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Surface charge properties of clays with emphasis on smectites

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***Abstract* – Smectitic clays display remarkable properties when dispersed in water due to their surface charge. This charge stems from various substitutions in their crystal structure both in tetrahedral and octahedral sites, which yield layer charge. Although the layer charge has been linked to several water-rock properties of smectitic clays namely cation exchange capacity, swelling and viscosity, it is a microscopic property referring to the unit cell i.e. at atomic level. In contrast smectite-water properties are macroscopic and refer to smectite particles. Therefore recently we introduced the term of *fundamental particle charge* (fpc) which pertains to the smectite particles rather than the unic cell. The Fpc is a macroscopic property which is useful in understanding the behaviour of smectite-water systems and interpreting smectite-water properties. In addition the fpc approach might be useful in soil stabilization, because it can assist in predicting failures.**

I. INTRODUCTION

Clay minerals are important components of soils, sediments and natural waters which often control the kinetics and deposition of different organic and inorganic species. Interfacial phenomena at clay/water interface are usually controlled by electrokinetic properties including zeta potential (zp), the structure of electrical double layer (EDL), surface potential, and isoelectric point (iep). These properties are linked to the charged surfaces of the clay minerals. Although most compounds acquire a surface electric charge, which is non-permanent, when immersed in a polar liquid such as water, several clay minerals like smectite, vermiculite and illite possess permanent negative charge (i.e. charge deficit) which controls their behaviour in soils and sediments. Most important, it affects soil stability, through swelling and flocculation/deflocculation, which in turn pose serious threats in engineering and construction works. In this sense, layer charge is an vital parameter which needs to be determined in order to interpret clay:water properties. Smectite is the most important clay mineral in terms of ion exchange, swelling, rheological and thixotropic properties [1]-[3], thus affecting the stability of soils. These properties are linked with the permanent layer charge, which in the case of smectite varies between 0.2 and 0.6 e/huc and which yields charged surfaces. Therefore the influence of layer charge and the surface charge properties of smectites on the organization of soil and the clay fraction is an important parameter which will be presented in this contribution.

II. LAYER CHARGE AND SMECTITE-WATER PROPERTIES

Layer charge is an important intrinsic property of smectites which stems from substitutions in the octahedral and/or tetrahedral sheet or from vacancies in the octahedral sheet. The layer charge is balanced by the interlayer cations which are exchangeable. There are four methods for determining layer charge: the structural formula method (SFM); the alkylammonium method AMM); the potassium saturation method (KSM) which has been calibrated with the SFM; and the recently proposed Li-fixation method [4]. The layer charge affects important physical water-rock properties of smectites. Smectites with high layer charge tend to form thicker quasicrystals than their low charge counterparts. Using the notion of [5], quasicrystals are stacks of 2:1 phyllosilicate layers oriented with parallel *c* axes and randomly oriented *a* and *b* axes (Figure 1b). Actually most clayey grains in soils consist of aggregates of quasicrystals (Figure 1a), which may break up into smaller ones by hydrodynamic forces and can be almost completely delaminated in dilute suspensions, when saturated with Na or Li cations (Figure 1c). Conversely, they may combine and form larger quasicrystals if their kinetic energy suffices to overcome the double layer repulsion [6].

Smectites with low layer charge have smaller cation exchange capacities (CECs) than their high-charge counterparts. This is expected because the CEC is directly associated with layer charge. However during crystalline swelling, the activity of water at which the transition from two to three water layers during hydration and dehydration follows a different trend, because it increases with increasing layer charge. This suggests that low-

