

Physicochemical and Hydrodynamic Aspects of Soil



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1 Introduction

Soil is a particulate material which is usually of natural origin. Its porous nature allows the movement of fluids within its interior. Solid soil particles are mostly of a mineral origin and, to a greater or lesser extent, chemically interact with the pore fluids, which are usually constituted by water. Due to the numerous thermal, hydraulic, mechanical, electrical, and even biological phenomena associated with the interaction between mineral particles and pore fluids, soil is a complex medium that is difficult to model and understand.

This chapter reviews the basic principles that govern the behavior of soils and influence the electrokinetic remediation processes of contaminated soils.

2 Origin of Soils

Soils are formed in a variety of ways, but the fundamental origin is the alteration of lithospheric rocks. The disintegration of the minerals that compose a rock gives rise to the particulate matter of soil. The type of soil that is generated depends on the different mechanisms responsible for decomposing the rocks and the subsequent process of aggregation of the mineral particles.

Residual soils are formed by the weathering (physical–chemical attack of environmental agents) of parent rock that is exposed on the earth's surface. The resulting

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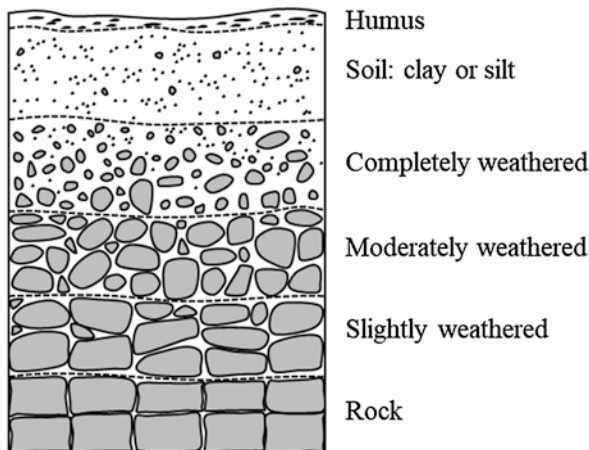


Fig. 1 Typical vertical profile of a residual soil

mineral particles or rock relicts are not transported, so they remain at the site where they were formed, eventually covering the underlying rock material.

Residual soils can be found in any region of the globe, but thicker soils are found in very humid climates [1]. Climatic, topographical, and, of course, lithological factors [2, 3] have a decisive influence on the genesis of residual soils. In general, residual soils present a high degree of heterogeneity because they are not classified according to particle size or reorganized by mechanical effects. Some rock relicts persist in their internal structure and are more abundant at lower depths (Fig. 1).

Colluvial soils are formed by the accumulation of weathered material in situ that is transported to low points of the terrain due to gravity. Different types of phenomena called landslide processes [4] are involved in their formation. Although they are very diverse in nature (from slow moving creep processes to sudden debris flow processes), residual soils have low or no internal organization and are very heterogeneous materials as a result [5, 6].

Soils of sedimentary origin (or transported soils [5]) come from the erosion, transport, and sedimentation of weathered material. Given that this type of soil transport involves a fluid (wind or water), the velocity of the fluid determines the size of the particles that can be mobilized [5, 7]. This factor confers a greater degree of homogeneity to sedimentary soils, at least on a small scale. However, at larger scales (tens to thousands of meters), the continuous variations in the velocity of the eroding and transporting agent generate significant spatial variability [8]. The transport process over long distances causes progressive wear of the particles, leading to rounded or subrounded grains. Another common characteristic of these soils is the existence of discontinuities due to stratification. Deposition usually occurs in subhorizontal layers and in different events, which favors the presence of bedding planes [2].

Soils that are formed by the action of water are called alluvial soils. They have a wide spatial distribution and are generally associated with large depressions of the terrain through which rivers flow. Given that these environments are ideal for human

settlements, alluvial soils often receive discharges of pollution. However, given that the flows of the river courses in these areas tend to be slow, the predominant soils are fine-grained (mainly clay and silts), with low permeabilities and for which electrokinetic remediation techniques are particularly recommended [9].

Soils formed by aeolian processes are characteristic of arid or semiarid zones, where wind action is the main erosive agent. These are well-sorted soils compared to alluvial soils. Sandy sediments derived from dune formation are the most recognizable, but the finest grained aeolian soils called loess are very important and are quite common in cold and arid areas [10]. Typically, aeolian soils have a very porous and metastable internal structure that can suddenly collapse in the presence of water [11, 12].

There are also soils for which humans are primarily responsible for their genesis. The main agent of erosion, transport, and sedimentation is construction machinery. In this manner, human beings determine the size of particles, their location, and their degree of compaction. These artificial soils are increasingly being used in urban infrastructure [13]. Common examples are large landfills for airport construction [14, 15], artificial islands, and land reclamation [16], all of which have considerable environmental impacts.

Based on the multiple factors that affect soil formation (climatology, vegetation, topography, fluvial, and/or aeolian regime, lithology, etc.) and the alteration factors that appear once a soil has developed (precipitation or dissolution of salts, compaction, etc.), each soil will be different because the combination of factors is almost infinite. The genetic conditioning of a soil is the influence that all factors have on its genesis, development over time, and final behavior [5].

3 Distribution of the Phases of a Soil

To be able to successfully address any soil remediation action, an abstraction and simplification of the associated processes should be performed. Due to their genesis and their temporal evolution, soils show very high internal and spatial variabilities. It is impossible to approach the study of a soil from an exhaustive point of view. Therefore, tools should be provided to obtain a qualitative and integrated description that allows rationally grouping, classifying, and organizing soils into types with homogeneous behaviors.

3.1 Phases of a Soil: Phase Diagram

The fluids inside the pores usually consist of water (with dissolved salts) and air (with a certain amount of water vapor). If we examine a soil sample point by point, the amount of water, air, or solid particles can change very abruptly. Thus, it is necessary to establish a series of hypotheses to rationally analyze the distribution of soil phases.

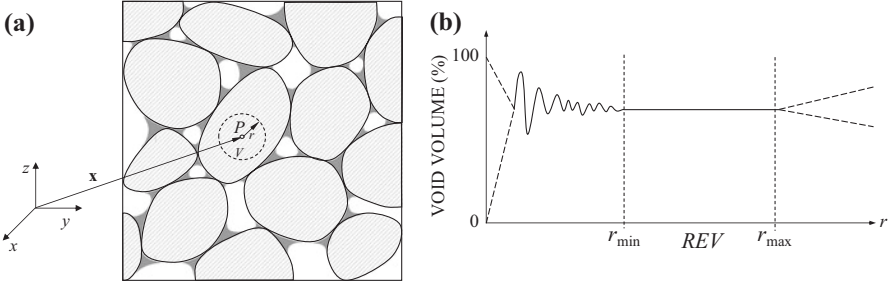


Fig. 2 (a) Sampling point P and its domain volume V . (b) Representation of average soil properties stabilization for representative elementary volume

If we take point P (Fig. 2a) and its immediate domain, as determined by a characteristic radius r that defines the volume V , the average properties of the domain highly depend on the position of the point. If P is on a mineral particle, 100% of volume V will be occupied by solid particles. If P is in a void, 100% of volume V may be occupied by air or water. As the value of r increases, there is a greater probability that the volume consist of a mixture of solid particles, liquid, and gases. As V continues to increase, the proportion of the volumes occupied by each of the phases is likely to stabilize around an average value that can be considered representative of the entire soil. Figure 2b shows how from r_{\min} the percentage of voids in the total soil volume remains constant until r_{\max} is reached. For small values of r the percentage fluctuates, in the most extreme case being 100% or 0% as discussed above. Between r_{\min} and r_{\max} lies the representative elementary volume (REV). The representative elementary volume [17] is the characteristic volume of a soil for which the average properties remain constant, even with small changes in that volume.

Based on this approach, the soil can be conceptualized as a multiphase mixture [18], with a series of index properties relating the volumes and masses of each phase. The variation of these average index properties is assumed to be continuous in space, and all these continua are superimposed at each point. Despite its particulate nature, the soil is assumed to be a continuous medium whenever it is possible to define a representative elemental volume.

