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Review on subsurface colloids and colloid-associated contaminant transport in saturated porous media

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Abstract

In this review article, authors presented up to date developments on experimental, modeling and field studies on the role of subsurface colloidal fines on contaminant transport in saturated porous media. It is a complex phenomenon in porous media involving several basic processes such as colloidal fines release, dispersion stabilization, migration and fines entrapment / plugging at the pore constrictions and adsorption at solid/liquid interface. The effects of these basic processes on the contaminant transport have been compiled.

Here, the authors, first presented the compilation on insitu colloidal fines sources, release, stabilization of colloidal dispersion and migration which are a function of physical and chemical conditions of subsurface environment and finally their role on inorganic and organic contaminants transport in porous media. This review article is superior over last two review articles by Elimelech and Ryan [3] and Kretzschmar et al. [6] respectively as (i) It gives not only complete compilation on colloidal fines-facilitated contaminant transport but also reviewed the new role of colloidal fines in contaminant retardation due to plugging of pore constrictions. This plugging phenomenon is also depends on various factors such as concentration of colloidal fines, superficial velocity and bead to particle size ratio. This plugging-based contaminant transport can be used to develop in containment technique in soil and groundwater remediation. (ii) It also presented the importance of "critical salt concentration (CSC)", "critical ionic strength for mixed salt, "critical shear stress" or "critical particle concentration (CPC)" on insitu colloidal fines release and migration and consequently their role on contaminant transport in porous media. (iii) This also reviewed the another class of colloidal fines called "biocolloids" and their transport in porous media. Finally authors are highlighted the future research based on their critical review on colloid-associated contaminant transport in saturated porous media.

Key words: Subsurface colloids, colloid-associated contaminant transport, biocolloids, plugging, saturated porous media.

Contents

1. Introduction:

Until some two decades ago, it was believed that only the soil liquid and gaseous phases were mobile and could facilitate the transport of chemicals and nutrients in subsurface flow. It is now generally accepted that also part of the soil solid phase is mobile under different geochemical conditions and that mobile organic and inorganic soil particles, colloidal in nature may facilitate or retard the contaminant transport [1-5]. Our knowledge and understanding of the colloidal fines-associated contaminant transport in porous media have increased substantially over the last one decade which is reviewed by Kretzschmar et al. [6] and Elimelech and Ryan [3] respectively. While the knowledge of colloid-associated transport of contaminants has been advanced in terms of an increased understanding of contaminant-colloidal fines associations and in terms of colloidal fines release, mobilization, entrapment or plugging and migration processes [1, 3, 7-8] still more research are currently underway concerning the uncertainties involved in the subsurface fate and transport of contaminants.

Major pathways and mechanisms for transport of contaminants may differ in the vadose and saturated zone, due to different conditions. In general, the vadose zone is characterized by the presence of oxygen, the presence of a gas-water interface, and the presence of relatively high concentrations of particulate organic matter and of relatively high microbial activity. Chemical conditions vary significantly with time and place, due to dilution with rainwater or concentration due to evaporation and due to large horizontal and vertical variations in the composition of the solid phase. Transport of contaminants in the vadose zone will be mainly vertical. The saturated zone on the other hand is in general characterized by much lower organic matter contents, much lower oxygen content and a lower sorption capacity of the solid phase. In comparison with the vadose zone, chemical conditions will be less variable in time and space because in general, the influence of dilution and evapotranspiration will be negligible and the composition of the solid phase in horizontal and vertical direction will be less variable. Transport of contaminants in the saturated zone will be mainly horizontal. The goal of this review is to compile and put in perspective the advance made in addressing these colloidal fines-associated contaminant transport in saturated porous media over the last decade.

This review article will be presented mainly the current state of the developments on sources, release and migration of inorganic colloidal fines and finally their new role on plugging phenomena as well as on contaminant transport in saturated subsurface zone. The new aspects of this review article over earlier review articles by Kretzschmar et al. [6] and Elimelech and Ryan [3] are mentioned in what follows. (a) It gives not only complete compilation of colloidal fines-facilitated contaminant transport but also reviewed the new role of colloidal fines in contaminant retardation due to plugging of pore constrictions. This plugging phenomenon depends on various factors such as concentration of colloidal fines, superficial velocity and bead to particle size ratio. This plugging-based contaminant transport can be used to develop in containment technique in soil and groundwater remediation, (b) It also accounts for the importance of "critical salt concentration (CSC)", "critical ionic strength for mixed salt, "critical shear stress" or "critical particle concentration (CPC)" on in situ colloidal fines release and migration and consequently their role on contaminant transport in porous media and (c) This review also include another class of colloidal fines called biocolloids such as virus, bacteria transport in porous media.

1.1 Contaminant transport in porous media:

The mobility of contaminants in saturated subsurface zone is dependent on their distribution between the immobile solid phase and the mobile aqueous phase. Many contaminants readily sorbs to immobile aquifer media and therefore considered to be virtually immobile in the subsurface, thus presenting little danger to, e.g., groundwater supplies. For example many metals and radionuclides bind strongly to mineral components and particulate organic matter of the solid phase, while many non-polar organic contaminants have a high affinity for binding to particulate organic matter [9]. Therefore, most predictions of contaminant transport were based on two-phase equilibrium adsorption models (a dissolved phase and a sorbed immobile phase). The greater the extent to which a contaminant partitions onto the immobile phase, the slower is its average transport velocity in the groundwater shown in Figure 1. This is the case of contaminant transport in the absence of mobile colloidal fines in subsurface environment.

The unexpected appearance of low-solubility contaminants some distance from known source or sooner than would be expected from their solubility, led to examination of the possible involvement of nonaqueous, mobile colloids in contaminant transport [1, 4-5, 9-12]. The presence of mobile colloidal fines can explain such observations and led to the thinking of three phases in contaminant transport models i.e. mobile liquid phase, mobile colloidal phase and the immobile solid phase (Figure 2). Figure 2 compares two and three-phase contaminant transport models. Figure 2 a shows a low solubility

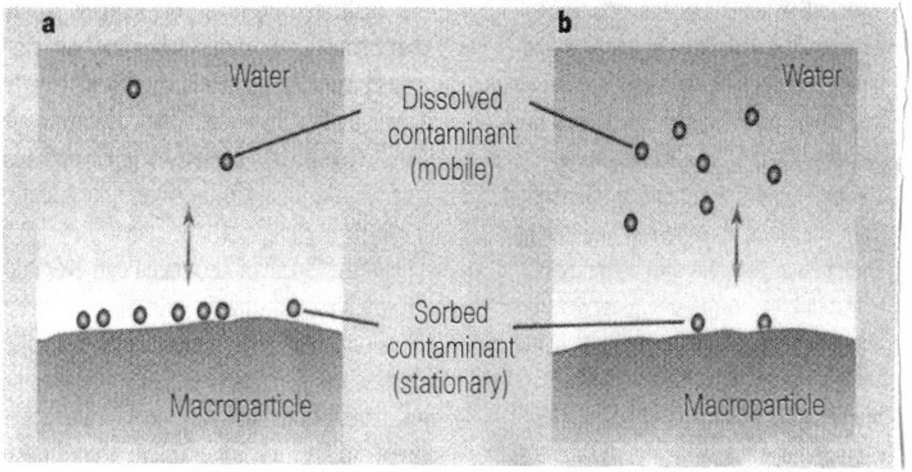

Figure 1: Contaminant transport in a simple two-phase groundwater system. (a) High sorption and therefore low contaminant solubility; (b) low sorption, high contaminant solubility.Macroparticles are the stationary components of a groundwater aquifer and include clays, metal oxides. Figure from reference [4] with written permission.

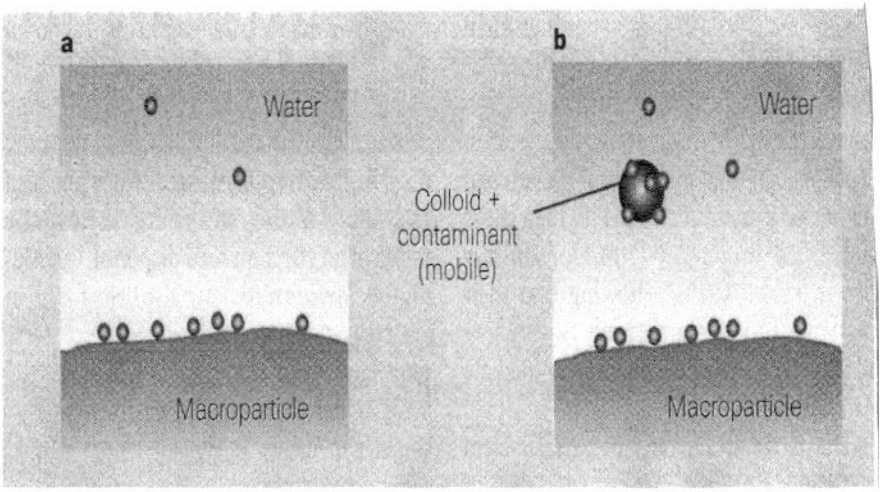

Figure 2: Comparison of generalized two and three-phase groundwater system. (a) Two phase; (b) three-phase. The third phase in b is a colloidal fines or microparticle, shown here with contaminant molecules sorbed to it, thus making them mobile. Figure from reference[4] with written permission.

contaminants distributed between an aqueous phase and immobile aquifer solids called the macroparticles. Colloidal fine materials can increase the apparent solubility of low solubility contaminants (Figure 2 b) if those contaminant strongly associate with the colloids and the colloids minimally interact with the stationary macroparticle phase. This contaminant transport has been known as "Colloid-facilitated contaminant transport" in literature.

Based on research progress towards the role of colloidal fines on the transport of contaminants, which is not limited to facilitation only, we shall term this phenomenon as "Colloid-associated contaminant transport" [1, 13].

In another class where colloidal fines not only act as carriers for contaminant transport but also acts as potential contaminant itself say virus, bacteria called "biocolloids transport". The transport of microbes in porous media is a topic of concern in bioremediation, water treatment, and public health.

2. Sources, mobilization and migration of colloidal particles

Ryan and Elimelech [14] mentioned that the first criteria for colloid-associated contaminant transport is that colloids must be present in sufficient amount to sorbs a significant amount of the contaminant. To predict the potential for colloid-associated transport, we need to identify the amount and nature of the colloidal particles present in the subsurface zone which in turn can indicate the sources of these fine particles and the basic processes responsible for colloid generation in underground flows. By colloidal fines, here we mean the small discrete solid or solid-like particles indigenously present in natural porous media such as rock and soil mass which can be mobilized by means of colloidal, hydrodynamic and other forces. These colloidal fines are termed as migratory fines with dimensions between 1 nm to 10μm [15-17] and generally possess electric surface charge on their surfaces [7]. A variety of inorganic and organic materials exist as colloids and small particles in groundwater, including mineral precipitates (mainly iron, aluminum, calcium, and manganese oxides, hydroxides, carbonates, silicates and phosphates), rock and mineral fragments, biocolloids (including viruses, bacteria and protozoans) and macromolecular components of natural organic matter [18]. These particles are involved in a wide range of environmentally relevant processes. This paper will focus mainly on inorganic colloids in saturated porous media and separately on the biocolloids transport. Field investigations have also shown that these small colloidal size range particles are mostly composed of clay minerals, oxides of Fe and Al, silica and /or natural organic matter [1,6]. Several potential sources of mobile colloidal particles in subsurface media have been identified. Such sources include in situ mobilization of particles that are naturally present, formation of colloidal particles by precipitation from supersaturated solutions and direct introduction of colloidal particles into the subsurface through waste management procedures, such as landfills, septic tanks, or groundwater recharge [1, 6, 13]. By migration of these fines here, we mean the entire sequence of occurrences of release or detachment of these particles present in the porous media, their motion with the flow and finally their capture at some pore sites or their migration out of the porous medium.

2.1 The statics of the release process

The statics of the release process has been analyzed for a fine particle adhering to a pore surface using potential energies of London-van der Waals attraction and electrical double layer repulsion. This single-particle analysis has been tested experimentally and has been shown to satisfactorily describe the conditions necessary for release [19-20]. In this approach, the total energy of interactions between a fine particle and the pore surface on which the particle adheres needs to be determined [7].

Figure 3 shows fine particles adhering to the surface of a pore chamber through which a permeating liquid is flowing. The distance of separation between a fine particle and the pore surface may be very small (order of 10^{-1} nm) [7] and therefore we expect both short-range and medium-range forces between macroscopic bodies to act. In addition, the fine particle will be subjected to hydrodynamic forces of the flowing fluid. Hence, there are several contributions to the total energy of interactions and if the net is repulsive, the fine particle may be released.

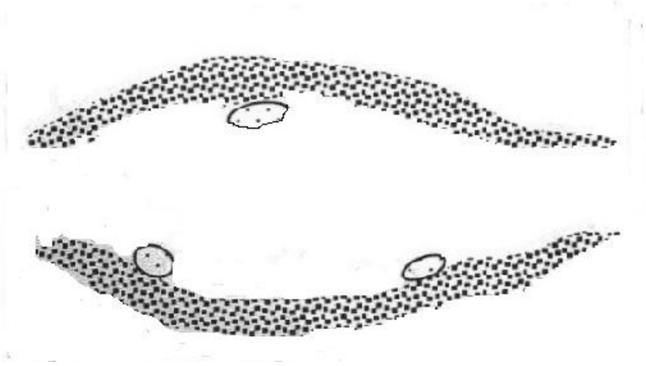

Figure 3. A conceptual picture of a system consisting of fine particles adhering to pore surface. Figure from [7].

2.1.1 Chemically induced release processes

The most common source of mobile colloids in soils and groundwater aquifer is in-situ particle release as a result of changes in solution chemistry [14, 21—26]. In-situ mobilization and transport of colloidal material in natural porous media has been demonstrated for various subsurface materials such as non-calcareous silt loam soil [27], sand soil [23] and highly-weathered aquifer sand [28-29]. The major factors inducing mobilization and subsequent transport are a change in solution ionic strength and pH; however, pH is often not that important for permanently charged clay minerals [27], unless the pH changes span several orders of magnitude or the pH change occurs close to the particles ‘zero point of charge’. Concentrations of mobilized particles can be large; up to a few hundreds of milligrams per liter have been reported for laboratory column outflow [27]. Numerous studies have shown that dispersion and release of particles in most soils is favored by high pH, high Na^+ saturation and low ionic strength [30-39]. Elimelech and Ryan [3] reviewed that addition of anions, surfactants and reductants to sediments also often results in colloid mobilization. Bergendahl and Grasso [40] presented a compilation on selected particle release experiments in natural and model systems under different chemical and physical conditions. They have also developed a particle detachment model under different geochemical conditions. The experimental evidence also suggests that, upon disturbances of ionic strength, in situ colloid mobilization may be an important transport mechanism for contaminant species[31]. If the disturbance of ionic strength occurs in combination with the presence of sorbing contaminants, the mobilized particles may also likely act as vectors for accelerated contaminant movement [41]. Saiers and Hornberger [31] also experimentally found that under conditions of low pore water ionic strength, the kaolinite colloids significantly accelerate ^{137}Cs transport through column packed with quartz sand. Kaolinite mobility and the affinity of kaolinite for sorbing ^{137}Cs diminish with increasing ionic strength. They have also reported that mobility of colloids increased with increasing pH and increasing flow rate.

Roy and Dzombak [22] experimentally found that a decrease in ionic strength can cause colloid mobilization (Figure 4).

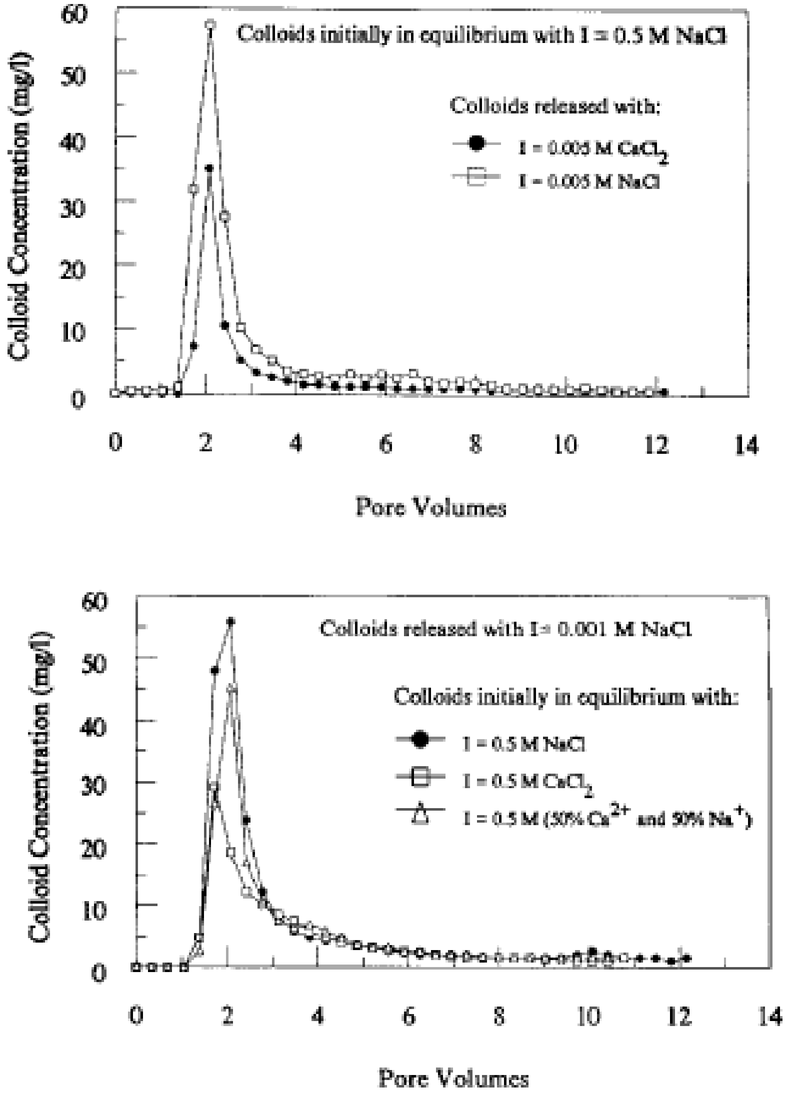

Figure 4: The effect of solution composition on the mobilization of colloids in porous media. In the upper graph, polystyrene latex microspheres deposited on glass in a 0.5 M NaCl solution are mobilized to a greater extent by lower ionic strength solutions of NaCl than by $CaCl_2$. In the lower graph, the amount of microspheres mobilized decreases as the calcium concentration of the deposition solution increases. Figure from [22] with written permission.

