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## Macroscopic properties of soils controlled by the diffuse double layer around particles

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### ABSTRACT

Physic and chemical properties of liquids and particle-fluid interaction (PFI) mechanisms control relevant soil properties. Chemical properties of pore fluids affect mainly the structure and hydraulic conductivity of fine soils with high specific surface. In this work, the hydraulic conductivity of three different soils (sand, silt and a bentonite-sand mixture) was measured using fluids with different chemical properties: deionized water, kerosene, 1N Sodium chloride solution and a solution with 20% of ethylic alcohol. The hydraulic conductivity was determined by following the falling head test procedure and using three different rigid-wall permeameters. Results show that the hydraulic conductivity of coarse granular soils does not depend on fluid chemistry since PFI have negligible effect on soil behavior. In this case, the dry density of soils and viscosity of fluids determine the observed behavior. On the other hand, the hydraulic conductivity of fine soils (silts and bentonite-sand mixtures) shows a dispersion of five orders of magnitude when tested at the same dry density but with different permeating fluids. © 2010 Trade Science Inc. - INDIA

### KEYWORDS

Flow;  
Particle-fluid interaction;  
Soil fabric;  
Double layer;  
Soil pollutant.

### INTRODUCTION

The hydraulic conductivity of porous media governs the displacement of fluids in the pore space, contaminant displacement, and pore pressure dissipation. These aspects are of fundamental importance for the strength-strain behavior of soils, landslide events, soil settlement analysis, etc. Hydraulic conductivity is affected by soil and liquid properties as explicitly shown in the Kozeny-Carman equation<sup>[11,12,13]</sup>. In the first case,

relevant soil properties include void ratio, saturation degree, particle size, soil fabric, and specific surface<sup>[17]</sup>. In the second case, significant properties of permeating liquids consist of density and viscosity<sup>[4]</sup>. In addition, there are a large amount of fine soils where the liquid-solid interaction can be the primary factor controlling the displacement of fluids inside the soil pores<sup>[14]</sup>. In general, particle-fluid interaction (PFI) mechanisms are of fundamental importance in the case of fine plastic soils<sup>[9,10]</sup>. This effect is related to soil microstructure,

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diffuse-double layer thickness, molding water content and compaction energy and method<sup>[9,10]</sup>.

The specific surface of soils increases as particle size decreases (higher wetted surface area per unit volume of particles). In this case, the interaction between the liquid phase surrounding particles and the mineral surface results in complex attractive and repulsive forces. This force balance, known as DLVO theory (named after Derjaguin and Landau, Verwey and Overbeek), governs fabric formation in soils<sup>[11,12,13]</sup>, entertains water molecules and hydrated counter ions at short distances from the mineral surface<sup>[1]</sup>, and restricts the fluid displacement through the soil<sup>[6]</sup>. Sivappalaiah<sup>[15]</sup>, Sridharan and Nagaraj<sup>[15,16]</sup>, and Lee et al.<sup>[8]</sup> show that the effect of PFI on permeability can be analyzed in terms of the induced changes in soil liquid limit and plastic index due to the chemical nature of the liquid phase (e.g. ion concentration, valence, or presence of non-polar molecules).

The primary purpose of this study is to analyze the influence of the affinity between different liquids and mineral particles on the hydraulic conductivity and liquid limit of soils. This effect is evaluated in three soils of varied specific surface: sands, silts and a sand–bentonite mixture. The interaction between these sediments and liquids is evaluated by using permeating fluids with different chemical and dielectrical properties. Obtained results allow us to identify the influence of the diffuse-double layer and PFI mechanisms on the hydraulic conductivity of low and high specific surface soil.

### PARTICLE-FLUID INTERACTION

#### Soil minerals in contact with water and inorganic pollutants

Interaction mechanisms arise when the specific surface of particles is significant since, in this case, the effect of electrical forces on soil behavior dominates with respect to the effect produced by gravity (the opposite takes place in the case of coarse soils). Above the point of zero charge, or the pH value at which the electrical charge density on a surface is zero, clay particles have negative surface charge that interact with the positive charge of cations adjacent to the surface<sup>[11,12,13]</sup>. In case of dry soils, these cations are found either fixed to the mineral surface or as precipitated salts. When the soil wets, these cations and anions hydrate and distribute in

the space forming the diffuse double layer influenced by the surface electric potential<sup>[9,10]</sup>. The double layer thickness,  $\vartheta$  (m), also known as Debye-Hückel length, is related to the liquid properties as follows<sup>[1]</sup>:

$$\vartheta = \sqrt{\frac{\epsilon_0 R \kappa' T}{2F^2 c_0 z^2}} \quad (1)$$

where  $R = 8.314 \text{ J}/(\text{K}\cdot\text{mol})$  is the universal gas constant,  $F = 9.6485 \times 10^4 \text{ C}/\text{mol}$  is the Faraday's constant,  $\epsilon_0 = 8.85 \times 10^{-12} \text{ F}/\text{m}$  is the vacuum dielectric permittivity,  $T = \text{temperature (K)}$ ,  $c_0 = \text{bulk electrolyte concentration (mol}/\text{m}^3)$ ,  $k' = \text{real relative permittivity}$ , and  $z = \text{ionic valence}$ . The change of any of these properties induces alterations in the soil microstructure affecting the hydraulic conductivity<sup>[6]</sup>.

#### Soil minerals in contact with organic pollutants

Different interaction mechanisms can be observed when soils are in contact with organic molecules. In the case of coarse grained soils, e.g. sand and gravel, the PFI becomes negligible and the liquid moves in the pores mainly governed by gravity and viscous forces. When the soil contains clay minerals, additional interaction mechanisms arise: a) intercalation, b) ion exchange, and c) adsorption<sup>[7]</sup>. If the organic molecules are non-polar, also known as non-aqueous phase liquids (NAPL), soils are more stable than in presence of water, clays behaves as non plastic and show no swelling potential<sup>[3]</sup>. Conversely, organic molecules containing polar groups with hydroxyl or carboxyl can form aqueous solutions, and hydrate ions. Then, a diffuse double layer develops around soil particles similarly to that expected in soil-water mixtures<sup>[5]</sup>.

Although these phenomena have being extensively studied in the past two decades<sup>[9,10]</sup> the relevant contribution of this research is to focus on the effect that produce polar and non-polar organic molecules on particle arrangements and two corresponding macroscopic emergent behaviors: a) soil liquid limit and b) soil hydraulic conductivity.

### MATERIALS AND METHODS

The soils tested in this study are sand, silt, and a mixture of bentonite (25%) with silica sand (75%). TABLE 1 shows the physical properties of these soils. The selected soils cover all the range of expected specific surface for any natural sediment, which is the fun-

TABLE 1 : Main physical properties of tested soils

Property	Bentonite	Silt	Sand
Passing sieve #200, %	100	96	1.2
Particle size lower than 2 $\mu$ m, %	80	4	0
Specific gravity	2.71	2.67	2.68
Specific surface, m <sup>2</sup> /gr	731	3	<0.01
Unified soil classification	CL	ML	SP

TABLE 3 : Influence of fluid properties on liquid limit (LL) and plastic index (IP)

Soil		Water	NaCl 1N	Kerosene	Ethylic alcohol
Sand	LL	13	13	5	12
	IP	0	0	0	0
Silt	LL	27	27	25	24
	IP	2.8	6.7	0	4
Bentonite	LL	301	111	33	388
	IP	231	55	0	339

damental property for the interaction mechanisms studied in this work.

The selected permeating fluids are: a) deionized water, b) 1N NaCl electrolyte, c) 20% ethylic alcohol solution (v/v), and d) kerosene. Some relevant physical and chemical properties of these liquids are summarized in TABLE 2. These liquids were selected due to their different dielectric permittivity and expected interaction with the electrical surface charges of soil particles. Kerosene has low real permittivity and behaves inside the soil pores as any other non-aqueous phase liquid (NAPL) when sorption and degradation are negligible. Water and the electrolyte have the higher expected dielectric permittivity and the different ionic concentration helps to evaluate the influence of electrical charges and hydrated ions surrounding soil particle. Finally, the ethylic alcohol has a permittivity that falls between that of water and kerosene.

Soils were oven dried at 105 Celsius degree, mixed with any of the liquids shown in TABLE 2, and compacted inside a rigid-wall permeameter in three layers of equal height by giving 25 blows per layer with a 10.95mm inner diameter blunt tip bar. The compaction moisture content was 10% in all cases except for the sand-bentonite mixture where the liquid content was higher than the bentonite liquid limit in order to ensure homogeneity. Hydraulic conductivity tests were performed by following the falling head method (ASTM D 5856<sup>[21]</sup>) and using as permeating liquid the same employed for compaction. The hydraulic gradient varied

TABLE 2 : Main physical properties of fluids (at 20°C)

Property	Water	Kerosene	Ethylic alcohol
Chemical formula	H <sub>2</sub> O	N/A	CH <sub>3</sub> -CH <sub>2</sub> -OH
Density, Kg/m <sup>3</sup>	1000	800	790
Viscosity, mm <sup>2</sup> /s	1.00	2.71	1.52
Dielectric permittivity	78.5	2.1	25.7

from 15 to 5 in all cases during tests. Each sample was tested several times until constant values of hydraulic conductivity were obtained.