Some of the most important and widely used index properties in soil characterization are:

1. Porosity (ϕ) is defined by the following expression:

$$\phi = \frac{V_V}{V_T}. \quad (1)$$

where V_V is the void volume, and V_T is the total volume of the soil (void volume plus volume of solids).

2. Void ratio. The void ratio (e) is given by the following expression:

$$e = \frac{V_v}{V_s}. \quad (2)$$

where V_s is the volume of solids contained in the soil.

Porosity and void ratio give us an insight into the amount of space available for the movement of fluids and the internal organization of the soil, so they are fundamental magnitudes for their characterization.

3. Gravimetric water content. The gravimetric water or moisture content (w) of a soil is given by the following expression:

$$w = \frac{M_w}{M_s} \approx \frac{M_L}{M_s} \quad (3)$$

where M_s is the mass of solid particles, and M_w and M_L are the water and liquid masses, respectively, which are assumed to be equal.

4. Degree of saturation. The degree of saturation is defined as the volume occupied by the liquid phase (V_L), which is assumed to be equal to the water volume (V_w), versus the volume of voids in a soil (V_v) and is given by the following expression:

$$Sr = \frac{V_w}{V_v} \quad (4)$$

The water content and the degree of saturation provide information on the importance of the liquid phase in the soil, since both index properties determine the thermodynamic state of the water and the type of movement it has within the porous medium.

5. Density of solid particles and specific gravity. The density of solid particles (ρ_s) is given by the following ratio:

$$\rho_s = \frac{M_s}{V_s} \quad (5)$$

where V_s is the volume occupied by the solid particles. The use of specific gravity (G) to characterize the minerals that make up a soil is quite common in the literature on soil mechanics. This variable is given by the following expression:

$$G = \frac{\rho_s}{\rho_w} \quad (6)$$

where ρ_w is the density of water. The value of G is dependent on the predominant mineralogy, although the most common minerals [19] have values between 2.6 and 2.8 [5].

6. Dry density. The dry density (ρ_d) is defined as:

$$\rho_d = \frac{M_s}{V_T} \quad (7)$$

where, as previously stated, M_s is the mass of solid particles, and V_T is the total volume of the soil.

7. Bulk density. The bulk density (ρ_b) of a soil is defined by the following expression:

$$\rho_b = \frac{M_T}{V_T} \quad (8)$$

where, as previously stated, M_T is the total mass (mass of solids, liquid, and gas, although the latter is usually disregarded), and V_T is the total volume of the soil.

8. Saturated density. The saturated density (ρ_{sat}) is defined as the bulk density when the soil is saturated, i.e., all pores are occupied by water.

The dry density and the saturated density are particular cases of the bulk density when the degrees of saturation are 0 and 1, respectively.

3.2 *Experimental Determination and Soil Phase Relations*

The determination of phase indices is usually not cumbersome and only requires very basic laboratory equipment. Furthermore, only a few indices need to be determined and the rest can be calculated from them. For these reasons phase distribution characterization in a soil can be performed easily and inexpensively in almost any laboratory.

The three most common characterization tests are:

- (a) Determination of the water content by mass [20] using oven drying. This test consists of measuring the mass of a soil sample before and after being placed in an oven with a temperature between 105 and 115 °C. The difference in mass between the two measurements returns the amount of water contained in the soil, and the last weighing provides the value of the mass of solid particles. With both masses, the gravimetric water content can be calculated using Eq. (3).
- (b) Determination of the specific gravity of soil solids using a water pycnometer [21]. This test can be somewhat more cumbersome, but, as previously specified, the density of solid particles presents a very low range of variation [5]. In many cases, in the absence of data, a value of 2700 kg/m³ is used [22].
- (c) Determination of the density (unit weight) of a soil specimen [23]. In this case, it is crucial to precisely determine the value of the total volume of the soil sample, which should remain unaltered after extraction. For this purpose, sampling tubes and paraffin wax are used for the samples [24].

From these values, the rest of the indices can be calculated. For this purpose, the use of the unit phase diagram is of special interest. Figure 3a shows a phase diagram of a soil for which the volume (to the left) and mass (to the right) are schematically represented. It is assumed that the mass of the gas phase is equal to zero. Dividing all the terms in the diagram in Fig. 3a by V_s (volume of solid particles) yields the

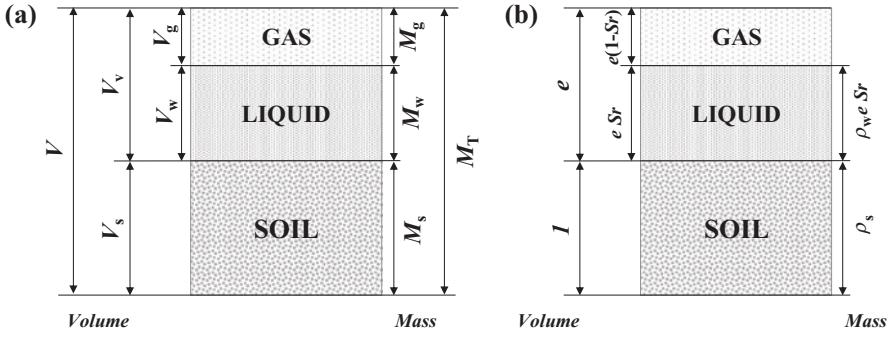


Fig. 3 (a) Soil phase diagram. (b) Unit diagram. All the masses and volumes of (a) are divided by V_s

Table 1 Soil phase relationships

Index property	Expressions in terms of ρ_s , e , and Sr	Expressions in terms of ρ_s , w , and ρ_b
e	e	$\frac{\rho_s + w\rho_s}{\rho_b} - 1$
φ	$\frac{e}{1+e}$	$1 - \frac{\rho_b}{\rho_s + w\rho_s}$
w	$\frac{\rho_w e Sr}{\rho_s}$	w
Sr	Sr	$\frac{w\rho_s \rho_b}{\rho_w (\rho_s + w\rho_s - \rho_b)}$
ρ_s	ρ_s	ρ_s
ρ_d	$\frac{\rho_s}{1+e}$	$\frac{\rho_b}{1+w}$
ρ_b	$\frac{\rho_s + \rho_w e Sr}{1+e}$	ρ_b
ρ_{sat} ($Sr = 1$)	$\frac{\rho_s + \rho_w e}{1+e}$	$\frac{\rho_b \left(\rho_s + \rho_w \left(\frac{\rho_s + w\rho_s}{\rho_b} - 1 \right) \right)}{\rho_s + w\rho_s}$

diagram in Fig. 3b, which is called the unit diagram because the volume of the solid particles takes the value of 1. From this diagram and the definitions of Eqs. (1)–(8), any index property can be obtained as a function of ρ_s , e , and Sr . For example, the gravimetric water content can be calculated as:

$$w = \frac{M_w}{M_s} = \frac{\rho_w V_w}{\rho_s V_s} = \frac{\rho_w \frac{V_w}{V_v} V_v}{\rho_s V_s} = \frac{\rho_w \frac{V_w}{V_v} \frac{V_v}{V_s}}{\rho_s \frac{V_s}{V_s}} = \frac{\rho_w S r e}{\rho_s} \quad (9)$$

where the expression can be obtained directly by dividing the terms on the right of the unit diagram that correspond to the mass of the liquid and solid phases. Thus, all indices can be obtained through the relationships shown in Table 1. These relationships can also be obtained as a function of ρ_s , w , and ρ_b (Table 1), which can be useful in the laboratory when calculating the distribution of phases of a soil.

Soils are characterized by all these index properties. Even if two soils are mineralogically and texturally identical, their behavior under same external actions will be completely different if their void ratio and degree of saturation are not equal. It is common in many studies (both in laboratory tests and in situ) to ignore the initial soil phase distribution and to compare the remediation efficiency with completely different initial conditions.

