Colloid transport in subsurface has received considerable attention recently because mobile colloids can facilitate the transport of heavy metals in soils to contaminate groundwater. Many studies on colloid mobility in the subsurface consider soils as well-defined porous media. Though similar in many aspects, soils are different from well-defined porous media. The authors emphasize the impacts of soil properties on soil-colloid deposition, release, and association with heavy metals to provide an overview of colloidal dynamics in natural soils. The electrical double layer and Derjaguin-Landau-Verwey-Overbeek (DVLO) theories are summarized in Section II as theoretical bases for further discussions of colloid dynamics in soils, and their interactions with heavy metals. After discussions of theory developments and experimental results on the characteristics of soil colloids in Section III and soil porous media in Section IV, the authors compare the deposition of colloidal particles in well-defined porous media with that in natural soils in Section V. In Section VI, processes that affect colloid release in soils are summarized and theories of ion transfer processes in soils during colloid release are reviewed and discussed. Finally, the authors give a brief overview of the adsorption and precipitation of heavy metals to soil colloidal particles and their influences on colloid surface charge development in Section VII. The authors conclude with remarks on the importance of colloid deposition and release in soils and their association with heavy metals.
KEYWORDS: colloid, contamination, DLVO theory, groundwater, heavy metal, soil

I. INTRODUCTION

It is well known that colloids, which are ubiquitous in soils, can be mobilized and transported by water flow to a distance in soil environments (Ryan and Elimelech, 1996; Sen and Khilar, 2006). The movement of colloidal particles in soil pores can be faster than that of water flows due to the size exclusion effect (Bradford et al., 2005; Kersting et al., 2004). As a result, the mobility of sparingly soluble heavy metals associated with colloids in soils can be enhanced (DiCarlo et al., 2006; Ma et al., 2005; Metreveli et al., 2005; Zhang and Selim, 2007). Colloid-facilitated transport has been considered one of the most important mechanisms making reactive heavy metals mobile in soils (Barton and Karathanasis, 2003; Grolimund and Borkovec, 2005; Kretzschmar and Schafer, 2005).

The term colloid generally applies to suspended particles between 1 nm and 10 µm (Stumm, 1977), which include abiotic colloids (e.g., clay, metal oxides, and humic substances) and biocolloids (i.e., virus, bacteria, and protozoa). Interactions among colloidal particles bigger than 1 µm (non-Brownian) are mainly controlled by physical forces (e.g., gravity and fluid drag). The interactions among submicron particles (1 nm–1 µm, Brownian), however, are mainly controlled by the interfacial characteristics of particle-solution (Stumm, 1977). Submicron colloids are of particular interest to us because of their large surface area to mass ratios and their high mobility in soils (Ryan and Elimelech, 1996). Although biocolloids are also very common in soils, in the present paper we focus only on abiotic soil colloids excluding colloidal-sized microbes.

Several processes responsible for colloid deposition and release in well-defined porous media have been established (Bradford et al., 2006; Johnson et al., 2007b). In principle, the Derjaguin-Landau-Verwey-Overbeek (DVLO) theory is widely accepted in describing the interactions between colloids and soil grains (Muller, 1994). The theory states that the net interaction energy between two particles is the sum of the interactions of electrical double layers (EDLs) and van der Waals-London (WL) forces, which vary with separation distance between particles. As particles approach each other, the net interaction energy experiences a secondary minimum first, then a primary minimum ($\phi_{\text{min}}$) after a maximum energy barrier ($\phi_{\text{max}}$; Figure 1). Particles may be attached or deposited when the net attractive forces are close to either the primary or secondary energy minimum (Figure 1). Both the magnitude of the energy barrier and the depth of the primary and secondary minimum, however, are affected by solution chemistry. In order for a deposited particle to be released, repulsive forces have to be generated between the surfaces.
of particles and stationary grains, perhaps as a result of changes in solution chemistry or flow velocity.

Understanding of colloid release and deposition is still far from complete. Colloid deposition under favorable conditions, in the presence of attractive interactions, can be predicted reasonably well using the DLVO theory. But colloid deposition under unfavorable conditions, in the presence of repulsive interactions, cannot be predicted by the theory (Grasso et al., 2002; Tufenkji and Elimelech, 2004b). Experimentally observed colloid deposition rates are many orders of magnitude greater than those predicted and are independent of the size of colloid particles. Elimelech (1994) presented an extensive discussion on possible explanation for these discrepancies. Although most of the studies on colloid deposition are developed for well-defined porous media, they are applicable to soils.

In this review we discuss only two characteristics of colloid deposition: transient phenomenon and straining. Though they are important to colloid deposition in natural soils, they received relatively less attention in the literature. Compared to colloid deposition, colloid release is even more poorly understood, which we emphasize in this review.

Investigations of colloid transport in the soil vadose zone have demonstrated that colloid particles tend to adsorb onto the water-air interface and the sorption process is almost irreversible (Sirivithayapakorn and Keller, 2003). These findings can trace their theoretical and experimental basis to the flotation discipline (Williams and Berg, 1992). Recent studies have
also revealed other governing mechanisms of colloid retention and release within soil pores (i.e., pore straining; Bradford et al., 2006), thin-water films (i.e., film straining; Wan and Tokunaga, 1997), air-water-solid interfaces (i.e., air-water interface capture; Gao et al., 2008), and immobile waters (i.e., immobile-water trapping; Gao et al., 2006). To maintain the simplicity, we focuses only on colloid dynamics in saturated soils excluding the vadose zone mechanisms.

Association of soil colloids with heavy metals has been an important issue in recent years (Hu et al., 2008; Zhang and Selim, 2007), but relatively less attention has been paid to the influences of colloid-metal associations on colloid mobility (Kretzschmar and Sticher, 1997). In the flotation processes widely used in mining industry, it is well documented that aqueous heavy metals can be potential determining ions (i.e., ions have the ability to preferentially dissolve over their counterions) or specific adsorbing ions (i.e., ions have the ability to be adsorbed to charged surfaces) to charged surfaces of minerals (Fuerstanau and Palmer, 1976), therefore the association of heavy metal with colloid surfaces may alter the surface charge significantly. The potential impact of the association on colloid mobility is emphasized in this review.

Most of the existing reviews on colloid transport in soils have focused on well-defined porous system (Bradford et al., 2006; Keller and Auset, 2007; Tufenkji et al., 2006). There are apparently differences between well-defined porous media and natural soils. In soils, ionic strength and pH of soil solution and redox potential of grain surface are influenced by rainfall, bioactivity, and changes in land use. The physiochemical heterogeneities in soils are not negligible, and various interfaces among grain, water, and air need to be taken into account to understand colloid mobility in soils. Colloid deposition and release in natural soils and their association with heavy metals are more dynamic and complicated than those in well-defined porous media. Though we do not cover all the differences between well-defined porous media and soils, we emphasize the unique electrochemical features of soils affecting colloid dynamics.

II. DLVO THEORY

The classic DLVO theory has been extensively used to describe colloid interactions and stability (Verwey and Overbeek, 1948). According to the DLVO theory, the total interaction energy ($\phi_{\text{Total}}$) between colloidal particles (or a particle and a stationary grain) is the sum of electrostatic repulsion energy ($\phi_{\text{EL}}$, arising from the overlap of electrical double layers) and attractive energy ($\phi_{\text{WL}}$, due to WL force), which is a function of particle separation distance. The generalized curve of interaction energy versus particle separation
distance shows one energy maximum ($\phi_{max}$) and two energy minimums (primary and secondary minimums; Figure 1). Aggregation or coagulation occurs when particles collide with sufficient kinetic energy to overcome the energy barrier ($\phi_{max}$) so they reach a distance within the $\phi_{min}$. On the other hand, if coagulated particles gain enough energy under perturbation to overcome the energy well ($\phi_{max} - \phi_{min}$) with increasing separation distance, they are released. The shape, intensities, and positions of the maximum and minimums are determined by the interactions between particle surfaces, which change with surface properties of particles and solution, and interfacial characteristics.