This effect has also been observed in Laboratory columns [23-24, 27-28, 42-47] and field-related studies ranging from secondary oil recovery [19, 48] to the sea water/freshwater interface [49-50] to artificial recharge of aquifers [51-52].

The double layer and the London-van der Waals forces between the colloidal fines and the aquifer grains are important for this chemically induced release of fines. The net effect of these attractive and repulsive forces is described by the DLVO (Derjaguin-Landan-Verwey-Overbeek) theory. The "DLVO" theory describes the potential energy profile (V_T / k_B T) for the colloidal particles and grain surfaces interaction by summing the effects of all forces over the interaction distance (h). A chemical perturbation due to decrease in ionic strength, increase in pH causes changes in these forces acting on the colloidal particles and the matrix surface [6-7, 14, 53].

Mobilization is caused by expansion of the electrostatic double layers around like-charged colloids and grains e.g. negatively charged clay mineral colloids and quartz grains) [3]. Kretzschmar et al. [6] pointed out that chemical conditions conductive to the release of colloidal particles can also occur during strong rainfall events, irrigation with Na^+-rich water of low ionic strength, or leaching of salt affected soils with fresh water [23, 54-55]. Although DLVO can predict the effect of these chemical perturbation on colloid release, however, in practice, surface heterogeneities, roughness and poor characterization of surface properties make theoretical predictions unreliable [3].

Figure 4 also shows that sodium chloride will mobilize more colloids than calcium chloride. Figures 5 to 7 are constructed for the dimensionless total interaction energy, (V_T / k_B T) vs separation of distance, h plots for kaolinite-pore wall system in

Berea sandstone for three different salt concentrations of NaCl, CsCl and $CaCl_2$ respectively [7, 37]. Here, V_T is the total interaction energy which can vary from negative values (attractive) to positive values (repulsive) depending on the relative magnitude of the various contributions and k_B is the Boltzman constant and T is the absolute temperature. Calculations have been done for kaolinite-pore wall system in Berea sandstone system [7, 37]. Acid-base (AB) interaction energy in the total interaction energy (V_T) equation is not considered in these calculations.

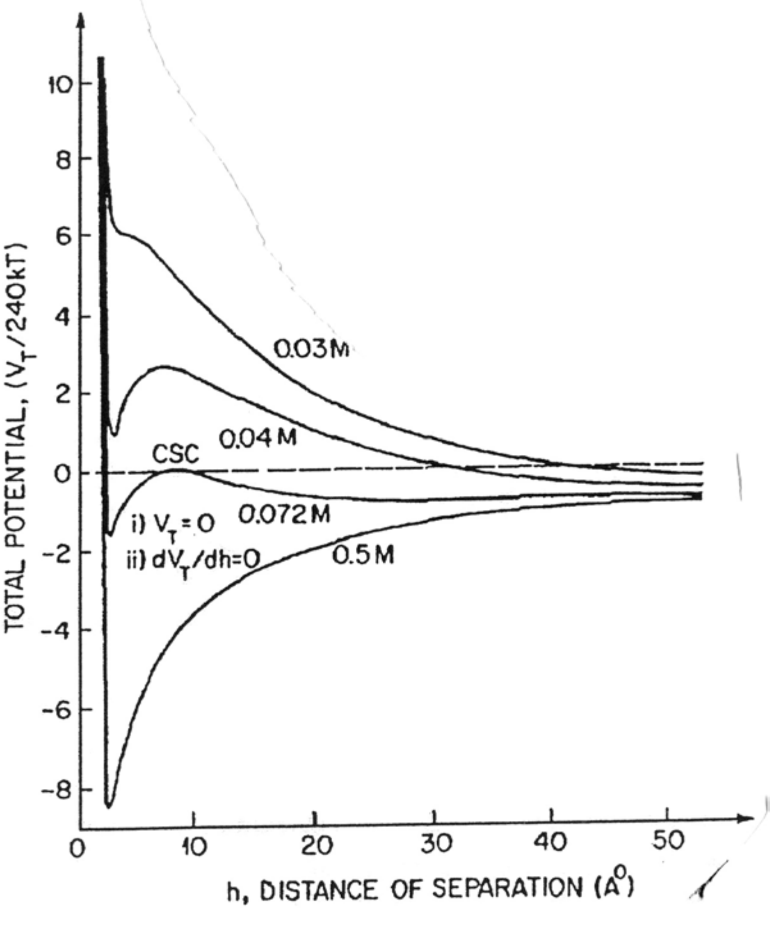

Figure 5. Total interaction energy plots for kaolinite-pore surface system with different concentration of NaCl solution. Here, Hamaker Constant A = 2.6 x 10^{-13} erg, and CSC is "Critical salt concentration" where V_T, total interaction energy = 0. Figure from [7].

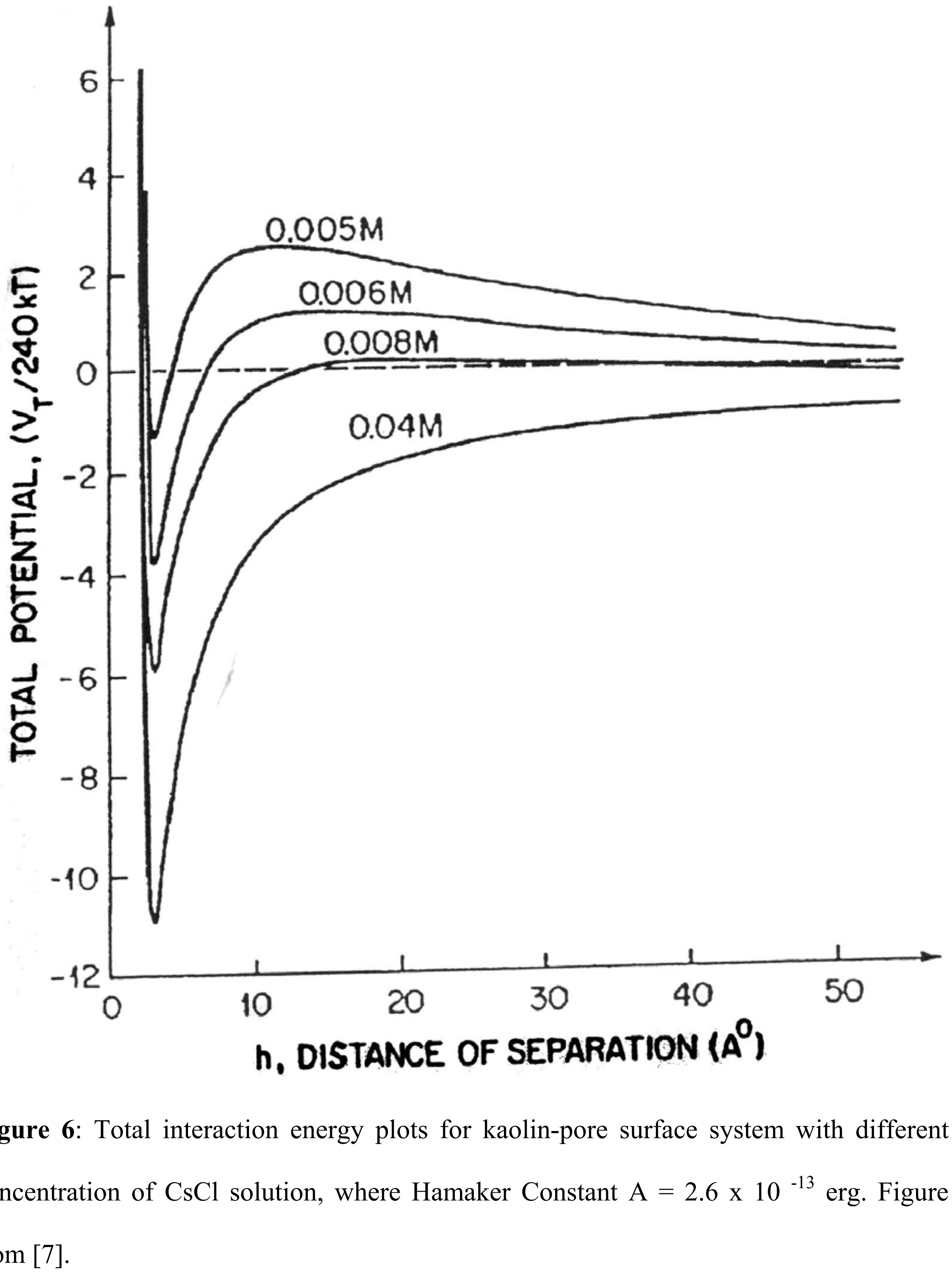

Figure 6: Total interaction energy plots for kaolin-pore surface system with different concentration of CsCl solution, where Hamaker Constant A = 2.6 x 10 $^{-13}$ erg. Figure from [7].

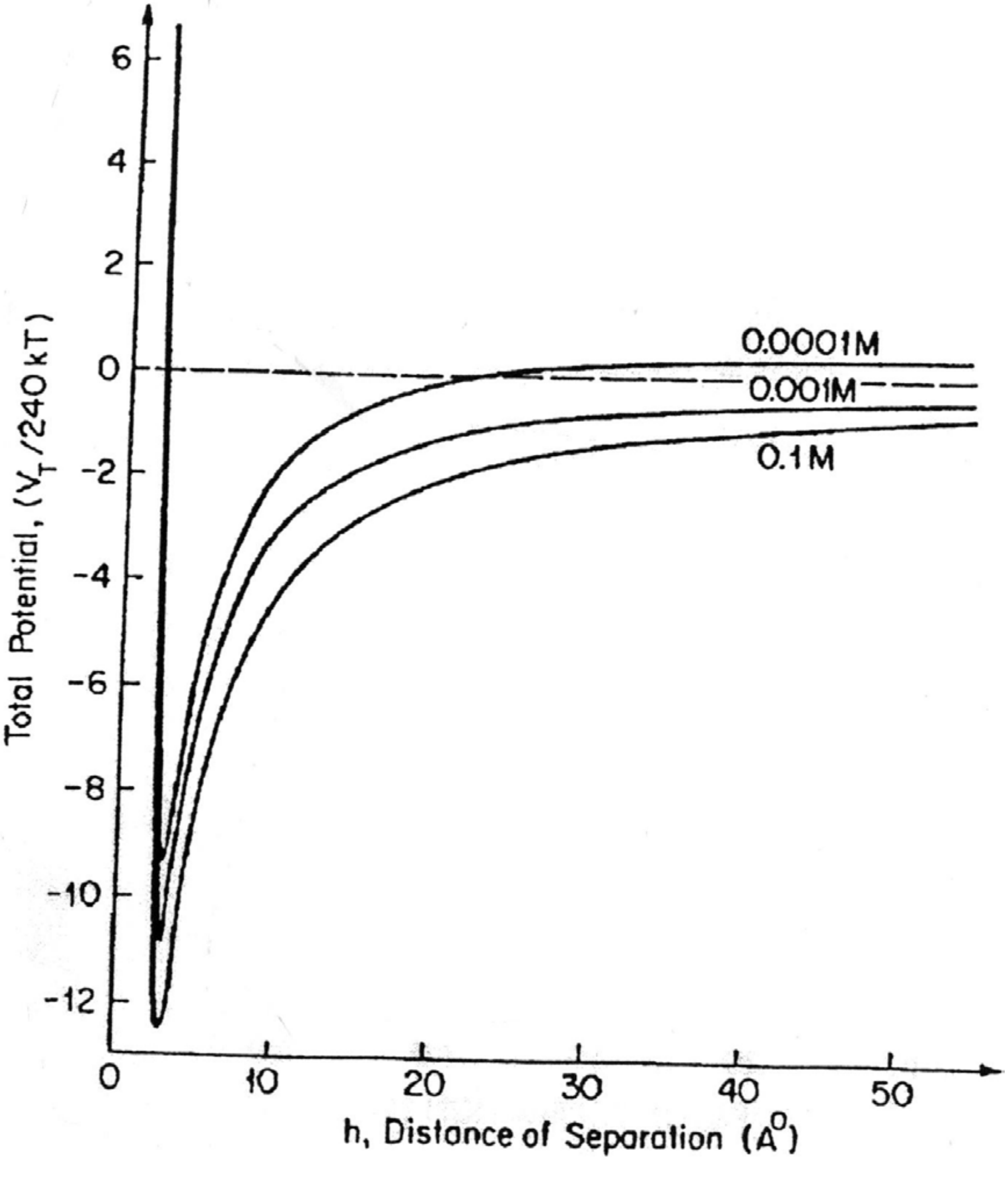

Figure 7: Total interaction energy plots for kaoline-pore surface system with different concentrations of $CaCl_2$ solution, where Hamaker Constant A = 2.6 x 10^{-13} erg. Figure from [7].

They found that while the nature of the plots remains virtually unaltered, the magnitude is strongly dependent on the type of salt solution. Figure 8 is presented for the same system at different pH of the solution. Figure 8 indicates that the interaction energy, V_T become increasingly repulsive (positive) with an increase in pH owing to the change in surface (zeta) potential.

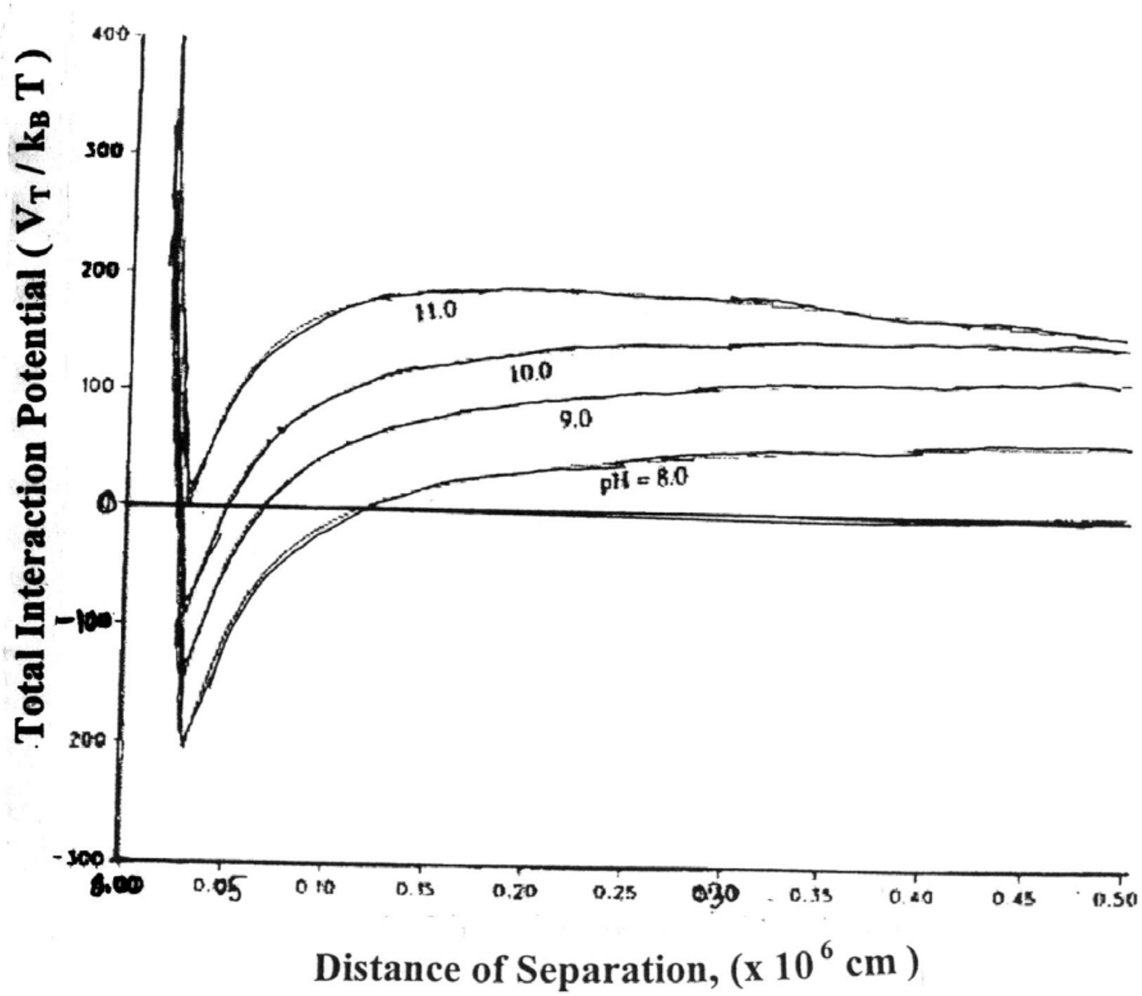

Figure 8: Total interaction energy plots for kaoline-pore surface system at different pH, Where Hamaker Constant A = 2.6 x 10 $^{-13}$ erg. Figure from [7, 56].

There are many investigators developed different theoretical models on colloidal fines release and deposition which are compiled by Ryan and Elimelech [14] and Khilar and Fogler [7] respectively. Grolimund et al. [30] experimentally found that the concentration of released particles can not be modeled with simple first-order kinetics but can be explained in terms of an exponential distribution of release rate coefficient. If colloid and grains are oppositely charged, decrease in ionic strength has no effect on colloid mobilization because decrease in ionic strength strengthens the electrostatic attraction between oppositely charged surfaces [24, 33]. On the other hand solution composition says for monovalent ions cause more release than bivalent ions for a particular ionic strength [7, 22-23, 31].

McCarthy and McKay [18] reported that increased deposition at higher ionic strength and much greater retention in the presence of divalent compared with monovalent, cations of comparable ionic strength is attributed to the screening of repulsive surface interaction energies between colloids and grain surfaces. These relationships have been extensively demonstrated in laboratory studies, including in experiments with natural soil minerals [12]. While aqueous chemistry may control the interactions between colloids and geochemical media, chemical and physical properties of natural geological materials may in some cases control the aqueous chemistry and thus the extent of colloid transport [3, 7, 18].

2.1.1.1 Condition for the release of colloidal fines: the concept of "critical salt concentration", (CSC).

Although a review by McCarthy and Zachara [9] focused attention on colloid-facilitated contaminant transport and subsequent reviews of the subject have highlighted the growing body of literature on colloid transport [6, 14]. The importance of critical salt concentration (CSC), critical total ionic strength (CTIS) for mixed salt on colloidal fines release and transport has however, been neglected. Colloidal particles, attached to grain surfaces, are abundant in the subsurface and under specific conditions they can be released from the matrix and subsequently transported with the mobile phase. This mechanism is of potential importance to the transport of contaminants that are typically adsorb to the solid phase. One of the mechanisms for sudden particle release is a decrease in pore water salt concentration to below the critical salt concentration (CSC) where repulsive forces between the fine particles and matrix surfaces exceeds binding forces which has been discussed earlier section.