4 The Solid Phase

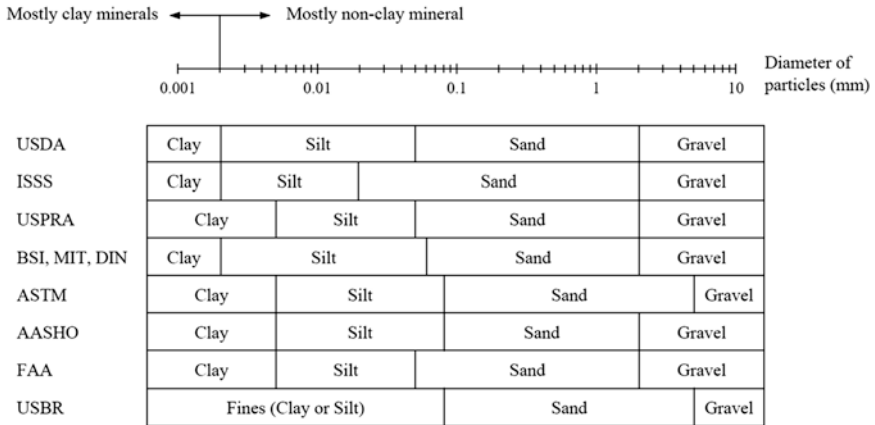
4.1 Soil Mineralogy

The mineralogy of soils varies greatly, depending on the parent rock and the physicochemical alterations subsequent to their formation. However, due to the nature of the composition of the terrestrial lithosphere, silicates, clay minerals, metal oxides, oxyhydroxides, hydroxides, carbonates, and sulfates predominate [19].

The reactivity of all these minerals generates a very significant range of pore waters that condition soil decontamination processes. Highly soluble minerals such as gypsum, calcite, or other carbonates, which can be important pH regulators in the electrokinetic treatment of contaminated soils [25, 26], are of special interest.

4.2 Soil Texture

The first approach for characterizing the soil texture is the granulometric analysis of the particles that compose the soil. Although the basic characterization tests for the analysis of the particle size distribution or gradation are sieving [27] and



USDA (US Department of Agriculture), ISSS (International Soil Science Society), USPRAs (US Public Roads Administration), BSI (British Standards Institute), MIT (Massachusetts Institute of Technology), DIN (German Standards), ASTM (American Society for Testing and Materials), AASHTO (American Association of State Highway Officials), FAA (Federal Aviation Agency) and USBR (US Bureau of Reclamation)

Fig. 4 Characteristic sizes of soil particles according to different classification systems

sedimentation [28], there are several techniques to determine the size distribution of solid particles, such as laser diffractometry [29], which is increasingly common. The predominant particle size marks the behavior of the soils, both mechanically [5] and hydraulically [30, 31]. The particle size variation in a soil can range immensely, from tens of centimeters to a micrometer in size. Although there is a convention regarding the characteristic sizes of each type of particle (see Fig. 4), there are various classifications, mainly from the perspective of agronomy (such as the USDA classification [32]) and civil engineering (such as the Unified Soil Classification System [33] and the AASHTO system [34]).

Traditionally, soil has been divided into two types of particles according to their size: a fine fraction, which is less than 0.074 mm in diameter, and a coarse fraction, which is above 0.074 mm in diameter. The division is marked by the difficulty of sieving below that size, but it is also conditioned by the presence of clay minerals that have a quite different behavior from the rest of the solid particles and play a fundamental role in soils of low or very low permeability.

Clay minerals are formed by weathering in an advanced phase of different materials of siliceous origin. They are formed by two types of planar mineral structures. The first structure is a phyllosilicate sheet that is formed by SiO_4^{4-} tetrahedra that share, by a covalent bond, the oxygen atoms in their bases (Fig. 5a). The second sheet structure is formed by metal hydroxides, generally $\text{Al}_2(\text{OH})_6$ (also called gibbsite) and $\text{Mg}_3(\text{OH})_6$ (also called brucite). Spatially, both hydroxides are in the form of octahedra combined by covalent bonding and share hydroxyl groups in the vertices (Fig. 5b). Because tetrahedral and octahedral sheets are not electrically neutral, they combine to form covalent bonds between the free apices of the tetrahedrons and the

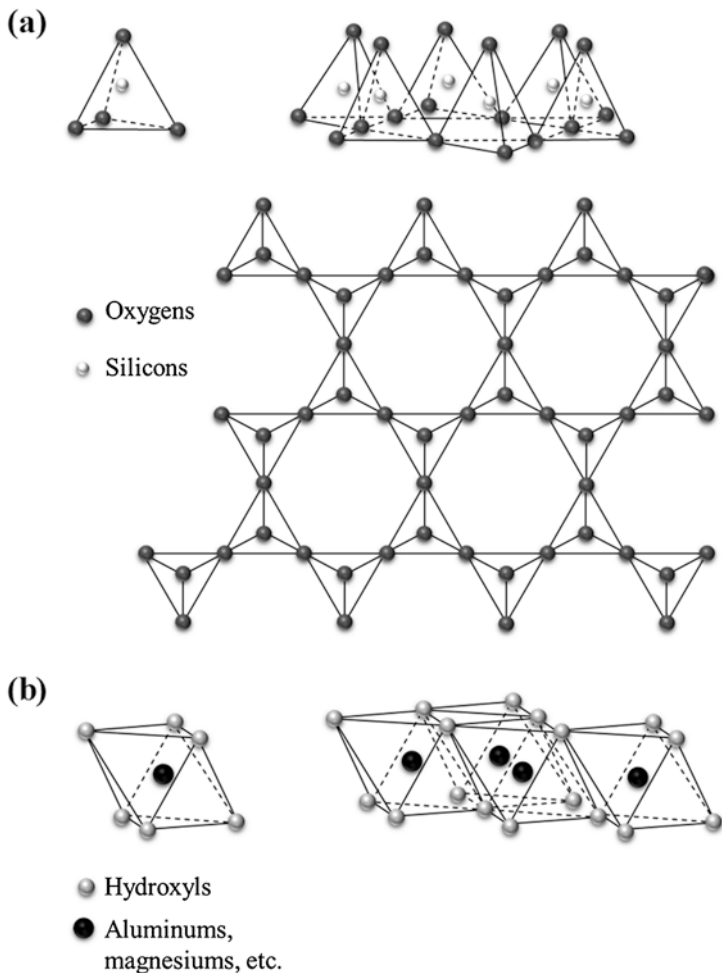


Fig. 5 (a) Structural diagram of phyllosilicates and (b) structural diagram of metal hydroxides

oxygen of the hydroxyl groups of the octahedra, giving rise to different clay minerals. The combination of one layer of phyllosilicates (tetrahedra) and one layer of hydroxides (octahedra) gives rise to a clay mineral type 1:1 (see Fig. 6a). In contrast, the sandwiching of an octahedral layer by two tetrahedral layers gives rise to a mineral type 2:1 (see Fig. 6b) or TOT (tetrahedron-octahedron-tetrahedron). These elementary pieces, in turn, have charge deficits and affinities for other like-layers, which give rise to a wide variety of minerals depending on the mode of combination [5, 35]. Most clay minerals are found in nature not as simple 1:1 or 2:1 sheets but as stacks of layers.

Regarding complexity, the phenomenon of isomorphic substitution must also be considered. During the formation of the clay layers, once the basic structure is formed, the silicon of the tetrahedra or the metallic cations of the octahedra can be displaced by elements with a lower charge without structural changes. Substitution

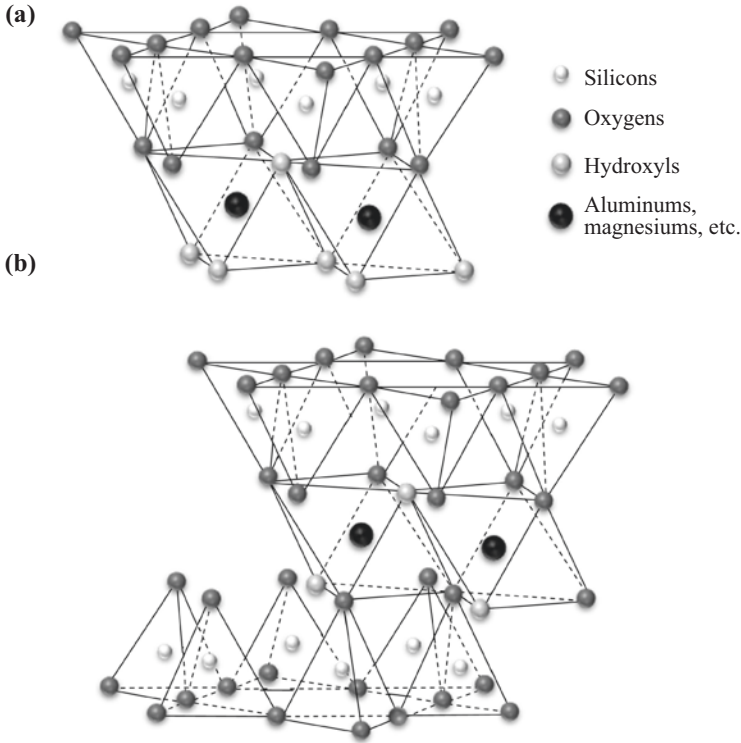


Fig. 6 (a) Structural diagram of a 1:1 clay sheet and (b) structural diagram of a 2:1 clay sheet

involves a loss of positive charges and, therefore, results in a net negative charge. The layers of clay become highly electrically charged planar structures, which give rise to behavioral phenomena and trends that are very different from those of soils formed only by large inert mineral particles [5].