Significant discrepancies have been found between experimental observations and the prediction based on the DLVO theory (Elimelech and Omelia, 1990; Tufenkji and Elimelech, 2004b). Various updated theories of colloid stability have been proposed in recent years (Grasso et al., 2002; Tufenkji and Elimelech, 2005). The accuracy of prediction is somewhat increased using more sophisticated models in some systems at the expense of simplicity. Nevertheless, stability of clay colloids in solution can be qualitatively described by the DLVO theory in some systems (Verwey and Overbeek, 1948). Although measured collision efficiency between colloids and porous media surfaces is much greater than the theoretical prediction (Elimelech and Omelia, 1990), colloid deposition and release can still be qualitatively described by the theory (Roy and Dzombak, 1996). It has been generally agreed that the concept of DLVO theory is correct even though it is incomplete (Swanton, 1995).

To reasonably predict colloid interactions in a natural system, the classic DLVO theory needs some modification. Direct measurements of colloid interactions indicate that additional forces exist between particles (Cail and Hochella, 2005). Interactions between polar electron acceptors (Lewis acids) in solution and polar electron donors (Lewis bases) from colloid particles are termed as AB force and are usually dominant in aqueous systems in addition to the electrostatic and WL forces (Grasso et al., 2002). It can account for up to 85% of interactions between soil mineral particles in aqueous solution; therefore, the DLVO forces combined with the AB force adequately describes some anomalous stability of mineral colloids (Wu, 2001). The approach to combine classic DLVO forces and non-DLVO forces to calculate total colloid interaction energy is termed as the extended DLVO theory. Besides the AB force, other non-DLVO forces between particles (e.g., osmotic and steric interactions) may also be important to colloid interactions in soils (Grasso et al., 2002). The extended DLVO theory should also be corrected for colloid surface roughness and heterogeneity of colloid compositions, charges and sizes (Johnson et al., 2007a; Tufenkji and Elimelech, 2005). Unfortunately, none of the theories or models has successfully taken all these factors into consideration. Nevertheless, the DLVO theory has provided a guideline to at
least qualitatively describe colloid interactions in soils (Elimelech and Omelia, 1990). A simple approach (Vanoss et al., 1988, 1990) of combining the AB force into the extended DLVO theory can present much better estimations of colloid interaction energies in soils:

\[ \phi_{Total} = \phi_{EL} + \phi_{WL} + \phi_{AB} \]  

The extended DLVO theory is more successful than the classic one in describing colloid behaviors (Vanoss et al., 1990). Detailed description of Eq. (1) can be found in Vanoss et al (1990).

As shown in Figure 1, in the presence of an energy barrier (\( \phi_{\text{max}} \)) the deposition of a particle from solution onto a surface is mainly affected by the magnitude and shape of this barrier extending from its maximum into the solution phase. These are primarily determined by long-range forces such as electrostatic, WL, and AB forces. In contrast, particle release depends on interaction at separations between the energy minimum and the barrier maximum, which is greatly influenced by additional repulsion at short separation (Born repulsion; Ruckenstein and Prieve, 1976). Over this region the energy profile is very sensitive to the specific characteristics of the interacting surfaces and intervening liquid layer. This may explain why colloid release is poorly understood at the present time.

III. CHARACTERISTICS OF SOIL COLLOIDS

A. Charge Development

A1. INTRODUCTION

Solid particles present in water are often charged. The mechanisms of charge development have been extensively investigated (Lopez-Garcia et al., 2007; Ottewill, 1994). Based on the nature of solid particles, charge development can be divided into three categories: (a) lattice substitution is the most common in clay particles and referred to as permanent charge; (b) specific chemical interactions between surfaces and solution, including hydrolysis of surface functional group (e.g., hydroxyl and carbonyl) and chemical adsorption; and (c) preferential dissolution resulting from preferential hydration of surface atoms.

In addition, based on the contribution from electrolytes in solution to the charges of particles, ions can be classified into three categories: potential determining ions, specific adsorbed ions, and indifferent ions. **Potential determining ions** are the constituent ions of solid particles (e.g., H\(^+\) and OH\(^-\) for Fe oxides, and Ca\(^{2+}\) and CO\(_3^{2-}\) for CaCO\(_3\)) and their concentrations primarily determine the surface potential of particles (Parks, 1967). **Specific adsorbed ions** (SAIs) can change the magnitude and sign of the surface
charge (e.g., Ca$^{2+}$ and Pb$^{2+}$) by adsorbing onto the surfaces and forming a stern plane in the EDL (Parks, 1975). Indifferent ions adsorb physically to surfaces and change the magnitude of the surface charge (e.g., Na$^+$ and Cl$^-$), and form the diffusive layer in EDL resulting from a balance of their electrostatic interaction with the surface and osmotic interaction with bulk solution (Parks, 1975).

Soil colloids are heterogeneous in composition and consist of inorganic and organic constituents, or a mixture of the two. They are combinations of various inorganic minerals and organic substances. Heterogeneity in the composition and structures of colloidal particles makes their charge development a complex process. This may be further complicated by the dynamic nature of soil solution chemistry, which may cause the interfacial composition and structure of colloidal particles to vary temporally. Nevertheless, numerous studies have shown that their charge developing process can still be described using the EDL theory (Grasso et al., 2002; Vanoss et al., 1990).

A2. Electrical Double Layer Between Metal Oxide-Water Interfaces

According to the EDL theory, a charged particle in solution is surrounded by two thin liquid shells: an inner region (Stern layer) where the counterions are strongly bound and an outer region (diffuse layer) where they are less firmly associated (Haydon and Ottewill, 1965). In this review we mainly discuss the EDL of metal oxides in water because metal oxides are important natural colloids and have been relatively well understood among various surfaces of colloid particles (Dzombak and Morel, 1990; Hofmann and Liang, 2007). When specific absorbing ions other than H$^+$ and OH$^-$ are absent in a system, the charge developing process on the surfaces can be described as follows (Schindler and Stumm, 1987):

$$
\text{SOH}_2^+ = \text{SOH} + H^+ K^{int}_{a1} \quad (2)
$$

$$
\text{SOH} = \text{SO}^- + H^+ K^{int}_{a2} \quad (3)
$$

Where SOH denotes a surface site and $K^{int}_{a1}$ and $K^{int}_{a2}$ are the intrinsic surface acidity constants. Schindler and Stumm (1987) summarized the intrinsic acidity constants ($K^{int}_{a1}$ and $K^{int}_{a2}$) of various metal oxides and found that the constants are generally correlated to those in solution. The affinity of protons to the surfaces of metal oxides, however, is much more complicated and influenced by changes in surface composition and structure (Koopal, 1996a; Preocanin and Kallay, 2006). The values of these constants are difficult to determine and different electrostatic models may give contradictory predictions. A simplified approach is often used by combining...
Eqs. (2) and (3):

$$\text{SOH}^+ = \text{SO}^- + 2\text{H}^+ K_a^{\text{int}}$$  \hspace{1cm} (4)

$K_a^{\text{int}}$ is simply related to the point of zero charge (PZC or pH$_0$), which is experimentally measurable and independent of electrostatic models for the solid-water interface (Bourikas et al., 2005). When the concentration of positively charged surface species is equal to that of the negatively charged species (i.e., a zero-charge surface), the pH$_0$ is related to the intrinsic equilibrium constant:

$$\text{pH}_0 = 0.5 \log K_a^{\text{int}} = 0.5 \log K_a$$  \hspace{1cm} (5)

This means that intrinsic acidity constant ($K_a^{\text{int}}$) is equal to the apparent acidity constant ($K_a$) at a surface potential of zero. Eq. (5) not only indicates that pH$_0$ is a measure of $K_a^{\text{int}}$, it also shows that the bonding of protons at metal oxide surfaces is more analogous to the bonding of similar complexes in an aqueous phase (Schindler and Stumm, 1987) or to that in bulk crystal structure (Sverjensky, 1993). The correlation between the surface acidity constants of metal oxides and those in solution supports the first scenario.

