

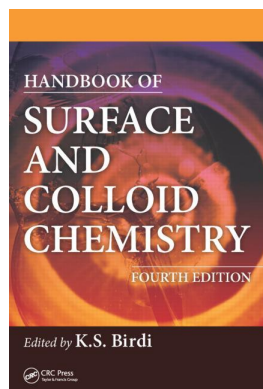
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## **Handbook of Surface and Colloid Chemistry Fourth Edition**

K.S. Birdi

### **Subsurface Colloidal Fines, Behavior, Characterization, and Their Role in Groundwater Contamination**

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# 5 Subsurface Colloidal Fines, Behavior, Characterization, and Their Role in Groundwater Contamination

*Tushar Kanti Sen and Chittaranjan Ray*

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## 5.1 INTRODUCTION

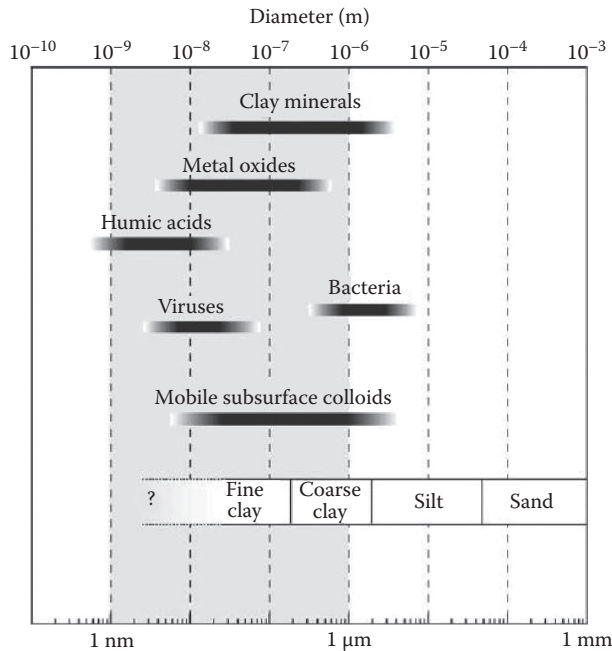
There are several classes of subsurface colloids—abiotic and biotic. The mobilization and migration of these subsurface colloidal particles take place under different physical and geochemical conditions (Massoudieh and Ginn, 2010; Sen, 2011; Sen and Khilar, 2006). Therefore, subsurface colloidal fines can enhance or retard the mobility and dispersion of various contaminants in groundwater flows (Sen and Khilar, 2009). There are two categories of colloid-induced subsurface contaminant transport: (a) colloid-associated contaminant transport and (b) transport of biocolloids. General research on subsurface colloid transport originated in the early 1930s (Kretzschmar and Schafer, 2005). First findings on the partitioning of aqueous solution constituents onto colloids appeared in the late 1970s, as summarized by Gustafsson and Gschwend (1987). Subsequently, reports on the transport facilitation of contaminants via association with subsurface colloidal fines emerged in the 1980s (Enfield and Bengtsson, 1988; McCarthy and Zachara, 1989). Our knowledge and understanding of the colloidal fines–associated contaminant transport in subsurface porous media have increased substantially over the last three decades, which is reviewed by various researchers from time to time such as Kretzschmar et al. (1999), Elimelech and Ryan (2002), Sen and Khilar (2006, 2009), and Bin et al. (2011). The focus of this chapter is to review subsurface colloidal fines, sampling methods and characterization, and their role in groundwater contamination. This has been

evidenced by various experimental, modeling, and field studies, which have been briefly compiled here and also partially updated in Chapter 4 (Sen and Khilar, 2009). Finally, authors here briefly discussed subsurface inorganic/organic colloid-associated contaminant transport in groundwater and their associated health effects.

## 5.2 SUBSURFACE COLLOIDAL FINES AND THEIR CLASSIFICATION

Within the subsurface systems such as soils, groundwater aquifers, sediments, or fractured rocks, colloidal particles/fines (particles with an average diameter between  $10^{-9}$  and  $10^{-10}$  m and carrying surface charge) are ubiquitous with a pronounced variability concerning morphology and chemical composition (Borkovec et al., 1993). There are several classes of subsurface colloids, such as abiotic and biotic (Auset and Keller, 2004). Basically, small colloidal particles of inorganic, organic, and microbiological variety exist in natural subsurface systems. These include silicate clays, iron and aluminum oxides, mineral precipitates, humic materials, microemulsions of nonaqueous phase liquids, viruses, and bacteria (Bradford et al., 2002; Sen and Khilar, 2006). In soils, the entire clay fraction is normally considered to be inorganic colloidal, since the clay minerals behave as colloids. The motion of colloids is more dominated by Brownian motions than by gravity. When colloids are stable, the low gravitational settling will render them in suspension for longer periods. Another of the important characteristics of the colloidal fines is that the specific surface is large ( $>10^2$  m<sup>2</sup>/g) (Kretzschmar et al., 1999). On the other hand, organic colloids can be viruses, bacteria, and protozoa collectively called biocolloids or macromolecular organic matter (OM) (when being smaller than 45  $\mu$ m often termed dissolved organic matter [DOM]) falls under these colloidal size ranges. Figure 5.1 indicates the size range of colloidal particles including a wide range of organic and inorganic components in the subsurface environment (Kretzschmar et al., 1999).

In general, colloidal fines possess a surface charge, of either permanent or nonpermanent (i.e., variable) nature (Sen and Khilar, 2006). Although a small portion of the colloids in soils are microorganisms and viruses, soil colloids are mostly complex assemblages of clay minerals,

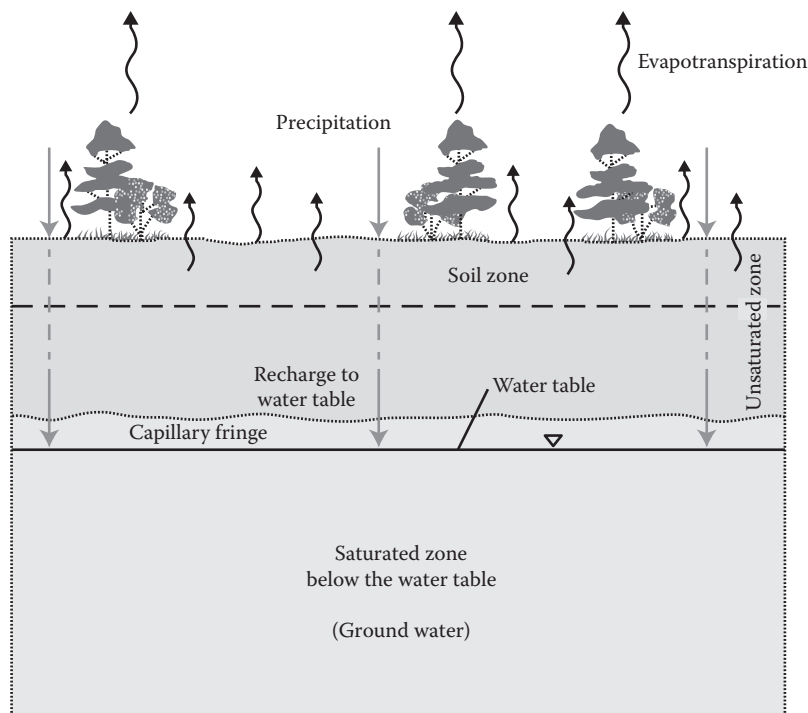


**FIGURE 5.1** Diameter range of various types of subsurface colloidal fines. (From Kretzschmar, R. et al., *Adv. Agron.*, 66, 121, 1999.)

