equation 2.12), without the sorption term $\partial S / \partial t$ as

$$C_s = \frac{C_{so}}{2}\left[erfc\left(\frac{L - vt}{2\sqrt{D_s t}}\right) - \exp\left(\frac{vL}{D_s}\right) erfc\left(\frac{L + vt}{2\sqrt{D_s t}}\right)\right] \qquad (3.5)$$

where, *erfc* = complementary error function, C_s = effluent concentration, C_{so} = influent concentration. Equation 3.4 can be rearranged to yield

$$\frac{C_s}{C_{so}} = 0.5\left[erfc\left(\frac{1 - P_v}{2\sqrt{D_s / vL}}\right) - \exp\left(\frac{vL}{D_s}\right) erfc\left(\frac{1 + P_v}{2\sqrt{D_s / vL}}\right)\right] \qquad (3.6)$$

In the above equations, D_S is equivalent to the longitudinal hydrodynamic dispersion coefficient since we are dealing with one dimensional condition whose principal flow direction is longitudinal. Thus, there is an assumption that transverse dispersion is negligible.

As Fetter (1993) outlined the concentration of the tracer in the effluent, C_{SO}, is measured for various values of P_V, and then C_S/C_{SO} is plotted as a function of $\left[(P_v - 1)/P_v^{1/2}\right]$ on a linear probability paper. If the data plot is a straight line, the diffusive form of the advection-dispersion equation is valid, and the slope of the line is related to the longitudinal hydrodynamic dispersion.

Equation 3.6 was used to estimate D_S using least squares, on the basis that other parameters are known from the experimental determination. Calculations were done using Mathematica software package. Selected properties of the packed columns are provided in Table 3.1.

Table 3.1 Some properties of the packed columns[a].

Column #	Length (cm)	B_Density (g/cm^3)	Porosity	Pore Vol. (cm^3)
15_1	15	1.53	0.42	114
15_2	15	1.53	0.42	115
30_1	30	1.54	0.42	226
30_2	30	1.54	0.42	227
60_1	60	1.64	0.38	414
60_2	60	1.64	0.38	413

[a] Column diameter = 4.8 cm; particle density = 2.645g/cm^3. The average calculated D_s is 0.418 +/- 0.072 cm^2/min. (calculated for the 30 cm column).

Results of tracer experiments are shown in Figure 3.5 for all three lengths. It can be noted that there is no significant difference in the three column lengths used. As a result, only one length (30 cm column) was chosen to show all subsequent results in the experiments. This allowed repetition of the experiments.

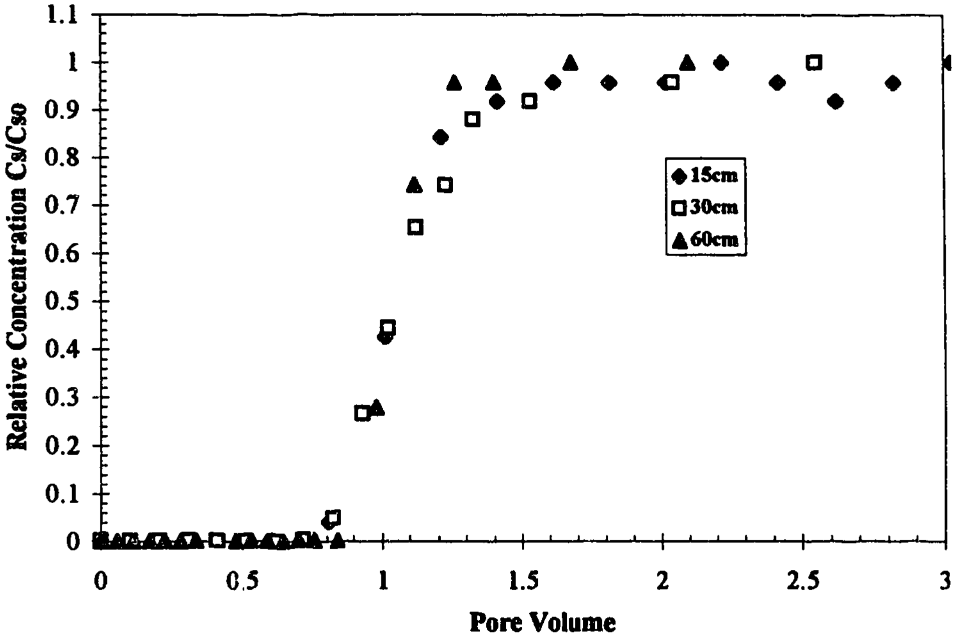

Figure 3.5 NaBr breakthrough curves for three column lengths (15, 30 and 60 cm).

Figure 3.6 shows results modeled using Equation 3.6. As already outlined above, only the results for the 30 cm column are shown because there was no observable differences in all the three lengths as depicted by Figure 3.5. The model results were used to determine D_s using least squares method. The average D_s obtained from calculation was 0.418 +/- 0.072 cm^2/min. Calculations were done based on an average velocity of 0.74 cm/min.

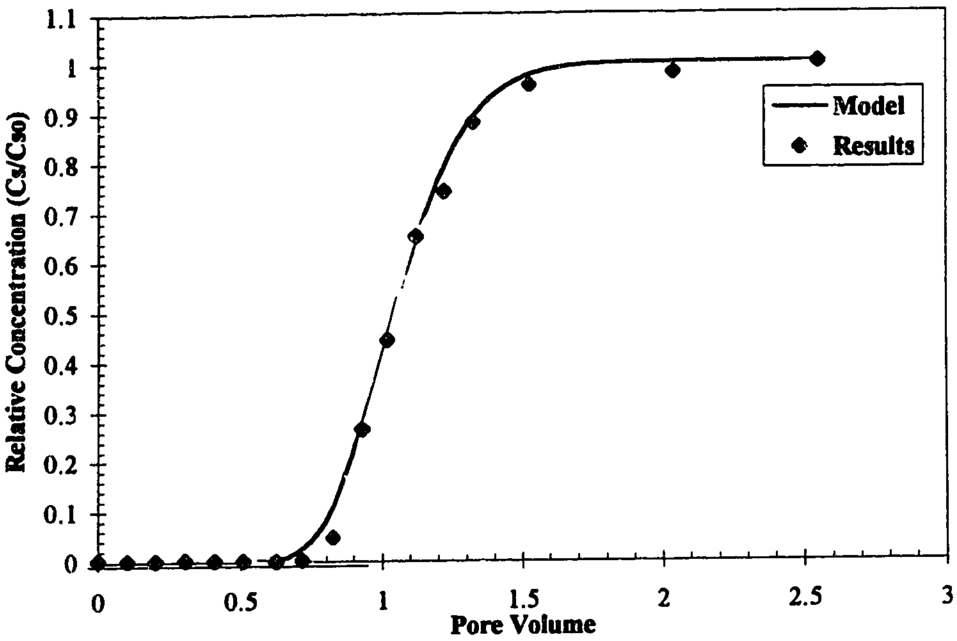

Figure 3. 6. Modeled NaBr breakthrough curve for a 30 cm column.