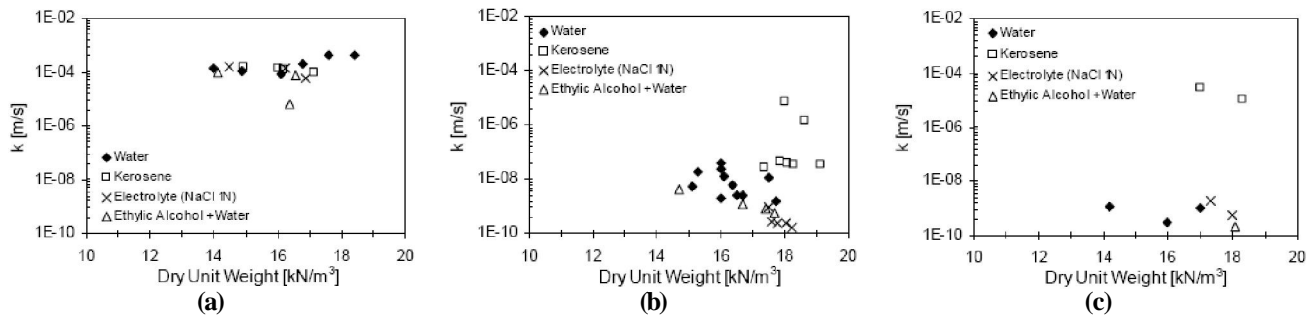
TABLE 3 shows the liquid limit (LL) and plastic index (PI) of each soil with all the fluids used as permeating liquids. The LL of bentonite measured with the NaCl solution is lower than that measured with water, as previously determined by Lee et al.<sup>[8]</sup>. In the case of the sand and silt specimens this effect cannot be detected probably because of the low effect of PFI in these low specific surface materials. In the case of kerosene all samples show no plasticity and a LL lower than that measured with water, since kerosene can neither hydrates counter ions nor develops double layer around mineral particles. Finally, in the case of the ethylic alcohol solution, the observed behavior is similar to that of soil-water mixtures.

## RESULTS

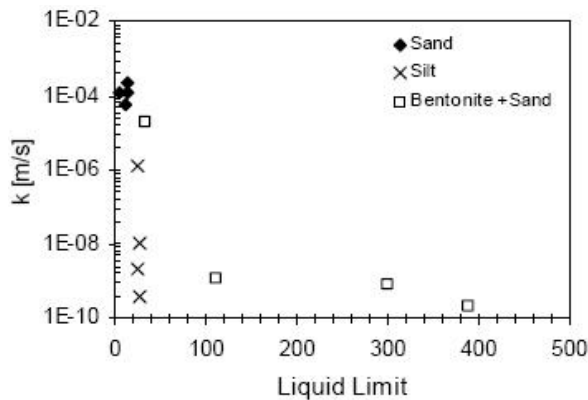
Figure 1 shows the hydraulic conductivity of compacted sand (a), silt (b) and sand-bentonite mixture (c) permeated with the liquids shown in TABLE 2, as a function of the dry unit weight. In the case of the tested sand, silt and sand-bentonite mixtures permeated with water, the change of unit weight (or void ratio) and specific surface are the main factors controlling the observed hydraulic conductivities, in agreement with the Kozeny-Carman model. In addition, the change of specific surface justify the several orders of magnitude of difference observed in soil permeability, while the dry unit weight and corresponding void ratio fall in a very narrow range for the three soils tested here.

The hydraulic conductivities of sand (Figure 1a) fall in a very narrow range of values, one order of magnitude, regardless the permeating fluid type. Then, the presence of ions or organic molecules in the permeating liquid produces negligible PFI mechanisms capable of alter the displacement of liquids inside the sand pores. In this case, the effect produced by gravity forces prevails over the electrical forces (DLVO) because of the

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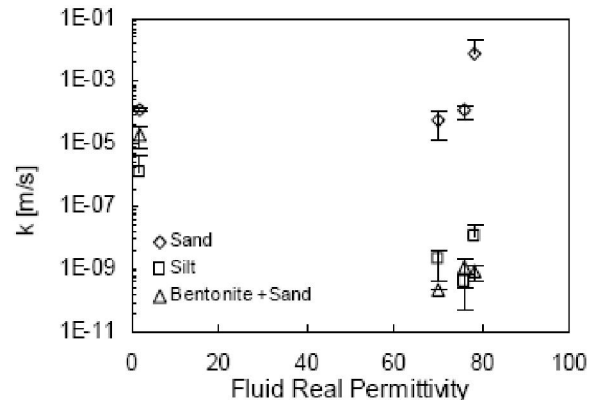
**Figure 1 : Influence of the permeating fluid on the hydraulic conductivity: a) sand, b) silt, and c) bentonite-sand mixture**