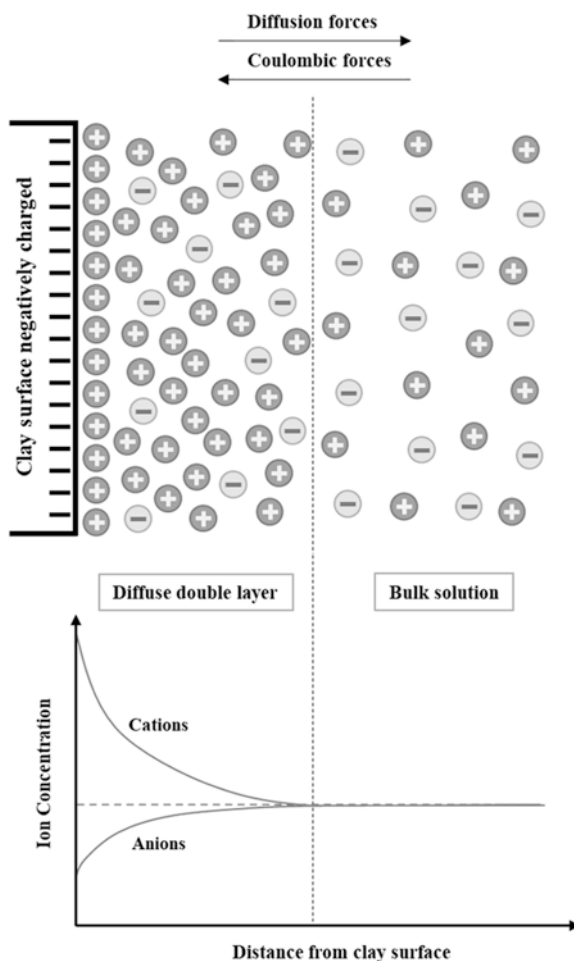
From the point of view of the electrokinetic remediation of soils, isomorphic substitution is responsible for many of the phenomena observed during treatment. Firstly, the clay sheets are able to attract water molecules that are electrical dipoles so that the mineral particles are hydrated and form a near crystalline structure. In addition, mineral surfaces are also able to attract a large amount of hydrated cations to compensate for negative net charges [35]. Both types of water molecules are virtually immobilized and are referred to as the water adsorbed on the surface of the clay particles. This water does not flow under conventional hydraulic gradients [36] and is responsible for the low permeability of this type of soils.

However, this property of clay soils makes them especially suited for electrokinetic remediation. When an external electric field is applied, the ions of the hydrating water travel toward the electrodes due to electromigration, which causes the entire liquid phase to flow. In clay soils, there are more cations than anions due to the excess negative charge of the clay particles, and more water is pulled toward the cathode than the anode; this phenomenon is called electroosmosis [9, 37, 38]. Some authors have confirmed [39] that if cationic surfactants are used, the electroosmotic

flow is reversed. Due to the positive charge of hydrophilic heads, more anions are required in the solution to attain electroneutrality, and the balance between anions and cations begins to equilibrate or even tend toward an excess of negative charges in the pore water with a subsequent electroosmotic flow toward the anode.

The study of the electrostatic properties of clay particles requires sophisticated equipment, which is unusual in most common commercial laboratories. For this reason, in the classification of soils, indirect tests that give an idea of the ability of a soil to retain water and solutes in its internal structure are used. The most common tests are the Atterberg limits [40, 41], which have been widely correlated with the macroscopic mechanical properties of soils [42–44], including the swelling capacity and the hydraulic conductivity [45, 46]. The methylene blue value [47–49] has also been used to characterize the behavior of clayey soils [50, 51]. These tests allow the classification of the fine fraction according to its nature whether it is

Fig. 7 Diffuse double layer in clays



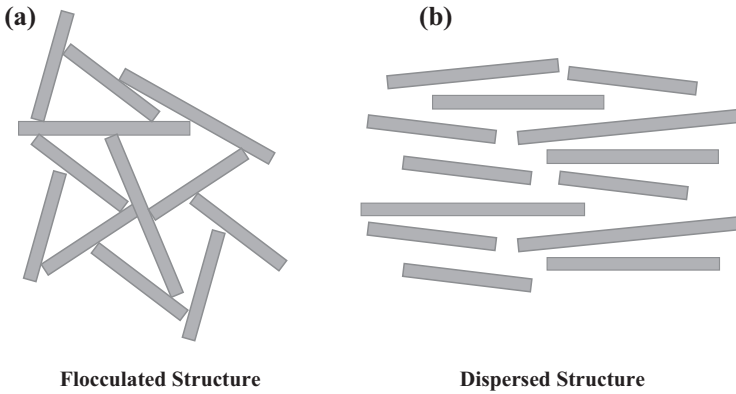


Fig. 8 Idealized representation of a clay with (a) flocculated structure and (b) dispersed structure

predominantly silty (with particles with a diameter of between 74 and 2 μm) or clayey (with a diameter of less than 2 μm). For this, the plasticity is studied, which is given fundamentally by the surface area and amount of charge of a soil, as measured through the cation exchange capacity (CEC) [19, 52].

As previously mentioned, the negative electric charge of clay particles results in an attraction of the cations toward their surface and a repulsion of the anions. This attraction alters the state of the pore water around minerals (Fig. 7), forming a diffuse double layer [52, 53] that consists of the mineral particle itself and its surrounding, which is affected by the electric field. The equilibrium between the electrostatic repulsive forces of clay surfaces and the attractive forces (London-van der Waals forces) cause the internal structure to be dispersed or flocculated [5] (see Fig. 8), with highly differentiated macroscopic behavior [5, 52].

Another additional effect of the nature of clays is the adsorption of contaminants on mineral surfaces. The electrostatic adsorption mechanism is very important, but it is not the only one [54]; many mechanisms can be superimposed for the same soil depending on the mineralogical composition, organic matter content, type of pollutant, and geochemical conditions of the pore water. For this reason, the adsorption of pollutants is usually described empirically through the use of sorption isotherms [19, 54, 55]. In many cases, the desorption of pollutants at high concentrations requires the use of anionic surfactants [56] that can alter the direction of water movement during electrokinetic soil remediation [39].

5 The Liquid Phase

5.1 Water

In virtually all soils in the natural state, water is present in its pores, even in small amounts. In soils with a high void ratio in saturated conditions, a greater volume of water than solid particles can be reached. Liquid water can be found in two forms. The first form is adsorbed water, as described above, which is strongly bound to the surface of the clay particles. It does not flow with conventional hydraulic gradients and can be considered immobile for all practical purposes [36]. Some authors have suggested that the molecular structure and thermodynamic properties of adsorbed water change [5, 57] and are different from the liquid-free water. In addition, it can remain in contact with the clay particles even if the soil is desiccated in an oven to determine the water content [20].