3.3.2 Colloid transport experiments

Results of colloid transport are presented in Figures 3.7. The breakthrough curve for colloid was found to be the same as that of the tracer shown in Figures 3.5 and 3.6. This implies that there was no retention of the colloids by the matrix. The reason could be due to packing and particle size of the colloids. However, it is possible that retention could be achieved if the pore water chemistry was changed by altering the ionic strength.

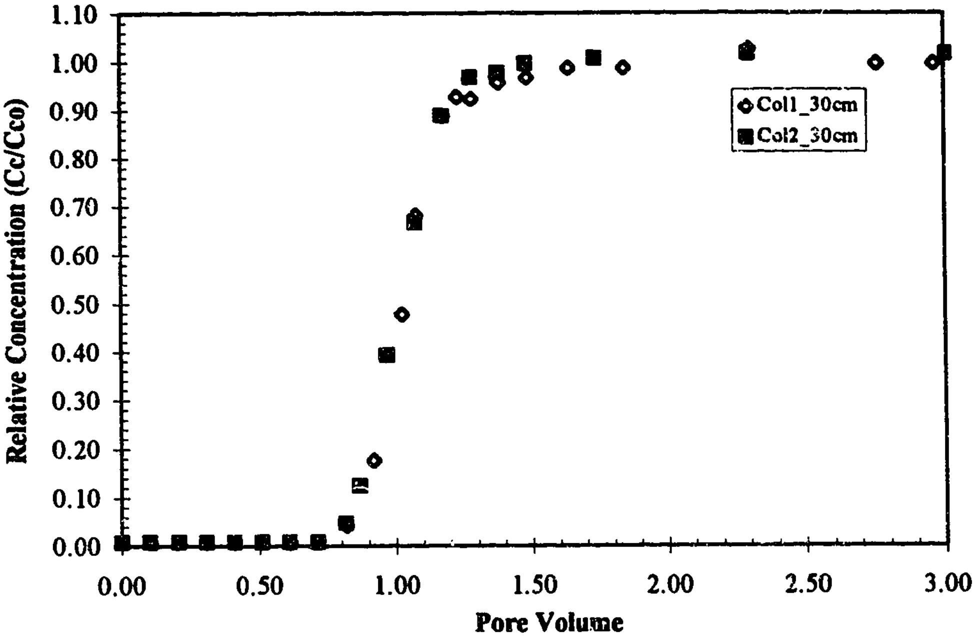

Figure 3. 7. Breakthrough curve for colloid transport for a 30 cm column (two runs).

3.3.3 Lead transport

Figures 3.8, 3.9 and 3.10 show breakthrough curves (BTC's) for Pb based on both time and pore volume, representing transport with and without adsorbent. It is clear from the BTC's that introducing an adsorbent changed the breakthrough time for Pb substantially (from 1 pore volume to 14.5 pore volume at the inflection point), suggesting the importance of sorption coefficients between the matrix and the contaminant, and between the colloids and the contaminant.

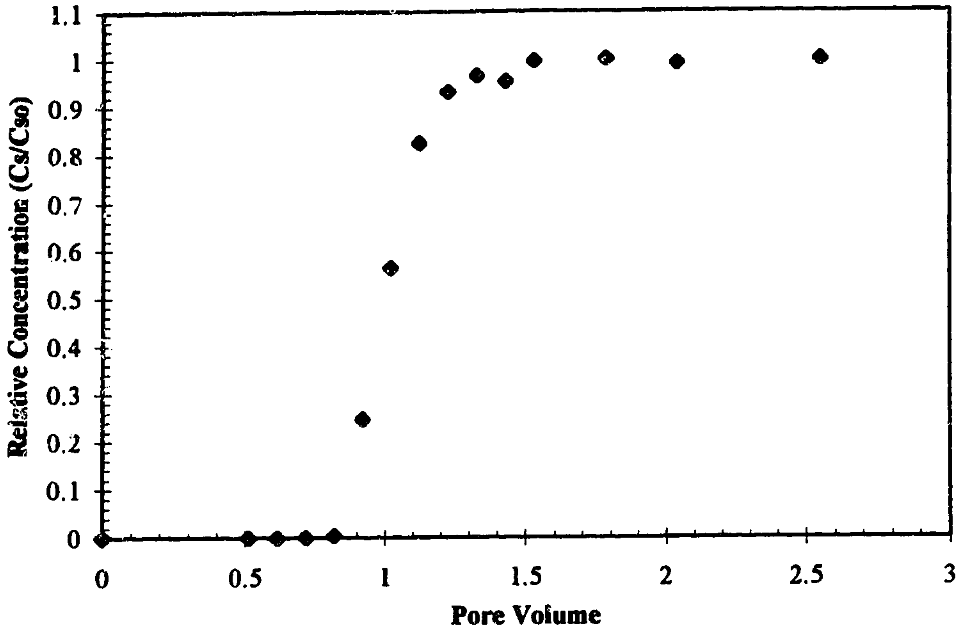

Figure 3. 8. Breakthrough curve of lead transport without adsorbent for a 30 cm column (based on pore volume).