Based on the concept of critical flocculation concentration, CFC, in describing the stability for colloidal suspension, Khilar and Fogler [7] proposed that the release of colloidal fines may begin at a specific salt concentration at which both total energy and total force acting on the fine particles are zero[19, 56]. Mathematically, the approximate CSC can be stated as:

$$V_T = 0 \text{ , and } -\frac{dV_T}{dh} = 0 \tag{1}$$

Figure 9 shows the variations of V_T as a function h at a specific salt concentration. Mohan [57] proposed that at CSC, the particles are neither adhered to the pore wall nor prevented from release by an energy barrier.

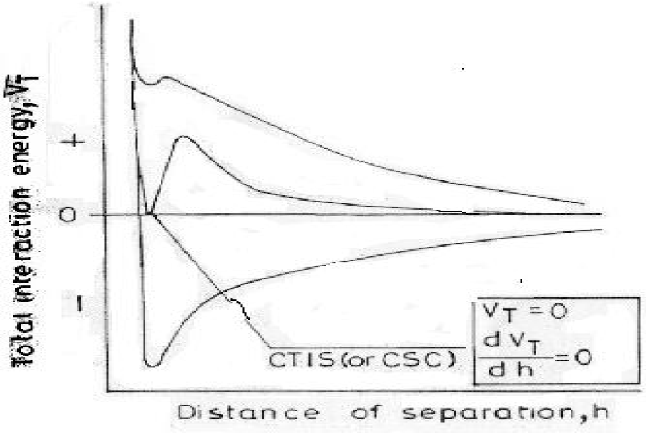

Figure 9: Interaction potentials showing the approximate critical ionic strength [20].

The “critical salt concentration for single salt systems observed by different investigators is shown in Table-1. We observe from this table that the CSC of a single salt system depends on (a) the valance of the cation, (b) the specific characteristics of cation (Na^+ vs Cs^-), (c) the pH of the solution and (d) the type of porous medium (pore surface to which particles are adhered) and (e) temperature of the system. Predictions of CSC based on the approach developed by Khilar and Fogler [19] and Mohan, [57] give excellent qualitative and reasonable quantitative agreements with measurement [20, 57-59].

In analogy with the CSC, the critical total ionic strength is defined as the total ionic strength of a mixed salt system below which the colloidal fines may be released. Khilar et al. [20] have experimentally measured CTIS of the NaCl and $CaCl_2$ system at different percentage of calcium of Berea sandstone. Their results are presented in Table 2.

2.1.2 Precipitation

In most natural subsurface environments colloid formation by precipitation is unlikely to be important because soil solutions tend to be either under saturated or in equilibrium with respect to the mineral phase present. However, human activities such as waste disposal, groundwater pumping or artificial recharge can induce quite drastic changes in water chemistry. Such hydro geochemical perturbations can lead to conditions that favor colloid formation by precipitation [6, 14]. One example is the infiltration of oxygen-rich water into an anoxic aquifer, a situation that may result from artificial recharge.

Table 1. Critical salt concentration for single salt system [7]

Authors	**Porous media**	**Salt**	**CSC (M)**	**(pH)**
Quirk and Schofield [55]	Packed bed of soil Clay content – 19% Kaolin-40% Illite – 40%	NaCl KCl $MgCl_2$ $CaCl_2$	0.25 0.067 0.001 0.0003	5.2 5.2 5.4 5.4
Rowel, Payne And Ahmed [60]	Packed bed of soil Clay content – 22 % Kaolin – 10-15 % Illite – 75-80% Montmorilite	NaCl	0.1	(-)
Hardcastle Mitchel [61]	Bed of compacted soil Clay content – 15 % Illite – 100 %	NaCl	0.05	
Kolakowski and Matijevic [62]	Packed bed of glass beads Chromium oxide	$NaNO_3$ $Ca(NO_3)_2$ $Co(dipy)_3(ClO_4)_3$	0.20 0.0001 0.00001	11.5 11.5 11.5
Khilar and Fogler [19]	Naturaully consolidated sandstone Clay content – 8% Kaolin – 88% Illite -12% Temperature = 303 K	NaCl LiCl KCl NH_4Cl CsCl $CaCl_2$	0.07 0.068 0.044 0.013 0.0006 < 0.0001	8.0
Kia, Fogler And Reed [59]	Same system as used by Khilar and Fogler (19840	NaCl	0.03 to 0.004	8.5 to 9.5

.

Table 2: CTIS for Berea sandstone and soil with clay at different calcium percentage (CP) [7].

CP	CTIS (M) (sandstone)	CTIS(M) (Soil)
0	0.071	0.05
5	0.025	-
10	0.005	0.017
15	<<0.001	0.011
20		0.009

Liang et al. [63] demonstrated in a field experiment that injection of oxygenated water into a anoxic sandy aquifer, in which dissolved Fe(II) was present, resulted in rapid precipitation of Fe(III) hydroxide colloids.

In another field investigation, Gschwend and Reynolds [64] collected groundwater samples near a secondary-sewage infiltration site and found that colloidal particles were formed by precipitation of sewage-derived phosphate with ferrous iron released from the aquifer solids

Several other situations may led to the formation of colloidal particles by precipitation, mostly in connection with waste disposal. Some radionuclides, such as the actinides have a strong tendency to undergo hydrolysis and form colloidal particles by precipitation [6, 65-67].

As a field study, a special situation exists at the Hanford tank farms, in USA, where solutions of high pH, high alkalinity, and high aluminate concentrations have leaked into the subsurface. It has been postulated and then experimentally demonstrated that when simulated Hanford tank solutions contact subsurface sediments, silica is solubilised from native minerals [68-70]. Certain minerals, like quartz and kaolinite are releasing silica and are dissolving under extreme chemical conditions [68-70]. The high silica concentrations from the sediments together with high aluminate concentrations from the tank solutions lead to the precipitations of the secondary mineral phases, which have been identified as zeolite, cancrinite and sodalite [68, 71-72]. These findings have important implications for the fate and transport of radionuclides below the Hanford waste tanks.

Although it is known and documented that changes in solution chemistry lead to the release of colloidal particles from soil and sediment matrices, the particle generation process is not well understood on a mechanistic level.

2.1.3 Hydrodynamically-induced release

The fine particles adhering to the pore surfaces of the porous media of relatively higher porosity and permeability can be released or detached by the hydrodynamic forces [7, 40]. Hydrodynamically induced release of fines is found to be of more common occurrence in loose soil embankments and in packed beds. There are two major reasons for this: (a) the flow velocity encountered is higher and (b) the fines are usually of large size and thereby experience a large drag force.

The statics of the release or detachment of fine particles induced by hydrodynamic forces is more complex than that induced by colloidal forces because hydrodynamic forces may act in more than one direction. The forces that can mobilize a colloid particle attached to the matrix surface due to a physical perturbation are:

- a lift force due to unsteady nature of viscous sub layer in the turbulent boundary layer,
- a hydrodynamic force along the surface causing the particle to slide, and
- a torque causing the particle to roll along the surface.

It has been observed that the fines are released only beyond a certain threshold value of a particular parameter, since a minimum perturbation is necessary to disturb the balance of colloidal and hydrodynamic forces. This parameter could be the "critical salt concentration" (CSC) in the case of colloid ally / chemically induced release, or ‘critical shear stress / critical velocity’ in the case of hydro dynamically released fines[73-75]. Extensive theoretical and experimental studies of the effect of shear on colloid release have been conducted in model system of spherical particles attached to flat walls [31, 76-80]. From these studies, we know that the rate and extent of colloid detachment increases as the flow velocity and particle size increase [73]. Elimelech and Ryan [3] presented detail literature survey on this issue.

It should be mentioned here that the fine particles released consists of clay, quartz and feldspar [74]. Furthermore, the flow velocity is higher. The influences of various parameters relating to the pore surfaces, fine particles, and permeating liquid on the magnitude of “critical shear stress” have not been systematically studied. Nevertheless, the studies of Arulanandan et al.[75] have shown that critical shear stress, ح$_c$ for the erosion of soil mass depends on the type of clay fines, the ionic strength and composition of the permeating liquid and the pH and temperature of the permeating liquid. In fact, these parameters are the same set of parameters that influence the “critical salt concentration", indicating that both colloidally induced release and hydrodynamically induced release are phenomenologically similar [7].

2.2 Capture of Fines and Plugging / Entrapment Phenomenon

The released colloidal fines from the pore surface while flowing with the liquid phase through the porous medium, can either readhere to the pore surface or flow without capture or get entrapped at the pore constrictions. The latter two occurrences are more common as the colloidal and hydrodynamic conditions that bring about their release are not likely to allow these particles to readhere back to the pore surface in the same conditions. Entrapment can occur in three forms, namely size exclusion, multiparticle bridging and surface deposition that are conceptually depicted in Figure 10. Migration of colloidal fines in porous media is a reasonably well-understood topic. Whether the particles get entrapped or not depends on various conditions as described next which could eventually lead to the plugging of the porous media [1, 7, 81]. The plugging results in drastic reduction in flow rates and therefore, there exists a possibility of reduction of contaminant transport and subsequent containment under a constant pressure gradient flow as it occurs in groundwater flows [1, 82]. In 1989, McCarthy and Zachara [9] gave credence to the growing suspicion that "Mobile colloids in the subsurface environment may alter the transport of contaminants" which is called colloid-facilitated contaminant transport and subsequent reviews of the subject have highlighted the growing body of literature on colloid-facilitated transport [6, 14]. But so far nobody gives importance on another important phenomena on in situ colloid release i.e. "plugging" phenomena at pore constrictions and their effect on retardation of contaminant transport [1, 82]. This plugging phenomena depends on various factors which are described below.

2.2.1 Pore Structure

Two important pore structure parameters that significantly affect the entrapment or piping of fines are the pore constriction size distribution and pore constriction to chamber interconnectivity. This interconnectivity can be described in terms of coordination numbers; the number of pore constrictions per pore chamber.

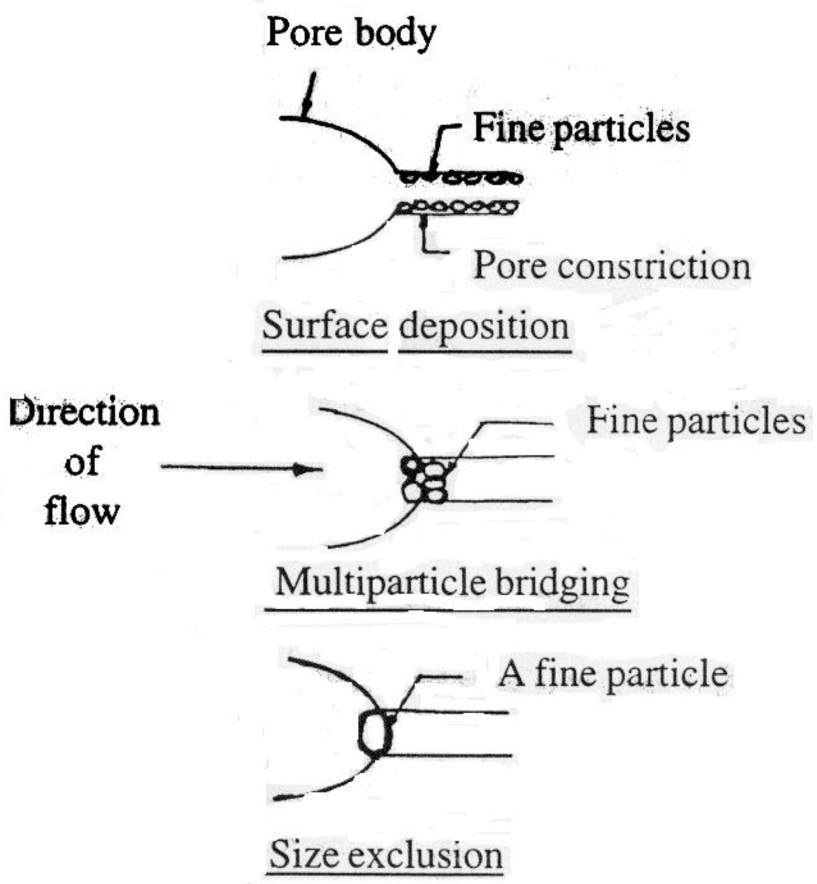

Figure 10: Conceptual diagrams for entrapment of fine particles at the pore constriction Figure from [13].

The probability of entrapment of fine particles is relatively high for porous media having small pore constriction size distributions and low coordination numbers,. The details literature on this area has been presented in Khilar and Fogler [7].

2.2.2 Size of colloidal fines

The size of fine particles, or more pertinently, the ratio of size of fines to that of pore constriction is a crucial parameter in determining entrapment / plugging phenomenon. If the fine size is equal to or greater than the size of the pore constriction, then entrapment or plugging will inevitably take place. In reality, however, both fines and pore constrictions will have respective size distributions. In such cases, Rege and Fogler [83] have shown that the higher the overlap between the size distribution of fines and that of pore constrictions, the higher is the extent of plugging and vice versa. Table 3 presents some qualitative results on whether plugging or other possible types of deposition would possibly occur as determined by the ratio of the size of fines to size of the pore constrictions [74, 84].

Table 3

Dependence of plugging on the ratio of size of fines to size of pore constrictions [7]

Size of fines / Size of pore constrictions	**Occurrence**
≥ 1	Plugging due to blocking or size exclusion
0.1 to 0.6	Plugging due to bridging and multiparticle blocking
0.04 to 0.10	Plugging due to surface deposition, bridging and multiparticle blocking
0.01 to 0.04	Surface deposition. Multiparticle blocking may or may not occur

Single particle plugging would occur when the fine size is comparable to that of the constriction size. When the ratio of fine size to constriction size is, however, between 0.1 to 0.01, then there will be possibility of multiparticle blocking, which depends on constriction of fines and flow rate. Retention of particles due to surface deposition at sites other than the constriction sites also takes place.

Pandya et al., [85] have shown that when the ratio of bead size to particle size (SR) is below 75, there exists a critical particle concentration (CPC) above which plugging occurs due to multi-particle jamming at the pore constrictions. Figure 11 indicates that the ratio of bead / particle size (SR) has a strong effect on plugging which is experimentally shown by Sen et al.[1, 13].

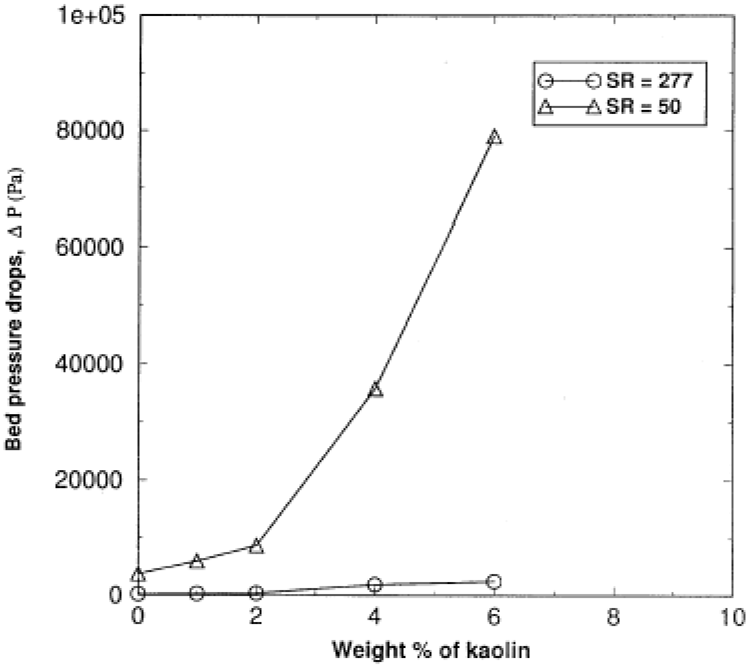

Figure 11. Effect of bead size to particle size (SR) on plugging phenomenon. L (length of packed bed) = 0.28 m, porosity = 0.29, superficial velocity = 0.000339 m / s. Figure from reference [1] with written permission.

Here, the extent of plugging by straining or convective jamming is decreased as the bead / particle ratio (SR) is increased for a fixed flow condition. Similar results have been found by Pandya et al. [85]. Multi-particle bridging or jamming appears to be the likely process leading to plugging [1, 7].

2.2.3 Concentration of fines

When the ratio of fines to size of pore constriction is in the range of 0.01 to 0.1, the concentration of fines assumes a high importance. To date, no studies have been reported delineating the role of concentration on entrapment [1,7]. In a study using glass bead packs and aqueous suspension of polystyrene latex particles, it has been shown that there exists a 'critical particle concentration'(CPC) beyond which the bead pack gets plugged due to multiparticle blocking [1, 85]. It is further shown that this critical particle concentration, CPC, is strongly dependent on the ratio of bead size to particle size. The CPC was found to increase from 0.35 % (v/v) to 9 % (v/v) when the ratio of bead size to particle size was increased from 12 to 40.

2.2.4 Hydrodynamic conditions

Hydrodynamic forces acting on the released fine particles affect the plugging phenomenon at the pore constrictions. If the flow velocity is small and the particle density and size are large, then sedimentation force will affect the trajectories of the particles, causing them to settle to the bottom wall of the pore space. In most cases of migration of fines in porous media, the size of the fines is small and therefore, the fines tend to follow the streamlines of the flow.

Small particles may form bridges at pore constrictions [86]. The structures of these bridges as well as the rate of formation depend on the hydrodynamic conditions of the flow. At higher flow rates, higher drag force acting on the bridge will tend to break them apart while at lower flow rates, the number of bridges formed may be greater. The flow velocity can also indirectly affect the plugging of pores by affecting the rate of release of particles [26, 82].

2.2.4.1 Effect of flow velocity on plugging

The Figure 12 show the steady state normalized pressure drop across the bed as a function of amount of kaolin present in the beds for a ratio of bead size to particle size (SR) of 50 for different flow rates [1,13]. 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 sand bed at the same flow rate ($\Delta P / \Delta P_0$). One can observe from this figure that at superficial velocities of 7.74×10^{-5} m / s and of 1.698×10^{-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 3.39×10^{-4} m / s, 5.095×10^{-4} m / s and 6.79×10^{-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 [81]. Such step rise indicates that plugging would have occurred in the bed. It should be mentioned here that by increasing the kaolin content, the sauter mean size and the porosity change slightly- decrease by less than 5 percent. Hence, increase of pressure drop due to the alterations in porosity and sauter mean size does not completely explain this steep rise. 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.