The second type of water is called free, capillary, or gravitational water and can flow with hydraulic gradients [36]. Due to the small size of the pores in which it is found, surface tension is of fundamental importance in its behavior. In partially saturated soils (Fig. 9), water adheres to solid particles to form curved surfaces called menisci. In the menisci, a balance of forces (Fig. 10) is established between the surface tension of the water and the forces exerted by the pressures of the liquid and gas. In the arrangement of Fig. 10, the equilibrium is given by the following expression:

$$P_G - P_L = \frac{2\sigma}{R} \quad (10)$$

where σ is the surface tension, P_G and P_L are the pressures of the gas phase and liquid phase, respectively, and R is the radius of curvature of the meniscus. In a three-dimensional arrangement, the menisci are warped surfaces in which two radii of curvature (R_1 and R_2) can be defined. Thus,

$$P_G - P_L = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (11)$$

The difference between the gas pressure (P_G) and the liquid pressure (P_L) shown in Eqs. (10) and (11) is called capillary suction (s). The greater the value of s , the smaller the radius of the meniscus, the closer the warped surface is to the solid particles, and the water content of the soil is, consequently, also lower. The function that relates the degree of saturation (S_r) and the capillary suction is called the soil water retention curve (SWRC). The SWRC can present hysteretic behavior (Fig. 11) with a main wetting path and a main drying path in which the hysteresis cycles are inscribed. However, especially for modeling purposes, these curves are simplified using the central tendency for both wetting and drying. There are many formulations for this type of curve [58–65], although their parameterization is usually simple (no more than four parameters). The SWRC is also called the characteristic curve because

Fig. 9 Water in unsaturated soils

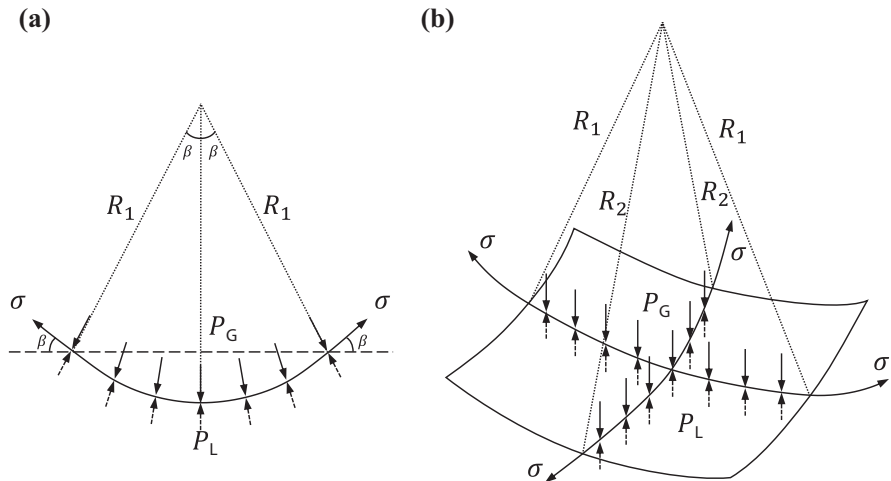
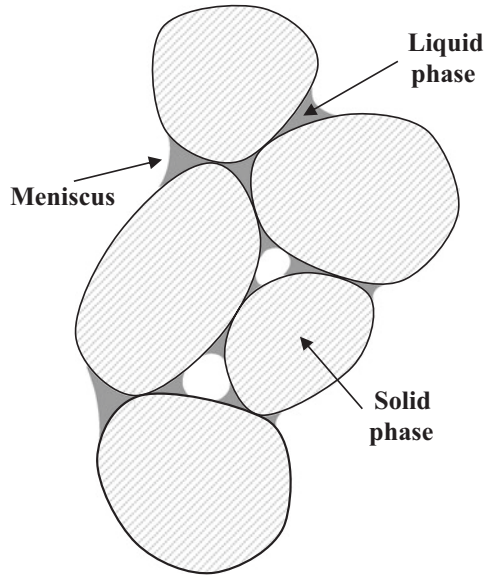


Fig. 10 Force balance of the menisci in (a) a two-dimensional configuration and (b) a three-dimensional configuration

it is representative of the type of soil [66]. As seen in Fig. 12, the curves for clay and sand are very different. The first type of soil has a more extended curve, with very high degrees of saturation, even for high suctions. However, the curve for a granular-type material, such as coarse sand, is much more step-like, with the soil changing from almost complete saturation to desaturation with only a small change in suction. The value of the suction in which the jump occurs for coarse granular materials is called the air entry pressure. Although in theory it also exists in clays and reaches much higher values, an abrupt jump in the value of S_r is generally not observed.

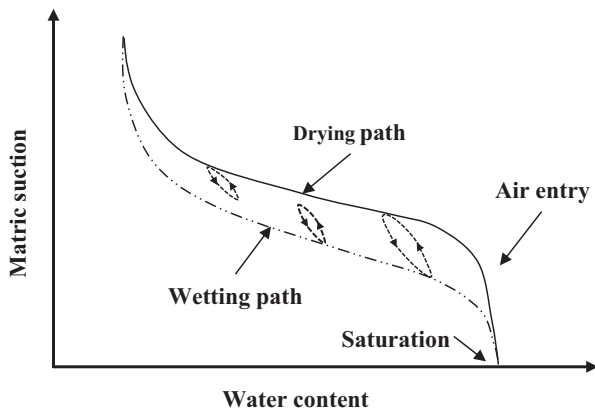


Fig. 11 Hysteretic behavior of the soil water retention curve

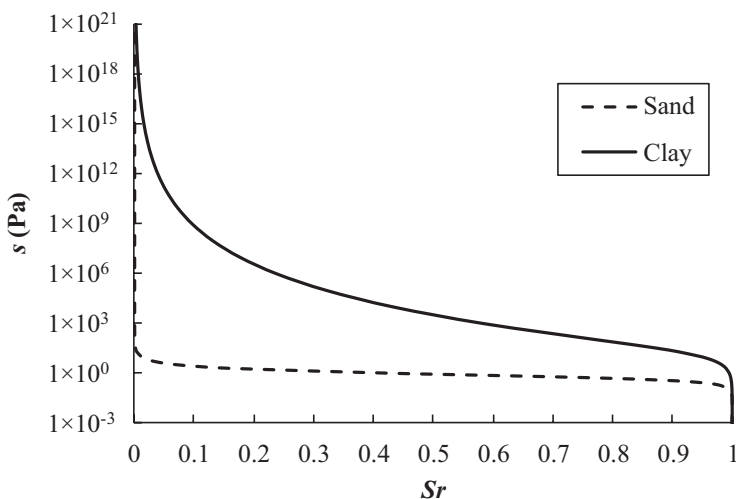


Fig. 12 Typical retention curves of a clayey soil and a sandy soil

If it is assumed that P_G is equal to or close to the value of atmospheric pressure (P_{atm}), which may be true in soils with a low degree of saturation, and $P_{atm} = 0$ (reference pressure level), P_L must be negative; therefore, its internal energy is lower than the water found in liquid form on the surface of the earth. For this reason, extraction for the subsequent treatment of pore water in a partially saturated soil is very complex and energy demanding.

5.2 *Solutes in the Liquid Phase*

Due to the chemical interaction of water with the gases present in the pores and with the minerals of the solid phase, the concentrations of the solutes in pore water are higher than in rainwater. Due to the composition of the lithosphere, the major ions in the water include Ca^{2+} , Mg^{2+} , Na^+ , and K^+ as cations and HCO_3^- , SO_4^{2-} , and Cl^- as anions [67, 68]. Other minor ions or trace elements can be present, and some of them can be considered as pollutants [69].

An effect of dissolved salts is that they alter the partial pressure of water vapor in equilibrium with the liquid phase. This variation induces an increase in suction called osmotic suction (s_o). Osmotic suction can be calculated as:

$$s_o = RT\rho_w \sum_{i=1}^j a_i \quad (12)$$

where R is the ideal gas constant ($8.314463 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature, and a_i is the activity of the i th species in the pore water solution.

Osmotic suction and capillary suction make up the value of the total suction (s_{TOT}), which will influence the mechanical behavior of the soil.

5.3 *Electrical Conductivity*

Another important effect that solutes have on pore water is the variation of the electrical conductivity of the soil. If this is taken as a parallel system with two conductivities, that of the solid phase and that of the liquid phase [70], the increase in the concentration of solutes substantially increases the total conductivity. There are several approaches to estimate water conductivity based on its chemical composition. A good compilation and comparison of the best-known approaches can be found in Tarantino et al. [71].