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charge smectites have greater swelling capacity than their high charge counterparts. In crystalline swelling 0 to 4 discrete layers of water molecules are intercalated in the interlayer between individual 2:1 layers within a smectite quasicrystal. Layer hydrates with 0, 1, 2, 3, and 4 layers of water molecules are distinguished by d*001* (basal) spacings of approximately 10.0, 12.5, 15.0, 17.5 and 20.0 Å, respectively. In contrast, data on the influence of layer charge on double layer (osmotic) swelling are inconclusive, although in general low-charge smectites have greater swelling capacity than high-charge smectites. Theoretical calculations based on the fundamental Gouy-Chapman equation in the diffuse double layer theory, which describes the relationship between the surface-charge density, the surface potential, the valence of exchangeable cations and the electrolyte concentration, do not predict significant influence of the layer charge for distances greater than 5 Å from the smectite surface [1]. In contrast, it has been well established by the pioneering work of [7] and verified by numerous subsequent workers, that double layer swelling is controlled by the electrolyte concentration of smectite suspensions. In this aspect the electrolyte concentration in solution controls the flocculation of smectite particles. This is an important property which affects the stability of smectitic soils and is related with soil creeping and landslides of clayey masses especially after heavy rainfalls along hill slopes.

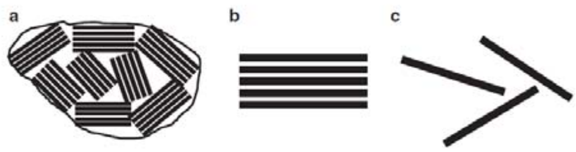

Fig. 1. Schematic representation of smectite (a) particle or aggregate (b) quasicrystal and (c) fundamental particles. The outline of the smectite particle (or aggregate) denotes a smectite grain (from [6]).

Smectites are often used in suspensions, which can display Newtonian, Bingham plastic, shear thickening (pseudoplastic) or shear thinning (dilatant) behaviour and may develop yield stress. Moreover they can develop time-dependent phenomena such as thixotropic or rheopectic (antithixotropic) behaviour. The limited existing data suggest that, in general, low-charge smectites form more viscous suspensions than their high-charge counterparts. In addition the area of the thixotropic loops in smectite rheograms were also found to be dependent on layer charge. This behaviour would be more or less expected, because due to the presence of electric charge, the colloidal properties of smectite particles are expected to depend on repulsive forces due to the overlap of their double layers (electroviscous effect) and on attractive interactive forces which lead to flocculation, in addition to Brownian forces and to hydrodynamic forces. However, due to the limited role of layer charge on osmotic swelling, its influence on the double layer swelling and the viscosity is attributed to the formation of quasicrystals and their ability to breakup by hydrodynamic forces under shearing rather than to the electroviscous effect and the particle interactions in suspension [1],[2]. Actually the real smectite suspensions consist of quasicrystals rather than isolated particles even if the smectites contain Na- or Li in the interlayer sites.

III. THE CONCEPT OF FUNDAMENTAL PARTICLE CHARGE

Notwithstanding the possibility for influence of layer charge on clay-water properties, still it is a property of the unit cell, i.e. it refers to the atomic level and it is not linked directly to the smectite particles. In contrast, the colloidal properties are macroscopic and refer to particles consisting of an unknown number of unit cells (Figure 2). The number of the unit cells per particle depends on the smectite particle size. Recently [8] proposed a model for calculation of the charge of fundamental particles of smectites and introduced the concept of '*fundamental particle charge*' (Fpc). Moreover, they examined how this charge may affect important smectite:water properties such as viscosity, free swelling and the tendency to form quasicrystals. The fundamental particles are individual or free particles that yield single-crystal electron diffraction patterns from the *ab* plane [9]. In the case of pure smectite, each fundamental particle is 10 Å thick, it has variable basal area and carries electric charge balanced by the exchangeable cations. The Fpc is given by the following equation [8]:

$$Fpc = 2 \times A \times \sigma_o$$

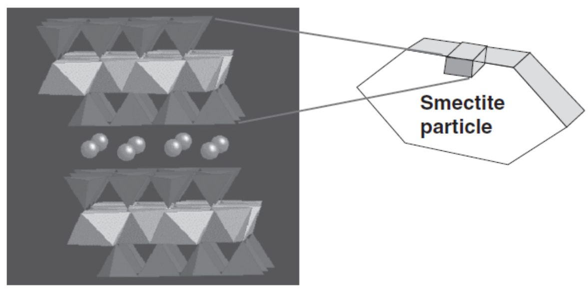

Fig. 2. Schematic relationship between unit cell and a fundamental smectite particle (from [6]).