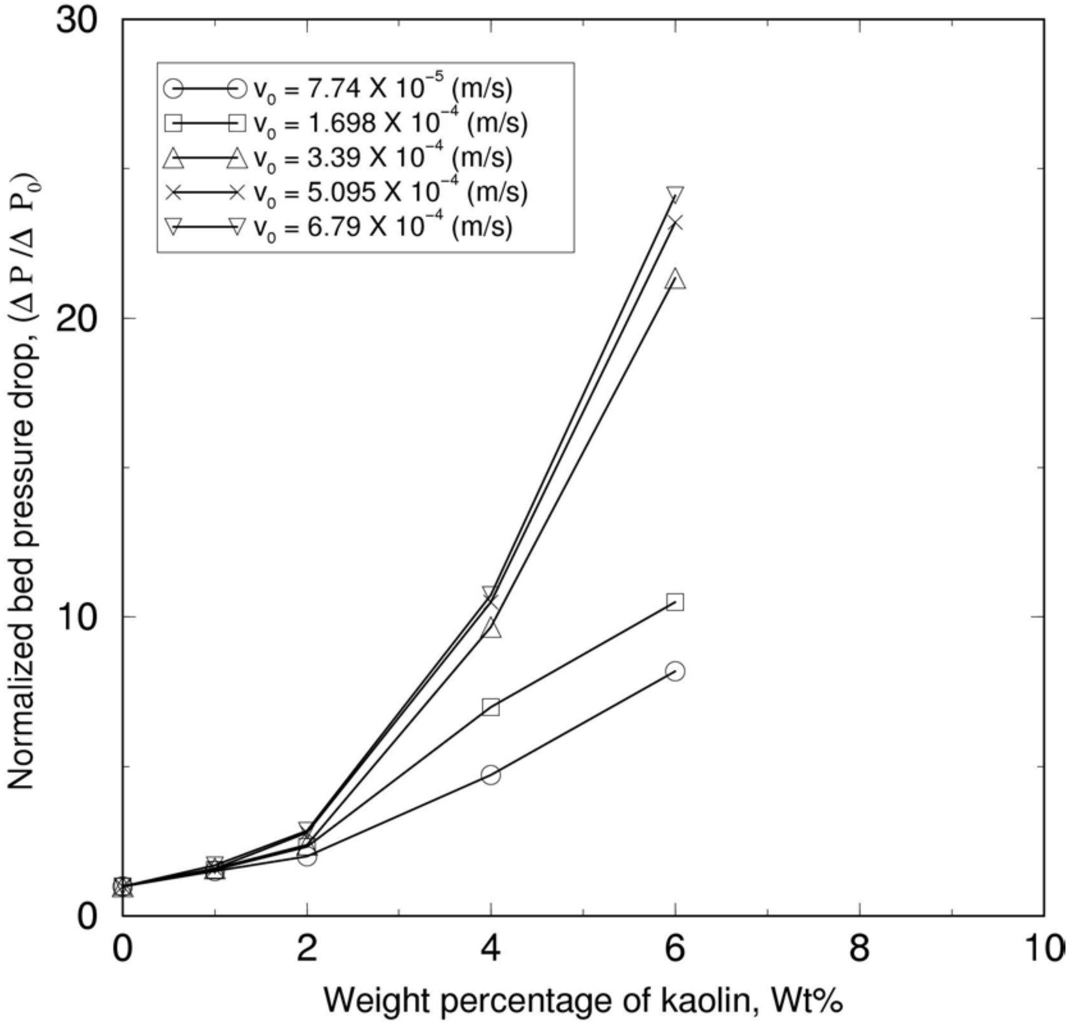

Figure 12: Effect of flow velocity on plugging phenomenon. L = 0.28 m, SR = 50, porosity = 0.29. Figure from reference[1] with written permission.

Amount of kaolin present in the bed determines the concentration of kaolin in pore liquid. The concentration in-turn influences the plugging phenomenon and the nature of 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 multi-particle bridging leading to plugging at the pore constrictions and thereby influences it [81-82]. 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 pore liquid. Therefore, as observed, flow rate is a strong parameter in the phenomenon of plugging [1, 13].

2.3 Stability of dispersed colloidal particles and their transport

A comprehensive amount of literature exists on the topic of colloid mobilization and transport in model and natural systems [7,10, 14 22, 24, 27,41, 87-88]. Considerable advances have been made on the prediction of colloidal transport using experimental laboratory and field studies as well as numerical models [87, 89-90]. Laboratory migration experiments [88, 90-91] have demonstrated that colloids can migrate with natural flow velocities, although compared to dissolved tracers, their migration is much more sensitive to flow velocity and flow path geometry [92]. Grolimund et al [90] found two differences between the colloidal particles and the conservative tracer which are (i) colloidal particles in the soil column travel considerably faster than a nonreactive tracer (earlier breakthrough) and (ii) only a fraction of the injected particles is recovered at the column effluent.

The fate of the contaminants and consequently their impact on the environment strongly depends on the nature and behavior of these potentially mobile colloids. The transportability of colloids and associated contaminants depends on the size and connectivity of pores and the size and stability of suspended colloids [10, 93]. After mobilization the life-time of colloidal particles is mainly determined by convective transport, particle (re-) deposition and the aggregation behavior. The three processes of particle mobilization, deposition and aggregation occur in general simultaneously.

However, relative importance of each of these process is strongly depends on the chemical and physical conditions of the system.

A variety of soil properties influences the dispersibility of colloids from aggregates. Besides the well-documented effects of clay mineralogy (e.g. Seta and Karathasis [34]) and solution ionic strength and pH [27, 41] on colloid dispersion, total clay content [94], soil moisture conditions [95], soil management [96] and interactions among these properties have also been shown to affect colloid dispersibility. Actually, interparticle forces such as vander Waals attraction and electrolytic repulsion determine colloidal fines stability. In addition hydration repulsive forces, hydrophobic attraction, polymer bridging or steric repulsions also contributes to the overall stability behavior of suspended soil colloids [97]. Experiments on the stability of dispersed colloids show that dissolved organic matter (DOM) and increasing pH contribute to the stabilization of colloids. In addition, DOM induced mobilization of dissolved Pb has often been observed [98].

Basically in the saturated zone colloid transport is described by several filtration models [14] but in the unsaturated soil zone, the mobilization, retention and migration of colloids is much less understood.

3. Overview of contaminant association with colloidal particles

For contaminants that are present in relatively low concentrations, it is generally accepted that association of the contaminants with colloids is another important basic concentration regulating process in subsurface environment [1, 3, 6, 18]. The contaminants may be cationic forms of metals (e.g., Cs^{+}, Cu^{2+}, Ni^{2+} etc), anionic forms of metals (e.g. CrO_4^{2-}, AsO_4^{3-} etc), nonpolar organic compounds (e.g. Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, DDT) and polar organic compounds. Colloidal particles are minerals with amphoteric surface (e.g. iron, aluminum and manganese oxides, carbonates) and fixed charge surfaces (phyllosilicate faces), organic matter coatings on mineral phases and bacteria. The basic mechanisms of contaminant association with colloidal particles are surface complexation, ion exchange and hydrophobic partitioning . Basically, the abundances of contaminant metal elements as well as their mobility or dispersability in soil, and water depends on their sorption characteristics at solid/ liquid interfaces, which in turn depend on environmental variables such as pH, salinity, presence of other competitive and/or complexing cations or anions, temperature, bedrock geology/ mineralogy, suspended particulate content and water velocity [6, 13, 99]. Cationic forms of metals (cations) are the most frequently reported contaminants influenced by colloid-associated transport [1, 3, 5, 100].There have been many experimental and modeling studies on the behavior of cations, particularly heavy metal ions, at mineral / aqueous interfaces (e.g.,, oxides, hydroxides and oxyhydroxides, kaolinite, illite) for different values of pH, metal ion concentration, solid / liquid ratio and ionic strength and only few are mentioned herewith [99-117]. Each of these sorption processes has also been reviewed by several recent researchers [100, 108]. The colloidal sorption capacity for hydrophobic chemicals is influenced by solution chemistry and nature of colloids. Colloid mineralogy and colloid-associated organic matter as well as ionic strength, valence of major cations and dissolved organic matter content of the suspension are important factors [93].

4. Biocolloids Transport

Another class of colloidal fines says viruses and bacteria also fall into the colloidal size range and called biocolloids. Such "bio-colloids" can pose serious health hazards if they occur in drinking water wells [118-119]. Therefore microbial contaminants (protozoa, bacteria, and viruses) pose a great risk in water resources. Historically, groundwater has been assumed to be free of pathogenic viruses, bacteria, and protozoa, but recent surveys indicate that a significant fraction of groundwater supplies are a source of water-borne diseases [120]. If at least four orders of magnitude reduction in virus, bacteria concentration can not be achieved between a potential microorganisms source (e.g. septic tank, leaking sewer line, or sewage infiltration beds, land application of sewage sludge) and a water supply well, the aquifer will be considered *"hydrogeologically sensitive"* [120]. Another major source of microorganisms in soils or groundwater aquifers is the controlled application or injection of selected bacteria strains for in situ bioremediation of contaminated sites via bioaugmentation [121] or as biocontrol organisms against certain plant diseases [120]. Therefore, knowledge about transport of bicolloids in porous media is necessary for safe disposal of wastewater and for the development of effective bioremediation strategies of contaminated soils and groundwater using introduced microorganisms strains [121].

McCarthy and McKay [18] and Sen et al., [122] mentioned in their article that there is a substantial body of published research on microbial transport in the subsurface, much of it focuses on transport in the saturated zone [119-131-134]. Transport of bacteria in porous media is mainly bounded with small scale batch and column studies. To better understand the process controlling the transport of microbes in porous media, models of microbe transport have been developed and tested against laboratory and field experiments which has been compiled by Kretzschmar et al [6] and Lis Wollesen et al [93] respectively. All these transport models incorporate advection, dispersion and a variety of terms accounting for microbe removal and growth. For viruses, the additional terms include attachment, release and inactivation. Physical and mathematical model for describing the fate of bacteria in porous media has been developed by few researchers [120-122, 131]. Bacterial transport in the subsurface is a complex and interacting process. Because bacteria are living organisms, their transport in the subsurface is more complex than in the case for colloidal solutes transport [17]. Not only are they subject to same physicochemical phenomena as are colloids [17] but they are also a number of strictly biological processes that affect their transport. Investigators are identified several environmental factors such as cell concentration, substrate concentration, captured to and release from the porous medium surfaces, growth and inactivation, chemotaxis and advection and dispersion [122,132] which having strong effects on bacterial fate and transport in porous media.

Moreover Bacteria can also dramatically accelerate the transport of heavy metals in ground water. Pang et al. [135] conducted both batch and column experiments to investigate adsorption of cadmium (Cd) onto bacillus subtilis spores or Escherichia coli vegetative cells and Cd transport in alluvial gravel aquifer media in the presence of these bacteria and they have found that Cd traveled 17 to 20 times faster when it traveled with mobile bacteria.

The dynamics of attachment of viruses to porous media will affect viruses transport over long-term release of viruses into the porous media. Properties of the porous media strongly affect biocolloids attachment, release and inactivation. The initial attachment of these microbes to porous media is controlled by electrostatic interactions between the surfaces of the microbes and the grains that comprise the porous media and the solution chemistry. In this way, “biocolloids transport” is quite similar to colloid transport. Therefore, the present review will not focus much on bacterial and virus transport; however, most analysis and treatments are also applicable to biocolloids transport.

5. Colloid-associated transport of contaminants

Here colloid-associated contaminant transport means not only facilitation of contaminants but also retardation of contaminant transport due to presence of colloidal fines. Majority of evidences for colloid-facilitated transport of contaminants are based on indirect field observations, model calculations and laboratory-scale column experiments. We first review the reported laboratory and field studies on the colloid-facilitated contaminant transport in porous media and then the studies concerning the modeling of this transport phenomenon and finally retardation of contaminants transport due to presence of colloidal fines under plugging conditions. Colloid-facilitated transport has been demonstrated for alkali and alkaline earth cations (Cs^+ and Sr^{2+}), transition metals (Ni^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}), oxyanions (arsenic and iodate), non-polar organic compounds (phenanthrene and pyrene) and a polar organic compounds (pesticide). Table 4 shows that over the last decade, colloid-facilitated transport laboratory experiments with a wide variety of contaminants and colloidal particles.

5.1 Colloid-associated transport of Inorganic ions

5.1.1 Colloid-facilitated transport of radionuclides

The study of radionuclide migration through the subsurface is an important issue in the safety assessment of nuclear waste repositories or radionuclide migration at former nuclear test sites. A number of investigations suggest that colloids dispersed in the groundwater provide an additional phase for radionuclides and enhance the transport of radinuclides [5-6, 67, 136-146]. Radionuclide elements, especially the actinides (e.g., U, Np, Pu, Am), have a strong tendency to undergo hydrolysis and to form colloidal particles by precipitation [65-67, 142, 147-148].

Table 4: A compilation on laboratory experiments on colloid-facilitated contaminant transport in subsurface zone. Travel time noted as either time or number of pore volumes (PV). Data are also taken from Elimelech and Ryan [3].

Contaminant	Colloids	Porous media	Travel time and distance	Comments	Reference
Co^{2+}, Sr^{2+}, Cs^{+}	Clay minerals from porous media; neutran-activated for colloid tracing.	Course sand (90%) and clay or zeolite (10%).	56 h, 15 cm.	High sodium phosphate concentration from waste form.	Torok et al. [149].
Arsenate	Hematite, 100-300nm, 5-10 mg /L.	Alluvial sand and gravel; quartz, fieldspar.	up to 4 PV, 0.8-3.4 m /d, 2.5-5.1 cm.	I 0.03.	Puls and Powell [150].
Cu^{2+}, Pb^{2+}, Ni^{2+}, Cr^{2+}	Clay and organic matter.	calcareous loam soil.	~10 cm	0.01(M)NaCl 01MCaMgaccetate.	Amrhein et al. [151].
Phenanthrene, pyrene.	Polystyrene latex, 76, 301 nm	Glass, 0.1, 0.2 mm, quartz sand ~ 0.12 mm.	250 PV, 20 cm.	0.05 mM KCL	Sojitra et al., [152].
Pb^{2+}	Clay minerals from soil; ~0.5-1μm dia.	Silt loam soil; noncalcareous	0.3 to 1 h, 10-12 cm	20-50 mM NaCl, 0.15 mM $CaCl_2$.	Grolimund et al., [12].

Cs^+	Montmorillonite	Quartz sand	30 PV	0.05-0.5 M NaCl	Faure et al. [43].
^{137}Cs	Kaolinite, 0-200 mg /L, ~ 0.5 µm	Quartz sand	100 PV, 5.2 cm.	I 0.002-0.1M, pH 7.2	Saiers and Hornberger [31, 153].
^{137}Cs, iodate	Goethite, 6-28 mg /L, 0.12 µm	Quartz sand	7.5-60 min, 6.cm	I 0.001 M, pH 4 and 10.5	Satmark et al. [154].
Ni^{2+}	Natural colloids from Lincoln sand, 250 mg /L	Ottawa sand	10 cm	I 0.001M, pH 8.3	Roy and Dzombak [22]
Cs^+, Sr^{2+}, Co^{2+}	Natural colloids from soil, < 5 µm	Sandy soil, quartz, feldspar	1-10 cm	pH 6.7	Tanaka and Ohnuki [155].
Phenanthrene	Latex microspheres, 100 mg/L	Eustis sand	10 cm	I 0.001M, pH 7.5, 9.8	Roy and Dzombak [8]
Cs^+	Silica, 100 nm, 200 mg/L	Glass beads, 150-210 µm	10 PV, 50 cm	pH 8.9, $NaHCO_3$	Noell et. Al. [156].
U, Th, Pu, Am, Np, Sr,	Smectitic bentonite colloids from bentonite backfill material <	Bentonite backfill material	19.8 PV -	-	Mori et al. [157]
Cs^+, I^-	clay colloids (montmorillonite), 360 nm	Sand column 10 cm	25 PV	-	Saiers [2]
Hydroxyatrazine (HA)	smectites colloids	Soil column		pH 4.8	Karathanasis, [158]
Zn^{2+} Ni^{2+}	6% (wt) kaolin, 2.8 µm	6 % (wt) kaolin-sand bed, 28 cm,	14 PV	-	Sen et al [1]
^{137}Cs	Natural colloid from Hanford sediment. Colloid conc. 50, 100, 37, 79, 45 mg/L.	Hanford sediment and silica Ottawa sand			Zhuang et al [159].
Pb^{2+}	Natural colloids from Zeolitized tuffs	Zeolitized tuff			Um and Papeles [160]

Radionuclides that are normally considered to be strongly sorbed (e.g. ^{137}Cs and ^{239}Pu) to colloidal particles consisting of clay minerals, oxides, and humic substances [66, 149, 161-163]. Complexes with organic matter can result in humic colloids that are transported under favorable conditions of solution composition and water content [164-167]. Contardi et al.[168], have shown that inclusion of colloids into a conceptual model of contaminant transport can result in a several order of magnitude reduction in the retardation factor for strongly retained ions like Am and Th. Mori et al. [157] have shown from their laboratory column experiments that migration behavior of the tri and tetravalent actinides Am and Pu was strongly mediated by the bentonite colloids. Colloid-mediated Pu transport in groundwater has been reported by Kersting et al.[5]. Using the ratio ^{240}Pu to ^{239}Pu, Kersting and her colleagues could unequivocally identify the source of the Pu as more than one kilometer away from the sampling site. Filtration of contaminated groundwater samples removed 99% of the Pu, indicating their association with colloidal material. Faure et al. [43] conducted packed column experiments with sand and 5% bentonite clay to study colloid and radionuclide transport induced by a salinity gradient. At the salt (NaCl) concentration > 0.16 M no colloid particles were leached from the column and ^{137}Cs was transported as the dissolved species. When the salt concentration was decreased below the critical threshold concentration of 0.16 M, particles started to be mobilized and colloid-facilitated ^{137}Cs transport was observed. Saiers and Hornberger [153] studied the influence of kaolinite colloids on the transport of ^{137}Cs through packed sand columns. Breakthrough curves for ^{137}Cs in the presence of different concentrations of colloidal particles in the influent are shown in Figure 13. The average travel time for the main ^{137}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 / liter. Of particular interest is the initial, unretarded breakthrough of ^{137}Cs in the presence of colloidal particles, resulting in a small plateau in the ^{137}Cs breakthrough curves (BTCs). Such unretarded contaminant transport in the presence of mobile colloids is of major relevance to risk assessment, because it leads to a rapid spread of the contaminant in the subsurface.