Blesa et al. (1990) pointed out that there is a difference in Gibbs free energy between forming aqueous and surface ion complexes, and inferred that the difference may result from the dehydration of the adsorbing ions. To favor adsorption, adsorbed species should occupy kinks, edges, or adatom positions where water molecules from the first coordination sphere must be removed. For observed difference between the hydrolysis in solution and the formation of the surface complex, the easy dehydration of anionic species should account, at least partially. Blesa et al. (1990) suggested that the solvation of metal ions must be considered. Following this point, combining crystal chemistry (Parks, 1965) and solvation theory (Sverjensky, 1993), Sverjensky (1994) showed that surface protonation on a wide variety of minerals can be accurately calculated from the dielectric constant of a mineral and the ratio of the Pauling bond strength to the cation-hydroxyl bond length of the solid particles. This suggests that much more emphasis should be placed on the analogy between the bonding of the surface protonated species and the bonding in the underlying crystal structure. In the approach of Sverjensky (1994), the property of crystals has been numeralized with its electric constant instead of qualitative terms such as kinks, edge position, and atom positions. The details on modeling or calculating pH$_0$ can be found in Kallay et al. (2007) and Preocanin and Kallay (2006).

Fokkink et al. (1989) demonstrated that pH and temperature congruencies exist in the surface charge development on various metal oxides. They measured the surface charge $\sigma_0$ in a number of oxides (TiO$_2$-rutile, RuO$_2$, and $\alpha$-Fe$_2$O$_3$-haematite) in KNO$_3$ solution as a function of pH, ionic
strength, and some other variables. When $\sigma_0$ is plotted as a function of $(\text{pH}-\text{pH}_0)$, where pH$_0$ is the PZC, the curves coincide for the three oxides within the experimental error at three levels of ionic strength even though they are different in pH$_0$. In other words, the individual identity of metal oxides makes no difference to the S-shaped plot of $\sigma_0$ versus pH-pH$_0$. In the measurements of temperature dependence of surface charge development, changes in temperature only affect the positions of PZC, not the trend of the surface charge development. They concluded that the EDLs in metal oxides can be functionally divided to a specific and a generic part, with respect to the natures of oxide and electrolyte. The specific part, which is determined by the specific interactions of a surface with protons on the surface, determines the PZC. The general part, which is controlled by the solution side of the double layer, determines the surface charge development once the surface charge deviates from pH$_0$. It can be well described by the Nernst equation ($\psi_0 = 2.303 RT/F (\text{pH}-\text{pH}_0)$).

In the presence of specific adsorbing ions (SAIs) such as Ca$^{2+}$ and Mg$^{2+}$ in solution, the charge developing process of a solid can be more complicated because its PZC will be shifted (Duval et al., 2002; Koopal, 1996b). In the presence of SAIs, observations have also shown the shifting of common intersection point (CIP) of titration curves under various ionic strengths. The CIP is the equal compensation point (Lyklema, 1987), at which charge-compensating cations and anions have an equal affinity to the surfaces. From this point of view, they explained CIP $\neq$ PZC in the case of specific adsorption as follows: at the PZC, adsorption of metal cations is favored over that of anions if cations have a higher affinity to the surface. To reach a situation where the intrinsic adsorbability of cations and anions is identical (equal compensation point), a positive charge on the surface has to be developed. This charge should be more positive with higher specific affinity of cations to the surface. Once the equal compensation point has been reached, further increase in concentrations of cations and anions do not lead to further shift (i.e., all successive curves at increasing concentrations will pass through the point). Similar reasoning applies when anions have a higher affinity over cations. This principle is important to understand the impact of soil solution chemistry on soil colloid charge development. Following this line, it is easy to understand the effects of changes in species of cations and anions in solution on PZC and CIP.

The previous discussion only applies to ideal crystal surfaces, where the dissolution is negligible using the surface complex approach. However, solubility of metal oxides be taken into account for surface charge determination, especially in the case of amorphous (hydr)oxides. Adsorption and desorption of hydrolyzed metal complex ions then may become an alternative to determine surface charge other than the surface complexation of H$^+$ and OH$^-$. Based on the minimum solubility theory (Bourikas et al., 2005; Reymond and Kolenda, 1999), PZC should be
identical to the *isoelectric point* (IEP) of an aqueous solution suspending the particles. The IEP is defined as the pH when the concentrations of positively and negatively charged complexes are equal in an aqueous phase (Parks, 1965), which is often found at the pH of minimum solubility of a solid. Blesa et al. (1990) found that the PZC and IEP for metal oxides do not coincide. However, the deviation from IEP can be well explained if considering the fact that the complex cations and anions require different dehydration energy when they are transferred from solution to surfaces. They explained that monomeric cations hydrate more strongly than anions in aqueous solution, so the shift should be small and negative when the charge is determined by monomeric surface complexes and the minimum solubility theory is generally valid. On the other hand, for polymeric species more specific behaviors are expected. Either relatively large positive or negative shifts may occur if the charge surface complexes are polymeric. The underlying assumption of these approaches is that the surface active site is more analogous to their solution species. This may be more suitable to soil environment where various amorphous minerals are abundant and aqueous species are better understood than surface species.

### A3. Charge Development of Soil Particles

Surface charge of soil particles can be classified into two types: permanent and pH-dependent charges. Detailed characterization of soil particle charges has been developed (Karak et al., 2005; Moulik et al., 2005). Charge development on soil particles is more complicated than that on the metal oxides because their surface composition and structure vary greatly and potential determining ions are not limited to just H\(^+\) and OH\(^-\). However, similar phenomena such as CIP have been observed, which is referred to as the point of zero salt effect (PZSE). It is often found that true PZSE deviates from CIP (Chorover and Sposito, 1995).

Different from ideal crystallized metal oxides, soil is a mixture of various minerals and organic substances including significant amounts of amorphous materials, such as amorphous Fe and Al. It is well documented that hydrolyzed species of Al and Fe on soil particles have significant impact on their pH-dependent charge (Itami and Fujitani, 2005; Marchi et al., 2006; Yu et al., 2005), and their complexation with organic matter further complicates the charge developing processes (Antelo et al., 2007). In addition, mineral dissolution may be significant for some soils and may affect the processes greatly (Blesa et al., 1997). Combining all these factors with the dynamic nature of solution chemistry (Dong et al., 2000), it can be concluded that at the present time it is difficult to accurately predict surface charge development of soil particles.

Blesa et al.’s (1997) approach may be promising to provide a guideline to estimate soil surface charge development. They emphasized the role of
the partitioning of charged species between solid surfaces and solution during surface charge development, which is driven by the difference in Gibbs free energy of a charged species between in solution and on surface. The underlying assumption is that the charged species in solution and on surfaces are similar. This approach has a relatively sound theoretical basis and experimental evidence, it is worth further examination.

A4. Charge Development of Mobile Colloids

Much research has been conducted to investigate charge development of water dispersive and mobile colloids (Itami and Fujitani, 2005; Kretzschmar et al., 1997). It is commonly observed that the stability of soil colloidal clays is many times greater than that of comparable reference clays. Clays isolated from surface soils were more dispersive than clays from the subsurface horizons of kaolinitic soils (Kretzschmar et al., 1997). Factors contributing to the high dispersibility of soil clays include the presence of adsorbed organic matter, minor quantity of smectite in kaolinitic clay, and larger surface roughness of soil clays compared with unweathered reference clays (Kretzschmar et al., 1995).