oxides and hydroxides, and OM. The clay minerals have fixed charge as well as a variable pH-dependent charge (Khilar and Fogler, 1998; Sen and Khilar, 2009), whereas oxides and hydroxides generally have a positive charge at neutral pH, but the charge is highly pH dependent (Cornell and Schwertmann, 1998). Waterborne viruses include *enteroviruses*, *coxsackievirus*, *echovirus*, *rotavirus*, *norovirus*, and *hepatitis A* and *B*. Bacteria of concern are chiefly enteropathogenic *Escherichia coli*, *Salmonella* and *Shigella* spp., *Campylobacter jejuni*, and *Aeromonas hydrophila*, among others. The main protozoa that have been transmitted by groundwater are *Cryptosporidium parvum* and *Giardia lamblia* (Macler and Merkle, 2000). Bacteria are microscopic (1–6  $\mu\text{m}$  in size) unicellular organisms with a nucleus; viruses are submicroscopic (20–120 nm in size) biological agents consisting of molecules of nucleic acids and a protein envelope (Nevecherya et al., 2005) and negatively charged at high pH (pH 7). With this unique feature of viral structure and colloidal physicochemical properties, the transport of viruses in soil and groundwater can act with a combination of characteristics ranging from solutes, colloids, and microorganisms. The contamination of subsurface water by migrating pathogenic bacteria and viruses has caused large outbreaks of waterborne diseases (Pekdeger et al., 1985; Stevik et al., 2004). The most important pathogenic germs that might possibly be transported on the subsurface water path are the bacteria *Salmonella* sp., *Shigella* sp., *Yersinia enterocolitica*, *Y. pseudotuberculosis*, *Leptospira*, *Dyspepsia coli*, enterotoxigenic *E. coli*, *Vibrio* sp., *Legionella* sp., and the infectious hepatitis virus, polio virus, *coxsackie viruses*, *rotavirus*, and *norwalk-like virus* (Pekdeger et al., 1985). Bradford et al. (2002) mentioned that these inorganic/organic colloid particles can be released into the soil solution and groundwater through a variety of hydrologic, geochemical, and microbiological processes including translocation from the vadose zone (Nyham et al., 1985), dissolution of minerals and surface coatings (Ryan and Gschwend, 1990), precipitation from solution (Gschwend and Reynolds, 1987), deflocculation of aggregates (McCarthy and Zachara, 1989), and microbial-mediated solubilization of humic substances from kerogen and lignitic materials (Quyang et al., 1996). Scientific interest in the way these colloidal particles are transported through the intricate pores of subsurface porous environments has been inspired by two facts affecting public health (Morales et al., 2011): colloids that can be contaminants by themselves (bacteria, viruses, organics) and colloids that can act as carriers for inorganic/organic contaminants (Elimelech and Ryan, 2002; Sen and Khilar, 2006, 2009). Basically, subsurface colloidal particles can be released into soil solution and groundwater through a variety of hydrologic and geochemical processes and also have been implicated in the transport of metals, radionuclide, and certain ionizable organic pesticides in laboratory and field tests, which has been reviewed by Sen and Khilar (2009, 2006), Flurry and Qiu (2008), Elimelech and Ryan (2002), Bin et al. (2011), and Massoudieh and Ginn (2010). It is now generally accepted that in situ release of subsurface soil particles, colloidal in nature, may facilitate the contaminant transport in groundwater (Flurry and Qiu, 2008; Kersting et al., 1999; Ryan and Elimelech, 1996; Sen and Khilar, 2009; Sen et al., 2002).

### 5.3 CLASSIFICATION OF SUBSURFACE ENVIRONMENT AND IMPORTANCE ON COLLOID-CONTAMINANT TRANSPORT

Major pathways and mechanisms for transport of contaminants may differ in the unsaturated (vadose) and saturated zones, due to different conditions. The vadose zone comprises the subsurface environment, situated between the land surface and the saturated subsurface zone (groundwater). The vadose zone is the first subsurface environment encountered by contaminants released through human activities. In general, the vadose zone is characterized by the presence of oxygen, gas–water interface, and relatively high concentrations of particulate OM and relatively high microbial activity (Figure 5.2). 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 (Sen and Khilar, 2006). The saturated zone on the other hand is in general characterized by much lower OM contents, much lower oxygen content, and a lower sorption capacity of the solid



**FIGURE 5.2** Classification of subsurface environment and characterization. (From USGS Circular 1186, General facts and concepts about groundwater in sustainability of ground water—Water resources, pubs.usgs.gov/circ/circ1186/html/gen\_facts.html.)

phase (Figure 5.2). 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 the horizontal and vertical direction will be less variable. Transport of contaminants in the saturated zone will be mainly horizontal (Sen and Khilar, 2006) and is important for the transport of inorganic contaminants. The transport of colloids/biocolloids through saturated and unsaturated porous media is of significant interest, from the perspective of protecting the groundwater supplies from contamination (e.g., Redman et al., 2001; Surampalli et al., 1997), assessment of risk from pathogens in groundwater (e.g., Bitton and Gerba, 1984; Bruins et al., 2000; Goyal et al., 1989; Morris and Foster, 2000; Nola et al., 2001; Rose et al., 2000; Scandura and Sobsey, 1997; Taylor et al., 2004; Yates and Yates, 1988), and design of better water treatment systems to remove biocolloids from drinking water supplies (e.g., Gerba and Goyal, 1985; Macler and Merkle, 2000; Schijven and Hassanizadeh, 2001). Because biocolloids are living organisms, their transport in the subsurface is more complex than in the case for colloidal solutes transport (Sen and Khilar, 2006, 2009). Not only are they subject to the same physicochemical phenomena as are colloids (Sen et al., 2004), but there are also a number of strictly biological processes that affect their transport. Three key features of the vadose zone play a critical role in colloidal movement: (1) the presence of air–water interfaces, (2) transients in flow and chemistry, and (3) soil structure and heterogeneity.

It has been found that the fate and transport of colloids and colloid-associated contaminants in saturated porous media are controlled by a combination of several basic factors including (1) the presence of colloidal particles in the subsurface environment; (2) their release, dispersion stability, migration, and straining/plugging at pore constrictions; and (3) association of contaminants with colloidal particles/solid matrix (Sen and Khilar, 2006, 2009; Sen et al., 2002, 2004, 2005). Similar observations by several investigators have been compiled by Sen and Khilar (2009).

Chemical colloidal and hydrodynamic forces are important to colloidal particle release, deposition, and straining/plugging in saturated porous media, which are also dependent on geochemical and hydrodynamic conditions of the subsurface medium (Ryan and Elimelech, 1996; Sen and Khilar, 2002, 2006). However, differences in the mobilization mechanisms and deposition behavior of colloids are vastly different for saturated and unsaturated systems: straining, for instance, is anticipated to be even more important in unsaturated than in saturated systems (Bradford et al., 2006; Gao et al., 2006). The retention of colloidal fines in saturated porous media is mainly due to attachment at the solid–liquid interface and the change in surface properties of solid and solution that has been well documented in literature (Kretzschmar et al., 1999; McCarthy and Zachara, 1989; Sen and Khilar, 2006, 2009; Sharma et al., 2008). But mechanisms of colloidal retention in unsaturated porous media may include adsorption (attachment/detachment processes) to the solid–water interface (SWI) (Ryan and Elimelech, 1996; Sen and Khilar, 2006, 2009), the air–water interface (AWI) (Nicole et al., 2004; Torkzaban et al., 2008; Zhang et al., 2010), the solid–water–air (SWA) straining (Bradford et al., 2006; Torkzaban et al., 2008), and film straining (Chin and Flurry, 2005; Kretzschmar and Schafer, 2005; Sen, 2011).

## 5.4 SAMPLING AND CHARACTERIZATION

As mentioned in earlier sections, a variety of small inorganic and organic materials exists in subsurface environment, termed as colloids. These subsurface colloidal fines include mineral precipitates (such as iron, aluminum, calcium and manganese oxides, hydroxides, carbonates, silicates and phosphates, and oxides and hydroxides of actinide elements), rock and mineral fragments, clay minerals, biocolloids (such as virus, bacteria, and microorganism), and natural organic materials (including humic substances and polymeric materials) (McCarthy and McKay, 2004). Because of their colloidal nature and smaller size, these materials play a significant role as contaminant carriers or blockers in water ecosystems, and these are well documented by experimental, laboratory, and field studies (Sen and Khilar, 2009, 2011).

To access the importance of subsurface colloids, their release, and their role on contaminant transport at a particular site, it is essential to know the information about their existence, the total mobile load of contaminants and colloids, and the distribution of subsurface contaminants between colloid and aqueous phase. In addition, it is also important to know the morphological and surface colloidal characteristics such as size, charge with solution chemistry, sorptive properties, and elemental composition. To know this information, groundwater sampling and characteristics of colloids are essential. Accurate data of colloids and groundwater are essential to develop colloid-associated contaminant transport model. Sampling and characterization of the truly mobile colloidal particles occurring in soils or groundwater aquifers is a challenging task. When collecting colloidal samples from groundwater, special care should be taken to avoid contamination and artifact formation. Factors controlling sampling artifacts are oxygen diffusion that leads to calcite precipitation in groundwater, pumping rates, and filtering techniques. Groundwater samples are routinely obtained by pumping from wells. New protocols should be formulated to minimize artifact formation (Backhus et al., 1993; McCarthy and Degueldre, 1993; McCarthy and McKay, 2004; Sen and Khilar, 2009). Authors are encouraged to go through the article by Takala and Manninen (2006). It is recommended that low pumping rates in the order of 0.2–0.5 L/min should be used (Puls and Barcelona, 1996). Water quality such as solution pH, conductance, dissolved oxygen content, turbidity, and temperature may be monitored during purging. Sometimes passive sample collection may be used for low-permeability formations that are carried out on a *dialysis cell*. Backhus et al. (1993) reported a standard sampling protocol with minimum artifacts (Table 5.1) for in situ mobile colloids, and the associated contaminant concentrations include prolonged slow pumping and groundwater chemistry conditions. They have also reported the case study on sampling of various natures of colloidal fines and their quantitative amounts at different measurement sites. Detailed information on sampling can also be found in Schurtenberger and Newman (1993), Buffle and Leppard (1995), Schulze and Bertsch (1996).