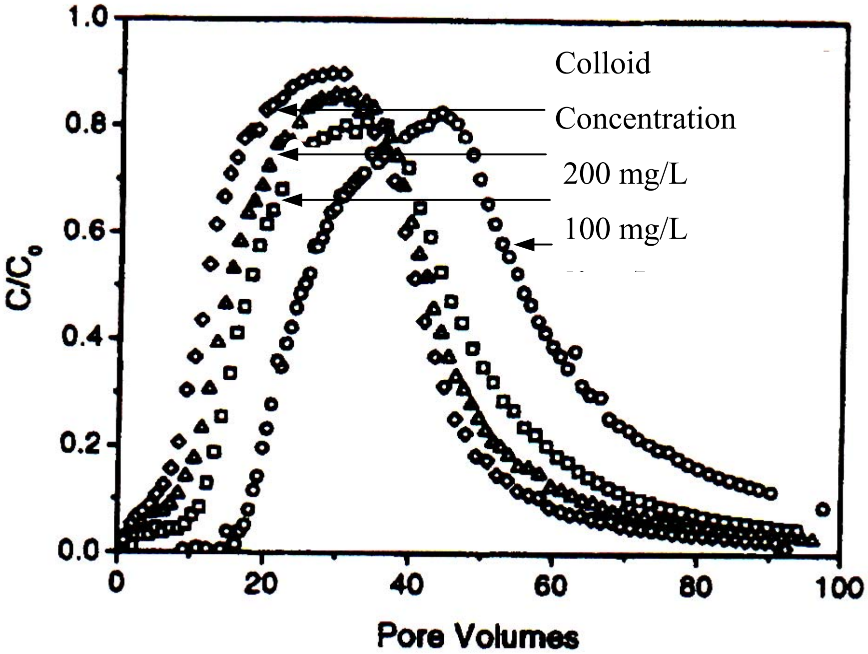

Figure 13 Transport of ^{137}Cs through columns packed with quartz sand in the presence and absence of kaolinite colloids (0-200 mg / liter). All feed solutions contained 0.35 ppb ^{137}Cs. Figure from [153]. C_0 is the initial input contaminant ^{137}Cs concentration.

Thus, mobile colloids potentially play a significant role as carriers of radionuclides in soils, groundwater aquifers, and rock fractures ([3, 6, 153, 157, 169]. Saiers and Hornberger [31] reported the results of their laboratory experiments on the co-transport of ^{137}Cs by inorganic colloids composed of kaolinite. They found that under conditions of low pore water ionic strength, the kaolinite colloids significantly accelerate ^{137}Cs transport through column packed with quartz sand. Immobilization of colloid increased as the ionic strength of the background electrolyte solution increased. Remobilization of initially deposited colloids occurs when the ionic strength of the background solution was reduced [31]. The mobility of colloid increased with increasing pH and increasing flow rate and consequently their effect on increase in contaminant transport [1, 31].

5.1.2 Laboratory studies on colloid-facilitated transport of other inorganic ions

Several recent experimental studies have found that colloidal fines in addition to radionuclides, (Table 4) can often carry contaminants such as metal ions and hydrophobic organic thus, significantly accelerate the transport of contaminants through porous media [1, 3, 8-10.12, 14, 42, 150, 153, 170-180]. Karathanasis [158] has observed experimentally that an increased transport of Zn in the presence of smectitic colloids through a soil column. Puls and Powell [150] have performed experiments on the transport of As^{2+} in the presence of colloidal ferric oxide particles and showed that colloid associated arsenate transport is 21 times faster than that of dissolved arsenate.

Experimental studies have been conducted for systems where the porous media contain the mobilizable colloidal fine particles, thus representing the underground soil mass [1, 8, 12, 43, 159,181-182]. Zhuang et al. [159] have conducted a series of saturated column experiments to investigate the effect of colloids on Cs^+ transport in two types of porous media, one being Hanford sediments characteristics of 2:1 clay minerals and another being silica Ottawa sand. The colloids used were obtained by reacting Hanford sediment with simulated tank waste solutions. They observed that due to the nonlinearity of Cs^+ sorption, the colloid-facilitated Cs^+ transport was more pronounced at the low Cs concentration (1.4 x 10^{-8} M) than at high concentration (7.5 x 10^{-5}M), when expressed relative to the inflow Cs^+ concentration. In the absence of colloids they found that there was no movement of Cs^+ through the 10 cm long column during the experiment within about 20 pore volumes except for high Cs^+ concentration in the Ottawa sand where a complete breakthrough was observed.

Roy and Dzombak [8] conducted a systematic laboratory investigation on Ni^{2+} contaminant transport in presence of in situ mobilized colloidal particles, through sand packed column. Significant enhancement of transport by colloids was observed. Without colloids, Ni^{2+} concentrations approached inlet concentration after about 15-pore volumes, whereas with colloids it reached only after 3-pore volumes. These experiments were conducted at a Ni^{2+} concentration of 10^{-6} M. When the experiments were performed at a higher concentration of Ni^{2+}, 10^{-4} M, the trends were quite different: the deposition efficiency of the colloids increased substantially and almost no colloids were measured in the effluent. The concentrations in the effluent were substantially lower than that for the low concentration Ni^{2+} experiment. In the experiment performed to observe colloid transport without Ni^{2+}, it was observed that the effluent colloid concentration was essentially identical to those for the 10^{-6} M Ni^{2+} case.

The potential of natural in situ mobilized colloids for facilitating the transport of strongly sorbing contaminants in natural porous media was demonstrated by Grolimund et al. [12]. In column packed with a non-calcareous soil material, they observed significant colloid release and mobilization of Pb^{2+} when feed solution was switched from 50 mM NaCl to 0.15 mM $CaCL_2$ (Figure 14).

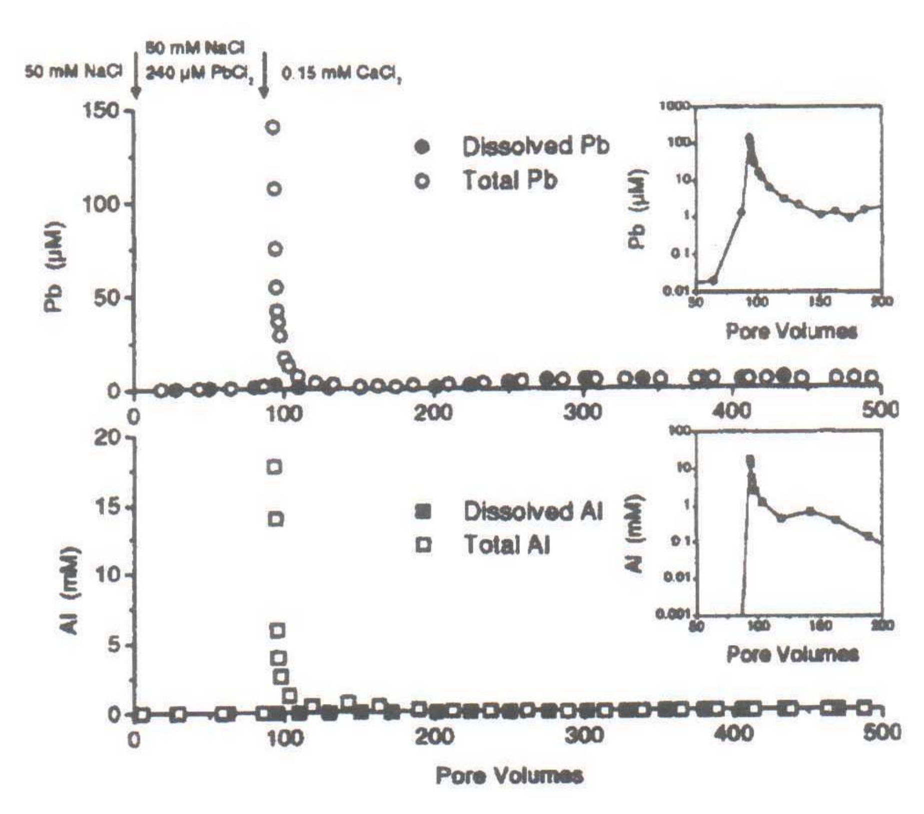

Figure 14 Transport of Pb^{2+} in association with in situ mobilized colloids in a packed, Na^{+}-saturated soil column following a decrease in solution ionic strength. Colloidal Al was used as a key element to quantify the colloid concentration. The inlets show that elevated colloidal Al and Pb^{2+} concentration were observed for at least 50 pore volumes after the change in feed solution. Figure from [12].

Figure 14 shows a typical experiment in which the soil column was first saturated with Na^{+} and then contaminated by leaching the column with about 90-pore volumes of 50 mM NaCl solution containing 240 μM $PbCl_2$. Because dissolved Pb^{2+} is strongly retarded, no breakthrough of dissolved Pb^{2+} was observed during these 90 pore volumes.

The feed solution was then switched to a 0.15 mM $CaCl_2$ solution, thereby decreasing the ionic strength and changing the major cation from Na^+ to Ca^{2+}. Such a change in feed solution results in two fronts moving through the porous medium, namely, an unretarded normality front at which the ionic strength decreases and a retarded Ca^{2+} for Na^+ exchange front. Between these two fronts, the conditions are favorable for colloidal Al, release and transport. Thus, a large colloidal Al peak appeared in the column effluent due to decrease in ionic strength and elevated colloid concentrations were detected for at least another 50-pore volumes, approximately the breakthrough of the Ca^{2+}-Na^+ exchange front. Correspondingly, a significant mobilization of Pb^{2+} in association with the soil colloids was observed. This colloid bound Pb^{2+} was mobilized in the contaminated part of the soil column and transported together with the colloidal particles through the uncontaminated part of the soil column. Small concentrations of dissolved Pb^{2+} appeared much later in the column effluent, approximately after 200-pore volumes. Therefore, mobilization of colloidal particles and subsequent colloid-facilitated contaminant transport can provide an unretarded pathway for strongly sorbing inorganic contaminants.

Several authors reported colloid-facilitated Pb transport to be a major pathway for Pb in soils [179-180]. Column experiments with insoluble Pb precipitates conducted in calcareous gravel-sand mixture showed that colloidal Pb is much more mobile than dissolved Pb^{2+} [183].

Sen et al. [1, 13] conducted laboratory column study on the effect of mobilization and migration of colloidal fines, kaolin on the transport of Ni^{2+} contaminant through sand beds containing 6 wt % kaolin particles under non-plugging condition (Figure 15). From

Figure 15, break through curves (BTC) for Ni^{2+} gives significant differences as compared to those for the BTC with sand bed.

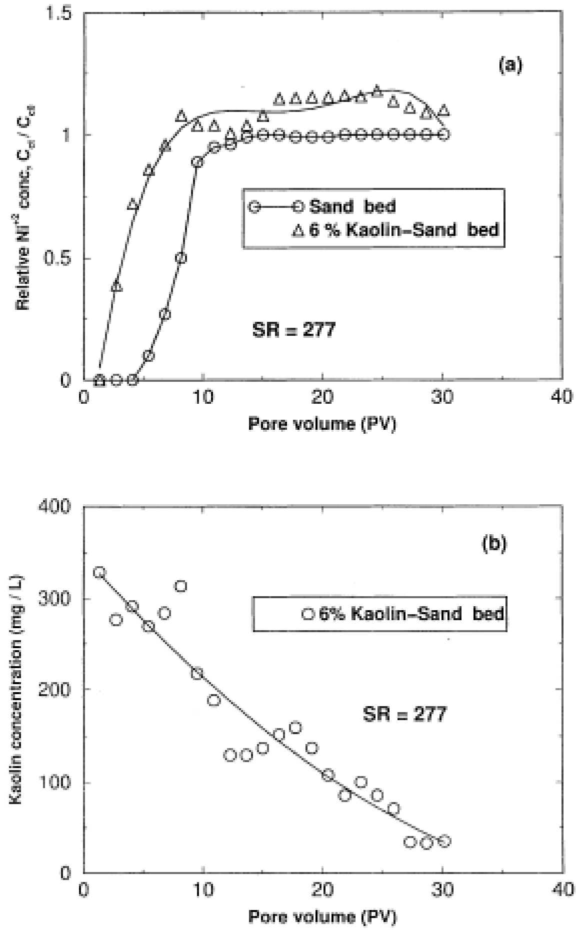

Figure 15: Role of mobilizing kaolin particles on the facilitation of Ni metal ions transport during flow through kaolin-sand bed under nonplugging condition. (a) Comparisons of experimental BTCs for Ni metal ions during upward flow through the sand bed and the 6% kaolin-sand bed; (b) Condition of effluent kaolin concentrations during flow through same bed. Initial Ni metal ion concentration = 11.0 ppm, length of bed (L) = 0.28m, Porosity (€) = 0.32, Superficial velocity = 6.69 X 10^{-4} m/s and SR = 277 (non-plugging). Figure from reference[1, 13] with written permission.

Breakthrough plots are presented as plots of C_c / C_{c0} against pore volume (PV), where C_c is the aqueous phase effluent Ni^{2+} concentration, C_{c0} is the influent Ni^{2+} concentration. SR represents the bead to particle size ratio.

First, the breakthrough has occurred earlier at around 6 pore volumes. Secondly, the dimensionless outlet of Ni^{2+} concentration has increased beyond 1.0 implying that colloidal kaolin particles with 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 Ni^{2+} transport process. The fact that colloidal particles were migrating out of the bed can be confirmed by the measurement shown in Figure 15 b. One observes from the figure 15 (b) that particles migrated out of the bed for about 25 pore volumes during which period, the dimensionless Ni^{2+} concentration was above 1.0. Such measurements carried out by Sen et al. [1] which clearly document the well-established phenomenon of colloid-facilitated contaminant transport. Further, it documents that the facilitation occurs as long as the fine particles are migrating out of the bed.

Um and Papelis [160] studied column experiments to investigate the effect of natural colloids on the transport of a strongly sorbing metal, lead (Pb^{2+}) under different geochemical conditions. Here, natural colloids were generated from zeolitized tuffs from the Nevada Test site (NTS). Their experimental results is that because of high sorption affinity of Pb^{2+} forzeolitized tuffs, the migration of Pb^{+2} without colloids was strongly retarded. The presence of mobile colloids, however, enhances the mobility of Pb^{2+}. Approximately 75-90% of the eluted Pb^{2+} was transported as a colloid-associated phase.

5.1.3 Colloid-associated retardation of inorganic ions due to plugging phenomena

The literature available so far has primarily focused on the facilitation of the contaminant transport due to presence of colloidal fine particles The focus of most of these studies has been on documenting this important phenomenon which have been reviewed first by McCarthy and Zachara [9] and subsequently by Ryan and Elimelech [14] and Kretzschmar et al [6] respectively.

Migration of colloidal fines in porous media is a reasonably well-understood topic. It has also been found out that under certain conditions which have been discussed earlier section in details, entrapment of the migratory colloidal particles can occur at the pore constrictions, which could eventually lead to plugging of porous media [1, 7, 81, 85]. This plugging results in drastic reduction in flow rate and thereby, there exists a possibility of retardation of contaminant transport and subsequent containment technique in soil remediation. No reported study has considered the possibility of occurrence of plugging of colloidal fine particles. Therefore, it is necessary to consider this plugging phenomenon on colloid-associated contaminant transport in porous media.

Sen et al. [1] presented their results on Ni^{2+}contaminant transport under plugging condition (Figure 16). Figure 16 presents the measured BTCs for different packed beds which indicates that the Ni^{2+} breakthrough gets delayed as the content of kaolin in the bed is increased. One further observes that the dimensionless effluent 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 occur. Plugging, however, occur for bed containing 4% and 6% kaolin. At this conditions, the dimensionless effluent Ni^{2+} concentration is below 0.65 after passing 18 pore volumes through the beds. At the same plugging conditions, the dimensionless effluent Ni^{2+} concentration is almost one after passing approximately 44 pore volumes for 4% bed and 54 pore volumes for 6% bed.

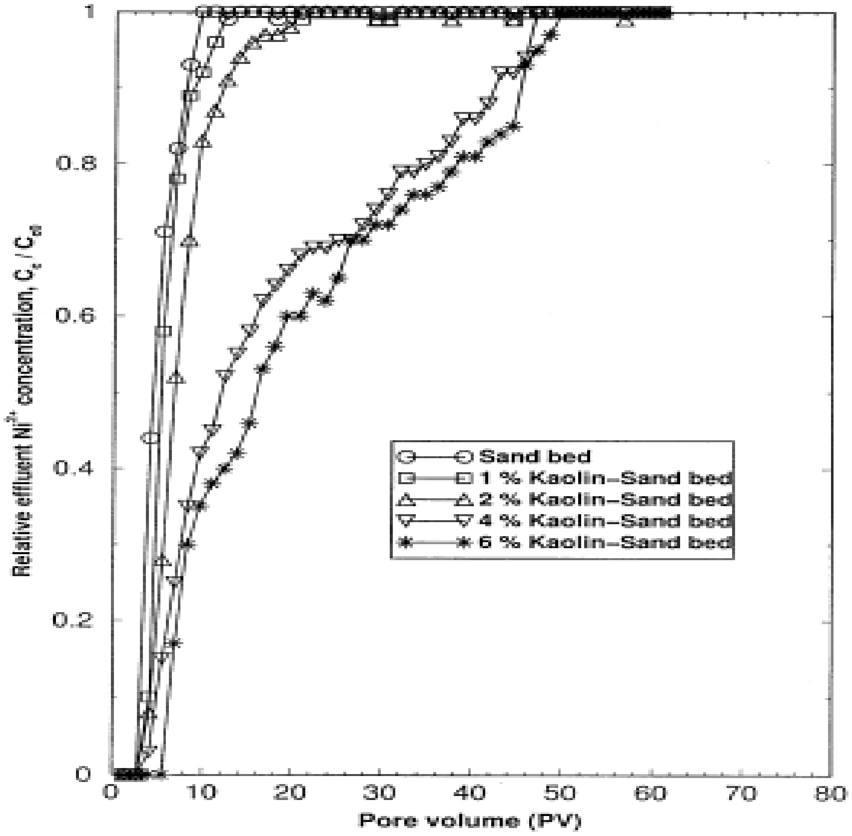

Figure 16: Experimental BTCs for Ni metal ions during upward flow through different composite kaolin-sand beds under plugging condition. Initial Ni metal ion concentration = 20.5 ppm, Length of bed (L) = 0.28 m, SR = 50, porosity (€) = 0.29 and superficial velocity = 3.39 X 10^{-4} m/s. Reproduced from reference [1] with written permission.