Organic matter is an important source of negative charges in soils. Well-decomposed humus may have cation exchange capacity (CEC) >300 cmol kg$^{-1}$, which is considerably greater than that of clays such as kaolinite (3–15), illite (30–40) and montmorillite (80–150; McBride, 1994). It has been estimated that 20–70% of the CEC of many soils are attributed directly to the soil organic matter alone (Vaughan and Ord, 1984). In soils, dissolved organic carbon (DOC) tends to adsorb onto solid particles such as clays and metal oxides, driven by ligand exchange, multivalent ion bridging, WL force, and hydrophobic interactions between DOC and the solid minerals (Murphy and Zachara, 1995). In particular, for Fe and Al oxides, when the pH of a system is lower than their PZC, adsorption of DOC onto the minerals increases significantly because of the electrostatic attraction between the two, resulting in significant increases of negative charge on the surfaces. There are numerous studies looking into the effects of organic coating onto metal oxides (Kretzschmar and Sticher, 1997) and clay minerals (Breiner et al., 2006) on surface charge. Heil and Sposito (1993a, 1993b) found flocculation of illitic soil colloids with organic coatings increased with pH in Ca solution, whereas it decreased when the organic matter is removed by H$_2$O$_2$. They concluded that competition between H$^+$ and Ca$^{2+}$ for the acidic functional groups of organic molecules is essential to the charge development on the coated colloids. A similar result was also obtained by Kretzschmar and Sticher (1997) in humic-coated kaolinic soil clay. On the other hand, it has been reported that the electrical properties of the quartz surface dispersed in river water is determined essentially by their interactions with inorganic cations such as Al and Ca instead of organic matter (Findlay et al., 1996). These results are consistent in that the surface electric properties of minerals are a result
of interactions in the interfaces of particle and solution, including particle organic matter, organic–inorganic ions, and particle inorganic ions. Particularly, types of cations and their concentrations are important for the charge development on particles in addition to organic matter.

Our ability to model surface charge development on soil colloids with reasonable certainty has not been fully realized; however, it has been conceptualized that soil particles can be treated as assemblages of crystalline and amorphous minerals and organic matters. Sophisticated models, such as the triple layer model, fail to describe the electrified interfaces of soil colloids because particle surfaces are irregular and the Stern layer often moves inward, inside the physical boundary of the particles. As a simple approximation, it is more practical to use the diffuse double layer theory to describe the interfaces of soil particles with a specific component (i.e., a charged surface) and a generic component (i.e., a diffuse layer). The surface charge development then can be described by the partitioning of charged species between solution and surfaces assuming the charged species are similar between the two phases.

B. Hydration

When water molecules orientate around immersed particles, they form a hydration shell (Clifford, 1975). When these particles with such a shell approach each other, additional forces between the particles arise. The origin of these forces is the interactions between polar electron acceptors (Lewis acids) in water and polar electron donors (Lewis bases) from colloidal particles, and termed AB forces as we discussed previously (Vanoss et al., 1990). Surface electron donicity of colloid particles is crucial for water molecules to be orientated along the surface. Strong surface electron donicity causes more ordering of water molecules along the surfaces, resulting in a repulsive force between the particles, while weak surface electron donicity causes less ordering of water molecules, resulting in an attractive force. Vanoss et al. (1990) demonstrated that between particles dispersed in water, the interaction free energy from AB, whether repulsive or attractive, is commonly as much as 100 times greater than WL energy, and ≥10 times greater than electrostatic repulsive energy at close range (1–5 nm). The AB energy can account for up to 85% of interactions between mineral particles in aqueous solution; therefore, the DLVO theory combined with the AB force can adequately describe some anomalous colloid stability that cannot be explained by the original DLVO theory (Vanoss et al., 1994a; Wu et al., 1994b). Wu et al. (1994a, 1994b) experimentally evaluated the particle interactions of montmorillonite and calcite by examining flocculation of their suspensions while increasing Ca$^{2+}$ concentration. They concluded that Ca$^{2+}$ not only reduced particle zeta potential, but also drastically lowered the electron donicity of the polar surface of the particles, resulting in an attractive AB force, which is primarily
responsible for the flocculation of the suspensions. It is suggested that surface electron donicity and $\zeta$-potential of particles are related; therefore, SAIs such as Ca$^{2+}$ alter not only $\zeta$ potential when they adsorb onto a particle, but also decrease the surface electron donicity (Wu et al., 1994a, 1994b).

C. Size Development of Mobile Colloids

The behaviors of colloids are size dependent. Individual colloidal particles may aggregate depending on the magnitude of the energy barrier of their interaction (Figure 1), which is similar to colloid deposition. If the energy barrier of an interaction is low, fast coagulation occurs and the colloid aggregation rate depends on particle diffusion rate; otherwise, the aggregation rate is controlled by the magnitude of the energy barriers. These two aggregation mechanisms result in two different fractal dimensions, which have been discussed by Riscovic et al. (1996). Direct measurements and theoretical simulations of colloid size distribution in natural system have shown that the concentration of colloids $<0.1 \, \mu \text{m}$ might be negligible because most of them coagulate instantly (Buffe and Leppard, 1995; Filella and Buffe, 1993). Kaplan et al. (1997) examined the possibility of mobile colloids’ aggregation from a reconstructed soil profile. They analyzed the size distribution of particles in the suspensions with or without sonification (which is supposed to break down the aggregates of particles in the suspension). They found that the suspension without sonification exhibits practically the same bimodal distribution of particle sizes as does the one with sonification. This holds for soil suspensions collected from two different soils: a loamy sand and a sandy soil. Their results suggest that colloid aggregation in soil pore space is limited especially when soil colloid particles are highly charged (Kaplan et al., 1997). Similar bimodal size distribution of mobile colloids were reported by Ronen et al. (1992) who characterized the suspended particles collected from groundwater in the coast plain phreatic aquifer of Israel. In the bimodal distribution, the colloids of smaller size ($<0.4 \, \mu \text{m}$) may result from long-distance translocation to sampling points, while those of larger size ($<1 \, \mu \text{m}$) may come from local dispersion at the points.

IV. CHARACTERISTICS OF SOIL POROUS MEDIA

Interactions between mobile colloids and surfaces of soil porous media may be more important than those between colloids in limited pore space. Therefore, pore structures and physicochemical surface characteristics have tremendous influence on colloid mobility. Extensive studies have been done in systems consisting of clean surfaces of porous media (Auset et al., 2005; Smith et al., 2008; Tong and Johnson, 2007; Tufenkji and Elimelech, 2005).
Large discrepancies, however, have been found in colloid deposition rate under unfavorable conditions between theoretical prediction and experimental observation. This has been attributed to the hydrodynamic effect of flow and surface heterogeneity of the porous media, such as surface roughness and local charge heterogeneity (Tufenkji and Elimelech, 2005). The latter has been considered to be the most promising approach to understand the interaction between colloids and porous media in clean systems (Schumacher et al., 2005). Several exhaustive reviews on the interactions between colloids and porous media are available (Elimelech, 1994; Ryan and Elimelech, 1996; Swanton, 1995).

Soil porous media are assemblages of a wide range of particles, which vary greatly in mineralogy, surface composition, and dimensions. Unlike systems with clean surfaces, where the surface properties of porous media may be far different from those of mobile colloids, the surfaces of soil porous media may consist of potential mobile colloids. In sandy soil, clay-sized particles of small amount may tend to pack closely along the surfaces of large sand grains driven by energy minimum. The arrangement between grain and colloidal particles has also been confirmed by fractal analysis (Bartoli et al., 1991). Based on this fact, the interactions between colloids and soil porous media can be treated, at a first approximation, as those between colloidal particles, which have actually been conventional assumption. Swanton (1995) suggested that in an undisturbed soil profile, the active sites may be completely occupied by mobile colloids. Ryan and Gschwend (1994a, 1994b) successfully related the observed colloid release rates from Fe oxide-coated sand columns to energy barrier \( \exp \left( \frac{\phi_{\text{max}} - \phi_{\text{min}}}{k_B T} \right) \), where \( k_B \) is the Boltzmann constant and \( T \) is absolute temperature). Their estimation of the energy barrier \( \phi_{\text{max}} - \phi_{\text{min}} \) is based on the interactions between colloids rather than those between colloids and porous media surface. The underlying assumption is that soil porous media surfaces are similar to colloid surfaces.

V. DEPOSITION OF COLLOIDS IN SOILS

A. Theoretical Background in Ideal Porous Media

Colloid mobility in porous media is mainly controlled by the net rate of colloid deposition and release. Deposition of colloids onto porous media can be viewed as a two-step process: transport of colloids from bulk solution to the proximity of the surfaces of porous media and then their attachment to the surfaces, which depends upon the nature of particles-surfaces interaction. If the energy barrier \( \phi_{\text{max}} \) is \( \leq 0 \), the colloid flux approaching to the surfaces is equal to that of the deposition and attachment efficiency of collectors (porous media) is 100% (Yao et al., 1971). The energy barrier must otherwise be overcome in order for a colloidal particle to attach to the
surfaces. Therefore, deposition rate constant \( (k_{dep}) \) is a function of energy barrier \( \phi_{max} \) with \( k_{dep} \propto \exp(-\phi_{max}/k_BT) \); Ryan and Gschwend, 1994b).