**TABLE 5.1**  
**Recommended Protocol for Groundwater Sampling of Colloids and Colloid-Associated Contaminants**

1. Measured depth to water calculates standing water volume.
2. (Optional) Make *dipstick* observation of any layering in the well (e.g., floating NAPL).
3. Slowly lower inlet/pump to sampling depth.
4. Inflate packer(s) to reduce well volume and isolate inlet from settled particles at well bottom or floating NAPL at the surface.
5. Initiate pumping at a slow flow rate (100 mL/min). Avoid surging. Observe air bubbles displaced from sample tube to assess progress of steady pumping until water arrives at the surface.
6. Measure volumetric flow rate and adjust pumping rate as necessary.
7. Use a flow-through cell to monitor temperature, specific conductivity, pH, Eh, and dissolved oxygen. Repeatedly collect water and assess turbidity.
8. (Optional) Initiate slow pumping at another well(s) on-site. In addition to sampling wells within the *contaminated* site of the aquifer, *background* wells should be sampled. The background well should be located outside the contaminated zone but constructed and developed in the same manner and screened in the same aquifer as the *contaminated* well.
9. After turbidity has stabilized, collect water samples for mobile contaminant analysis in suitable flow-through vessels. Minimize contact with air. Do not filter for groundwater analyses. Preserve as appropriate (e.g., store in cold and dark for organics).
10. (Optional) Collect colloid samples on membrane filters and store for characterization (SEM/EDX and XRD analysis).

*Source:* Adapted from Backhus, D.A. et al., *Ground Water*, 31, 466, 1993.

Different techniques are usually used to collect water sample from the vadose zone such as free drainage lysimeters, suction cups or porous plates, and fiberglass wicks or rock wool samplers (Takala and Manninen, 2006). The suitability of fiberglass wicks for colloidal sampling was tested by Czinany (2004). A zero-tension lysimeter is used to sample colloidal particles and to routinely monitor colloidal concentrations in field soils (Thompson and Scharf, 1994). Such zero-tension lysimeters are installed at a certain depth below undisturbed soil cores and these basically consist of a sampling cup with an air inlet tube and a sampling tube. Field flow fractionation (FFF), a rapid and high-resolution fractionation technique, may be used for the characterization of low concentration natural colloids (Beckett and Hart, 1993). This sampling technique is based on colloid interaction with an externally applied force field in a thin, ribbon-like flow channel.

Sampling and analysis of microorganisms in groundwater are especially problematic because traditional analytical methods (APHA, 1995) are based on culturing of viable cells and many pathogens of interest are not readily culturable in the laboratory (Maier et al., 2000; Sen and Khilar, 2009). This problem has been partly solved by the development of nucleic acid-based analysis, which can detect both viable and nonviable microorganisms (Josephson et al., 1993; McCarthy and McKay, 2004).

The nature of colloidal materials is complex and several properties should be considered to characterize the dispersion of colloids. Different techniques for characterization of colloids and nanofines (synthetic or natural) have been presented in different articles (Hasselov et al., 2008; Hennebert et al., 2013; McCarthy and Degueldre, 1993; Schurtenberger and Newman, 1993). When characterizing colloidal particles, one is usually primarily interested in composition (mineralogy, elemental composition, and organic components), concentration (mass concentration, number concentration), size and shape (size distribution), and surface characteristics (specific surface area (SA), surface charge, and sorption capacity). Some important techniques that can be used to analyze subsurface colloids are summarized in [Table 5.2](#), which is updated and taken from our earlier publication (Sen and Khilar, 2009). The elemental and morphological analysis of colloidal particles can be done either from large single particles (<500 nm) or from agglomerate of the colloidal particles or from a filter cake with an energy dispersive x-ray spectroscope, SEM/EDS (Takala and Manninen, 2006).

Mineralogical characteristics of colloidal particles can be found from XRD analysis. Wang and Keller (2009) collected three bulk agricultural soils and one sediment (denoted as Ag#1, Ag#2, and Ag#3, and sediment from the topsoil layer of Santa Barbara, CA) and separated natural colloids and analyzed various properties, which are presented in Table 5.3. From Table 5.3, although natural colloids only vary from 2.7% to 13.8% by weight, they have significantly higher organic carbon (OC), cation exchange capacity (CEC), and BET SA than their bulk soils and sediments and hence have strong implications in the colloid-associated contaminant transport.

There are only few studies dealing with the release and characterization of colloids from solid waste. Hennebert et al. (2013) reported potential colloidal release and their various characterizations

**TABLE 5.2**  
**Various Methods Used for the Characterization of Colloidal Particles in Subsurface Systems**

Colloid Property	Method	Information
Particle composition	Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectroscopy (ICP-MS)	Bulk elemental composition for most elements with atomic number >10, isotopic analysis with ICP-MS, mass concentration if all constituent elements are analyzed
	Energy dispersive analysis of x-rays (EDAX)	Elemental composition of single particles viewed by SEM or TEM, analysis of most elements with atomic number >10, element mapping
	X-ray diffraction analysis (XRD)	Mineralogical composition
	Fourier transform infrared spectroscopy (FT-IR, FT-IR image)	Mineralogical composition and organic functional groups
	Thermogravimetric analysis (TGA), differential thermal analysis (DTA)	Quantitative analysis of minerals
	Mossbauer spectroscopy	Oxidation state and structure of Fe-containing minerals
Morphology and size distribution	Light microscopy	Particle number, morphology
	Transmission electron microscopy (TEM)	Particle morphology, size distribution
	Atomic force microscopy (AFM)	Particle morphology, size distribution
	Static light scattering (SLS)	Particle size and shape with the small angle option for particle size distribution in the range of 0.1–100 $\mu\text{m}$
	Dynamic light scattering (DLS)	Average hydrodynamic radius of particles <1 $\mu\text{m}$ , upper size cut-off for polydisperse samples from multiangle measurements
	Sedimentation analysis	Particle size distribution based on sedimentation velocity in a gravitational field, size range 1–50 $\mu\text{m}$
	Centrifuge techniques	Particle size distribution based on sedimentation velocity in a centrifugal field, analytical and preparative techniques, wide size ranges from 1 to 1000 nm
	Field flow fractionation (FFF)	Size distribution based on sedimentation velocity or diffusion coefficient
Particle surface characteristics	Electrophoretic mobility measurement (EM), zeta analyzer	Electrophoretic mobility, which is an indicator of surface charge (zeta potential)
	Gas adsorption (BET)	Specific surface area, microporosity

*Sources:* Adapted from Kretzschmar, R. et al., *Adv. Agron.*, 66, 121, 1999; Sen, T.K. and Khilar, K.C., Mobile subsurface colloids and colloid-mediated transport of contaminants in subsurface soils, in: Birdi, K.S. (Ed.), *Handbook of Surface and Colloid Chemistry*, 3rd edn., Taylor & Francis Group/CRC Press, 2009, pp. 107–130.



**TABLE 5.3**  
**Measured Properties of Natural Colloids, Bulk Soils, and Sediment**

Soil	Weight (%)	OC (%)	CEC (cmol/kg)	Surface Area (m <sup>2</sup> /g)	Exchangeable Ca <sup>2+</sup> + Mg <sup>2+</sup> (cmol/kg)	Fe Content (%)
<i>Ag#1</i>						
Bulk	100	1.51	6.20	3.5	5.8	0.19
Colloids	5.3	4.95	40.2	30.8	39.0	
<i>Ag#2</i>						
Bulk	100	1.50	15.2	9.4	14.1	0.14
Colloids	6.8	4.36	59.0	53.1	57.5	
<i>Ag#3</i>						
Bulk	100	1.52	15.4	14.1	15.1	0.17
Colloids	13.8	4.50	54.4	63.1	53.6	
<i>Sediment</i>						
Bulk	100	1.12	5.4	2.0	5.2	0.19
Colloids	2.7	6.02	42.2	36.6	40.7	

Source: Adapted from Wang, P. and Keller, A.A., *Langmuir*, 25(12), 6856, 2009.