The BTCs in the plugging condition, exhibit a long, slow increase in effluent Ni^{2+} concentration with variations in the slope of the curve (Figure 16). Therefore at plugging condition retardation of Ni^{2+} transport occurs and it is due to increase in adsorption. 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 concentration of kaolin [1, 13].

5.1.4 Laboratory studies on colloid-associated transport of organic contaminants

Organic contaminants in natural porous media is strongly influenced by physicochemical properties of the organic molecules, in addition to soil-dependent factors such as organic matter content, water regime, and biological activity. The most important carrier in colloid-associated transport for hydrophobic organic compounds in subsurface environments is probably "dissolved" organic carbon (DOC) which consists primarily humic substances and natural organic matter (NOM) [6, 18, 184-185]. Therefore, the role of DOC in facilitating the transport of hydrophobic organic contaminants has been studied experimentally and theoretically by several investigators [2, 186-190]. Magee et al. [189] 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. Some researchers have employed polystyrene latex spheres as model carrier colloids to study colloid-facilitated transport of hydrophobic organic compounds in porous media [8, 152].

Colloid-facilitated transport of phenanthrene through columns packed with natural sands was studied by Roy and Dzombak [8]. In the first set of experiments, the role of colloidal particles mobilized by decreasing ionic strength on the mobilization of previously adsorbed phenanthrene was studied (Figure 17). Figure 17(a) presents the total phenanthrene concentrations (dissolved and colloid-associated), normalized by influent concentration C_0 during the sorption stage, and Figure 17(b) presents colloid concentrations for sorption and mobilization stages in experiments with three Lincoln sand columns.

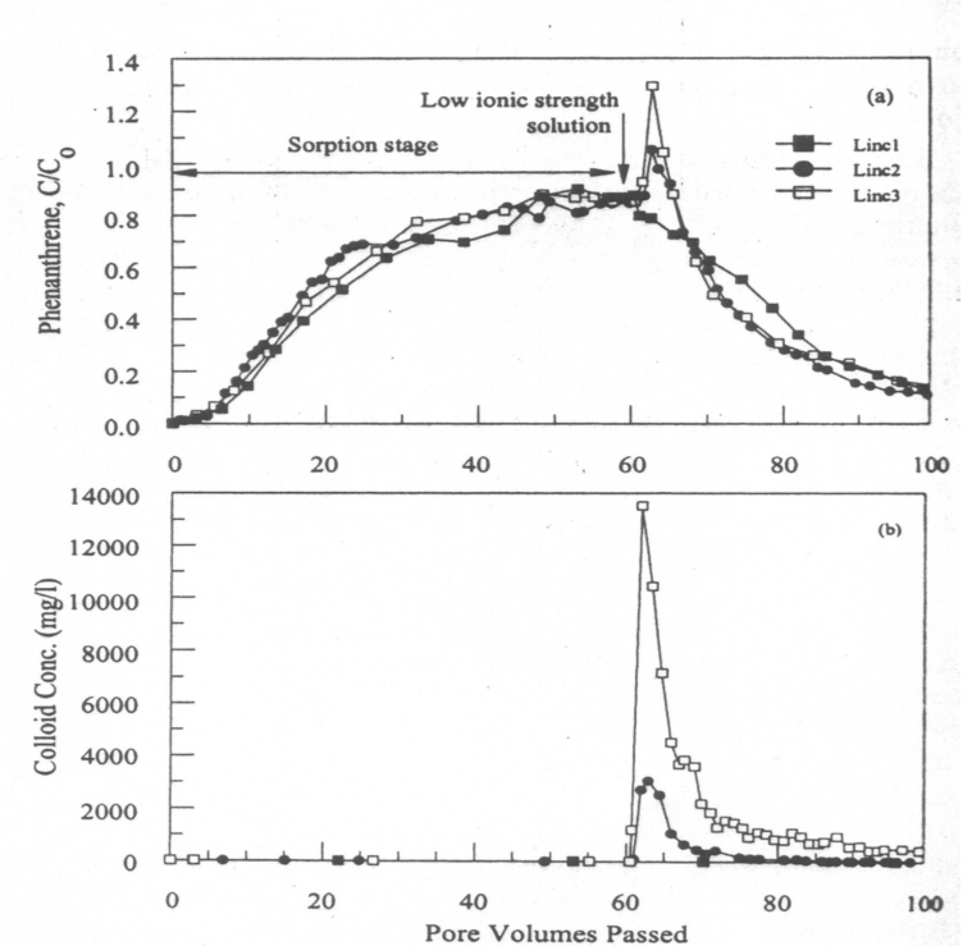

Figure 17 (a) Total phenanthrene concentrations (dissolved and colloid-associated), normalized by influent concentration C_0 during the sorption stage, and **(b)** colloid concentrations for sorption and mobilization stage in experiments with three Lincoln sand columns. Figure from [8].

The influent during sorption was a 1 mg / L (5.6×10^{-6}M) solution of ^{14}C-labeled phenanthrene with 0.1 M NaCl, and the influent during mobilization was 0.1 M (Linc 1), 0.01 M (Linc 2), or 0.001 M NaCl (Linc 3), with no phenanthrene. The influent pH was

9.0 in all cases. The breakthrough of phenanthrene through Lincoln sand was retarded significantly: after the passage of 61-pore volumes, the effluent concentrations were about 0.9 times the inlet concentrations. For the column experiment where the influent was changed to 0.01 M NaCl, there was a small peak in the total phenanthrene concentration soon after ionic strength reduction (peak concentrations about 1.1 times the inlet concentrations). For the column experiment at 0.001 M NaCl (which corresponds to nearly complete removal of colloids, approximately 0.019 g / g of sand), the peak was significantly larger: peak concentrations about 1.4 times inlet concentration. Four or five-pore volumes after the reduction of the ionic strength, total phenanthrene concentrations were at levels similar to those without colloid mobilization. In the second set, the influence of injected latex colloids on phenanthrene was tested (Figure 18). Here, the columns were injected with 4-6 pore volumes of water at 0.1M NaCl, followed by a 1 mg / L (5.6×10^{-6} M) solution of phenanthrene at pH 7.5 in equilibrium with 100 mg / L latex colloids (Eust1), at pH 9.8 with 100 mg / L latex colloids (Eust 2), or at pH 9.8 with no colloids (Eust 3) sands respectively. From Figure 18, it has been found that, for the experiments performed at pH 7.5 with 100 mg / L latex colloids in the inlet, the effluent concentrations were low. There was a significant increase in the concentrations when the same experiment was performed with 100 mg / L colloids at pH 9.8. In an experiment performed at pH 9.8, but with no colloids at the inlet, the effluent phenanthrene concentrations were very low (less than 5% of influent concentrations), indicating clearly the role of the colloidal particles in transport enhancement. However, this paper will focus primarily on inorganic colloids and biocolloids and therefore will not discussed further on organic colloid-mediated contaminant transport in porous media.

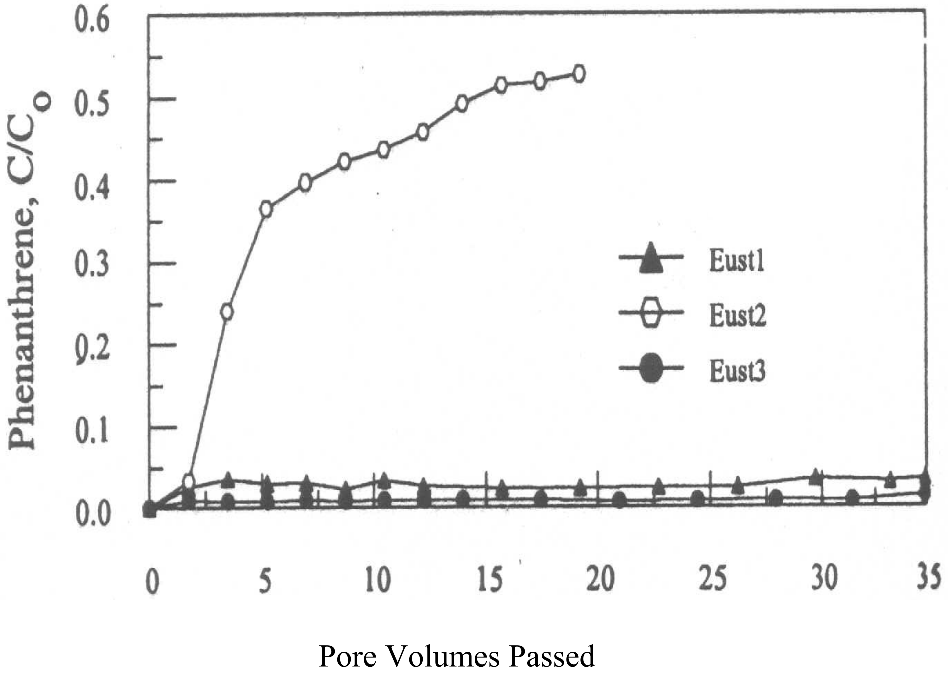

Figure 18 Total phenanthrene concentrations (dissolved and colloid-associated), normalized by influent phenanthrene concentration C_0 . Figure from [8].

5.1.5 Field studies on colloid-associated contaminant transport

Kretzschmar et al. [6] have mentioned in their review article that only a few field studies provide evidence for colloid-facilitated transport of contaminants. This has been advanced in compilation by Elimelech and Ryan [3]. Generally, studies on colloid-facilitated transport in the field are dominated by actinides and transition metals (Table 5). Magaritz et al. [191] were able to show that the metals associated with the colloid fraction recovered in their passive groundwater samplers were enriched relative to the metal content of the surrounding sediment. Mori et al. [157] have presented the results of the colloid and radionuclide retardation (CRR) experiment for in situ migration behavior of selected actinides and fission products in the absence and presence of bentonite colloids in fractured rock at nagra's Grimsel Test Site (GTS) in the central Swiss Alps. Bentonite colloids were stable in the groundwater and the in situ monitored breakthrough of the tri and tetravalent actinides Am and Pu and Cs followed the colloid breakthrough indicating some degree of colloid-mediated migration of these radionuclides in the experimental shear zone. Many other investigators also reported that strongly sorbing contaminants can travel much faster than anticipated from traditional transport models calibrated by batch sorption data [5, 148, 192-194].The existence of mobile colloids acting as carriers of contaminants may offer a plausible explanation for this unexpected mobility [192-194]. However, transport along preferential flow paths as a result of physical heterogeneity or the presence of dissolved organic ligands forming anionic metal species may also explain the observed discrepancies between measured and predicted contaminant retardation. For example, Champ et al. [148] have reported that, due to complexation by organic ligands, anionic species dominated for many radionuclide elements (e.g., Co, Eu, Zr, Ni, Pu) present in contaminant plumes at the chalk river Nuclear Laboratories. More direct evidence for colloid-facilitated transport was provided by studies where the contaminants were found to be associated with colloidal particles, suggesting that colloids indeed acted as contaminant carriers [192-194].

Table 5: A compilation on field studies of colloid-facilitated contaminant transport in natural porous media. Some data are also from reference [3]

Contaminant	Colloids	Porous media	Travel time and distance	Comments	Reference
U, ^{230}Th	Quartz, muscovite, lepidocrocite, 1:1 and 2:1 clay minerals.	Alligator river U deposit, Australia.	< 1 to 14 km.	0.01-2.0 ^{238}U and 0.3-39% ^{230}Th in colloidphase. -	Airey [195]; Short et al., [196]
Mn^{2+}, Co^{2+}, Ce^{2+}, Eu, Ru, Sb^{2+}, Cs	Quartz, feldspar, clay minerals.	Nevada Test Site	~ 25y, 300 m		Buddemeier and hunt [194].
PAHs	Clay minerals, iron oxyhydroxide, iron sulphide, quartz, > 10 nm, ~ 5 mg/L, 18 % organic matter	Marine sands; creosote contamination	80 m	5-35% in colloid phase > 90% in colloid phase	Villholth [197]
^{137}Cs, Co^{2+}, Eu, Pu	Illite, smectite, zeolite, 7nm to > 1 μm	Nevada test site	1-80 m y, 1.3 km		Kretzschmar et al [6]
U, ^{230}Th, Pu, Am, Np, Sr, Cs, I and Tc	Smectitic bentonite colloids.	Grimsel Test site (Swis).			Mori et al [157].
U, ^{230}Th, Eu	Natural colloids	Granite from Grimsel Test site (GTS, Swiss)			Schater et al. [136]
Pb^{2+}	Natural colloids	Zeolitized tuffs from Nevada Test site (NTS)			Um and Papelis [160].

Marley et al. [198] have reported field evidence for the mobilization and movement of Pu, Am, Th, and Ra in a shallow sandy aquifer after injection of colloidal and macromolecular natural organic matter. Carboxylic-rich fulvic acids were most mobile and had the greatest potential to dissolve and mobilize radionuclides from the mineral matrix in the aquifer. These field studies provide evidence of colloid facilitated transport of contaminants in underground soil. A series of lab-scale and field-scale leaching experiments involving undisturbed soil monoliths and lysimeters were conducted to assess the effect of the mineralogical composition of soil colloids on their capacity to mediate the transport of heavy metals and herbicides in subsurface soil environments [158]. V. Cvet kovic et al. [199] investigates the potential impact of inorganic colloids on plutonium transport in the alluvial aquifer near Yacca Mountain, Nevada. They found that if sorption on colloids is reversible and relatively rapid, then the effect of colloids on nuclide transport is negligible in most cases. Only if binding of tracers on colloids is irreversible (or slowly reversible) relative to the time scale of the transport problem, may colloids play a potentially significant role in subsurface contaminant transport which is also reviewed by Ryan and Elimelech [14].

In order to assess the role of colloidal fines on the transport of metal ions in soil under long term land use (a podzol under a forest, a cultivated luvisol and a luvisol under a metallophyte grassland, Citeau et al. [200] collected gravitational waters in situ by ‘zero-tension-lysimeters’. They separated dissolved and colloidal fraction of metals by ultracentrifugation and colloids were studied by transmission electron microscope (TEM) coupled with energy dispersive X-ray analysis (EDS), shown in Figure 19. Their results show that the colloidal fraction was found to be significant only for Pb^{2+} ion in the two studied luvisols (on average 70-77%) whereas this fraction was much lower for Zn^{2+} and Cd^{2+} in all soils as well as for Pb^{2+} in the podzol. Zn^{2+} and Cd^{2+} were found in dissolved forms and as free ions or labile complexes. The nature of colloids (i) were mainly organic in the podzol; (ii) consisted of a mixture of organic (bacteria) and mineral materials in the agricultural soils; and (iii) were exclusively minerals. This results clearly indicates that specific soil physico-chemical conditions induced by soil type and corresponding land use govern the nature of colloids circulating in gravitational waters and consequently their role on metal ions transport in soils under different land use.

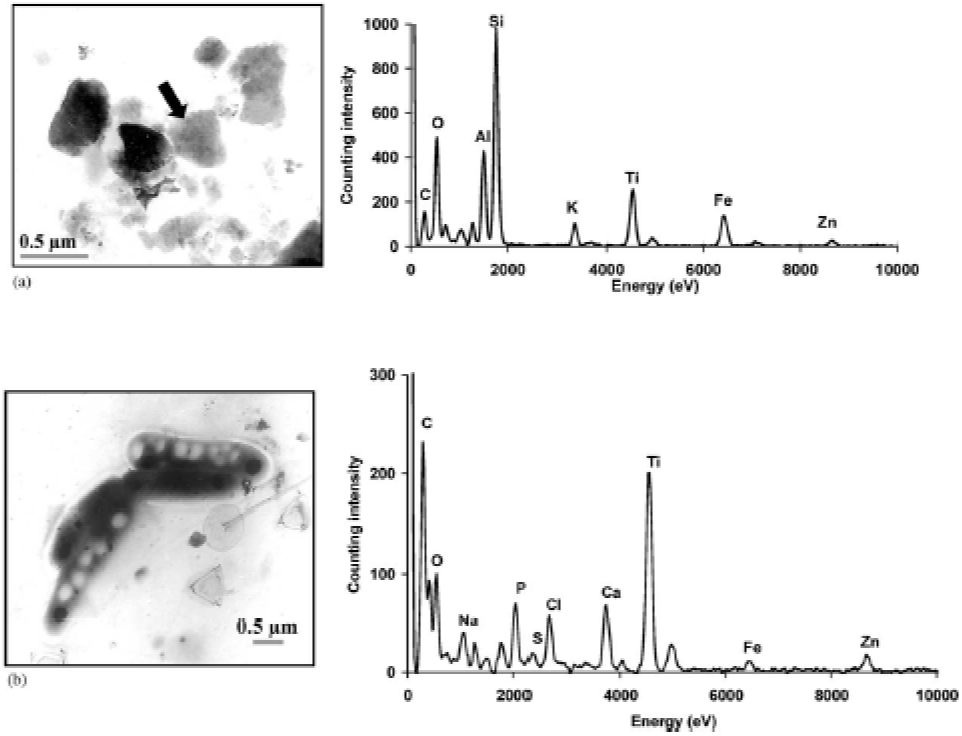

Figure 19: TEM images and EDS analysis of colloidal phases bearing metals isolated from gravitational waters of the surface horizon of the agricultural soil (a) phyllosilicate and (b) bacteria. Figure from [200].

Pb^{2+} was found mainly in colloidal form and consequently colloids are likely to play an active role in facilitating the transport of Pb^{2+} through the soil towards the water table, strongly limiting interaction of Pb^{2+} with reactive soil constituents, whereas colloids seem to have a minor role in Zn^{2+} and Cd^{2+} transport through the soil profile. On the other hand, Zn^{2+} and Cd^{2+} can more easily interact with soil reactive constituents during migration towards the water table.

Also a greater number of field studies did not detect any significant colloid-facilitated transport [3, 192, 201].

5.2 Theoretical modeling on colloid-associated contaminant transport in porous media

Transport modeling can be considered to be an integral part of characterization and remedial design of any contaminated sites, especially sites with groundwater contamination. Several models have been reported to describe the transport of contaminants in subsurface systems. These models have traditionally been based on a two-phase approach: the mobile fluid phase and the immobile solid phase. However due to presence of subsurface colloids and their role on contaminant transport, the old two-phase model should be modified as a three-phase model with two solid phases, that is, mobile colloidal particles and stationary solid matrix.