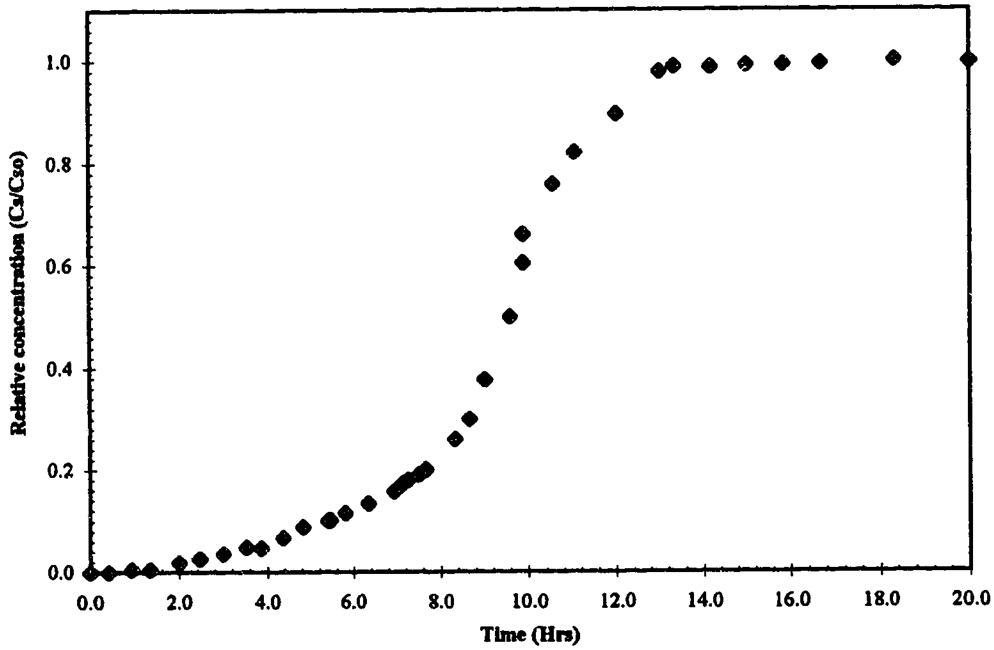

Figure 3. 9. Breakthrough curve of lead transport with adsorbent (Amberlite®) for a 30 cm column based on time.

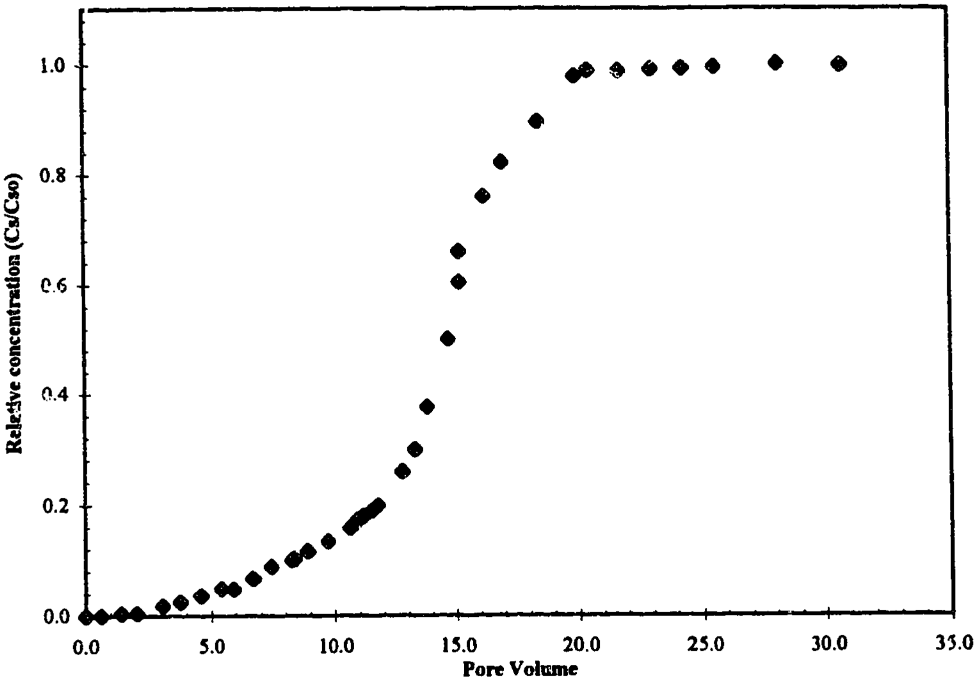

Figure 3. 10. Breakthrough curve of lead transport with adsorbent (Amberlite®) for a 30 cm column based on pore volume.

3.3.4 Lead and colloid transport

BTC's for Pb, colloids and tracer without adsorbent are shown in Figure 3.11. These can be compared with Figure 3.10 which shows that the presence of adsorbent has significantly caused the retardation of Pb. In the absence of Amberlite® there was no observable differences between Pb, colloids and NaBr breakthrough. As a result there was no need to perform simultaneous Pb and colloid transport experiments. It is assumed that the Pb transport will be dependent upon the extent of sorption onto both the matrix and the colloids. This has significant implications on the role of colloids on contaminant transport. In the presence of a highly adsorbing medium, the colloids would play an important role in transporting the contaminant. The transport of contaminants will also depend on the kinetics of desorption from both the colloids and matrix. There is lack of data in the area of contaminant desorption from colloids and kinetics of dissolution (Puls, 1990). In this investigation these studies were not done.

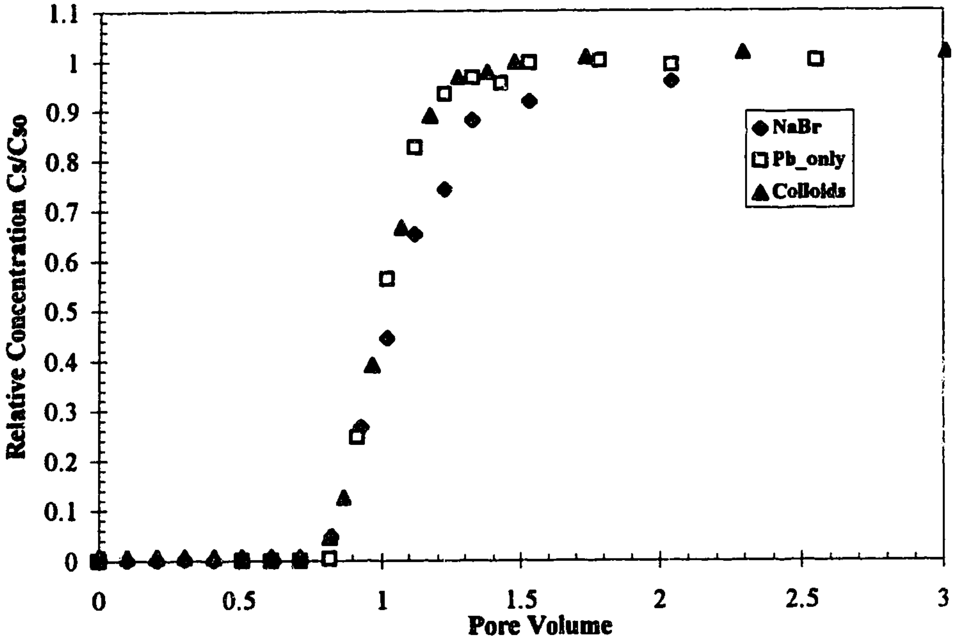

Figure 3. 11. Breakthrough curves for NaBr, Pb and colloid transport for a 30 cm column, without adsorbent.