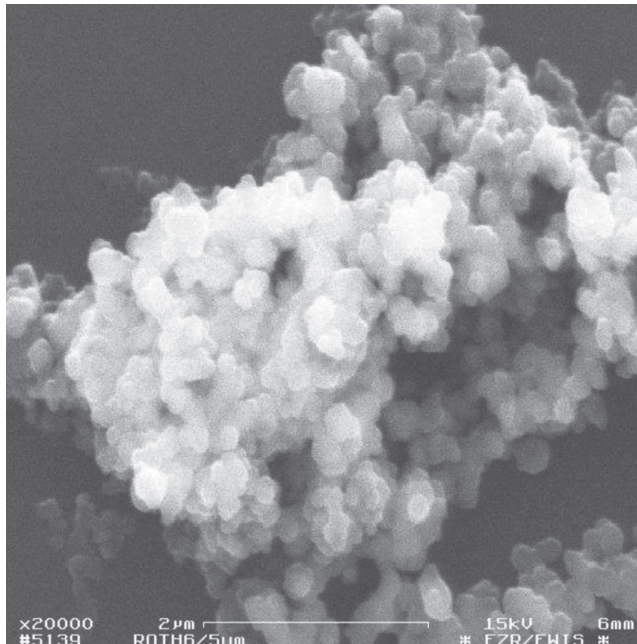
Abbreviations: CEC, cation exchange capacity; OC, organic carbon

from solid industrial and municipal waste leachates, contaminated soil, contaminated sediments, and landfill leachates. Potentially released colloids and their characterization were carried out with standard leaching, membrane filtration, and elemental determination of filtrate fraction (ICP), and visible morphological characteristics of colloids were done by the TEM-EDS system. They have reported that Mn, As, Co, Pb, Sn, and Zn always had a colloidal form and total organic carbon (TOC), Fe, P, Ba, Cr, Cu, and Ni had a partially colloidal form that existed in various waste leachates and contaminated soil. Koster et al. (2007) show the release of Cu, Pb, Zn, and Cr in colloidal form from municipal solid waste incinerator's bottom ash.

#### 5.4.1 PARTICLE SIZE

The particle size distribution is one of the most important characteristics of mobile colloidal particles. The size distribution has a large influence on the specific SA of the colloidal particles, which is directly related to the capacity for contaminant sorption and hence in the colloid-associated contaminant transport. The size distribution of colloids is usually determined by light scattering techniques. Colloids are small colloidal fines (10–1000 nm, commonly 20–450 nm) that are present as stable suspension of subsurface environment (Takala and Manninen, 2006). Colloidal fines may be either single solid fine or agglomerates of several smaller solid particles. Figure 5.3 presents SEM of colloidal particles agglomerating from the mine drainage tunnel (Zanker et al., 2000). The size and shape of particles also play a crucial role in determining whether or not plugging will occur and hence colloid-associated contaminant retardation or facilitation takes place. Table 5.4 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 (Khilar and Fogler, 1998; Sen and Khilar, 2006). Typically, the dimensions of the migratory colloidal fines vary from 0.1 to 10 μm (Khilar and Fogler, 1998). The size of the migratory fines in soil mass is usually below 5 μm. Seldom are migratory fines larger than 10 μm.

In case of the last two entries of low size ratios in Table 5.4, there exists a critical particle concentration (CPC) above which the plugging may occur (Pandya et al., 1998).



**FIGURE 5.3** SEM micrograph of an agglomerate of the colloidal particles from mine drainage tunnel. (From Zanker, H. et al., *A Separation and Detection Scheme for Environmental Colloids*, Institute of Radiochemistry, Dresden, Germany, 2000, [www.fz-rossendorf.de/FWR/COLL/Coll\\_2.htm](http://www.fz-rossendorf.de/FWR/COLL/Coll_2.htm); Takala, M. and Manninen, P., Sampling and analysis of groundwater colloids—A literature review, Working report 2006-15, Posiva, Finland, 2006, (29), 43, <http://www.posiva.fi/tyoraportit/WR2006-98web.pdf>)

**TABLE 5.4**  
**Dependence of Plugging on the Ratio of Size of Fines to Size of Pore Constrictions**

Size of Fines/Size of Pore Constrictions	Occurrence
$\geq 1$	Plugging due to blocking or size exclusion.
0.1–0.6	Plugging due to bridging and multiparticle blocking.
0.04–0.10	Plugging due to surface deposition, bridging, and multiparticle blocking.
0.01–0.04	Surface deposition. Multiparticle blocking may or may not occur.

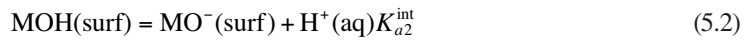
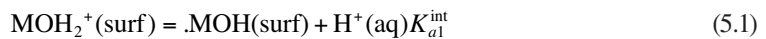
Source: Khilar, K.C. and Fogler, H.S., *Migration of Fines in Porous Media*, Kluwer Academic Publishers, Dordrecht, the Netherlands, 1998, Chapters 1, 3, 9.

### 5.4.2 SURFACE CHARGE AND ZETA POTENTIAL

It is very important to know the surface charge and surface potential (zeta potential) of subsurface colloidal fines in aqueous solution because the adsorption/desorption of ionic species on its surface is determined by the electrical properties at the colloidal fines/aqueous solution interface. Further stability of colloidal fines in subsurface aqueous phase also depends on surface charge of particles. A particle with a zeta potential  $>30$  mV is considered as electrostatically stable (Hasselov and Kaegi, 2009). Solid particles present in water are often charged and depend on particles and geochemical solution chemistry. The mechanisms of charge development have been extensively investigated (Bin et al., 2011; Lopez-Garcia et al., 2007). Fine colloidal particles, in general, carry a surface charge, the origin of which depends on how the fines were formed. A negatively charged

surface can exchange its portable cations present on the surface for cations present in the solution. The amount exchanged at equilibrium is known as the CEC. Likewise, we can define anion exchange capacity (AEC) of positively charged colloidal fines. The CEC of several clay minerals has been listed by Grim (1968). For migratory clayey fines such as kaolin and illite, the CEC is of the order of 3–15 meq/g (Khilar and Fogler, 1998). Further soil colloids are heterogeneous in composition and consist of inorganic and organic constituents or a mixture of the two. Therefore, charge development of soil colloids in geochemical environment is a complex process due to heterogeneity in the composition and structures of colloidal particles (Bin et al., 2011).

The surfaces of oxide colloidal particles or silicate minerals in contact with aqueous solutions are charged positively or negatively by adsorption or desorption of  $H^+$  ions. An electrical double layer at solid/liquid interface is formed by adsorbing counterions from the aqueous solution to its surface (Sen and Khilar, 2009). The charge developing process on the surfaces can be represented as follows (Cornell and Schwertmann, 1998):



where

MOH denotes a surface site

$K_{a1}^{\text{int}}$  and  $K_{a2}^{\text{int}}$  are the intrinsic surface acidity constants

Schindler and Stumm (1987) summarized the intrinsic acidity constants of various metal oxides/minerals under solution chemistry. In this system,  $H^+$  and  $OH^-$  are potential determining ions and the surface charge and surface potential are defined by the pH of the solution. There is a particular pH at which the surface charge becomes zero, that is, the point of zero charge (pzc) or the isoelectric point (iep).  $K_a^{\text{int}}$  is correlated to the pzc, which is as follows (Bin et al., 2011):

$$\text{pzc} = 0.5 \log K_a^{\text{int}} = 0.5 \log K_a \quad (5.3)$$

Here intrinsic acidity constant ( $K_a^{\text{int}}$ ) is equal to the apparent acidity constant ( $K_a$ ) at a surface potential of zero. Point of zero charge (pzc) can be measured by electrophoresis as the pH at which there is no motion of the particles in suspending medium under an applied external electric field. Table 5.5 presents the point of zero charge of simple hydro(oxides) and other materials (Kosmulski, 2004; Sen and Khilar, 2009).

The more relevant and useful method of surface charge characterization of colloidal fines is, however, the measurement of zeta potential of the particle. The zeta potential of kaolinite has been studied by several investigators (Herrington et al., 1992; Hussain et al., 1996; Khilar and Fogler, 1983; Kia et al., 1987; Williams and Williams, 1978). The kaolinite face zeta potential varies from approximately –35 to –25 mV at a pH of 6.5 in the range of sodium chloride concentration between  $10^{-4}$  and  $10^{-2}$  M (VanOlphen, 1977). Hussain et al. (1996) measured the zeta potential of kaolinite, illite, and chlorite clay minerals against pH and found to have negative zeta potential in the pH range of 2.5–11. The kaolinite is the most negative clay, ranging in zeta potential value from –24 to –49.5 mV. There have been numerous investigations of the electrochemical properties of goethite, hematite, and ferrihydrite (Atkinson et al., 1967; Breeuwsma and Lyklema, 1971, 1973; Crawford et al., 1996; Davis and Leckie, 1978; Onoda and Debruyne, 1966; Park, 1967; Puls and Powell, 1992).