Majority of the studies concerning the development of mathematical models to describe the colloid-facilitated transport of contaminants have been carried out by various researchers during past ten years [1-2, 17, 42, 137, 153, 169, 176-177, 189, 202-203]. Most of these studies have assumed equilibrium interactions between the colloidal particles and the contaminant in the dissolved phase [176, 189, 202-203] and analogous to model developed by Corapcioglu and Jiang [177]. These models predict a reduction of the effective retardation arising out of sorption on to the solid matrix depending on the concentration of the colloidal fines and the partition coefficient for contaminant sorption on the colloidal fines. A considerable amount of literature exists on the modeling the influence of colloid-facilitated transport of radionuclides involving reversible and irreversible sorption processes in porous media [2, 82, 168, 204-210].

Mathematical models for colloid and colloid-facilitated transport are usually based on the advection-dispersion equation (ADE) of colloidal particles, their deposition and release from the surface of the fixed porous medium and interactions between contaminants and the three solid phases (the attached and suspended colloidal phases and fixed solid phase).The ADE is then coupled with different types of colloid-contaminant-soil-matrix interactions. Colloid interactions with the stationary solid phase are usually described by means of filtration theory, where the overall reaction can be formulated as first-order kinetics. Recent advances have been made by considering two-site attachment, langmuir-type reaction kinetics [211], sorption site blocking [212-213] and solid phase heterogeneity [214].

Corapcioglu and Jiang [177] have proposed, first time the following equilibrium mathematical model to describe the facilitated contaminant transport. This model consists of mass balance equations for fine particles as well as for the contaminants. Since the contaminant species reside in four different sites (mobile fines, captured fines, liquid and solid phase), mass balance equations are written for each site.

Their model has been developed based on the following assumptions and considerations.

- A single species of contaminant is considered.
- Contaminant partitioning among the three phases, namely solid matrix, mobile colloidal fines, and aqueous phase.

- The variations in concentrations are significant only in the axial direction.
- Porosity of the medium remains constant.

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

$$\frac{\partial \varepsilon C}{\partial t} = D_B \frac{\partial}{\partial x}\left(\varepsilon \frac{\partial C}{\partial x}\right) - v_0 \frac{\partial C}{\partial x} + r_r - r_c \tag{2}$$

Where, C is the concentration of fines in aqueous phase, ε is the porosity of the medium, v_0 is the superficial velocity, D_B Brownian diffusivity of fine particles, and it can be neglected if particle size greater than 1 μm. r_r is the rate of release of the fines from the solid matrix and r_c is the rate of capture of fine particles.

Similarly, unsteady mass balance for the contaminant on the colloidal fine particles in suspension can be written as

$$\varepsilon \frac{\partial (X_1 C)}{\partial t} = \varepsilon D_B \frac{\partial^2 (X_1 C)}{\partial x^2} + v_0 \frac{\partial (X_1 C)}{\partial x} + r_r X_3 - r_c X_1 + b_1 \varepsilon K_a C_c - \varepsilon K_d C X_1 \tag{3}$$

Where, X_1 is the mass fraction of the contaminant species adhered to colloidal particles in suspension, C_c is the concentration of contaminant species in the aqueous phase, K_a and K_d are the rate constant for sorption and for desorption from the fine particles respectively; b_1 represents the fraction of total adsorption that takes and D_B Brownian diffusivity of fine particles. In equation (3), the only term on the left hand side represents the rate of accumulation of contaminant on the fines in suspension. The first two terms on the right hand side represent the flux of contaminants due to the Brownian and convective motion of the fines. The third and fourth terms on the right hand side represent the flux of contaminant resulting from the release and capture of fines and last two terms represent the contributions of adsorption and total adsorption that takes place on the fines in suspension.

Unsteady state mass balance for the contaminant species on the captured fines can be written as:

$$\frac{\partial(\sigma_2 X_2)}{\partial t} = r_c X_1 + b_2 \varepsilon K_a C_c - K_d X_2 \sigma_2 \tag{4}$$

Where, X_2 is the mass fraction of contaminant species adhered to the captured colloidal particles, b_2 represents fraction of total adsorption that occur on the captured fines and σ_2 is the concentration of fines captured at pore constrictions. In equation (4) the term on the left hand side represents the rate of accumulation of contaminant species on the captured fines and the first term on the right hand side indicates the influx of contaminant species due to capture of colloidal fines. The last two terms represent the rate of the adsorption and desorption of the contaminant respectively as regard to captured fines.

Finally an unsteady mass balance for the contaminant in the liquid phase and on the solid matrix together yields:

$$\frac{\partial(\rho_b X_3)}{\partial t} + \varepsilon \frac{\partial C_c}{\partial t} = \varepsilon D_c \frac{\partial^2 C_c}{\partial x^2} + v_0 \frac{\partial C_c}{\partial x} - (b_1 + b_2) \varepsilon K_a C_c + \varepsilon K_d C X_1 + K_d \sigma_2 X_2 \tag{5}$$

Where, D_c is the longitudinal dispersion coefficient of the contaminant species, ρ_b is the bulk density of solid matrix. In equation (5) the first term on the left hand side is the rate of accumulation of contaminant on the solid matrix while the second term represents that in the liquid phase. The terms on the right hand side are similar to other equations except first term which indicates the flux of the contaminant species due to hydrodynamic dispersion.

Linear equilibrium partition equation between the liquid phase and solid phase is

$$X_3 = K_e C_c \tag{6}$$

Where, X_3 is the mass fraction of contaminant species adhered to the solid matrix, based on dry mass of solid and K_e is the partition coefficient of the contaminant on the solid matrix.

These equations (2) to (6) coupled with release and capture equations and also with appropriate initial and boundary conditions are numerically solved for a system of finite length and where the fine particles, contaminant species and fluid are fed at a constant rate to the system. They carried out simulations describing the variations in total mobile concentration of contaminant as a function of time and axial length for various values of the system parameters. The total mobile concentration C_{ct} is the sum of the concentration in the liquid phase, C_c and that on the fines in suspension, $\sigma_2 X_2$, where X_2 is the mass fraction of contaminant species adhered to the captured fine particles, σ_2 is the amount of captured fines. Figures 20 and 21 show some of their simulation results. We observe from these figures that, the total mobile concentration, in general, is higher when compared with the concentration without migration of fines. Their simulations also showed that higher rate of sorption of contaminant species as well as higher rate of release significantly facilitates the transport of contaminants. On the other hand, higher rates of desorption and capture of fine particles, weakly facilitate the transport.

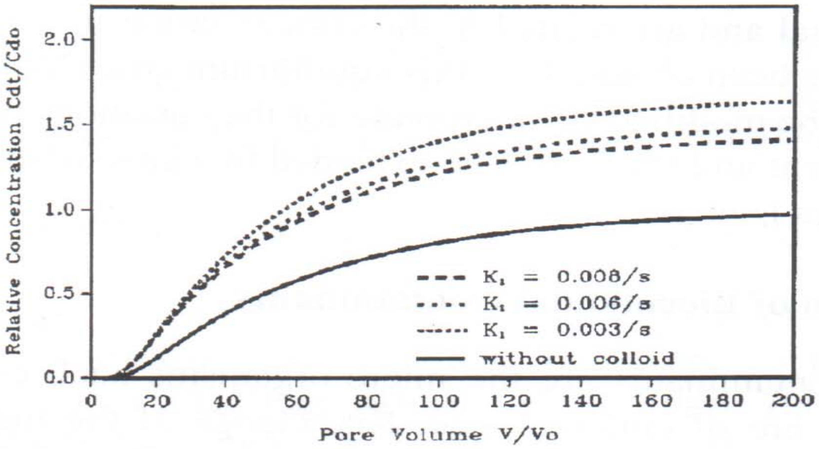

Figure 20: Total mobile contaminant concentration at different capture coefficients.

Figure from [7, 177]

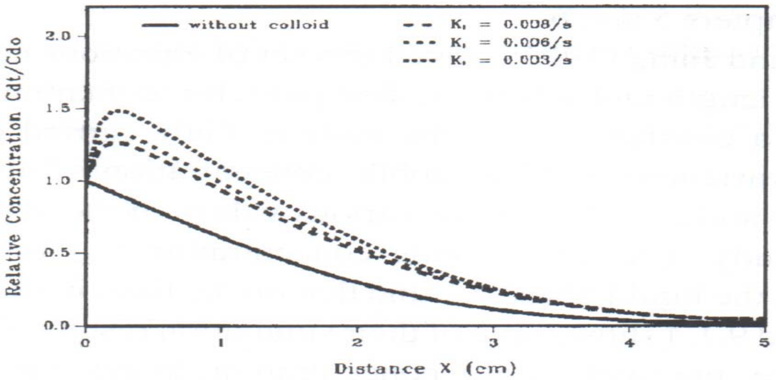

Figure 21: Spatial variations of total mobile contaminant concentration at different capture coefficients. Figure from [7, 177].

Saiers and Hornberger [153] developed a three-phase model, analogous to the model developed by Corapciglu and Jiang [127], that can successfully explain the transport behavior of ^{137}Cs in the absence and presence of kaolinite colloids through sand packed column. Their model is based on independently determined parameters for first order colloidal fines deposition kinetics, ^{137}Cs sorption equilibrium and sorption kinetics on kaolinite and quartz sand, and hydrodynamic solute dispersion in the porous medium.

Roy and Dzombak [8] studied colloid-facilitated transport of phenanthrene through columns packed with natural sands that has been discussed in earlier section. These experimental data were modeled under consideration of colloidal fines deposition and release kinetics as well as equilibrium and nonequilibrium sorption and desorption of phenanthrene to colloidal particles and matrix grains [42]. Model calculations show that slow desorption kinetics of the contaminant from the colloidal particles is an essential prerequisite in order for colloid-facilitated transport to become significant. If the contaminant would desorbs rapidly, it would be transferred to binding sites on immobile matrix surfaces as the colloidal particles move into an uncontaminated zone of the porous medium. Slow desorption kinetics are of particular importance under natural field conditions where water flow velocities are commonly much lower than in most laboratory column experiments.

A one-dimensional model for coupled colloid and contaminant transport in a porous medium is also reported [174]. Here, calculated breakthrough curves (BTCs) during contamination and decontamination have shown systematically the effects of nonlinear and kinetic interactions on contaminant transport in the presence of reactive colloidal fines.

All these above models do not incorporate the effects of entrapment of particles which have also been experimentally found by Sen et al. [1, 13] and have already discussed in details in our earlier section. Therefore Sen et al. [82, 17] developed a comprehensive one dimensional mathematical model which has been formulated in a manner analogous to that of existing models such as the model developed by Corapcioglu and Jiang [127]. The new aspects of their model are: (i) porosity of the porous medium changes due to plugging phenomenon, (ii) the release of fines occurs due to hydrodynamic forces and (iii) the coefficient of capture of colloidal fines is negligibly small until the concentration of fines reaches the critical particle concentration (CPC). Beyond CPC, the porous medium gets plugged due to convective jamming and the flow stops [13, 82]. Their model also based on the equilibrium adsorption of a contaminant, hydrodynamic release, migration and capture of colloidal fines in groundwater flows. Additional equations, apart from four unsteady state mass balance equations for colloidal fines as well as for contaminant developed by Corapcioglu and Jiang [127], relating to release and the variations in permeability, as well as porosity due to entrapment/plugging, have been incorporated which are given below:

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

$$\frac{d\varepsilon}{dt} = \frac{r_r\,\varepsilon}{\rho_f} \tag{7}$$

Where, ρ_f is the material density of the fines and all other terms as per earlier equations.

The rate of release is given by [7]

$$r_r = \alpha_h A_s (\tau_w - \tau_c) \text{ for } \tau_w > \tau_c$$

$$= 0 \text{ for } \tau_w < \tau_c \tag{8}$$

Where α_h is the release coefficient, A_s is the pore surface area per unit pore volume, τ_w is the wall shear stress; τ_c is the critical shear stress. To account for the change in porosity and permeability due to erosion, we need a model for the pore structure.

Using a capillary model consisting of capillaries of diameter δ, we get,

$$A_s = \frac{4}{\delta} \tag{9}$$

$$\varepsilon = \varepsilon_0 \left(\frac{\delta}{\delta_0}\right)^2 \tag{10}$$

$$\delta^2 = \frac{32K}{\varepsilon} \tag{11}$$

$$\tau_w = \left(\frac{8\mu}{\varepsilon\delta}\right) v_0 \tag{12}$$

Where, δ is the diameter of the pore, K is the permeability of the medium. The subscript " o" refers to the initial condition.

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

$$K = K_0 \left(\frac{\varepsilon}{\varepsilon_0}\right)^2 \tag{13}$$

Where K_0 is the initial permeability and ε_0 is the initial porosity of the medium.

The critical particle concentration, CPC, is expected to increase with increase in porosity. Very little knowledge is available on CPC, let alone its variations with relevant parameters. A recent study has shown that CPC varies with the ratio of bead to particle diameters [1, 82]. Without any knowledge on its variations with porosity, we have assumed a constant value for the CPC [13, 82].

Darcy's law gives the velocity of flow in the porous medium,

$$v_0 = \frac{K}{\mu} \quad (-\frac{\Delta P}{L}) \tag{14}$$

Where μ is the viscosity of the suspension, $\Delta P / L$ is the pressure gradient across the medium.

The low contaminant concentrations generally encountered in ground water permits us to assume linear adsorption isotherm,

$$X_3 = K_e C_c \tag{15}$$

$$X_1 = K_f C_c \tag{16}$$

Where, K_e and K_f are the partition coefficients for the matrix and the colloidal fines respectively. All other terms have been defined in earlier section It is shown later that the adsorption process can be assumed to be at equilibrium. Otherwise, equations describing the rate of adsorption are required as follows

$$Q_{cf} = k_a C_c - k_d X_1 \tag{17}$$

Sen et al [13, 82] numerically solved the above equations along with appropriate initial and boundary conditions using a finite difference method. A simulation is carried out and the model parameters used in the simulation were taken from published work [8, 31,82]. Influent solutions of colloidal fines and contaminants are continuously fed at a constant pressure drop across a porous cylinder. Breakthrough curves are presented as plots of C_{ct} /

C_{c0} against time, where C_{ct} is the total mobile contaminant concentration ($C_{ct} = C_c + X_1 C$). C_{ct} is chosen as the ordinate because it accounts not only for the contaminants in the aqueous phase but also accounts for the contaminants on the mobile colloid phase. It is thus a more realistic representation of the concentration of contaminant.

This model predicts both facilitation and retardation of the transport of contaminants depending on the flow and other conditions. Figure 22 presents the retardaded breakthrough curves (BTCs) for Ni^{2+} transport through different wt% of sand-kaolin bed obtained by developed three-phase model under plugging condition (solid line) and has been verified with experimental results (symbols) of Sen et al. [1, 13]. Their developed three-phase model also verified with published experimental results [2, 8, 82]. They have concluded from their model sensitivity analysis that the key parameters for determining whether facilitation or retardation would occur are the ratio of grain size to particle size, initial permeability, the release coefficient and the initial colloidal fines concentration. Some of their simulation results are shown in Figure 23 and Figure 24 respectively. Figure 23 depicts the case of enhancement of contaminant transport due to adsorption of contaminants on the colloidal fines. The value of the partition coefficient K_f seems to have significant influence on the extent of enhancement. At low value of K_f implies that the association between the contaminants and the colloidal fines is weak. A lesser amount of contaminants gets sorbed onto the colloidal fines and hence, lesser total contaminant concentration is observed in the effluent. Further, as shown in this figure, the release of colloidal fines from the pore surface enhances the contaminant transport to even greater extent.

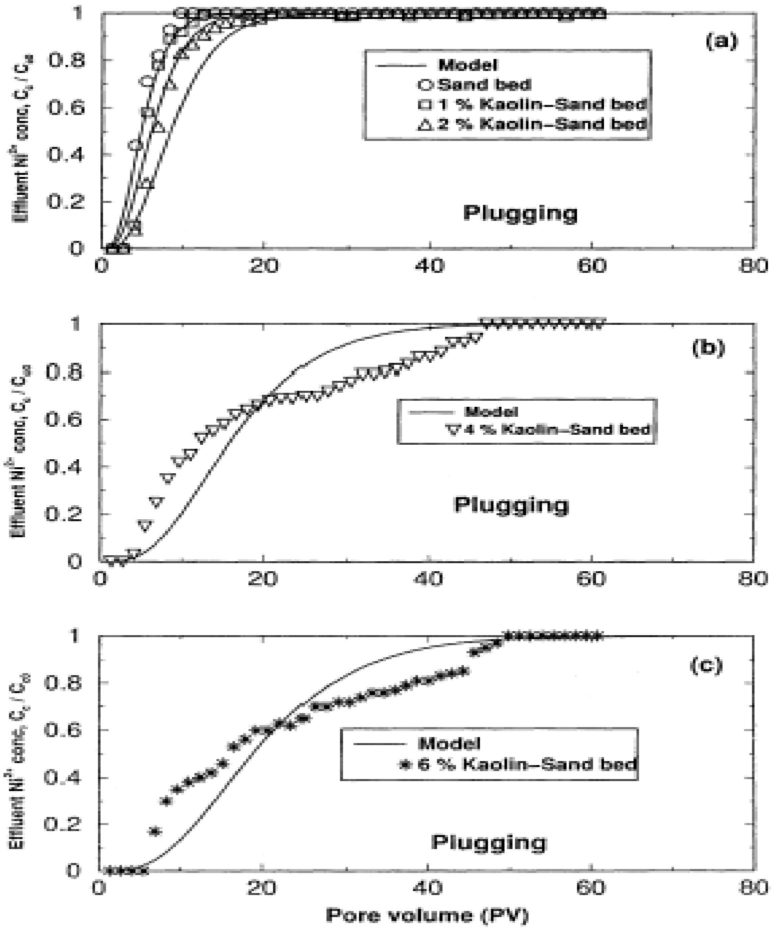

Figure 22 Dimensionless concentrations: prediction by the equilibrium three-phase model (solid line) and experimental measurement (symbols) for Ni metal ion migration through different composite beds. (a) Low weight % kaolin present in the bed; (b) 4 weight % kaolin present in the bed; (c) 6 weight % kaolin present in the bed. Length of the bed (L) = 0.28 m, porosity of bed (ϵ) = 0.29, superficial velocity (v_0) = 3.39 X 10 $^{-4}$ m/sec. Figure from reference [13, 82] with written permission.