3.4 CONCLUSIONS

Although no investigation was done on the effect of ionic strength on colloid transport mechanism, from the results on Pb sorption and literature reviewed, it can be concluded that colloids may play a significant role in the transport of contaminants in highly sorbing media. This would, however, be determined by the kinetics of adsorption between the contaminant and both the colloids and the medium. The adsorption of Pb by montmorillonite remained relatively high (53.6 meq/100g) at high electrolyte concentration (0.01M NaCl), indicating that colloids could still play a significant role in contaminant transport.

The results also show that colloids were not retained by the medium, as colloid BTC's were similar to tracer BTC's. This might be different if the porosity was relatively low and the ionic strength high, since these factors would be expected to increase retention.

A simple method of determining relatively low colloid concentrations was also developed. Although the method was found to be relatively reliable, there is a need for further development by testing with other material.

3.5 NOTATION

M = mass of sand (M)

n = porosity of sand

ρ_b = bulk density (L^3/M)

ρ_s = particle density(L^3/M)

Pv = Normalized pore volume

V = volume (L^3)

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CHAPTER FOUR

SIMULATION OF COLLOID - FACILITATED TRANSPORT IN SAND PACKED COLUMNS

4.1 INTRODUCTION

Mathematical modeling of contaminant migration allows prediction of sorptive behavior and transport of contaminants under given conditions. This approach plays an important role in risk assessment of contaminants such as lead which occurs in high levels in sewage sludge and industrial wastes, and how this may vary depending on prevailing soil conditions.

In Chapter 2 of this thesis a model was developed to describe colloid-facilitated contaminant migration based on the convective-dispersive transport equation and filtration theory. A schematic diagram illustrating the framework for the model that accounts for colloid-facilitated transport was shown in Figure 2.1 (Chapter 2).

The purpose of this Chapter is to provide a solution to the colloid-contaminant migration equations presented in Chapter 2. Colloid-facilitated breakthrough curves (BTC's) obtained will be compared with colloid-free BTC's to assess the effect of the colloids presence. Sensitivity analyses to assess various parameters will also be conducted as well as comparison with experimental data.

4.2 SOLUTION OF THE MODEL

A complete set of governing equations for the co-transport of contaminant in one-dimensional form based on Equations 2.6, 2.9 and 2.25 is given by Equations 4.1, 4.2 and 4.3 respectively. These are:

$$\frac{\partial \sigma}{\partial t} = -K\sigma \frac{q}{K_{cond}} + \lambda C_c v \tag{4.1}$$

$$\theta \frac{\partial C_c}{\partial t} = D_c \frac{\partial^2 C_c}{\partial x^2} - q\frac{\partial C_c}{\partial x} + K\sigma \frac{q}{K_{cond}} - \lambda C_c v \tag{4.2}$$

$$\left(1 + K_{p_c} C_c + \frac{K_{p_c}\sigma + K_{p_s}\rho_b}{\theta}\right)\frac{\partial C_s}{\partial t} = \frac{D_s}{\theta}\frac{\partial^2 C_s}{\partial x^2} - \left(v + v_c C_c K_{p_c}\right)\frac{\partial C_s}{\partial x} \tag{4.3}$$

where, D_s is solute dispersion. In Equations 4.1, 4.2 and 4.3, C_c, C_S and σ are unknowns, and from the previous equations,

$$\lambda = \alpha\eta \frac{(1-\theta)}{a}, \tag{4.4}$$

$$v = \frac{q}{\theta} = \frac{Q}{\theta A}, \qquad (4.5$$

$$D_c = \varepsilon d_m v \tag{4.6}$$

$$D_s = \mu D_0 + \frac{\varepsilon d_m}{1 + \gamma D_0 / d_m v} v \tag{4.7}$$

$$v_c = \frac{J_c}{C_c \theta} \tag{4.8}$$

$$J_c = -D_c \frac{\partial C_c}{\partial x} + qC_c \tag{4.9}$$

$$\rho_b = (1-\theta)\rho_s \tag{4.10}$$

where ρ_S is particle density. The values of K_{pc} and $K_{ps'}$ can be estimated from the adsorption-desorption processes as modeled by the Freundlich or Langmuir type relationships for both colloids and matrix. In this study, the Langmuir-type equation was used.

In order to solve the transport model given by the above equations, the appropriate boundary conditions must be specified. In this study, the analysis was restricted to steady-state water flow conditions in a homogeneous, saturated column having uniform moisture content distribution. Therefore, the water flux, q, and moisture content, θ, were assumed to be at maximum and constant and are considered time invariant. It is also assumed that a solute solution or colloid suspension of known concentration (C_{so} or C_{co}) is applied continuously at the column surface. The boundary conditions for both colloids and dissolved solute associated with such a system are expressed as (Jiang and Corapcioglu, 1993; Corapcioglu and Jiang, 1993; Montero *et al.*, 1994):

$$C_c(x,t) = C_{c0} \qquad \text{at } x=0,\ \ t \geq 0 \tag{4.11}$$

$$\frac{\partial C_c(x,t)}{\partial x} = 0 \qquad \text{at } x=L, \quad t \geq 0 \qquad (4.12)$$

$$C_c(x,t) = 0 \qquad \text{at } t=0, \quad x \geq 0 \qquad (5.13)$$

$$C_s(x,t) = C_{s0} \qquad \text{at } x=0, \quad t \geq 0 \qquad (4.14)$$

$$\frac{\partial C_s(x,t)}{\partial x} = 0 \qquad \text{at } x=L, \quad t \geq 0 \qquad (4.15)$$

$$C_s(x,t) = 0 \qquad \text{at } t=0, \quad x \geq 0 \qquad (4.16)$$

$$\sigma(x,t) = 0 \qquad \text{at } t=0, \quad x \geq 0 \qquad (4.17)$$

where equations 4.13, 4.16 and 4.17 represent the initial conditions for the column of length *L*. Equations 4.11, 4.12, 4.14 and 4.15 are associated with the inflow and outflow boundary conditions of the porous material column.