Park (1967) summarized the factors controlling the sign and magnitude of surface charge of oxide and mineral oxides, especially hydrous metal oxides.

**TABLE 5.5**  
**Point of Zero Charge (pzc) of Simple Hydro(oxides) and Other Materials**

Material	Description	Salt	<i>T</i>	Method	pzc	References
Al <sub>2</sub> O <sub>3</sub>	γ, >99%	0.1 mol/dm <sup>3</sup> NaCl	25 60	pH	9.3 9	Fein and Brady (1995)
Al <sub>2</sub> O <sub>3</sub>	α	0.01 mol/dm <sup>3</sup> NaCl	25	IEP	8	Guo et al. (1997)
Al <sub>2</sub> O <sub>3</sub>	α, A16, Alcoa	None		IEP	8.5	Yang and Troczynski (1999)
Al <sub>2</sub> O <sub>3</sub>	γ, from <i>sec</i> -butoxide	0.001–0.1 mol/dm <sup>3</sup> KNO <sub>3</sub>	25	CIP	8.6	Ardizzone et al. (2000)
Al <sub>2</sub> O <sub>3</sub>	Riedel Haen, purity 98%	0.01 mol/dm <sup>3</sup> KCl	20	IEP	8	Ramos-Tejada et al. (2002)
Al <sub>2</sub> O <sub>3</sub>	α, AKP-30	0.01 mol/dm <sup>3</sup> NaNO <sub>3</sub>	22	IEP	9	Hackley et al. (2002)
Al <sub>2</sub> O <sub>3</sub>	γ, spherical, NanoTek	0.01 mol/dm <sup>3</sup> NaCl		IEP	9.6	Tang et al. (2002)
Al <sub>2</sub> O <sub>3</sub>	γ, Aldrich, mesoporous	0–0.1 mol/dm <sup>3</sup> NaCl		CIP	9.1	Wang et al. (2002)
Al <sub>2</sub> O <sub>3</sub>	Fisher	0–0.1 mol/dm <sup>3</sup> NaCl		CIP	8.7	Wang et al. (2002)
Al <sub>2</sub> O <sub>3</sub>	γ, from nitrate	HNO <sub>3</sub> + KOH	25	IEP CIP pH	8.2 8.6 8–8.4	Vakros et al. (2002), Bourikas et al. (2003)
Al <sub>2</sub> O <sub>3</sub>	α, sapphire	0.001 mol/dm <sup>3</sup> KBr, KNO <sub>3</sub>		IEP	5	Franks and Meagher (2003)
Al <sub>2</sub> O <sub>3</sub>	γ	0.001–0.1 mol/dm <sup>3</sup> NaCl	25	IEP	8.4	De Lint et al. (2003)
Al <sub>2</sub> O <sub>3</sub>	Alcoa			Acousto	7.8	Cordelair and Greil (2003)
Al <sub>2</sub> O <sub>3</sub>	Aldrich, 99.5%, α			IEP	9	Sun and Berg (2003)
Al <sub>2</sub> O <sub>3</sub>	Alfa Aesar, 99.9%	0.01 mol/dm <sup>3</sup> KCl		IEP	9.1	Hu and Dai (2003)
Al <sub>2</sub> O <sub>3</sub>	γ, Merck	0.1 mol/dm <sup>3</sup> NaNO <sub>3</sub>	25	CIP	8.2	Lefevre et al. (2004)
AlOOH, Al(OH) <sub>3</sub>	Six different recipes	HCl + KOH	25	IEP	8.5–9	Katatny et al. (2003)
Co <sub>3</sub> O <sub>4</sub>	Thermal decomposition of nitrate at 400°C	0.005–0.3 mol/dm <sup>3</sup> KNO <sub>3</sub>		CIP	7.2	Faria and Trasatti (2003)
Cr <sub>2</sub> O <sub>3</sub>	From chloride	0.1 mol/dm <sup>3</sup> KCl		pH	4	Onija et al. (2003)
Cr <sub>2</sub> O <sub>3</sub>	Fluka	0.001–0.1 mol/dm <sup>3</sup> KCl	22	pH	6.7	Onija and Milonjic (2003)
Cr(OH) <sub>3</sub>	From chloride	0.1 mol/dm <sup>3</sup> KCl		pH	4.7	Onija et al. (2003)
CuO	Tenorite, Merck	0.001 mol/dm <sup>3</sup> KClO <sub>4</sub>		pH	6.9, 7.6	Gonzalez and Laskowski (1974)

(Continued)

TABLE 5.5 (Continued)

## Point of Zero Charge (pzc) of Simple Hydro(oxides) and Other Materials

Material	Description	Salt	<i>T</i>	Method	pzc	References
CuO	Aldrich			IEP	8.5	Rao and Finch (2003)
Fe <sub>3</sub> O <sub>4</sub>	Magnetite, Sweden	0.01, 0.1 mol/dm <sup>3</sup> KCl		Intersection	6.5	Laskowski and Sobieraj (1969)
Fe <sub>3</sub> O <sub>4</sub>	Magnetite, synthetic	0.002–1 mol/dm <sup>3</sup> NaCl		IEP CIP	8 7.9	Illes and Tombacz (2003)
Fe <sub>2</sub> O <sub>3</sub>	From nitrate	0.1 mol/dm <sup>3</sup> NaNO <sub>3</sub>	25	pH	8.5	Liger et al. (1999)
Fe <sub>2</sub> O <sub>3</sub>	Baker, washed	0.001–0.1 mol/ dm <sup>3</sup> NaCl		IEP CIP	8.5 8.5	Jeon et al. (2001)
Fe <sub>2</sub> O <sub>3</sub>	Hematite, Laborchemie Apolda	0.01 mol/dm <sup>3</sup> NaCl	25	IEP	7	Chibowski and Wisniewska (2002)
Fe <sub>2</sub> O <sub>3</sub>	Hematite, Alfa	0.01 mol/dm <sup>3</sup> KNO <sub>3</sub>	25	pH	6.3	Preocanin et al. (2002)
Fe <sub>2</sub> O <sub>3</sub>	Hematite, spherical, from FeCl <sub>3</sub>	0.01 mol/dm <sup>3</sup> NaCl	25	pH	8.5	Pochard et al. (2002)
Fe <sub>2</sub> O <sub>3</sub>	Aldrich			IEP	6.8	Rao and Finch (2003)
Fe <sub>2</sub> O <sub>3</sub>	Aldrich, >99%	0.001, 0.01 mol/ dm <sup>3</sup> NaNO <sub>3</sub>		IEP	8	Ramos-Tejada et al. (2003)
Fe <sub>2</sub> O <sub>3</sub>	Natural, Clinton, NY	0.01 mol/dm <sup>3</sup> NaNO <sub>3</sub> and 0.01 mol/dm <sup>3</sup> KNO <sub>3</sub>		IEP	<4	O'Reilly and Hochella (2003)
Fe <sub>2</sub> O <sub>3</sub>	Natural, Italy	0.01 mol/dm <sup>3</sup> NaNO <sub>3</sub> and 0.01 mol/dm <sup>3</sup> KNO <sub>3</sub>		IEP	6.8	O'Reilly and Hochella (2003)
Fe <sub>2</sub> O <sub>3</sub>	Synthetic	0.01 mol/dm <sup>3</sup> NaNO <sub>3</sub> and 0.01 mol/dm <sup>3</sup> KNO <sub>3</sub>		IEP	7.3	O'Reilly and Hochella (2003)
Fe <sub>2</sub> O <sub>3</sub> – <i>n</i> H <sub>2</sub> O	Synthetic	0.01–0.1 mol/dm <sup>3</sup> NaNO <sub>3</sub>	25	CIP	7.2 7.9	Trivedi et al. (2003)
Fe <sub>3</sub> HO <sub>8</sub> –4H <sub>2</sub> O	From chlorate VII	0.2 mol/dm <sup>3</sup> NaClO <sub>4</sub>	25	pH	8.3	Spandini et al. (2003)
Fe <sub>3</sub> HO <sub>8</sub> –4H <sub>2</sub> O	Synthetic	0.01 mol/dm <sup>3</sup> NaNO <sub>3</sub>		IEP	6.8	O'Reilly and Hochella (2003)
FeOOH	Goethite, synthetic	0.01 mol/dm <sup>3</sup> NaCl		IEP	9.1	Pozas et al. (2002)
FeOOH	Goethite, from nitrate	0.001–0.1 mol/ dm <sup>3</sup> NaNO <sub>3</sub>	25	IEP	8.7	Kosmulski et al. (2003)
FeOOH	Natural goethite	0.01 mol/dm <sup>3</sup> NaNO <sub>3</sub>		IEP	7	O'Reilly and Hochella (2003)
FeOOH	Synthetic goethite	0.01 mol/dm <sup>3</sup> NaNO <sub>3</sub>		IEP	9.2	Luxton and Eick (2003)