The main mechanisms of colloid contact to a collector are inertial impaction, interception, sedimentation, electrostatic forces, Brownian diffusion, and straining (Tien, 1989). The overall single collector contact efficiency can be theoretically calculated based on the filtration theory that considers the processes of interception, sedimentation, and Brownian diffusion (Tufenkji and Elimelech, 2004a). The single collector contact efficiency only represents the physical processes of colloid filtration in porous media, which is independent of the chemistry of the system. In the classic filtration theory, a separate term, removal efficiency \( (\alpha) \) is used to reflect the role of chemistry in colloid deposition in porous media.

The classic filtration theory has been widely used in predicting colloid deposition and transport in porous media; however, a great discrepancy between the prediction and experimental observation under unfavorable deposition conditions has been observed. This has been attributed to the distribution of surface and physical properties, surface charge heterogeneity of solids, surface roughness, interfacial electrodynamics, and colloid deposition in secondary minimum (Tong and Johnson, 2007; Tufenkji and Elimelech, 2004a). In addition, as particles deposit on a collector, the deposition rate may change after initial stage of deposition depending on the nature of particle–particle interaction (Yao et al., 1971). If the net interaction is repulsive, the collector surfaces become progressively occluded as particles accumulate and colloid deposition rate should decline accordingly. This surface exclusion phenomenon is termed blocking. There are several excellent recent reviews on this topic (Bradford and Bettahar, 2006; Ryan and Elimelech, 1996; Swanton, 1995).

B. Colloid Deposition in Soils

B1. Transient Phenomenon in Colloid Deposition

Because there are no clean surfaces in soils, the results obtained in ideal porous media cannot be directly extrapolated to describe colloid deposition in soils. At a given time, in most soils, the most favorable deposition sites may already be occupied. If there is an influx of mobile colloids in soil, the deposition site may be limited during the early stages of exposure because all favorable deposition sites are filled, which is different from the clean porous media. Over a prolonged period of exposure for a colloid flux, soil porous media may develop surfaces that are similar to those of mobile colloids (Swanton, 1995), which will also limit the deposition of colloids. Therefore, colloid deposition may just be a transient phenomenon in soil porous media.
Dispersion of soil clays by exhaustively shaking in water provides a measure of the fraction of colloid that can potentially become mobilized. Miler and Baharuddin (1986) observed that the amount of colloidal particles remaining in suspension after 36 hr of shaking was highly correlated to surface soil loss in southeast USA under high intensity rainfall. Kaplan et al. (1997) found that mobile colloids are similar in mineralogy to the water dispersible clays in two soils and that they are many orders of magnitude lower than the amount of water dispersible clays. There is a significant amount of potentially mobile colloids attached to the soil porous media (de Jonge et al., 2004); however, during that period of time they functioned as a part of stationary porous media. They may be detached from the porous media (mobilized) once they are exposed to a chemical or hydrological perturbation (Saiers and Lenhart, 2003; Zhuang et al., 2007). The mobilization of these loosely attached colloids is referred as transient phenomena in colloid deposition, which is important for understanding the distinctive features of colloid mobility in soil porous media. Take surface soil, for example, a perturbation occurs often from the top such as rainfall. This type of perturbation may result in the release of deposited colloids (Ryan and Elimelech, 1996), and the mobilized colloids move down over the surfaces of porous media consisting of the deposited colloids. Therefore, at the front of the downward-moving perturbation, there are two opposite processes operating simultaneously: the deposition and release of soil colloids. The deposition is mainly influenced by the blocking effect, and the release is discussed in Section VI.

B2. PORE STRAINING

If the effective size of a colloid particle is larger than the pores through which water flows, the particle is retained in porous media, which is referred to as straining. Straining occurs in granular bed filtration if the ratio of the suspended particle diameter to the grain diameter is greater than some critical values (Bradford et al., 2004; Xu et al., 2006). It is reported that straining is one of the most important mechanisms of colloid deposition in well-defined porous media (Bradford and Bettahar, 2005; Bradford et al., 2006; Xu et al., 2006). Previous studies have also examined pore straining of colloids in soil porous media. Seta and Karathanasis (1997) examined the transportability of water dispersible clay through intact soil columns and found that pore straining is one of the most important factors in determining the concentrations of colloids in leachates. They concluded that relatively low colloid transportability in some soils they studied is attributed to larger sizes of soil colloids (i.e., straining). Jacobsen et al. (1997) examined the transportability of illite through soil columns containing macropores and found that illite concentrations moving through the soil columns are related to the sizes of active macropores in the soil columns. They also found that there was no significant difference in mobility between the illite and that coated with humic acid through the columns. These results suggest that size straining is a...
physical process that is not affected by changes in surface potentials resulting from the coatings of humic acid. This was further confirmed by the fact that colloid concentrations in leachates increased with the intensity of infiltration because high intensity of infiltration depresses the effect of straining. Kretzschmar et al. (1995), however, found that coating colloids with humic acid results in much lower collection efficiency in columns packed with clean saprolite particles. This contradiction demonstrates the difference of colloid deposition between soil porous media and clean porous media.

VI. COLLOID RELEASE IN SOILS

Different from colloid deposition, which is essentially determined by the interactions at larger separation distance, colloid release depends on interactions at separation between the surface and energy barrier (Figure 1) and is greatly influenced by additional repulsion at short separation. Colloid release is generally expected from the repulsion between porous media and colloids. The efficiency of colloid release depends on whether the process is caused by diffusion alone or by an applied external force. Without external forces the rate of particle release is a function of the diffusional escape probability of the deposited colloids through the energy barrier (i.e., the energy well: $\phi_{\text{max}} - \phi_{\text{min}}$; Ryan and Elimelech, 1996). It can also be reflected by the shape of interaction energy profile between the energy minimum and the primary maximum (Figure 1): the smaller the slope $(d\phi/db)$ of the curve the less force it is needed for colloid release, where $b$ is the separation distance.

It is clear that the two opposite processes, colloid deposition and release, are controlled by different mechanisms and factors. For a given system, mobile colloid concentration is determined by the relative magnitude of colloid deposition and release rates (Sen and Khilar, 2006). The residence time of colloid-carrying solution in the system also plays an important role. A longer resident time represents a condition closer to the equilibrium of colloid deposition and release, while a short one may favor deposition over release and vice versa. For example, colloid dispersion in a batch experiment is a result of balancing between colloid deposition and release because of the longer residence time in general, whereas colloid release from a short column may be free of redeposition effect (Smith et al., 2008). Extra caution must be taken when extrapolating colloid stability obtained from a batch experiment to colloid transportability in a column experiment where kinetic effect is more pronounced.

A. Processes of Colloid Release

Similar to colloid deposition, colloid release rate is generally determined by both colloid detachment from porous media and transport to bulk solution.
Ryan et al. (1994b) examined the release rates of colloidal hematite from hematite-coated sand columns under different ionic strengths and flow rates, and found that colloid release rates decrease as ionic strength increases. In addition, colloid release rate also decreases with increasing flow rate, which is contrary to the expectation that greater mobilization would occur at greater flow rate due to greater hydraulic stress on deposited colloids (Ryan and Elimelech, 1996). They suggested that the rate-limiting step in colloid release is the transport of detached colloids to the bulk fluid when rapid colloid release corresponds to conditions where the energy barrier has vanished from the potential energy profile. Coincidentally, a similar phenomenon was observed by Jacobsen et al. (1997) in intact soil-column experiments where natural particles are leached with tap water. Their results showed that particle mobilization is not influenced by increases in flow rate. The plot of accumulated amount of mobilized particles versus square root of time showed a fairly linear relation, implying diffusion limited kinetics.