A numerical solution of the model involves solving equations 4.1, 4.2 and 4.3 using the Crank-Nicolson approach with boundary conditions as described above[1]. This approach was chosen for its stability and consistency in linear one-dimensional problems (Bear and Verruijt, 1987; Remson *et al.*, 1971). The model has 3 different submodels that calculate solute transport, colloid transport and retention/mobilization. At each time step the colloid model is called first and the information obtained is used in the solute transport model and in retention/mobilization. The program iterates, going back to recalculate the concentration until convergence occurs, and progresses to next time step.

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[1] The model solution is available on request

The input parameters for the model are listed in Table 4.1. In assessing the mode, these parameters were varied accordingly.

Table 4.1 Model input parameters*.

Parameter	**Values**
a (cm)	0.015
α	0.02
η	0.05
θ	0.42
C_{co} (mg/L)	100
C_{so} (mg/L)	50
K_{cond} (cm/min.)	0.06
K (s^{-1})	0.03
K_{ps} (ml/mg)	10
K_{pc} (ml/mg)	100
ε	20
[illegible] (cm)	0.03
	0.2
[illegible]$_o$ (cm^2/min.)	0.000567
γ	1.08
Q (ml/min.)	5.76
L (cm)	30
A (cm^2)	18.1

***Other parameters that were calculated within the model: D_s (cm^2/min.) = 0.431+/- 0.072, D_c (cm^2/min.) = 0.442+/- 0.072, v (cm/min.) = 0.737.**

4.3 RESULTS AND DISCUSSION

The model proposed for colloid-facilitated transport of contaminant has been applied to simulate the migration of a reactive contaminant along a finite column. Influent solutions of colloids and contaminant were continuously fed with a constant velocity. Breakthrough curves were obtained as fractions of the aqueous phase mass concentration C_s/C_{s0} where C_{s0} is the influent contaminant mass concentration at x=0. Colloid-facilitated contaminant breakthrough curves were compared with the colloid-free curve to observe the effect of the presence of colloids.

4.3.1 Results of the model and sensitivity analysis

In order to investigate the effect of various model parameters on results, a sensitivity analysis was conducted. The range of various parameters depends on the surface characteristics of colloids and/or medium as well as the chemistry of the pore water.

There are several parameters and assumptions of importance that need to be assessed in colloid-facilitated transport as seen from the equations developed. However, as noted earlier, in this study only a few were investigated. The main parameters include sorption coefficients between both the colloids and matrix, and colloid concentrations. It should be noted that not all of the parameters considered in the sensitivity analysis were determined experimentally.

Figure 4.1 shows that introducing an adsorbing matrix delays the breakthrough time. K_{ps} represents equilibrium distribution coefficient or adsorption coefficient of the dissolved contaminant with the solid matrix. Figure 4.1 illustrates that the model shows a fairly high sensitivity for sorbing matrix. Increasing sorption by 5 times resulted in an increase of more than 10 pore volumes.

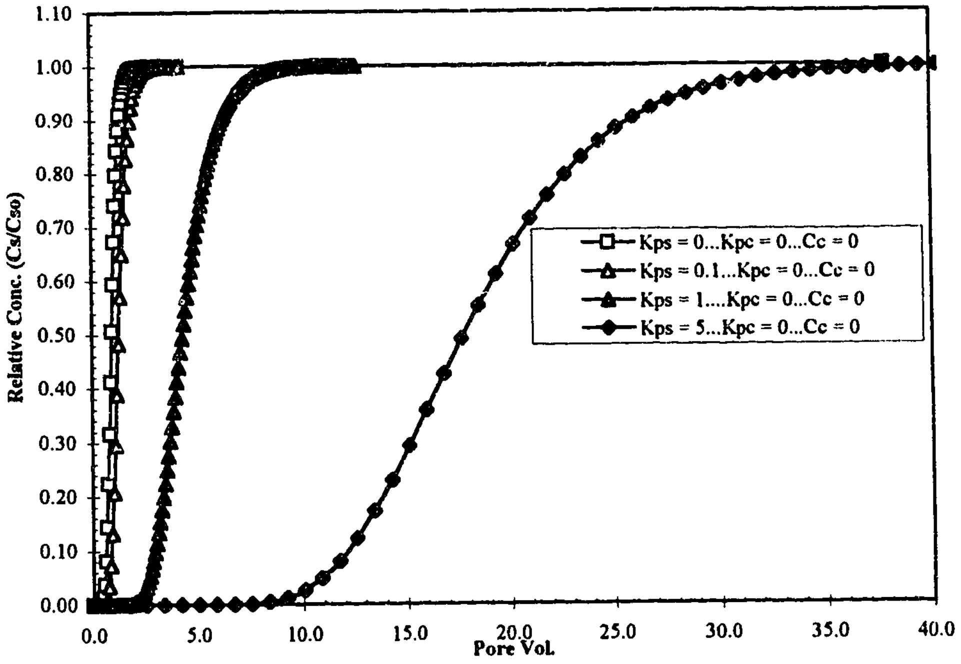

Figure 4.1 Sensitivity of the model to contaminant-matrix distribution coefficient (Kps)

Figure 4.2 shows that introducing the colloids does reduce breakthrough time. This agrees with the results reported in Chapter 3 were it was found that the absence of sorption onto matrix (i.e., Kps = 0), renders consideration of the colloids as carriers unnecessary. Changing colloid concentration also reduces the breakthrough time. Thus the importance of colloids is more pronounced when the matrix is adsorbing. Nevertheless, one might expect the colloids to move faster if the pore size and colloids were relatively small. That is, factors such as size exclusion would come into effect. Accelerated transport of contaminants by the presence of colloids in aqueous phase can be attributed to the local velocity of colloidal particles which is larger than that of the groundwater (Corapcioglu and Jiang, 1993).