(Continued)

**TABLE 5.5 (Continued)**  
**Point of Zero Charge (pzc) of Simple Hydro(oxides) and Other Materials**

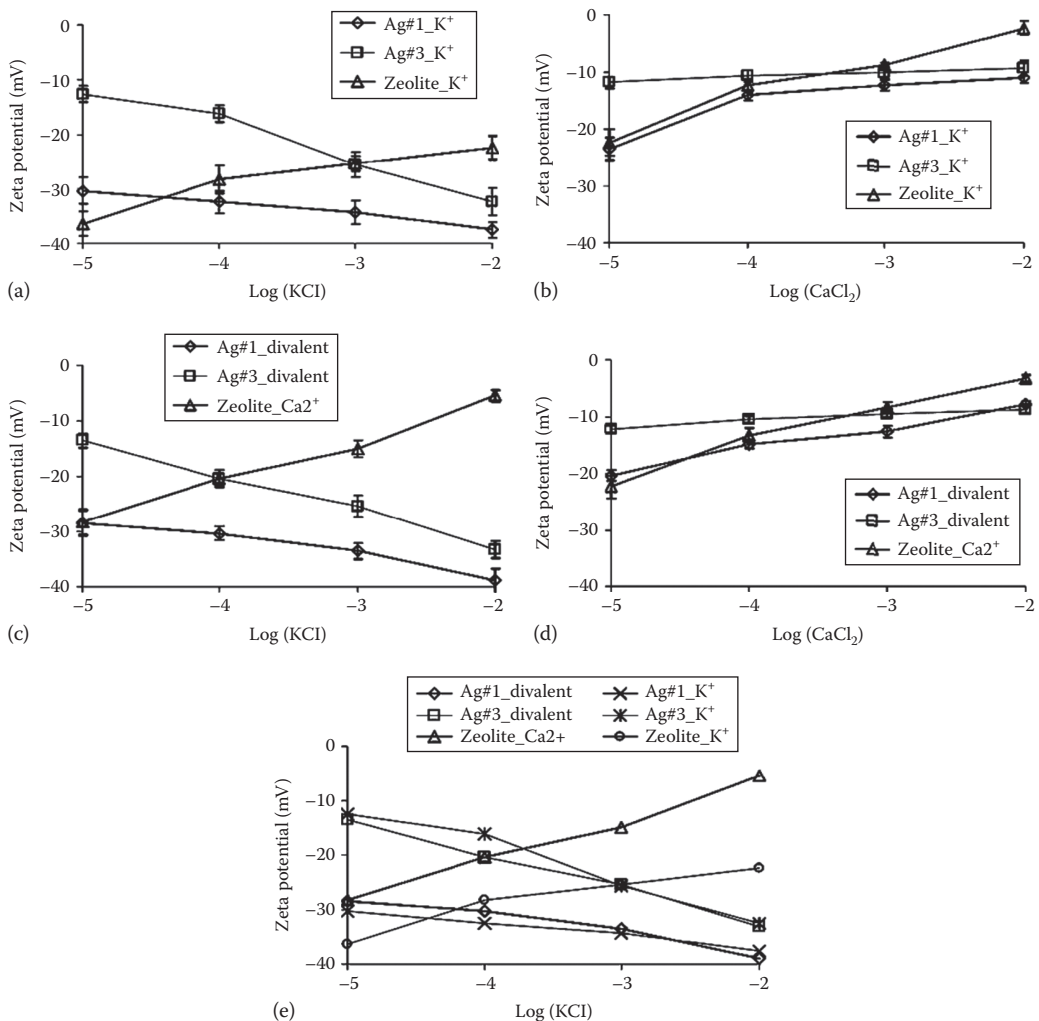
Material	Description	Salt	<i>T</i>	Method	pzc	References
MgO	Merck, 97%	HNO <sub>3</sub> + KOH	25	IEP	12	Vakros et al. (2002)
				CIP	10	
				pH	10.2–10.9	
MgO	Aldrich, >99%, fused			IEP	12.4	Sun and Berg (2003)
MnOOH	Ground natural manganite	0.1 mol/dm <sup>3</sup> NaNO <sub>3</sub>	23	CIP	5.4	Weaver et al. (2002)
MnO <sub>2</sub>	γ, Union Carbide	0.0001–0.01 mol/dm <sup>3</sup> KNO <sub>3</sub>		IEP	5.6	Natarajan and Fuerstenau (1983)
MnO <sub>2</sub>	γ, electrolytic, Union Carbide	0.0001, 0.001 mol/dm <sup>3</sup> NaNO <sub>3</sub>		IEP	5.3	Fuerstenau and Shibata (1999)
MnO <sub>2</sub>	Ramsdellite, synthetic	0.001–0.1 mol/dm <sup>3</sup> KNO <sub>3</sub>	25	CIP	<2.5	Prelot et al. (2003)
MnO <sub>2</sub>	Commercial, Sedema	0.001–0.1 mol/dm <sup>3</sup> KNO <sub>3</sub>	25	CIP	3.7	Prelot et al. (2003)
MnO <sub>2</sub>	Electrochemically synthesized, Delta	0.001–0.1 mol/dm <sup>3</sup> KNO <sub>3</sub>	25	CIP	6.7	Prelot et al. (2003)
NiO	Aldrich			IEP	7.8	Rao and Finch (2003)
PbO	In situ precipitated from nitrate	0.01 mol/dm <sup>3</sup> KCl		IEP	11	Liu and Liu (2003)
SiO <sub>2</sub>	Merck	0.01 mol/dm <sup>3</sup> NaCl		IEP	<3 if any	Jada et al. (2002)
SiO <sub>2</sub>	Davisil, Aldrich	0.001 mol/dm <sup>3</sup> KCl	25	IEP	3.5	Pettersson and Rosenholm (2002)
TiO <sub>2</sub>	Baker, 99.9%, anatase			IEP	6.7	Sun and Berg (2003)
ZnO	Aldrich			IEP	7.5	Rao and Finch (2003)
Kaolinite	KGa-2	0.001–0.1 mol/dm <sup>3</sup> NaCl	25 ± 3	pH	2.8	Appel et al. (2003)
Montmorillonite	Fluka		25	IEP	<1 if any	Juang et al. (2002)
CaCO <sub>3</sub>	Iceland spar		50	IEP	ζ ≤ 0	Moulin and Roques (2003)
Kaolin	From China			IEP	2.8–3.8	Hu and Liu (2003)
Activated carbon	CS-1501	0.1 mol/dm <sup>3</sup> NaCl	20	pH	7.5	Faur-Brasquet et al. (2002)

*Sources:* Taken from Kosmulski, M., *J. Colloid Interface Sci.*, 275, 214, 2004; Sen, T.K. and Khilar, K.C., Mobile subsurface colloids and colloid-mediated transport of contaminants in subsurface soils, in: Birdi, K.S. (Ed.), *Handbook of Surface and Colloid Chemistry*, 3rd edn., Taylor & Francis Group/CRC Press, 2009, pp. 107–130. More data are available in Kosmulski, 2004.



Crawford et al. (1996) measured the zeta potential of amorphous hydrous iron (III) oxide (HFO) and amorphous hydrous chromium (III) oxide (HCO) as a function of pH during adsorption and coprecipitation of  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$ . For sand materials, the zeta potential is negative and it increases as the pH increases (Elimelech et al., 2000).

Hennebert et al. (2013) measured the zeta potential of solid industrial and municipal waste leachates under different conditions, and it was found that six leachates had a positive zeta potential ( $<8$  mV) and all others had a negative zeta potential ( $-15$  to  $-38$  mV). A particle with a zeta potential  $>-30$  mV is considered as electrostatically stable (Hasselov and Kaegi, 2009). The measured zeta potentials for the three types of natural colloids (Ag#1, Ag#2, Ag#3) and engineered zeolite particles under different salt concentrations are presented in Figure 5.4 (Wang and Keller, 2009). Detailed mechanistic explanations are given in Wang and Keller (2009). The zeta potential of all the natural colloids showed similar trends (Figure 5.4).



**FIGURE 5.4** Zeta potentials of the original and cation-exchanged natural colloids (Ag#1 and Ag#3) and engineered zeolite as a function of log molar concentrations of KCl and CaCl<sub>2</sub> (pH 7.0): (a) K<sup>+</sup> saturated colloids with KCl in the bulk solution, (b) K<sup>+</sup> saturated colloids with CaCl<sub>2</sub> in the bulk solution, (c) divalent cation saturated colloids with KCl in the bulk solution, (d) divalent cation saturated colloids with CaCl<sub>2</sub> in the bulk solution, and (e) comparison of K<sup>+</sup> and divalent cation saturated colloids with KCl in the bulk solution. (From Wang, P. and Keller, A.A., *Langmuir*, 25(12), 6856, 2009.)