6 The Gas Phase

The gas phase in a soil consists mainly of air (a mixture of nitrogen, oxygen, and other minor constituents) that is enriched by other gases due to interactions with minerals and the pore water. For example, the content of CO_2 or methane will be strongly related to biological activity and pH of the water. However, the gas most dependent on the physicochemical state of the pore water is water vapor. If a thermodynamic equilibrium between water vapor and free water is assumed, then the psychrometric equation or Kelvin's equation is fulfilled. This equation is given by the expression [72]:

$$P_V = P_V^o \exp\left(\frac{WMM}{RT\rho_W} s_{TOT}\right) \quad (13)$$

where P_V is the partial vapor pressure, P_V^o is the saturation vapor pressure (equilibrium partial vapor pressure for a planar surface of water) that is only temperature-dependent, WMM is the water molecular mass, ρ_W is the density of pure water, and s_{TOT} is the total suction, which is equal to

$$s_{TOT} = s + s_O \quad (14)$$

where s is the capillary suction, and s_O is the osmotic suction. Given that P_V / P_V^o is the relative humidity, if we are able to measure this ratio in the soil pores, the total suction can be determined. Subtracting the osmotic suction from the total suction yields the capillary suction. From the SWRC of the soil, the degree of saturation and water content can then be obtained. This is the operating principle of psychrometers, which are suitable for determining the suction in soils with low degrees of saturation. For other conditions (low suction and greater degree of saturation), tensiometers [73] are more appropriate and are capable of determining capillary suction directly. There are also other methodologies to obtain the soil water content based on the measurement of thermal and electrical conductivities [74] or on the dielectric properties of the soil [73]. Therefore, there are a variety of techniques to measure the suction or water content, both in the laboratory and on site.

7 Coupled Hydromechanical Behavior of Soils

The cornerstone of soil mechanics is the principle of effective stress [73–75]. In the formulation of this principle, for a saturated soil, the effective stress ($\hat{\sigma}$), which is responsible for the soil strains, is given by:

$$\hat{\sigma}' = \sigma - P_L \mathbf{I} \quad (15)$$

where σ is the tensor of total stress to which the soil is subjected, P_L is the pressure of the liquid phase, and \mathbf{I} is the identity tensor. For unsaturated soils, the formulation of the effective stress is slightly different [76].

$$\hat{\sigma}' = \bar{\sigma} - \chi \cdot s \cdot \mathbf{I} \quad (16)$$

$$\bar{\sigma} = \sigma - P_G \cdot \mathbf{I} \quad (17)$$

where χ is the Bishop factor [77], which is usually formulated as a function of the degree of soil saturation and $\bar{\sigma}$ is the net stress tensor. Consequently, there is a

coupling between mechanical and hydraulic behaviors in soils. This interdependence can generate unexpected phenomena [78] when applying electrokinetic remediation techniques that generate significant changes in the distribution of water pressure and the degree of soil saturation [79].

8 Flows in Soils

The high microscopic and macroscopic variability of soils, the changes in the environmental variables, and the human actions cause flows of a diverse physicochemical nature. The gradients of chemical potential experienced by all soil components involve flows of matter and energy in all phases and, consequently, in all species.

Any flow \mathbf{q}_i in a soil can be formulated generically by the following expression [80]:

$$\mathbf{q}_i = \sum_{j=1}^n \mathbf{L}_{ij} \nabla X_j \quad (18)$$

where \mathbf{L}_{ij} is the coupling coefficient tensor that links the flow \mathbf{q}_i and the gradient of the driving variable X_j , and n denotes the total number of driving variables and types of flow considered.

In most of the conceptual and numerical models that have been used to simulate electrokinetic remediation treatments, movements in the solid or gaseous phase have not been considered. However, they have been used in other applications, such as the analysis of engineered barriers for the storage of radioactive waste [81, 82].

The flows that are most commonly considered in electrokinetic remediation processes include the water mass, which is practically equal to that of the entire liquid phase, the mass of chemical species, heat and electric charge. The most intuitive part of the description of the flows is to consider only those in which $i = j$, that is, those in which the flow and driving force are of the same nature. Thus, the mass flow of water is given by Darcy's Law.

$$\mathbf{q}_w^h = -\mathbf{K}^h \nabla h \quad (19)$$

where \mathbf{q}_w^h is the hydraulic water flux, \mathbf{K}^h is the hydraulic conductivity tensor, and ∇h is the hydraulic gradient, being h the water head, it is defined as:

$$h = z + \frac{P_L}{\gamma_w} \quad (20)$$

where z is the vertical coordinate, P_L is the liquid pressure, and γ_w is the specific weight. An additional term to the water head, which corresponds to kinetic energy

of the porewater, is not included because the velocity of water movement in the soil is very low.

The flow of solutes is driven by gradients in the concentration of chemical species and is given by Fick's Law.

$$\mathbf{j}_i = -\mathbf{D}_i \nabla C_i \quad (21)$$

where \mathbf{j}_i is the diffusive flux of chemical species i , \mathbf{D}_i is the diffusion/dispersion tensor, and ∇C_i is gradient of the concentration of the species considered.

In the case of conductive heat flux (\mathbf{q}^t), the formulation using Fourier's law is similar to the previous ones and is given by the expression:

$$\mathbf{q}^t = -\mathbf{K}^t \nabla T \quad (22)$$

where \mathbf{K}^t is the thermal conductivity tensor and ∇T is the temperature gradient in the soil.

Finally, the electrical current (\mathbf{I}^e) is given by Ohm's law can be obtained by as:

$$\mathbf{I}^e = -\boldsymbol{\sigma}^e \nabla E \quad (23)$$

where $\boldsymbol{\sigma}^e$ is electrical conductivity tensor, and ∇E is the electric potential gradient.

In certain cases, it is necessary to include in the conceptual model coupled flows ($i \neq j$ in Eq. 18) for which the nature of the flow and that of the driving force are different. In the case of electrokinetic remediation treatments, the most important coupled flows to consider are the electroosmotic flow and the electromigration. The first is given by the following expression:

$$\mathbf{q}^{eo} = -\mathbf{K}^{eo} \nabla E \quad (24)$$

where \mathbf{K}^{eo} is the electroosmotic conductivity (or permeability). In the same way, charged species experience electromigration due to the presence of an electric field. This chemical flux can be expressed as:

$$\mathbf{q}_i^{em} = -\mathbf{U}_i \nabla E \quad (25)$$

where \mathbf{q}_i^{em} is the electromigratory flow, and \mathbf{U}_i is the ionic electromobility tensor of chemical species i .

Many other coupled flows can occur (see Table 2 adapted from [5]), and it can be shown [82] that due to Onsager reciprocal relations, the coupling coefficients must be symmetric; thus, according to Eq. (18),

$$\mathbf{L}_{ij} = \mathbf{L}_{ji} \quad (26)$$

The hydraulic, electroosmotic, thermal, and electrical conductivities, diffusion/dispersion, and electromobility ion coefficients are phenomenological and are

Table 2 Coupled flows in soils

Flow	Driving force (∇)			
	Chemical concentration	Hydraulic head	Temperature	Electrical current/potential
Chemical species	Fickian diffusion	Streaming current	Soret effect	Electrophoresis
Fluid	Chemo-osmosis	Darcyan conduction	Themo-osmosis	Electroosmosis
Heat	Dufour effect	Isothermal heat transfer	Fourier conduction	Ohmic conduction
Electric current	Diffusion and membrane potentials	Streaming potential	Thompson effect	Peltier effect

Adapted from [5]

therefore dependent on other variables. Although tensor is used in a general way in Eqs. (19)–(25), if the medium is isotropic, these coefficients are taken as constants so that

$$\mathbf{L}_{ij} = l_{ji} \mathbf{I} \tag{27}$$

where \mathbf{L}_{ij} is the coupling tensor, l_{ij} is the scalar coupling coefficient, and \mathbf{I} is the identity tensor.

The presence of all these coupled transport phenomena, together with the chemical reactivity of the mineral and liquid phases, makes any chemical–physical process of remediation in soils extremely complex. Therefore, from the point of view of modeling and understanding the phenomena, many of these mutually coupled equations are disregarded based on their lower relative importance. However, such an evaluation must be careful when there are changes in scale or changes in soil or environmental conditions. For example, the influence of thermal effects due to ohmic heating of the electrodes is usually disregarded in the analysis of electrokinetic remediation processes. Nevertheless, it has been shown that it is relevant when the process is scaled up [83, 84].