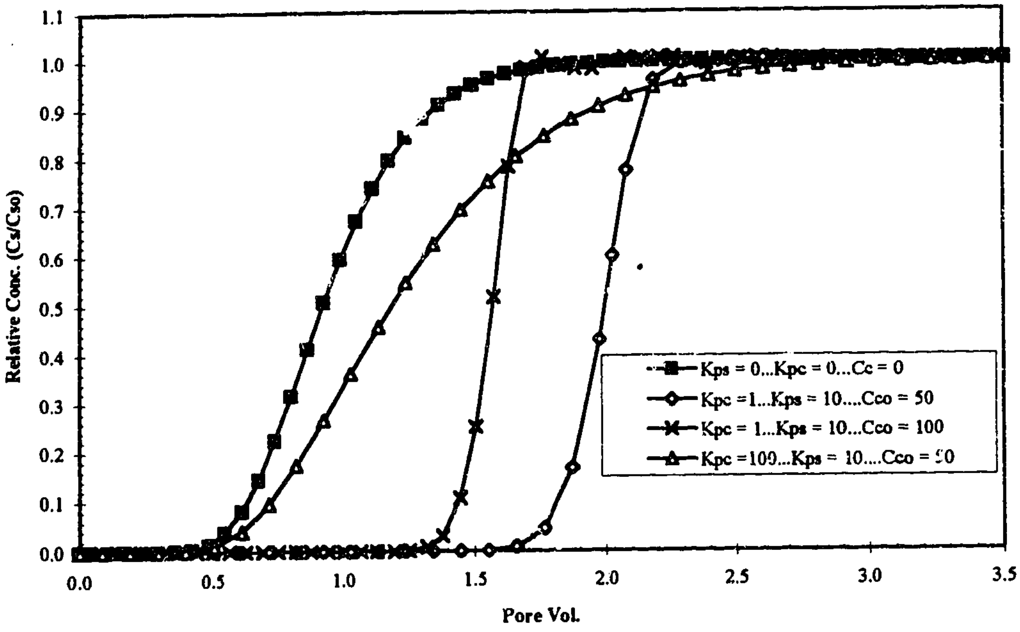

Figure 4.2 Variation of solute concentration as affected by colloid concentration

Figure 4.3 shows the difference in the adsorption coefficient for colloids (Kpc). Increasing Kpc does reduce breakthrough time at a given colloid concentration. This can be attributed to the relative increase in sorption of contaminant by the colloids.

The relevance of adsorption coefficients in colloid facilitated transport will also depend on the kinetics of adsorption of the contaminant with the matrix and colloids. If the rate of sorption between the aqueous phase and colloids is faster than the flow rate, then the equilibrium assumption is applicable. However, if the flow rate is relatively large in comparison with sorption rate, then it may be necessary to consider reaction kinetics.

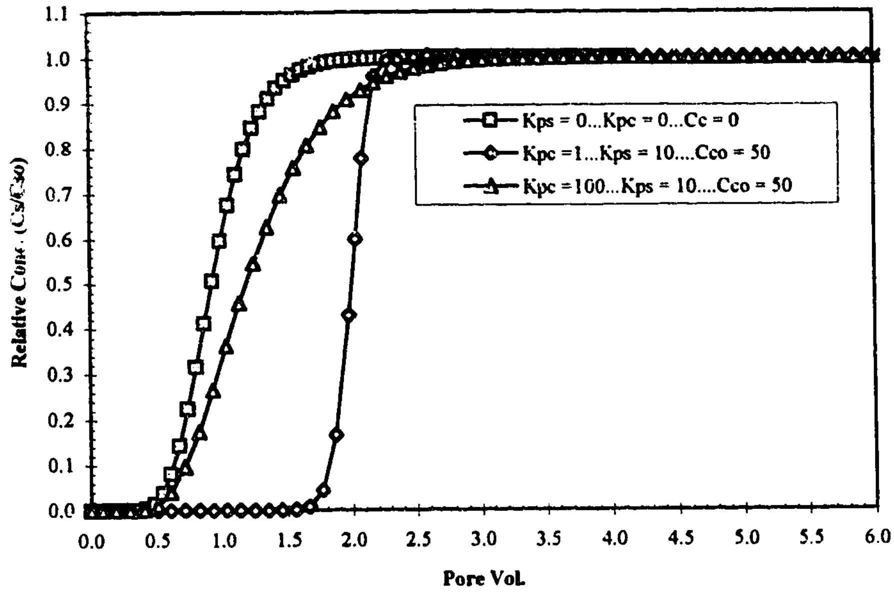

Figure 4.3 Effect of change in contaminant-colloid distribution coefficient (Kpc)

Other parameters that may be looked at include mass of particles deposited per total volume, σ, and rate coefficients, K, and λ which relate to the release of and retention of colloids. As noted above, the velocity will also be of importance because it will affect the kinetics of sorption between the dissolved contaminant and colloids and solid matrix.

Figure 4.4 shows colloid BTC and its sensitivity to the colloid mobilization rate coefficient (K). As seen in Figure 4.3 the mobilization rate coefficient affects the colloids concentration. At smaller and larger values of pore volumes the colloidal effect is much less significant. σ is also affected in a in a similar manner as shown in Figure 4.5.

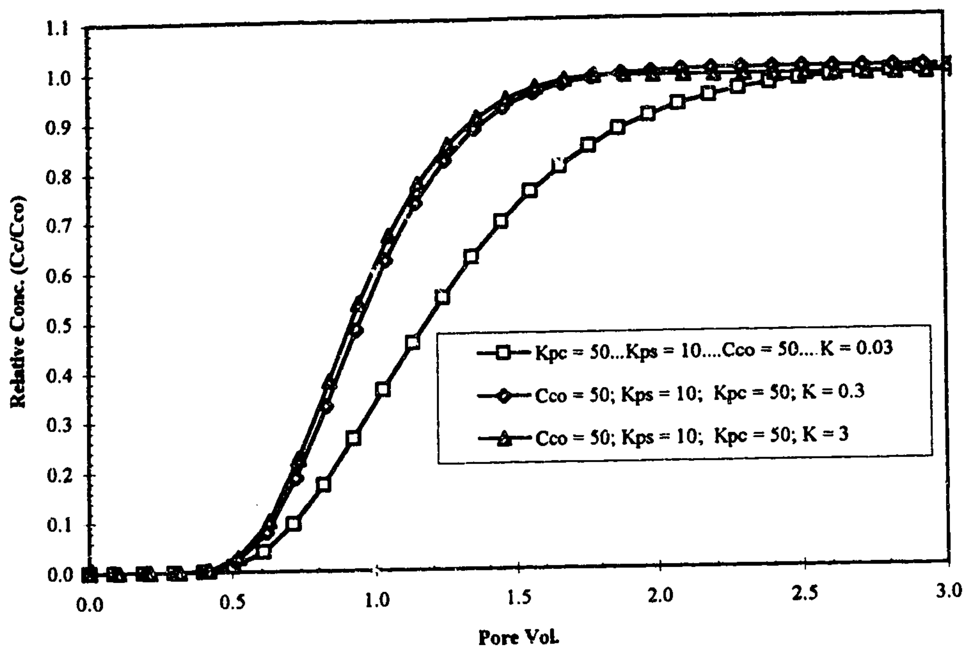

Figure 4.4 Colloid breakthrough curve and sensitivity to colloid mobilization rate (K).