One necessity for diffusion kinetics being dominant is that the barrier maximum of mobile colloids vanishes, which may be very common in soil because of the transient phenomena we discussed previously. The lack of flow rate effect in Jacobsen et al. (1997) may be caused by the larger slope of energy barrier for potential mobile colloids at a given condition, which may otherwise be overcome by increases in hydraulic stress. Subsequently, these colloids will not become mobile. This is based on the heterogeneity of the interactions between colloids (mobile and potential mobile colloids) and media in soil discussed previously. In addition to ionic strength and flow rate, other physicochemical effects (e.g., charge and steric effects and pH perturbations) also play an important role in governing colloid release in soils (Grolimund et al., 2001a, 2001b).

### B. Mobile Colloids and Water-Dispersible Clay

Kaplan et al. (1997) examined the release of colloids from an Ultisol soil in the southeast United States. Mobile colloids were collected during and after mild rain events from the reconstructed pedons. They found that the mobile colloids are similar to the water-dispersible clay in mineralogy, which is consistent with the results of Seta and Karathanasis (1997).

However, there were some differences between the two results. Kaplan et al. (1997) found that the sizes and compositions of the mobile colloids differed from those of the water-dispersive clays, with the former being smaller and generally enriched with kaolinite, Fe oxides, gibbsite, and organic carbon. In addition, compared to the total clay fractions in the reconstructed pedon, the mobile colloids were more dilute in quartz and hydroxy-interlayered-vermiculite. Based on the results from scanning electron microscopy and photon-correlation spectroscopy, essentially all the mobile colloids (>90%) had diameters of about 230 nm and moved through
the soil as discrete, nonaggregated particles. They concluded that the particles enriched in mobile colloids are not only readily dispersible but also smaller in size than water dispersive clay. Moreover, they proposed colloid mobilization in the pedons is a result of two consecutive processes: dispersion of highly charged particles due to changes in soil chemistry and/or induced water flow, which is determined by particle composition and can be evaluated by water dispersibility of a soil, and their transport through a pedon, which is size dependent.

C. Influences of Colloid Stability on Mobilization of Water-Dispersible Soil Colloids

The dispersability of water-dispersable clay has been studied extensively (Kjaergaard et al., 2004; Koopmans et al., 2005; Shaw et al., 2003). Even though we do not fully understand dispersability of soil colloids at the present time, it is undoubtedly affected by factors such as pH, ionic strength, DOC, and exchangeable sodium percentage. In their column leaching study, Seta and Karathanasis (1997) found that colloid release in soils strongly depends on pore water pH and total exchangeable bases. The effect of pH on colloid release can be explained by its effect on colloid stability: the higher the pH above the pH0, the greater the colloid stability. The strong correlation between total exchangeable bases and colloid recovery is anticipated because of its high correlation with pH. Using similar soil leaching studies, Kaplan et al. (1997) found that colloid release is highly correlated to the exchangeable sodium percentage (ESP) of the soils. The positive correlation between soil colloid dispersability and ESP has also been found by other researchers (Redman et al., 1999; Suarez et al., 1999).

There are sufficient evidences to show that ESP is consistently correlated to the dispersability of soil colloids in a soil. Rengasamy and Oades (1977), however, demonstrated that even Ca-saturated clay (i.e., ESP = 0) could be dispersed provided that a soil has been free of electrolyte by dialysis. Further, in a soil system, solution chemistry is dynamic and therefore concentrations and types of cations in soil solution and exchangeable sites may vary greatly. Parameters such as total exchangeable bases, which take cations besides Na+ into account, may be more reasonable than ESP to describe colloid transportability. The effects of cation exchange reactions on colloid release have been demonstrated by many studies, which are discussed in the following section.

D. Ion Transfer Processes During Colloid Release

D1. Ion Transfer During Colloid Release in Well-Defined Systems

Kallay and Zalac (2001) examined the effects of pH-neutral electrolytes on the detachment of spherical colloidal particles of goethite from glass surfaces in basic media. They found that colloid release is enhanced with increasing
Colloid Deposition and Release in Soils

concentration of NaNO$_3$, which is unexpected. This behavior corresponds to a double layer that undergoes relaxation during particle detachment. As the distance between the particle and the surface increases, to keep the potential constant, the adsorption of the potential determining ion (OH$^-$) must occur with consequent equilibration of all ionic species in the Stern and diffuse layers. During particle detachment, ion transport from solution phase into the interfacial layer is accelerated with increasing distance between the surfaces due to solution influx from bulk. Kallay and Zalac (2001) summarized that this unusual behavior can be observed under the following conditions: colloid redeposition is minimal (short column), particles and media have alike charges, and surface potentials are constant during colloid detachment. This apparently unusual behavior can be understood by taking into consideration of the energy profile as a function of distance near the surfaces (Figure 1). The probability of colloid detachment depends on the depth of energy well ($\phi_{\text{max}} - \phi_{\text{min}}$), however, the probability of colloid deposition depends on the height of the energy maximum ($\phi_{\text{max}}$). As the concentration of NaNO$_3$ in the system increases, the depth of energy well may be reduced, resulting in an increased rate of colloid detachment; at the same time the energy maximum may decrease, resulting in an increased rate of deposition. The amount of colloidal particles one observed in effluents is determined by the net rate of these two opposite processes.

Kallay and Zalac’s (2001) rationale is that a change in electrical environment of the interfaces resulted from colloid detachment may induce ion flow between solution and interfaces (EDL), which may facilitate colloid detachment. This has been known as so-called surface charge or potential regulation, which has been discussed by Chan et al. (1975). They showed that there may be significant ion flow between solution and interfaces during EDL interaction if the particles carry pH-dependent charge. This suggests that ion transfer may also be important during colloid release because pH-dependent charge is generally abundant in soil colloid particles.

D2. Ion Transfer During Soil Colloid Mobilization

Shainberg et al. (1981a, 1981b) examined the effects of electrolyte concentrations on hydraulic conductivity of a sodic soil. They found that both clay dispersibility and hydraulic conductivity (HC) of the soil were very sensitive to the levels of exchangeable Na$^+$ and to the salt concentrations of a percolating solution. When salt concentration in the solution was 3.0 meq/L, clay dispersion increased and HC decreased with ESP only if ESP $>$12%. Conversely, when salt concentration was maintained at $\sim$0.5 meq/L, clay dispersion increased and HC decreased with ESP even when ESP $>$1–2%. These results indicate that ESP itself cannot determine soil dispersibility, and salt concentrations in solution have to be taken into account. A simple principle behind this is that colloids flocculate when the critical flocculation concentration of a salt is reached. Shainberg et al. (1981a, 1981b) concluded
that the response of soils to low ESP and leaching with low-electrolyte water depends on the concentration of electrolytes in the soil solution that the solid phases of a soil maintain. Their results demonstrated that salt concentration in soil solution was determined by the dissolution rate of soil minerals. Higher rate of mineral dissolution depresses the impact of exchangeable Na on soil dispersion. Based on these studies, it is recognized that the interaction between cations on exchangeable sites and bulk solution significantly impacts colloid mobilization.

There is sufficient evidence that exchangeable Na has significant influence on colloid release from soil at low ionic strength. Cummins and Kelley (1923) first demonstrated the hydrolysis of exchangeable Na\(^+\) in soil, or the replacement of exchangeable Na\(^+\) by H\(^+\) from the dissociation of water. They found that in the absence of CaCO\(_3\) and CO\(_2\), a Na-saturated soil leached with distilled water yields a NaOH solution. In an experiment with Na-montmorillonite, where the hydrolysis products are removed continuously, Baron and Shainberg (1970) found a yield of 0.1 M Na\(^+\) solution. Shainberg (1973) demonstrated that Na-montmorillonite releases Na\(^+\) even when the reaction products are not removed and the specific conductance of the clay suspension was proportional to the square root of time. These observations are consistent with a hydrolysis mechanism consisting of two consecutive reactions: a rapid exchange between exchangeable Na\(^+\) and H\(^+\) in solution, which results in an acidic surface, and a slower, first-order transformation of H\(^+\) clay to Mg\(^{2+}\) or Al\(^{3+}\) clay, which increases the amount of exchangeable Na\(^+\) release.