**TABLE 5.6**  
**Range in Chemical Composition of Migratory Clays**

Clay	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O
Kaolin	40–49	35–40	0–13	0–2	0–0.8	0–0.5	0–0.10	0–0.2
Illite	50–56	18–31	2–5	0–0.8	0–0.2	1–4	—	0–1
Chlorite	31–38	18–20	—	—	—	35–38	—	—
Montmorillonite	45–55	19–50	0–3	—	—	0–2	—	—

Source: Khilar, K.C. and Fogler, H.S., *Migration of Fines in Porous Media*, Kluwer Academic Publishers, Dordrecht, the Netherlands, 1998, Chapters 1, 3, 9.

### 5.4.3 CHEMICAL CHARACTERIZATION OF FINES

Chemical characterization of fines implies the elemental and mineral compositional analysis of migratory fines in porous media. Khilar and Fogler (1998) presented the range in chemical composition of migratory clays primarily of kaolinite, illite, montmorillonite, and chlorite particles in Table 5.6. We observe from this table that silica, SiO<sub>2</sub>, and alumina are the major minerals.

## 5.5 BRIEF DESCRIPTION OF THE ROLE OF INORGANIC COLLOIDAL FINES—ASSOCIATED CONTAMINANT TRANSPORT IN GROUNDWATER FLOWS AND ASSOCIATED HEALTH EFFECT

Numerous experimental, theoretical, and field studies have confirmed that subsurface colloidal fines can either facilitate or retardate the transport of inorganic and organic pollutants (Arab et al., 2014; Katzourakis and Chrysikopoulos, 2014; Massoudieh and Ginn, 2011; Sen, 2011; Sen and Khilar, 2009; Wang et al., 2014). There are a couple of review articles published from time to time such as the articles by Ryan and Elimelech (1996, 2002), Kersting et al. (1999), Sen and Khilar (2006, 2009), Sen (2011), and Bin et al. (2011) where a large number of observations on colloid-associated contaminant transports have been compiled. Colloid-facilitated transport has been demonstrated for alkali and alkaline earth cations (Cs<sup>+</sup> and Sr<sup>2+</sup>), transition metals (Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>), oxyanions (arsenic and iodate), nonpolar organic compounds (phenanthrene and pyrene), and polar organic compounds (pesticide) (Sen and Khilar, 2009).

Sun et al. (2010) reported the colloidal fines kaolinite facilitated lead (Pb<sup>2+</sup>) transport through saturated porous media. Similarly soil humic acid (HA)-mediated transport of copper (Cu) was studied by Paradelo et al. (2012). The influence of pH and Cu<sup>2+</sup> concentration on Cu–HA binding and retention of Cu–HA complexes in the matrix was analyzed with the colloid-surface attachment model. The effect of ionic strength reduction and flow interruption enhanced colloid-facilitated Hg<sup>2+</sup> transport in contaminated soils, which was reported by Zhu et al. (2014). They have concluded that a large amount of colloidal Hg was associated with colloidal OM, which can be transported over long distances causing environmental pollution. Sen et al. (2002) present experimental studies of colloid-associated contaminant transport in the subsurface. They conducted column experiments to study the effects of the mobilization of colloidal fines, kaolin on nickel transport in sand beds containing kaolin particles under plugged and unplugged conditions. Nickel transport was facilitated when colloidal kaolin present in the sand bed migrated out. Without migration and plugging of kaolin particles, the kaolin-sand bed acted as a poor filter for nickel. However, when migration as well as plugging occurs, the retardation of nickel transport increases and such enhancement in sorption can be attributed to sorption sites that become more accessible as well as higher sweeping a higher pressure drop and higher concentration of kaolin.

Colloids are known to mobilize strongly sorbing compounds (Honeyman, 1999; Kersting et al., 1999; Roy and Dzombak, 1997, 1998; Saiers and Hornberger, 1996). When highly mobile colloids

carry with them the attached contaminants, the phenomena have been termed as *colloid-facilitated transport* (McCarthy and Zachara, 1989).

Nanoparticles have found their way for many human use products over the years. They are in the colloidal or subcolloidal size range. Nowack and Bucheli (2007) present a review of classes of nanoparticles relevant to the environment and summarize their formation, emission, and occurrence in the environment. At elevated concentrations, they reported the toxic ecotoxicological effects of certain nanoparticles.

Silver nanoparticles are widely used for their antimicrobial properties. Toxic effects of soluble silver on humans are presented in a review by Panyala et al. (2008). In recent years, the regulating agencies are concerned about the widespread use of inorganic nanoparticles, including the use of carbon nanotubes (CNTs) in various items used by human. Choi et al. (2010) show that nanoparticles that have a hydrodynamic diameter less than 34 nm and have noncationic surface charge can translocate rapidly from the lungs to the mediastinal lymph nodes. Nanoparticles with hydrodynamic radius less than 6 nm can traffic rapidly from lungs to lymph nodes and blood streams. However, the kidney may subsequently clear them. Colvin (2003) is one of the early researchers to alarm about the widespread use of nanoparticles in products for human use. She pointed out that a few studies have investigated the direct or indirect exposure to nanoparticles and no clear guidelines exist to quantify their effects.

Lam et al. (2006) conducted a review of potential CNT toxicity. From rodent studies they summarized that regardless of the synthesis methods or metals used, CNTs caused inflammation, epithelioid granulomas (microscopic nodules), fibrosis, and biochemical/toxicological changes in the lungs. Their review suggests that single-walled CNTs are toxic than quartz (which is considered as a serious occupational hazard when chronically inhaled).

## 5.6 BRIEF DESCRIPTION OF THE ROLE OF BIOCOLLOIDS IN GROUNDWATER CONTAMINATION AND ASSOCIATED HEALTH EFFECT

Many biocolloids, such as viruses, bacteria, and certain protozoa, being pathogenic can cause disease if they are ingested through drinking waters or recreational waters. Groundwater contamination from biocolloids has been reported over the decades. Crane and Moore (1984) concluded in their review that physical factors such as soil properties, clay content and moisture regime, and pore size distribution along with biological factors such as pH, temperature, nutrient supply, and soil moisture content affect the rate and quantity of bacterial migration through soil. Sen (2011) conducted a review of processes affecting the transport of pathogenic biocolloids in saturated and unsaturated porous media. He suggested that basic processes such as physical, chemical, and biological affect the transport of biocolloids. These factors affecting the transport of biocolloids include advection and dispersion as well as diffusion through water, straining, and physical filtration through the porous media as the biocolloids move, adsorption, and biological processes such as adhesion/detachment, survival, and chemotaxis. For viruses, removal in unsaturated zone seems to be greater than that in the saturated zone and it has been observed by many researchers over three decades (Bitton and Gerba, 1984; Jin et al., 1997; Powelson and Gerba, 1994; Powelson et al., 1990). Chu et al. (2001) suggest that once viruses are adsorbed to the AWI, they are considered to be effectively removed.

Most intestinal (enteric) diseases are infectious and are transmitted through fecal waste. Pathogens—which include virus, bacteria, protozoa, and parasitic worms—are disease-producing agents found in the feces of infected persons. These diseases are more prevalent in areas with poor sanitary conditions. These pathogens travel through water sources and interfuses directly through persons handling food and water. Since these diseases are highly infectious, extreme care and hygiene should be maintained by people looking after an infected patient. Hepatitis, cholera, dysentery, and typhoid are the more common waterborne diseases that affect large populations in the tropical regions (BIONFATE Newsletter, 2013). Tables 5.7 and 5.8 show information about the water-transmitted

**TABLE 5.7**  
**Selected Waterborne Bacterial and Protozoan Diseases, Their Agents, Symptoms, and Sources in Water Supply**

Disease	Bacterial Species or Genera	Symptoms	Sources in Water Supply
Amoebiasis	<i>Entamoeba histolytica</i>	Diarrhea, bloating, fever	Sewage-contaminated water
Typhoid	<i>Salmonella typhi</i>	Very high temperature, sweating, etc.	Fecal-contaminated water
Cryptosporidiosis	<i>Cryptosporidium parvum</i>	Watery diarrhea, flu-like symptom	Unfiltered water containing animal manure
Giardiasis	<i>Giardia lamblia</i>	Diarrhea, abdominal discomfort	Untreated water, water from beaver and muskrat ponds
Cholera	<i>Vibrio cholerae</i>	Watery diarrhea, nausea, vomiting, etc.	Drinking water contaminated with the bacterium
Leptospirosis	Bacteria genus <i>Leptospira</i>	Flu-like symptom followed by meningitis, liver damage, etc.	Water contaminated by animal urine carrying the bacterium
Legionellosis	Bacterial genus <i>Legionella</i>	Fever, chills, pneumonia, etc.	Contaminated water-cooling towers
<i>Escherichia coli</i> infection	<i>Escherichia coli</i>	Diarrhea and can lead to death in people with weak immune response	Water contaminated with the bacterium
Dysentery	Bacterial genera <i>Shigella</i> and <i>Salmonella</i>	Frequent passing of feces with blood and/or mucus	Water contaminated with the bacteria
Botulism	<i>Clostridium botulinum</i>	Dry mouth, blurred vision, slurred speech	Bacterium enters through wounds or gastrointestinal tracts
Campylobacteriosis	<i>Campylobacter jejuni</i>	Dysentery with high fever	Drinking water contaminated with feces

Source: Kolwzan, B. et al., *Introduction to Environmental Microbiology*, Oficyna Wydawnicza politechniki wroclawskiej, Nigeria, 2006, <http://www.oficyna.pwr.wroc.pl>.