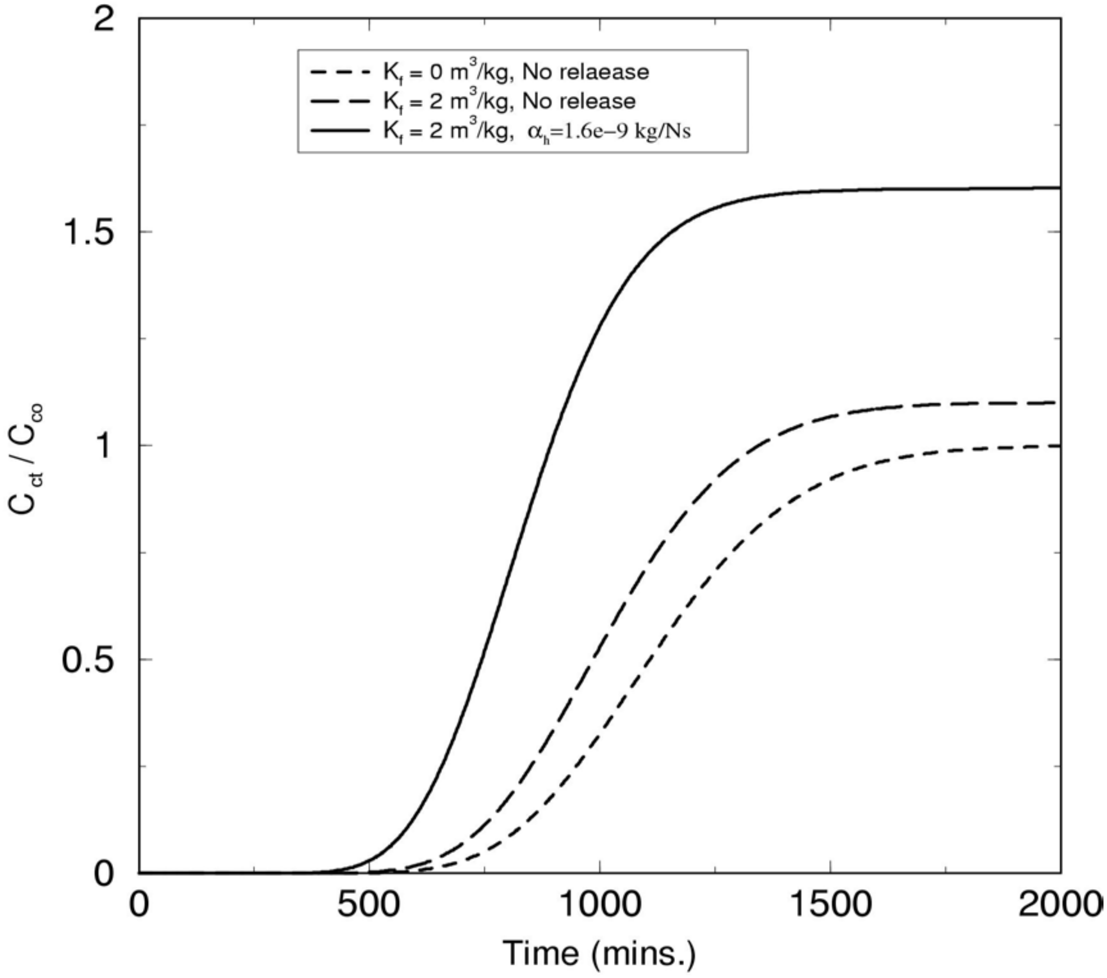

Figure 23: Model predictions of enhancements in contaminant transport due to release and migration of colloidal fines. Figure from [13, 82] with written permission.

New role of colloidal fines i.e. retardation of contaminant transport by plugging has been shown in Figure 24. The phenomenon of plugging occurs when the concentration of colloidal fines reaches the critical particle concentration (CPC) provided the ratio of pore size to particle size is not very high. It has been found that, at any given time, the concentration of colloidal fines is maximum at the outlet [1, 13]. As the water front traverses the porous medium, it collects the fines released from the solid matrix. As a result, the concentration of colloidal fines in the aqueous phase is found to be maximum at the outlet. Hence, plugging may take place near the outlet. It is thus sufficient to monitor the effluent colloidal fines concentration to examine the conditions that lead to plugging [1, 13, 82]. As shown in Figure 24, initially, there is a rapid build up of the colloidal fines concentration. After that, the concentration increases slowly. Initially, the concentration gradient along the length of the porous medium is negative. As a result, the convective rate of input becomes greater than the convective rate of output in the mass balance equation and leads to a rapid build-up of colloidal fines concentration. Afterwards, the concentration gradient becomes positive and thereby, the concentration of colloidal fines increases slowly with release of particles as the source [13].

CPC should increase with the increase in porosity. Without the knowledge on this dependency, CPC has been assumed constant in this study. The value of CPC is taken from the measurements of Pandya et al. [85]. It is implicitly assumed that the ratio of pore size to particle size is not very high and therefore plugging can occur [1]. The slope of the graph after the initial build-up increases with increase in α_h. Higher α_h implies higher rate of release and hence higher rate of increase of fines concentration. For $\alpha_h = 2.50 \times 10^{-8}$ kg / N-s at t= 1238 min, the effluent fines concentration reaches CPC and hence plugging occurs (Fig. 24). At this situation, the flow of the solution more or less stops completely, and the spreading of contaminant is prevented. This is the case of inhibition of contaminant transport due to plugging and a new containment technique can be developed based on this plugging based retardation of contaminant transport. The time required for plugging to occur decreases with increase in α_h, which is also shown in Figure 24.

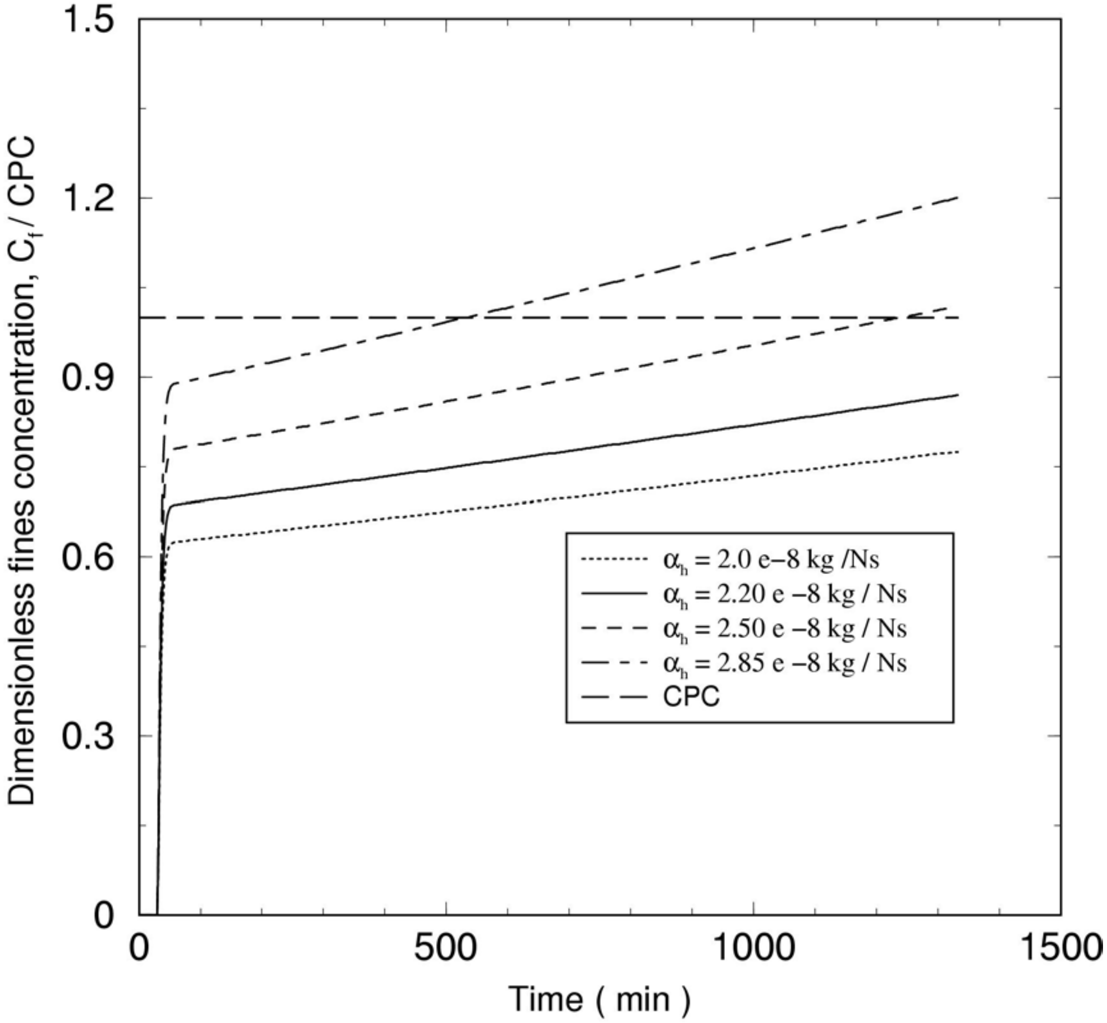

Figure 24: Effects of release coefficient on the temporal variations in effluent colloidal concentration and on plugging time. Figure from [13].

Sen et al. [17] also developed another equilibrium three-phase model based on colloidal induced release, migration and finally capture of these colloidal fines at pore constriction leading to plugging phenomenon. Hydrodynamically induced release of colloidal fines is not considered in this model. Their model simulations again indicates that presence of colloids can either facilitate or inhibit the spreading of contaminants depending on the values of parameters, such as the inlet colloid concentration, the release coefficient and more significantly on the sensitivity of the permeability to the concentration of captured fines at the pore constrictions.

Bekhit and Hassan [215] developed two-dimensional latest model of colloid-contaminant transport in physically and geochemically heterogeneous porous media. The model accounts both spatially varying conductivity (physical heterogeneity) and the spatially varying distribution coefficient and colloid attachment coefficient (chemical heterogeneity). One of their finding is that the presence of colloids reduces variability in mass arrival times to a downstream control plane. Their study also indicates that the effect of geochemical heterogeneity is important only if it is correlated to physical heterogeneity.

6. Conclusion and future research

We have reviewed comprehensively experimental, modeling and field studies addressing an important topic on subsurface colloidal particles and their role on contaminant transport in saturated porous media. This complex phenomenon in porous media involving several basic issues and processes such as (i) presence of colloidal particles in subsurface environment, (ii) their release, dispersion stability, migration and entrapment/plugging at pore constrictions, (iii) association of contaminants with colloidal particles and also with subsurface solid matrix and colloid-associated contaminant transport. These processes depend on physical and chemical conditions of subsurface environment. The followings are the major conclusions from this review article:

- It is well known that a variety of inorganic and organic materials exits as colloidal particles and small particles in subsurface, including mineral precipitates (such as iron, aluminum, calcium and manganous oxides, hydroxides, carbonates, silicates and phosphates and also oxides and hydroxides of actinide elements), rock and mineral fragments, biocolloids (such as viruses, bacteria) and natural organic matter (NOM).

- Most of these colloidal particles in subsurface zone are generated by chemical and physical perturbations that mobilize colloidal sized soil and sediment particles. In general two major types of forces are responsible for the release of these fines, namely colloidal and hydrodynamic forces. The main sources of these mobile fines are insitu colloidal particles release due to changes in solution chemistry (such as pH, ionic strength, addition of surfactant), surface chemistry and flow velocity. The decrease in ionic strength, increase in pH, and increase in velocity enhance the particle release. The retention of particles is much greater in presence of divalent ion with respect to monovalent ion. The mechanistic explanations are based on classical 'DLVO' theory. These phenomena are well established and reviewed here. However, release and mobilization of mixed colloidal particles from complex natural system needs further research.
- Some colloids may be generated by precipitation of saturated porous media but their existence may be two transitory to be of great concern in colloid-associated contaminant transport.
- Hydrodynamically induced particle release is more complex than colloidally induced release because of this forces acts in multiple directions.
- The importance of "critical salt concentration (CSC)", "critical ionic strength " for mixed salts, "critical shear stress" or critical velocity" and "critical particle

concentration (CPC)" on colloidal particles release, mobilization and finally on entrapment/plugging phenomena has also been compiled and presented up to date development. Although it is well-established that changes in solution chemistry lead to release of colloidal particles from soil and sediment matrix, the particle generation process still needed further research on a mechanistic level.

- The released colloidal particles from the pore surface while flowing with the liquid phase through the porous medium can either readhere to the pore surface or flow without capture or get entrapped at the pore constrictions. The latter two occurrences are more common as the colloidal and hydrodynamic conditions that bring about their release are not likely to allow these particles to readhere back to the pore surface in the same conditions. Entrapment can occur in three forms: size exclusion, multiparticle bridging and surface deposition. This entrapment/plugging phenomena depend on pore structure, size of colloidal fines or bead to particle size ratio, concentration of colloidal particles and superficial velocity that has been reviewed here.
- Both field and laboratory research have clearly demonstrated that colloidal particles can be transported through subsurface zone under certain hydrogeochemical conditions. If present in sufficiently large concentrations, existing mobile colloidal particles can provide potentially relevant transport pathways for strongly sorbing contaminants. These colloidal particles act as highly mobile contaminant carrier and thereby enhance the spreading of sorbing pollutants in groundwater flows. Here, the contaminats may be inorganic or organic, must bind strongly and essentially irreversible to the colloids for colloid-

facilitated transport to occur. This is not a new phenomenon as per present day research work is concern which is established first by McCarthy and Zachera[9] in the year of 1989 and advancement has been done by subsequent reviews by Ryan and Elimelech [14] and Kretzschmar et al [6]. This present review article which is not limited to facilitation only but also presented the compilation of retardation of contaminant transport under certain conditions due to entrapment /plugging conditions. Therefore, depending on geoenvironmental conditions, colloidal particles not only facilitate the contaminant transport but also retarded in transport in subsurface flows.

- The conditions leading to inhibition/retardation of contaminant transport due to plugging are: high release coefficient, low initial porosity, high fines concentration, high superficial velocity respectively. When migration and plugging of colloidal 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 drop and at high concentration of particles.
- Although there is a substantial body of published research on ‘bio-colloids’ transport in the subsurface, much of it focuses on transport in the saturated porous media. Therefore understanding the transport behavior of biocolloids is particularly important in the vadose zone as sources of pathogens in drinking water are: septic tanks, land application of sewage sludge or animal waste or leaking sewer lines. The vast majority of published studies are based on

laboratory experiments or modeling studies with very few based on actual field studies of virus/bacteria transport in the vadose zone.

In our view, the most important research needs the followings:

(a)The principal scientific issue that limits prediction is understanding of how colloids behave in natural subsurface systems. Natural systems have complex solution chemistry and include mixed colloidal fines and phases. Further chemical and physical heterogeneity affects colloid behavior at a range of spatial and temporal scales.

(b) More advancement has to be made towards release and migration of colloidal fines and their role on contaminant transport at the microscopic scale such as (i) arrangement and nature of surface functional groups, (ii) surface hydrophobicity, (iii) charge heterogenecis, (iv) porous structural net work which indicates the intricacy of the porous media.

(c) Understanding colloidal transport and their role on contaminant transport in partially saturated porous media is a major challenge due to presence of an air phase in addition to the solid and water phase present in saturated media.

(d) More work should be on colloid-associated contaminant transport in real-world field situations.

(e) Development on practical methods for characterization of the distribution of surface charge, solution chemistry, or flow regime in natural system.

(f) Studies to develop a new containment technique based on the selected plugging of porous media in soil and groundwater remediation.

(g) As colloidal fines can carry contaminants adsorbed on their surface, they can also carry beneficial molecules to a contaminated site and therefore, research needs to development of ‘smart colloids’ or ‘nano-colloidal materials’ in environmental cleanup.

The above list is not meant to be complete; it only lists selected aspects that currently considered to be important. These challenges need to be addressed because mobile in-situ colloidal fines transport can have a significant impact on (i) petroleum engineering such as in oil production, (ii) geochemical engineering such as in failure of earthen dams, (iii) environmental engineering such as in soil and groundwater contamination and (iv) chemical engineering such as in filtration operation.

Nomenclature

A_s = Pore surface area per unit pore volume, m^2/m^2

C_f = Concentration of free colloids in aqueous phase, kg/m^3

C_c = Concentration of contaminants in the aqueous phase, kg/m^3

C_{ct} = Total mobile contaminant concentration in the aqueous phase, kg/m^3

C_{c0} = Inlet concentration of contaminants in the aqueous phase, kg/m^3

C_{f0} = Inlet concentration of colloidal fines in the aqueous phase, kg/m^3

D = Dispersion coefficient of colloids, m^2/s

D_B = Brownian diffusion coefficient, m^2/s

D_c = Longitudinal dispersion coefficient of the contaminant species, m^2/s

K_0 = Initial permeability, m^2

K = Permeability of porous medium, m^2

K_e = Partition coefficient of the contaminant on the solid matrix, m^3/kg

k_a = Rate constant for adsorption, 1/s

k_d = Rate constant for desorption, 1/s

K_f = Partition coefficient for the colloidal fines, m^3 / kg

L = length of column, m

Q_{cf} = Net rate of transfer of contaminants from the aqueous phase on the fines.

v_0 = Superficial velocity, m / s

V_t = Empty column volume , m^3

V_0 = Void volume, m^3

V = Cumulative volume, m^3

$\Delta P / L$ = Pressure gradient across the medium, Pa / m.

ΔP = Pressure drop across the composite bed, Pa

ΔP_0 = Pressure drop across 0% bed, Pa

X_1 = Mass fraction of the contaminant species adhered to colloidal fines in suspension, kg/kg

X_2 = Mass fraction of contaminant species adhered to the capture fine particles, kg / kg.

X_3 = Mass fraction of the contaminant species adhered to the solid matrix, kg/kg

Greek letters

α_h = Release coefficient, kg / N.s

δ = Diameter of pore, m

ε = Porosity of the medium

ε_0 = Initial porosity

μ = Viscosity of the suspension, Pa.s

ρ_f = Bulk density of fines, kg / m^3

τ_w = Wall shear stress, Pa

τ_c = Critical shear stress, Pa

σ_2 = Amount of captured fines, kg / kg

σ_0 = Surface charge, C /m^2

ϕ_s = Sphericity of material

Abbreviations

BTCs = Break through curves

CEC = Cation exchange capacity

CSC = Critical salt concentration

CPC = Critical particle concentration

PV = pore volume

SR = Bead size / Particle size.

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