9 Conclusions

Because of their special multiphase and multicomponent nature, soils are highly complex porous media. Their character as natural materials makes them highly heterogeneous at all scales. In addition, multiple physical–chemical phenomena take place within soils when the initial equilibrium conditions are altered, leading to unexpected or irregular behaviors in many cases.

From the point of view of electrokinetic treatments, empirical approaches have often been used for understanding the main behavioral trends; however, these methods fail to understand all the intrinsic complexity of soils. To achieve this objective,

it is necessary to completely characterize the distribution of the soil phases, the mineralogical composition, the geochemistry of the pore water, and the coefficients that govern the different flows of matter and energy in soil. Clearly, this characterization is an extremely complex task, but it should not be forgotten that an oversimplification of conceptual approaches can omit relevant phenomena in the behavior of soil.

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References

1. I.M.R. Duarte, C.M.G. Rodrigues, Residual Soils, in *Encyclopedia of Engineering Geology*, ed. by P. T. Bobrowsky, B. Marker, (Springer International Publishing, Cham, 2018), pp. 751–752
2. L.D. Wesley, *Geotechnical Engineering in Residual Soils* (Wiley, Hoboken, 2010)
3. B.B.K. Huat, D.G. Toll, A. Prasad, *Handbook of Tropical Residual Soils Engineering* (CRC Press, Boca Raton, 2012)
4. L.M. Highland, P. Bobrowsky, *The Landslide Handbook—A Guide to Understanding Landslides* (Geological Survey Circular 1325, Reston, 2008)
5. J.K. Mitchell, K. Soga, *Fundamentals of Soil Behavior* (John Wiley & Sons, Inc., Hoboken, 2005)
6. T. Zádorová, V. Penížek, Formation, morphology and classification of colluvial soils: a review. *Eur. J. Soil Sci.* **69**, 577–591 (2018)
7. R.P.C. Morgan, *Soil Erosion and Conservation*, 3rd edn. (Blackwell Science, Hoboken, 2005)
8. R.E. Hunt, *Geotechnical Engineering Investigation Handbook*, 2nd edn. (Taylor and Francis Group, Abingdon, 2005)
9. A.T. Yeung, S. Datla, Fundamental formulation of electrokinetic extraction of contaminants from soil. *Can. Geotech. J.* **32**, 569–583 (1995)
10. A.S. Goudie, *Arid and Semi-Arid Geomorphology* (Cambridge University Press, New York, 2013)
11. A. Assadi-Langroudi, S. Ng’ambi, I. Smalley, Loess as a collapsible soil: some basic particle packing aspects. *Quat. Int.* **469**, 20–29 (2018)
12. S.L. Houston, W.N. Houston, C.E. Zapata, C. Lawrence, Geotechnical engineering practice for collapsible soils. *Geotech. Geol. Eng.* **19**, 333–355 (2001)
13. M. Bendixen, J. Best, C. Hackney, L.L. Iversen, Time is running out for sand. *Nature* **571**, 29–31 (2019)
14. G. Mesri, J.R. Funk, Settlement of the Kansai International Airport Islands. *J. Geotech. Geoenviron.* **141** (2015)
15. The construction record of Kansai International Airport. *World Dredg. Min. Constr.* **37**, 6–30 (2001)
16. S.Y. Chee, A.G. Othman, Y.K. Sim, A.N. Mat Adam, L.B. Firth, Land reclamation and artificial islands: walking the tightrope between development and conservation. *Glob. Ecol. Conserv.* **12**, 80–95 (2017)
17. J. Bear, *Dynamics of fluids in porous media* (Dover, New York, 1972)
18. M. Hassanizadeh, W.G. Gray, General conservation equations for multi-phase systems: 1. Averaging procedure. *Adv. Water Resour.* **2**, 131–144 (1979)
19. G. Sposito, *The Chemistry of Soils* (Oxford University Press, Cary, 2008)

20. ASTM, ASTM D2216-19. Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass (2019)
21. ASTM, ASTM D854-14. Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer (2014)
22. Skaven-Haug, S.V.: Volumetric relations in soil materials. Proceedings of the Fourth International Peat Congress, Espoo (1972)
23. ASTM, ASTM D7263-09. Standard Test Methods for Laboratory Determination of Density (Unit Weight) of Soil Specimens (2018)
24. ASTM, ASTM D4531-15. Standard Test Methods for Bulk and Dry Density of Peat and Peat Products (2015)
25. R. López-Vizcaíno, E.V. dos Santos, A. Yustres, M.A. Rodrigo, V. Navarro, C.A. Martínez-Huitle, Calcite buffer effects in electrokinetic remediation of clopyralid-polluted soils. *Sep. Purif. Technol.* **212**, 376–387 (2019)
26. T. Grundl, C. Reese, Laboratory study of electrokinetic effects in complex natural sediments. *J. Hazard. Mater.* **55**, 187–201 (1997)
27. ASTM, ASTM D6913/D6913M—17. Standard Test Methods for Particle-Size Distribution (Gradation) of Soils Using Sieve Analysis (2017)
28. ASTM, ASTM D7928-17. Standard Test Method for Particle-Size Distribution (Gradation) of Fine-Grained Soils Using the Sedimentation (Hydrometer) Analysis (2017)
29. A. Bieganski, M. Ryżak, A. Sochan, G. Barna, H. Hernádi, M. Beczek, C. Polakowski, A. Makó, Chapter 5: Laser Diffractometry in the Measurements of Soil and Sediment Particle Size Distribution, in *Advances in Agronomy*, ed. by D. L. Sparks, (Academic Press, London, 2018), pp. 215–279
30. A. Scheuermann, A. Bieberstein, Determination of the Soil Water Retention Curve and the Unsaturated Hydraulic Conductivity from the Particle Size Distribution, in *Experimental Unsaturated Soil Mechanics*, ed. by T. Schanz, (Springer Berlin Heidelberg, Berlin, Heidelberg, 2007), pp. 421–433
31. M.D. Fredlund, G.W. Wilson, D.G. Fredlund, Use of the grain-size distribution for estimation of the soil-water characteristic curve. *Can. Geotech. J.* **39**, 1103–1117 (2002)
32. Soil Science Division Staff, Soil Survey Manual, in *USDA Handbook 18*, ed. by C. Ditzler, K. Scheffe, H. C. Monger, (Government Printing Office, Washington, 2017), p. 603
33. ASTM, ASTM D2487-17. Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System), (2017)
34. ASTM, ASTM D3282-15. Standard Practice for Classification of Soils and Soil-Aggregate Mixtures for Highway Construction Purposes (2015)
35. F. Bergaya, G. Lagaly, *Handbook of Clay Science* (Elsevier, London, 2013)
36. T.A. Hueckel, Water–mineral interaction in hygromechanics of clays exposed to environmental loads: a mixture-theory approach. *Can. Geotech. J.* **29**, 1071–1086 (1992)
37. A.T. Yeung, C.-n. Hsu, R.M. Menon, Physicochemical soil-contaminant interactions during electrokinetic extraction. *J. Hazard. Mater.* **55**, 221–237 (1997)
38. D.H. Gray, J.K. Mitchell, Fundamental aspects of electro-osmosis in soils. *J. Soil Mech. Found. Div.* **93**, 209–236 (1967)
39. R. López-Vizcaíno, C. Sáez, P. Cañizares, V. Navarro, M.A. Rodrigo, Influence of the type of surfactant on the mobility of flushing fluids for electro-remediation processes. *Sep. Sci Techn.* **46**, 2148–2156 (2011)
40. K.H. Head, *Manual of Soil Laboratory Testing. Volume 1: Soil Classification and Compaction Tests* (Whittles Publishing, Dunbeath, 2006)
41. ASTM, ASTM D4318—17e1. Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils (2017)
42. B. Voight, Correlation between Atterberg plasticity limits and residual shear strength of natural soils. *Geotechnique* **23**, 265–267 (1973)
43. L.D. Wesley, Residual strength of clays and correlations using Atterberg limits. *Geotechnique* **53**, 669–672 (2003)