**Figure 2 : Influence of liquid limit on the hydraulic conductivity**

low specific surface of sand. The compacted silts specimens (Figure 1b) have hydraulic conductivities that vary from  $7.5 \times 10^{-6}$  to  $1.6 \times 10^{-10}$  m/s depending on the chemical properties of the permeating liquid. In general, the specimens compacted and permeated with water, electrolyte or water-alcohol solutions have lower conductivities than that observed with kerosene. A similar trend is observed for the sand-bentonite mixtures but in this case, the increase of the hydraulic conductivity of specimens compacted and permeated with kerosene in comparison with those permeated with water is close to 5 orders of magnitude. Nevertheless, the differences in fluid density and viscosity shown in TABLE 2 are not sufficient to explain these trends.

Soil properties that depend on PFI mechanisms (e.g. LL and  $k$ ) are significantly influenced by the chemical properties of the liquid surrounding particles when the specific surface of soil particles is higher than  $1\text{m}^2/\text{g}$ <sup>[11,12,13]</sup>. In the case of LL, the expected changes are related to the relative importance of the diffuse double layer respect to the volumetric content of free water inside the pores<sup>[9,10]</sup>. The figure 2 summarizes the influence of the LL on the mean hydraulic conductivity of compacted specimens determined with different liquids. The low specific surface of sand is responsible of the



**Figure 3 : Relationship between hydraulic conductivity and real dielectric permittivity of the fluid inside the pores**

insignificant effect of fluid chemistry on  $k$ . For high specific surface materials,  $k$  reduces when the LL increases as a result of PFI mechanisms<sup>[8,15,16]</sup>. This phenomenon was clearly identified in the bentonite-sand mixtures as shown in figure 2.

Behavior of silt and clay in contact with the electrolyte and alcohol solution depends on the thickness of the diffuse double layer (Eq. (1)), because the displacement of hydrated ions is affected by the negative electrical surface charge of minerals which also affects fluid displacement inside the pores. However, all soils show similar behavior when are permeated with kerosene since this liquid can neither hydrate ions nor form a double layer regardless the soil specific surface.

Figure 3 shows the influence of the real dielectric permittivity of the permeating liquid on  $k$ . Error bars represent  $\pm 1$  standard deviation. The variability of  $k$  respect to any liquid is mainly affected by the specimen void ratio (assumes that the chemical properties of the permeating liquid do not change). In addition, the mean value of  $k$  is associated to the fluid chemical properties. In the case of sand,  $k$  is almost the same no matter what is the liquid real dielectric permittivity. However, in the case of fine soils,  $k$  decreases when the liquid has higher dielectric permittivity which enlarges the thick-

ness of double layers (Eq. (1)). These results reveal the relevance of the chemical properties of liquids and the interaction between liquid and minerals on  $k$ .

## CONCLUSIONS

This work analyzes the relevance of PFI mechanisms on the hydraulic conductivity of sand, silt and sand-bentonite mixtures permeated with water, electrolytes and organic fluids. The main conclusions of this work can be summarized as follows:

- In contact with kerosene, all soils show no plasticity because of the non-polar nature of this liquid, their incapacity to hydrate ions and to form diffuse-double layers around soil particles. Then, the measured hydraulic conductivity respect to kerosene results higher than that measured with water since the total pore space is available for the displacement of the liquid.
- Particle-fluid interaction becomes of relevance in soils with high content of clay and high specific surface materials. In this case, the hydraulic conductivity may vary up to 5 orders of magnitude depending on the chemical and dielectrical properties of the permeating liquid, which control electrochemistry at short distance from the particles. Conversely, sand and very low specific surface materials have conductivities that fall in a narrow range regardless the dielectric constant of the fluid surrounding soil particles. In this last case the relative importance of the water forming the diffuse-double layer respect to bulk water and the mass of soil particles becomes negligible.
- At higher soil plasticity measured with water, higher is the observed increase of hydraulic conductivity when the soil is permeated with non-polar liquids (e.g. kerosene, NAPLs). The thickness of the diffuse-double layer is responsible of the low hydraulic conductivity observed in soils with high plasticity (and liquid limit).

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