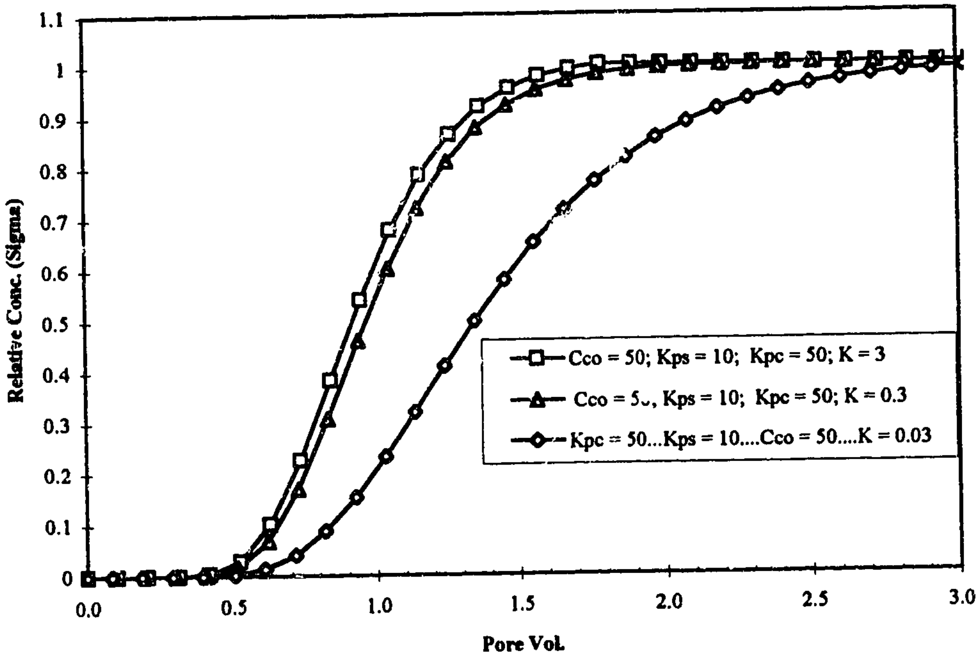

Figure 4.5 The effect of colloid mobilization rate on retained collides (σ)

4.3.2 Comparison with data

The proposed model of Equation 4.3 has been applied to simulate column transport of Pb in a porous media in the presence of montmorillonite particles. The experimental results illustrated the importance of an adsorbing medium, by introducing a cation exchange resin (Amberlite®). Figure 4.6 shows Pb BTC without an adsorbent, compared with the model results. The adsorption coefficients were set at zero because, as noted earlier the sand did not adsorb any Pb. The results fitted the model relatively well. The slight difference can be attributed to numerical dispersion.

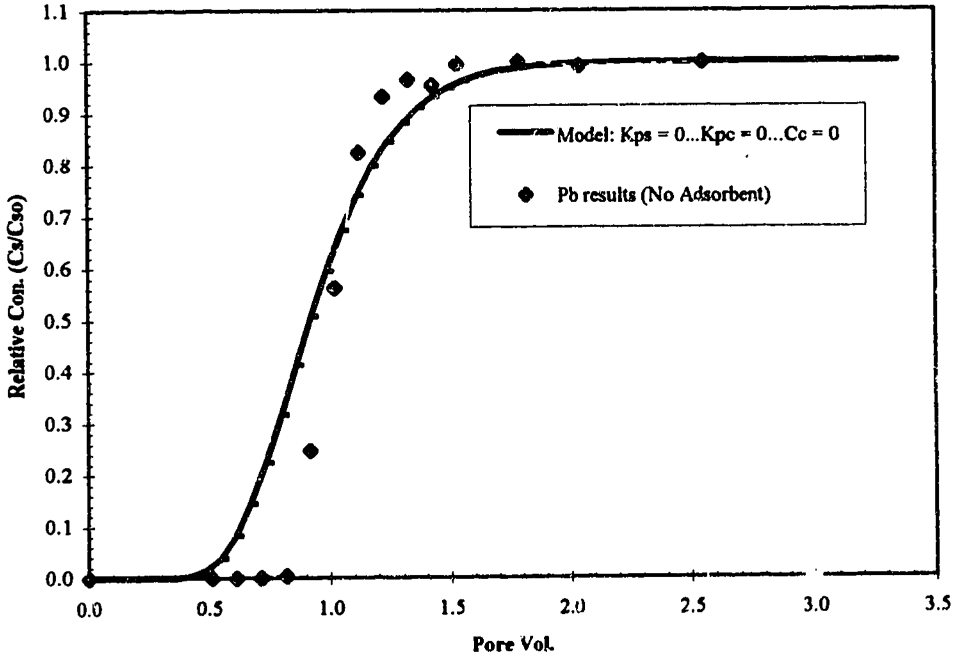

Figure 4.6 The breakthrough curve for Pb results and the model for a 30 cm Column.

Figure 4.7 shows the BTC for Pb after the addition of Amberlite®,which is a highly sorbing material. Although the shape is different and offset, it appears that the results would fit the model. The difference could be due to the difference in the adsorption coefficient for Pb and the adsorbent. In addition, only one experiment was conducted, and that the introducion of the resin could have slightly changed the column properties. Thus the results would require more verification.