44. M.A. Kanji, The relationship between drained friction angles and Atterberg limits of natural soils. *Geotechnique* **24**, 671–674 (1974)
45. J.M. Lee, C.D. Shackelford, C.H. Benson, H.Y. Jo, T.B. Edil, Correlating index properties and hydraulic conductivity of geosynthetic clay liners. *J. Geotech. Geoenviron.* **131**, 1319–1329 (2005)
46. A. Bouazza, S. Jefferis, T. Vangpaisal, Investigation of the effects and degree of calcium exchange on the Atterberg limits and swelling of geosynthetic clay liners when subjected to wet-dry cycles. *Geotext. Geomembr.* **25**, 170–185 (2007)
47. E. Çokça, Relationship between methylene blue value, initial soil suction and swell percent of expansive soils. *Turkish J. Eng. Environ. Sci.* **26**, 521–529 (2002)
48. J. Zhang, J. Peng, Y. Chen, J. Li, F. Li, Estimation of soil-water characteristic curve for cohesive soils with methylene blue value. *Adv. Civil Eng.* (2018)
49. M. Schaeffner, Introduction of methylene blue value of a soil into soil classification of recommendation for road earthworks. *Bull. Liaison Lab. Ponts Chaussees*, 9–16 (1989)
50. J.C. Santamarina, K.A. Klein, Y.H. Wang, E. Prentke, Specific surface: determination and relevance. *Can. Geotech. J.* **39**, 233–241 (2002)
51. Y. Yukselen, A. Kaya, Suitability of the methylene blue test for surface area, cation exchange capacity and swell potential determination of clayey soils. *Eng. Geol.* **102**, 38–45 (2008)
52. D. Hillel, *Introduction to Environmental Soil Physics* (Elsevier Science & Technology, Burlington, 2003)
53. D.G. Strawn, H.L. Bohn, G.A. O'Connor, *Soil Chemistry* (John Wiley & Sons, Incorporated, Somerset, 2015)
54. R.N. Yong, M. Nakano, R. Pusch, *Environmental Soil Properties and Behaviour* (CRC Press LLC, Baton Rouge, 2012)
55. N.M. Nagy, J. Konya, A.T. Hubbard, *Interfacial Chemistry of Rocks and Soils* (CRC Press LLC, Baton Rouge, 2009)
56. S.D. Haigh, A review of the interaction of surfactants with organic contaminants in soil. *Sci. Total Environ.* **185**, 161–170 (1996)
57. R.T. Martin, in *Adsorbed Water on Clay: A Review*, ed. By E. Ingerson. *Clays Clay Miner.* (1962), pp. 28–70
58. R.H. Brooks, A.T. Corey, *Hydraulic Properties of Porous Media* (Colorado State University, Fort Collins, 1964)
59. G.S. Campbell, A simple method for determining unsaturated conductivity from moisture retention data. *Soil Sci.* **117**, 311–314 (1974)
60. D.G. Fredlund, X. Anqing, Equations for the soil-water characteristic curve. *Can. Geotech. J.* **31**, 521–532 (1994)
61. W.R. Gardner, Some steady-state solutions of the unsaturated moisture flow equation with application to evaporation from a water table. *Soil Sci.* **85**, 228–232 (1958)
62. P.H. Groenevelt, C.D. Grant, A new model for the soil-water retention curve that solves the problem of residual water contents. *Eur. J. Soil Sci.* **55**, 479–485 (2004)
63. K. Kosugi, Lognormal distribution model for unsaturated soil hydraulic properties. *Water Resour. Res.* **32**, 2697–2703 (1996)
64. M. Kutílek, Soil hydraulic properties as related to soil structure. *Soil Till. Res.* **79**, 175–184 (2004)
65. M.T. van Genuchten, A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* **44**, 892–898 (1980)
66. Meyer, P.D., Rockhold, M.L., Gee, G.W.: Uncertainty Analyses of Infiltration and Subsurface Flow and Transport for SDMP Sites, Pacific Northwest National Laboratory. U.S. Nuclear Regulatory Commission., (NUREG/CR-6565, PNNL-11705) NRC Job Code W6503 (1997)
67. Hem, J.D.: Study and Interpretation of the Chemical Characteristics of Natural Water. Water Supply Paper, U.S. Geological Survey, Reston, VA (1985), p. 263
68. Bartos, T.T., Ogle, K.M.: Water Quality and Environmental Isotopic Analyses of Ground-Water Samples Collected from the Wasatch and Fort Union Formations in Areas of Coalbed

- Methane Development—Implications to Recharge and Ground-Water Flow, Eastern Powder River Basin, Wyoming. Water-Resources Investigations Report 02-4045, USGS, Cheyenne, Wyoming (2002)
69. J.D. Rhoades, N.A. Manteghi, P.J. Shouse, W.J. Alves, Soil electrical conductivity and soil salinity: new formulations and calibrations. *Soil Sci. Soc. Am. J.* **53**, 433–439 (1989)
 70. R.B. McCleskey, D.K. Nordstrom, J.N. Ryan, Comparison of electrical conductivity calculation methods for natural waters. *Limnol. Oceanogr.-Meth.* **10**, 952–967 (2012)
 71. A. Tarantino, A.M. Ridley, D.G. Toll, Field Measurement of Suction, Water Content, and Water Permeability, in *Laboratory and Field Testing of Unsaturated Soils*, ed. by A. Tarantino, E. Romero, Y.-J. Cui, (Springer Netherlands, Dordrecht, 2009), pp. 139–170
 72. R. Bulut, E.C. Leong, Indirect Measurement of Suction, in *Laboratory and Field Testing of Unsaturated Soils*, ed. by A. Tarantino, E. Romero, Y.-J. Cui, (Springer Netherlands, Dordrecht, 2009), pp. 21–32
 73. K. Terzaghi, *Erdbaumechanik* (Deuticke, Vienna, 1925)
 74. A.W. Skempton, in *Terzaghi's Discovery of Effective Stress*. From Theory to Practice in Soil Mechanics (1960), pp. 42–53
 75. R. de Boer, W. Ehlers, The development of the concept of effective stresses. *Acta Mech.* **83**, 77–92 (1990)
 76. E.E. Alonso, J.M. Pereira, J. Vaunat, S. Olivella, A microstructurally based effective stress for unsaturated soils. *Géotechnique* **60**, 913–925 (2010)
 77. A.W. Bishop, The principle of effective stress. *Teknisk Ukeblad.* **106**, 859–863 (1959)
 78. R. López-Vizcaíno, V. Navarro, M.J. León, C. Risco, M.A. Rodrigo, C. Sáez, P. Cañizares, Scale-up on electrokinetic remediation: engineering and technological parameters. *J. Hazard. Mater.* **315**, 135–143 (2016)
 79. R. López-Vizcaíno, A. Yustres, M.J. León, C. Saez, P. Cañizares, M.A. Rodrigo, V. Navarro, Multiphysics implementation of electrokinetic remediation models for natural soils and porewaters. *Electrochim. Acta* **225**, 93–104 (2017)
 80. A.T. Yeung, J.K. Mitchell, Coupled fluid, electrical and chemical flows in soil. *Geotechnique* **43**, 121–134 (1993)
 81. V. Navarro, E.E. Alonso, Modeling swelling soils for disposal barriers. *Comput. Geotech.* **27**, 19–43 (2000)
 82. D.W. Pollock, Simulation of fluid flow and energy transport processes associated with high-level radioactive waste disposal in unsaturated alluvium. *Water Resour. Res.* **22**, 765–775 (1986)
 83. S. Barba, R. López-Vizcaíno, C. Saez, J. Villaseñor, P. Cañizares, V. Navarro, M.A. Rodrigo, Electro-bioremediation at the prototype scale: what it should be learned for the scale-up. *Chem. Eng.* **334**, 2030–2038 (2018)
 84. R. López-Vizcaíno, C. Risco, J. Isidro, S. Rodrigo, C. Saez, P. Cañizares, V. Navarro, M.A. Rodrigo, Scale-up of the electrokinetic fence technology for the removal of pesticides. Part II: Does size matter for removal of herbicides? *Chemosphere* **166**, 549–555 (2017)