Similar phenomena have been observed in soils. Oster and Shainberg (1979) demonstrated that by washing three arid-zone soils with distilled water the release of electrolytes can be related to the square root of time exhibiting two linear rates. They concluded that the rate of the first, the more rapid of the two, which occurred right after the washing (<1~2 hr), depends on exchangeable Na. Increasing ESP causes increases in the release rate in electrolytes.

Ma and Dong (2004) examined how colloid mobility in a Pb-contaminated soil, collected from Montreal, Canada, is affected by water-flooding incubation. The soil packed in short columns was incubated approximately for 3, 20, and 80 days, respectively. After the standing water on the top of soil columns was removed, 0.01 mM CaCl\(_2\) solution was pumped through the soil columns until the soil was saturated with CaCl\(_2\). This is designed to eliminate the artifacts resulting from column packing and to use Ca as an index for ion transfer during the following colloid release. The influent was then switched from CaCl\(_2\) to deionized distilled water (DDW) and effluent of \(~12\) mL was continuously collected using a fraction collector. Total and dissolved metal concentrations were analyzed. The relation among colloidal Al, colloidal Fe, dissolved Ca, and pH with pore volumes of the effluent is presented in Figure 2.
It is expected that, after saturating the soil columns with 0.01 mM CaCl$_2$, Ca was the dominant cation in both bulk solution and EDL surrounding colloidal particles or stationary solid phases in the soil. When the influent was switched from 0.01 mM CaCl$_2$ to DDW, the release of Ca from the soil may be determined by various mechanisms, which came to play probably
sequentially. At the beginning stage of switching influent to DDW, Ca release was from the bulk solution, which was confirmed by the fact that Ca concentrations and pH in the effluent at pore volume = 1 were approximately those of the influent ([Ca] = 0.01 mM, pH = 6.95; Figure 2). At the second state, Ca diffusion from EDL to the bulk solution driven by a concentration gradient may occur. Once Ca in the bulk solution was depleted, Ca cations moved against electrostatic attraction away from the surfaces, extending EDL surrounding colloids and solid phases to mobilize colloids. Any significant expending of EDL and resulted colloidal mobilization had to be associated with significant amount of Ca released into bulk solution. The excess Ca$^{2+}$ in the diluted bulk solution may be combined with hydroxyl to release proton (Ca$^{2+}$ + H$_2$O $\leftrightarrow$ [CaOH]$^+$ + H$^+$; Oster and Shainberg, 1979), resulting in perturbations in pH, which is consistent with the data shown in Figure 2. Generally, Ca hydrolysis is weak in solution, it is thus not likely for it to cause notable changes in pH; however, the heterogeneity of the system may enhance Ca hydrolysis in bulk solution to cause the perturbations.

Although further validations are still needed, the results can be used as a mechanistic illustration for ion transfer between EDLs and bulk solution described by Eq. (5). Studies on ion transfer (Ca and OH$^-$) during the colloid release provides a very useful tool to evaluate colloid mobility in soils because current understanding of colloid mobility in soils is still limited, especially in respect to heterogeneous systems.

VII. ASSOCIATION OF COLLOIDS WITH HEAVY METALS

There are two major issues involved here: sorption capacity of heavy metals to soil colloidal particles, which has been well documented (Hayes and Bolt, 1991; Kim and Tobiason, 2004), and influences of metal sorption on colloid mobility. The association of colloids with heavy metals can be classified into adsorption, precipitation (and surface precipitation), and ion exchange. Their influences on surface charge are possibly by virtue of heavy metal ions functioning as specific adsorbing, potential determining, and indifferent ions, respectively. Since most heavy metals are low in solubility in soil and their concentrations are much lower than those of electrolytes in soil solution, it is unlikely for them to function as indifferent ions. The same reasoning may also apply to the role of heavy metal ions to play as potential determining ions. It has been realized that adsorption is one of the most important mechanisms for heavy metal association with colloids (Hayes and Bolt, 1991) and colloid-facilitated heavy metal transport (Grolimund and Borkovec, 2005; Sen and Khilar, 2006).

In soils, colloids are heterogeneous, including weathered minerals (e.g., clay and metal oxides), CaCO$_3$, silica, large organic molecules, and cellular
debris. However, it may be classified by surface functional groups: surface hydroxyl, carbonyl, or organic complexation group. In this review, the surface functional group hydroxyl is used as an example to discuss the association of heavy metals with colloids.

A. Adsorption of Heavy Metals to Surface Hydroxyl Groups of Colloids

Surface hydroxyl-bearing minerals are abundant in soils (metal oxides, quartz, and the edge of kaolinite). Similar to the expression for the deprotonation processes as described in Section III, surface complexation reactions of surface hydroxyl with heavy metals can be written as (Hayes and Bolt, 1991):

\[
\begin{align*}
\text{SOH} + M^{z+} &= \text{SOM}^{z-1} + H^+ & \text{K}_{1}^{\text{app}} \\
2\text{SOH} + M^{z+} &= (\text{SO})_2M^{z-2} + 2H^+ & \text{K}_{2}^{\text{app}}
\end{align*}
\]

Where SOH denotes a surface site and \(M^{z+}\) represents a metal cation. \(K_{1}^{\text{app}}\) and \(K_{2}^{\text{app}}\) are the apparent surface equilibrium constants, and can be expressed as

\[
\begin{align*}
K_{1}^{\text{int}} &= K_{1}^{\text{app}} \exp((z - 1)F\psi/RT) \\
K_{2}^{\text{int}} &= K_{2}^{\text{app}} \exp((z - 2)F\psi/RT)
\end{align*}
\]

where \(\psi\) is the potential difference between the binding site and bulk solution. The exponential term accounts for the coulombic contribution to the intrinsic equilibrium constants. Because the surface potential cannot be determined experimentally, it is generally formulated based on a variety of models, such as constant capacitance, diffuse layer, and triple layer models. It has been found that stability constants of surface complexes correlate with those of the hydroxyl complexes in aqueous phase (Schindler and Stumm, 1987). This supports Eqs. (6–9), which assume that surface complex is analogous to aqueous complex and that Gibbs free energy of sorption is the sum of intrinsic and coulombic terms. Blesa et al. (1997) pointed out the importance of ion hydrolysis during adsorption, and Sverjensky (1993) divided the intrinsic term into two: a solvation contribution and a remaining term. Thus the overall free energy of adsorption of an ion can be written as

\[
\Delta G_{\text{ads}} = \Delta G_{\text{ii}} + \Delta G_{S} + \Delta G_{\text{coul}}
\]

In this equation, the coulombic term (\(\Delta G_{\text{coul}}\)) represents its contribution to the overall free energy of adsorption owing to the interaction between the ion and surface charge, the solvation term (\(\Delta G_{S}\)) accounts for the role of solvation during sorption of the ion, and the remaining term, named as
ion-intrinsic term ($\Delta G_{ii}$), is assumed to be a property of the ion alone. With this approach the experimental adsorption data for Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Mg$^{2+}$, and Ca$^{2+}$ can be closely reproduced (Sverjensky, 1993).

When there exist ligands other than H$_2$O and OH$^-$ in solution (e.g., Lewis acids or bases, which is often the case in soil), competition may occur among dissolved ligands, heavy metals, and surface adsorption sites. Formation of aqueous metal-DOC complexes stabilizes the metal in solution and effectively decreases the amount of aqueous metal ions available for adsorption. Similarly, anions such as sulfate and phosphate compete with surface sites of solids for metal cations, reducing the metal adsorption on solids. Metal sorption may be enhanced by the formation of ternary surface complexes. To our knowledge, no theory can describe these complicated processes well. However, partition of any aqueous species may be described under the framework of Eqs. (6–10; Blesa et al., 1997; Sverjensky, 1993).