**TABLE 5.8**  
**Selected Waterborne Viral Diseases and Symptom**

Disease and/or Agent	Symptoms	Sources in Water Supply
Poliomyelitis (polio virus)	Minor or no symptoms to headache, fever, etc.	Feces-contaminated water
Hepatitis A	Fatigue, fever, abdominal pain	Can manifest in water and food
Severe acute respiratory syndrome	Fever, lethargy, cough, sore throat	Manifests in improperly treated water
Coxsackie A	Herpangina, hemorrhagic conjunctivitis, meningitis	Feces contamination
Enteroviruses	Meningitis, encephalitis, hemorrhagic conjunctivitis, fever	Similarity with polio virus
Enteric cytopathic human orphan (ECHO) virus	Meningitis, respiratory system problems, rash, diarrhea, fever	Feces contamination
Norwalk virus	Diarrhea, fever	Feces contamination
Adenoviruses	Respiratory problems, diarrhea, eye infection	Respiratory droplets, fecal route in water
Rotaviruses	Severe diarrhea	Fecal–oral route exposure

Source: Kolwzan, B. et al., *Introduction to Environmental Microbiology*, Oficyna Wydawnicza politechniki wroclawskiej, Nigeria, 2006, <http://www.oficyna.pwr.wroc.pl>.

pathogenic microorganisms (bacteria and virus), waterborne bacterial infections, and intestinal viruses that may be transmitted by water and diseases caused by them (Kolwzan et al., 2006).

In rural areas, human and animal waste sources contribute to groundwater contamination. For example, septic tanks and cesspools used for human waste disposal have traditionally been considered as source of fecal contamination of groundwater. Additionally, animal waste lagoons and stockyards are becoming important sources for fecal contamination of shallow groundwater in rural landscapes and the number of these units and the animals housed in the facilities are becoming more and more. Yates (1985) states that septic tanks contribute 800 billion gallons of water per year to subsurface, and this subsurface water is a source of pathogens including bacteria and viruses. She points out that in regions having more than 40 systems per square mile (1 system per 16 acres), the Environmental Protection Agency (EPA) estimates high potential for groundwater contamination. Ahmed et al. (2005) conducted biochemical fingerprinting enterococci and *E. coli* to relate possible migration of these organisms from septic tanks to surface water (a creek).

In 1976, cryptosporidiosis was first recognized to infect humans and the symptoms were diarrhea that generally ends in 2–3 weeks. Among the most well-known public health concerns involving biocolloids is the outbreak of cryptosporidium in the water system of the city of Milwaukee, Wisconsin, in 1993 (MacKenzie et al., 1994). Contamination occurred as the sand filtration system at the Howard Avenue Water treatment Plant on the shore of Lake Michigan failed to remove the oocysts of cryptosporidium during rapid sand filtration. Because of a storm even in early spring season (when cows were out in open areas), the oocysts in manure mixed in runoff water ended up near the intake of the treatment plant. The filtration system was not operating optimally and that led to a bypassing of the oocysts during the backwash of the filters. Over a period of 2 weeks (March 23 to April 8, 1993), over 400,000 people became infected and more than 100 weak or immune-compromised individuals died.

An outbreak of cryptosporidiosis in a disinfected groundwater supply occurred in Warrington, a town in Northwest England, between November 1992 and February 1993 (Bridgeman et al., 1995). A total of 47 cases were recorded over this period, and the bypass flow of surface water containing animal feces to aquifer was attributed to the cause. The bypass flow did not take advantage of filtration in natural sandstone present in subsurface. Once the source (e.g., well) was taken out of service, the outbreak quickly subsided. The fecal samples from infected patients showed the presence of oocysts of cryptosporidium. Chlorination appeared not to have complete disinfection potential in the outbreak.

The town of North Battleford, Saskatchewan, Canada, suffered a cryptosporidium outbreak (Sterling et al., 2001). The mechanism for failure was the defect of the sand filtration units and cryptosporidium oocysts being resistant to chlorine passed through the treatment plant to the distribution system. The outbreak occurred between late March and early May of 2001. Between 5800 and 7100 people were affected by the outbreak that included many visitors. Confirmed 275 cases of cryptosporidiosis were found by May 30, 2001. Again, failure of filtration was attributed to the outbreak. The source water was surface water and the parasites must have entered the river some point upstream from the intake.

Another serious case of contamination of the water supply of Walkerton, Ontario, Canada, with O157:H7 strain of *E. coli* led to the death of 7 people and sickening of 2500 people in year 2000 (Hrudey et al., 2002, 2003). Contaminated surface runoff entered the well possibly due to bypass flow. The operators were held liable for misconduct.

The resort on the island of South Bass in Lake Erie, Ohio, witnessed an outbreak of gastroenteritis in 2004 (Fong et al., 2007; O'Reilly et al., 2007) that exposed the visitors and the local residents. Fong et al. (2007) concluded the following:

Massive groundwater contamination on the island was likely caused by transport of microbiological contaminants from wastewater treatment facilities and septic tanks to the lake and the subsurface, after extreme precipitation events in May–July 2004. This likely raised the water table, saturated the

subsurface, and along with very strong Lake Erie currents on 24 July, forced a surge in water levels and rapid surface water–groundwater interchange throughout the island. Landsat images showed massive influx of organic material and turbidity surrounding the island before the peak of the outbreak. These combinations of factors and information can be used to examine vulnerabilities in other coastal systems. Both wastewater and drinking water issues are now being addressed by the Ohio Environmental Protection Agency and the Ohio Department of Health.

Understanding the fate and transport of biocolloids in environmental systems is quite important because they pose a serious water quality risk. Biocolloids may remain infectious and may survive for long periods of time in natural environmental systems (Chrysikopoulos et al., 2010). In order to estimate the potential health risk associated with aquifers contaminated by various biocolloids, the prediction of biocolloid fate and transport is necessary.

Virus adsorption has some correlation with soil moisture; whereas its transport is faster when water saturation in pores is high. It has been proved that virus adsorption on AWI in unsaturated porous media is governed by temporal and spatial water saturation fluctuations. Virus adsorption is stronger on AWIs than on liquid–solid interfaces. However, virus inactivation is enhanced under the presence of AWIs. Released viruses in water or wastes can be adsorbed on the sand surface, clays, bacterial cells, natural colloidal dispersions, and sludge particles. Adsorbed viruses survive for longer time periods than viruses suspended in the aqueous phase. The prevailing mechanisms for biocolloid adsorption onto clays are not well defined and they vary for varying kinds of biocolloids. The electrostatic interactions and chemical properties such as ionic strength and pH are dominant parameters for the adsorption of a virus on mineral surfaces (Chrysikopoulos et al., 2010).

## 5.7 CONCLUSIONS

Within the subsurface systems such as soils, groundwater aquifers, sediments, or fractured rocks, colloidal particles/fines (particles with an average diameter between  $10^{-9}$  and  $10^{-10}$  m and carry surface charge) are ubiquitous with a pronounced variability concerning morphology and chemical composition. There are several classes of subsurface colloids—abiotic and biotic. These include silicate clays, iron and aluminum oxides, mineral precipitates, humic materials, micro emulsions of nonaqueous phase liquids, viruses, and bacteria. The mobilization and migration of these subsurface colloidal particles take place under different physical and geochemical conditions. The contamination of groundwater and soil due to these migrating colloidal particles is well recognized and is classified into two categories: (a) colloid-associated contaminant transport and (b) transport of biocolloids. This chapter has briefly reviewed these subsurface colloidal fines, classifications, sampling methods, and characterization, and finally their role in groundwater contamination. Groundwater contamination due to mobilization and migration of these colloidal fines and associated health effects has also been presented here.

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