where A is the is the basal area of the smectite fundamental particle and σ_o is the surface charge density in C/m^2 given by the formula: $\sigma_o = 1.602 \times 10^{-19} \times \xi / (\alpha \times \beta)$, were 1.602×10^{-19} is the elementary charge of one electron in Coulombs, is the layer charge in e/huc and α and β are the dimensions of the smectite unit cell. The Fpc is the sum of the layer charges in Coulomb of all the unit-cell charges in the fundamental particle [8]. It contains additional information about the electric charge of the smectite particles compared to the layer charge, because it combines the data of the surface-charge density and the area of each of the two basal surfaces (size of the fundamental particle). In addition, the approach normalizes the particle populations in the suspensions relative to a reference sample with minimum number of quasicrystals, i.e. to that closer to complete isolated particles rather than to a constant smectite concentration (i.e. w/v). This is because two suspensions with similar concentration will have different smectite-water properties if they contain quasicrystals with different thickness, because they will contain different number of particles.

IV. IMPORTANCE OF THE FUNDAMENTAL PARTICLE CHARGE

The Fpc is a new concept for smectites and it is useful in understanding the behaviour of smectite-water systems and interpreting smectite-water properties. This is because smectites with small layer charge may well form particles with large Fpc values if the particle area is large and *vice versa*. For instance this is the case of Wyoming smectites. It follows that the difficult part of this approach is to determine the basal area of the smectite fundamental particle A, because as it was noted before the smectite suspensions do not consist of free particles, but contain quasicrystals of unknown thickness. On the other hand estimation of σ_o can be easily achieved by any of the methods described before (i.e. SFM, AAM, KSM or Li-fixation), and after determination of the *a* and *b* parameters of the smectites. This is easily achieved by routine XRD analysis of random powder of the clay fractions containing the smectite.

The importance of the fundamental particle charge, which also is a macroscopic property, has been evaluated and the results are promising. Indeed, an important outcome of this approach is the observation that smectites with greater fpc tend to form larger quasicrystals and simultaneously greater swelling and viscosity, which might be considered as an apparent contradiction. However this contradiction might be resolved if it is considered that quasicrystals consisting of larger particles i.e. having large fpc, also break up easier to thinner particles when dispersed in water and subjected in hydrodynamic shear force. On the other hand the dependence of smectite-water properties on layer charge can also be explained, considering that these experiments were performed on suspensions containing smectites formed under very similar geological conditions. In this case the average smectite crystallite size is expected to be comparable among the various samples and the differences in smectite-water properties might be directly linked to layer charge. However, this might not be the case when smectites formed under different geological environments and mechanisms are compared.

Finally, in the case of soil stabilization, the fpc approach will be useful because it can assist in predicting failures. For instance, the deflocculation of clay minerals present in soils has been invoked as an important mechanism triggering soil creeping and eventually landslide incidents. In natural soils systems, most of the water present in pore solutions resides in intraaggregate porosity and only a fraction is directly adsorbed on the clay surface if the clay is flocculated. The latter occurs if the pore solution has a high concentration of electrolytes, as is the case with soft marine sediments and the soils developed upon them. If deflocculation occurs by dilution of the pore water, swelling of smectite will take place, initially crystalline and then if the water:soil ratio is adequate, osmotic. In this case swelling will be affected by the fpc of the particles of the swelling minerals mostly smectite. Determination of the fpc of the smectites present will assist in assessing the swelling capacity of the soils and thus in predicting their deflocculation behaviour and their capacity to induce landmass movements.

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