B. Effects of Heavy Metal Adsorption on Surface Charge of Soil Colloids

Many studies indicated the importance of particle-solution interactions in determining the surface properties of colloids in natural waters. Electrokinetic measurements of natural particles dispersed in seawater and natural fresh waters showed that their electrophoretic mobilities tend to fall within very limited ranges of negative values. The apparent uniformity of the surface electrical property has been attributed to the adsorption of organic materials, particularly humic compounds, at the particle surfaces, which has been supported by a number of studies (Breiner et al., 2006). It is indicated that the effects of adsorbed organic compound on the surface properties of minerals present in natural waters are modified to some extent by additional ion interactions (Citeau et al., 2006). The interactions of heavy metals with the surfaces of soil colloids cannot be simply described by the interactions between heavy metals and pure minerals because of the complexed surfaces of real soil colloids, which include the irregularity of colloid shapes and three-dimensional interfaces between solution and colloids. Metal oxides are often used as mimics of soil colloids because they possess not only similar composition with soil colloids but also three-dimensional interfaces (Breiner et al., 2006; Day et al., 1994).

There has been fair amount of research on how ionic strength or pH affects the mobility of colloids and colloid-metal complexes in soils (Klitzke et al., 2008; Zachara et al., 2007; Zhang and Selim, 2007). However, little is known about the effects of heavy metals on colloidal charge development and stability of the complex colloids. Kretzschmar and Sticher (1997) explicitly took into account the effects of Pb$^{2+}$ and Cu$^{2+}$ adsorption onto humic-coated-oxide colloids on colloid charge development and colloid transportability, and found that replacement of Ca$^{2+}$ with Pb$^{2+}$ resulted in a slight
decrease in electrophoretic mobility of humic-coated hematite colloids while holding the total concentration (Ca$^{2+}$ + Pb$^{2+}$) constant. When Ca$^{2+}$ was completely replaced by Pb$^{2+}$, the suspensions were destabilized and aggregated within 20 hr. In contrast, replacement of Ca$^{2+}$ by Cu$^{2+}$ had little effect on electrophoretic mobility and colloidal stability. Both Pb$^{2+}$ and Cu$^{2+}$ are known to bind much more strongly to humic substances and Fe oxide surfaces than Ca$^{2+}$. At the pH of the suspensions investigated (pH 5.7), Cu$^{2+}$ has a higher affinity for humic substances than Pb$^{2+}$, whereas Pb$^{2+}$ adsorbs more strongly to hematite than Cu$^{2+}$. It is expected that the effect of the destabilizing of suspensions is more pronounced by replacing Ca$^{2+}$ with Pb$^{2+}$ than with Cu$^{2+}$, therefore, humic-coated oxide colloids can be stable and mobile in the presence of strongly adsorbing trace metals.

C. Partitioning of Heavy Metals in Soil Colloids

The ability of colloids in facilitating heavy metal transport depends on the distribution of heavy metal among solution, mobile colloids, and stationary grains. Several mathematical models successfully incorporated partition coefficients to simulate colloid-facilitated metal transport in porous media (Kim and Kim, 2007; Li et al., 2004); however, there still exits a knowledge gap in understanding metal distribution among different phases. This is mainly due to the complexities of the dynamic feature of soil colloid mobility (e.g., introducing heavy metal to soil alters the distribution of colloids between water and solid phases).

Amrhein et al. (1993) examined the potential of colloid-facilitated transport of heavy metals in roadside soils receiving deicing salts (i.e., NaCl and calcium magnesium acetate-CMA). In their experiments, a series of 60 mL syringes were packed with 30 g of soil. The columns were leached on a centurion vacuum extractor with three consecutive 30 mL aliquots of either 0.1 ml L$^{-1}$ NaCl or CMA. After initial leaching with either of the salts, the columns were leached with three consecutive 30 mL aliquots of deionized water. A portion of each leachate was saved without any further filtration and the remainder of each solution was filtered through a 0.45 µm membrane filter. Then the filtrates were immediately placed into a stirred ultrafiltration cell with a membrane of 1000 MWCO. This procedure separates the particles into three fractions: >450 nm, between 1.0 and 450 nm, and <1.0 nm. Their results showed that the cumulative leached metals through the entire procedure vary with the initial salt input, and NaCl tended to mobilize more soil colloids compared with CMA (Amrhein et al., 1993). Because of the possibility of artifacts resulting from column packing in their study, it is more reasonable to examine the cumulative leached metals excluding the first several pore volumes.

Figure 3 is a plot of leached cumulative metals after switching the influent from salt solution to deionized water, showing mobilization of soil
colloids upon reduction in ionic strength based on their data. The concentrations of heavy metals (Cu, Pb, Fe, Ni, and Cr) are consistently higher in the leachate from soil columns preleached with NaCl than those with CMA in all three size fractions. Among other fractions, the concentration of each metal is much higher for the columns preleached with NaCl than those with CMA. This is because Na promotes colloid mobility and facilitates the release of colloid-associated metals in soil. Metals in fraction 1.0–450 nm are much higher than those in fraction >450 nm for the columns preleached with CMA, whereas they are not significantly different for the columns preleached with NaCl, except Fe and Cu. This suggests that CMA is more selective in mobilizing smaller colloidal particles than NaCl. Colloidal Cu does not correlate well with DOC (data not shown) between the two fractions for the columns preleached with NaCl, nor does colloidal Fe with other colloidal metals preleached with CMA (Figure 3). This suggests that the mobility of heavy-metal-bearing colloids varies with both size and solution chemistry.

Ma and Dong (2004) examined the effect of water flooding incubation on colloidal Pb mobility in soil columns. Detailed description about experiment procedures can be found in Section VI-D 2. As shown in Figure 4, colloidal Pb concentrations in leachates varied with incubation, with longer incubation resulting in lower concentrations (Figure 4). Interestingly, there was no significant difference in the colloidal Fe and Al in the first several pore volumes when the columns were incubated from 3 to 20 days (data not shown), while the concentrations of colloidal Pb decreased approximately 4

![Figure 3](image-url)
times from 3 to 20 days (Figure 4). These results indicate that water flooded incubation reduces the releases of Pb from soil by decreasing either the mobility of soil colloids or the associations between Pb and mobile colloids.

VIII. CONCLUDING REMARKS

Compared with well-defined porous media, soils have distinctive features influencing colloid mobility and colloid-metal complex. Our ability to accurately predict colloid mobility and colloid-facilitated transport of heavy metal in soils has not been fully realized.

Soil colloids are exposed to solutions with dynamic chemistry. It is difficult to predict charge development of soil colloids because of the various interactions between surfaces and solution. Point zero charge of mineral particles suspended in a simple solution can be theoretically predicted, but little success has been achieved in soils because soil particles are assemblages of crystalline or amorphous minerals, and organic matters. Sophisticated models such as the triple layer model failed to describe the electrified interfaces of soil particles because their surfaces are irregular and the Stern layer often moves inward inside the physical boundary of the particles. It is more practical to model the particle-water interfaces as a diffusive double layer. The surface charge development may be described by partitioning of charged species between solution and surfaces assuming the species are similar in the two phases. Similarly, association of heavy metals with colloids may have
significant influences on colloid mobility, which is also subject to changes in
dynamic solution chemistry.

Different from clean porous media, the surfaces of soil stationary phases
consist of deposited colloids, which cause blocking effects and may enhance
colloid mobility in soils. In addition, these deposited colloids may be released
back to the solution upon physicochemical perturbations, which is referred to
as transient phenomena in deposition. There are two simultaneous, opposite
processes controlling colloid mobility in soils—deposition and release—their
relative effects on colloid transport in soils rely on flow residence time in the
system.

The DLVO theory provides a theoretical framework in describing colloid
dispersion in soils, and colloid deposition and release under ideal conditions.
However, modern colloid theories (including the DLVO theory) always fail to
describe colloid dynamics in soils because of the heterogeneities in soil and
colloid surfaces. Phenomenological and empirical approaches are commonly
used in present research of colloid deposition and release in soils. Experimental
studies always found that colloid deposition and release in soils are
coupled with significant ion transfer between EDLs and bulk solution. By
evaluating the possibility of the ion transfer, it is possible to estimate colloid
mobility in soils, at least qualitatively.

To better understand the mobility of heavy metals in soils, it is important
to consider the role of soil colloids. The complexity in the characteristics
of colloids and soils makes it difficulty to model the behaviors of colloid-
facilitated transport of heavy metals in heterogeneous media like soils, which
merits further study.

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