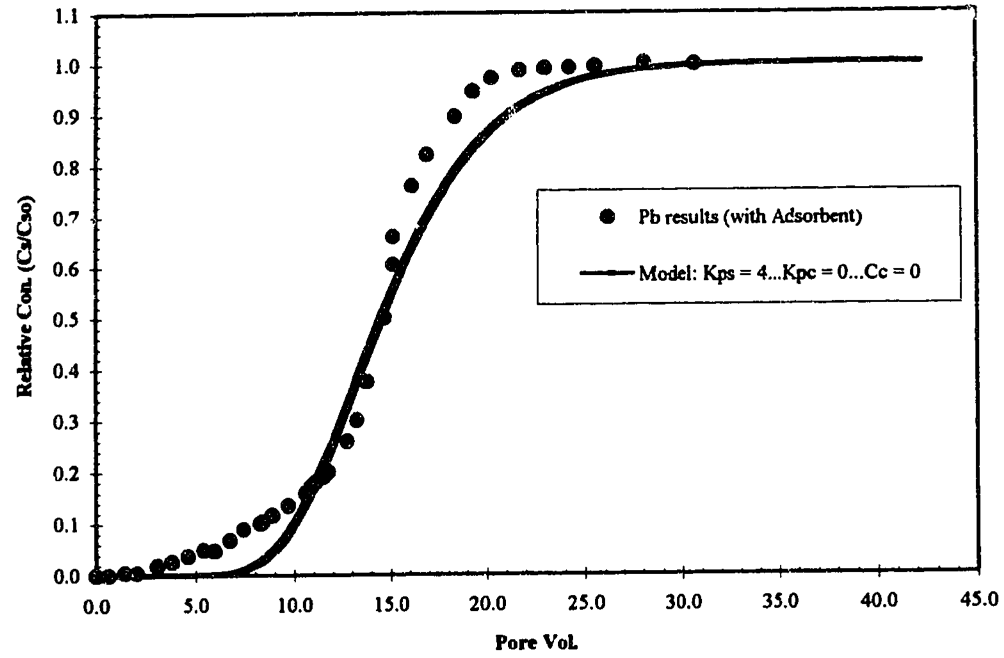

Figure 4.7 The breakthrough curve for Pb results with a sorbant and the model for a 30 cm Column.

4.4 CONCLUSIONS

In this Chapter, a solution to a mathematical model to describe the transport of a reactive solute in saturated sand columns in the presence of mobile colloids was presented. The model consists of mass balance equations for mobile and captured colloidal particles and the stationary matrix. Colloid-contaminant mass partitioning was formulated by employing the local equilibrium assumption. Results were presented for a one dimensional system. It has been shown that the presence of colloids is more significant when the porous medium is adsorbing. For the conditions examined it is clear that the contaminant would be expected to migrate faster in the presence of colloids than in colloid-free environment. A relatively significant sensitivity to the model parameters, particularly adsorption coefficients with mobile colloids and immobile matrix was observed. It is evident that despite the uncertainty of parameter values and lack of enough information, the model appear favorable, at least for the processes that were considered. What is important is whether these trends could occur in real life situations.

4.5 NOTATION

a = grain radius of bed/matrix (L)

α = attachment coefficient or sticking probability

A = total cross-sectional area of a column (L^2)

η = collector efficiency

λ = filter coefficient

σ = mass of particles deposited/total volume (M/L^3)

θ = porosity or water content in saturated condition (fraction)

ρ_b = bulk density (mass of solids/total vol.) (M/L^3)

ρ_s = density of deposited particles (M/L^3)

C_{c0} = influent colloid concentration (M/L^3)

C_c = colloid concentration (M/L^3)

C_{s0} = influent solution-phase solute concentration (M/L^3)

C_s = solution-phase solute concentration (M/L^3)

d_m = effective average particle diameter (L)

D_o = molecular diffusion coefficient of solute in water (L^2/T)

D_c = dispersion coefficient for colloids (L^2/T)

D_s = diffusion-dispersion coefficient (L^2/T)

K_{cond} = Hydraulic conductivity (L/T)

K = mobilization rate coefficient

K, μ, ε, γ = empirical coefficients

K_{ps}, K_{pc} = partition or distribution coefficients for immobile and mobile solid phases, respectively (L^3/M)

q = specific discharge (= Q/A) (L/T)

Q = volumetric flow rate (L^2/T)

t = time (T)

v = average pore water velocity or Darcy velocity [$v = q/\theta$] (= velocity of dissolved component) (L/T)

v_c = velocity of colloid components (L/T)

x = distance in flow direction (L)

4.6 REFERENCES

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CHAPTER FIVE

OVERALL CONCLUSIONS

The overall objective of this study was to establish the basis for the significance of mobile colloidal particles in the contaminant transport. We also set out to develop a simple transport model for contaminant migration and to examine some of the parameters that may be important in the colloid-facilitated transport of contaminants. Although there is ample evidence pointing to the existence of colloids, from the literature reviewed (e.g. McCarthy and Degueldre, 1993; Mills and Liu, 1989; Mills *et al.*, 1991), it is apparent that mechanisms of contaminant-colloid interactions and factors governing the colloid behavior in subsurface environment are still poorly understood. In addition there is lack of data on colloid behavior in subsurface environments. It is in this light that the experimental set up was designed to be relatively simplified to ensure proper and reliable results.

Other studies have demonstrated the strong binding and enormous sorption capacities of colloidal particles of inorganic and organic contaminants (Puls, 1990); however, for the significance of this as a contaminant transport mechanism to be adequately determined, additional data concerning the kinetics of desorption and dissolution reactions are needed.

Within the uncertainty of the parameter values used, assumptions and limitations of the model developed, some conclusions can be drawn. Transport of inorganic colloids through sand and gravel aquifers could play an important role in contaminant transport under certain hydrogeochemical conditions.

The presence of colloids reduces the retardation factor and increases the effective velocity. Neglecting colloidal mobility in predictive contaminant transport models may underestimate both transport rate and mass flux (Puls and Powell, 1992).

If colloids exist *a priori* as stable suspensions, and remain stable after association with the contaminant, they should theoretically reach the outlet of a hydrological system within a relatively short period (van der Lee *et al.*, 1993). The significance of colloids in transporting contaminants will depend highly on the reactivity of both the mobile colloids and immobile matrix. As indicated by the results, in some cases, it is necessary to have an adsorbing matrix for colloids to have an effect as carriers.

The colloid facilitated groundwater contaminant transport model developed in this study could be a starting point in assisting in evaluating the significance of the presence of colloids. Furthermore, such an approach would be useful in understanding the importance of individual modes of transport on the overall behavior of reactive solutes. Other possible scenarios where the study could be applied include clean up operations for reactive contaminants, were the colloids may be introduced or 'flushed' through the medium. As McCarthy and Zachara (1989) pointed out, manipulation of colloid mobilization and deposition could be a useful tool for the mitigation or remediation of waste sites.

Evidently there is a need for further research in order to establish the necessary information for adequate assessment of contaminant transport. Sufficient tests for other parameters such as mobilization and immobilization of colloidal particles require further attention. Other parameters of importance include the chemical effects on colloid transport such as the effect of ionic strength. To date, experiments on studies related to colloid contaminant transport have generally excluded the chemistry of pore water and its effect on colloid behavior.

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