Nanomorphology of montmorillonite particles: Estimation of the clay edge sorption site density by low-pressure gas adsorption and AFM observations

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ABSTRACT

Dry and in situ (fluid-cell) Atomic Force Microscopy (AFM) and Low-Pressure Gas Adsorption experiments were used to investigate the surfaces of pure Na-smectite particles. These two techniques permit the identification of different surfaces of the platelets (lateral, basal, and interlayer surfaces) and to quantify their surface area. Calculation of the surface area was done for AFM, by measuring directly the dimensions of the clay particles on AFM images, and for gas adsorption experiments, by applying the Derivative Isotherm Summation (DIS) procedure designed by Villiéras et al. (Villiéras et al. 1992, 1997a, 1997b).

In the present study, we find a discrepancy between measurements of the basal and interlayer surface area. This difference is due to the stacking of platelets in dry conditions compared to their dispersion in aqueous suspension. A particle is estimated to be formed of nearly 20 stacked layers in the dehydrated state used in the gas adsorption experiment, whereas it is estimated to be composed of only 1 or 2 layers in aqueous suspension, on the basis of AFM measurements. However, the two techniques give similar results for the lateral surface area of the platelets (i.e., about 8 m$^2$/g) and the perimeter to area ratio value of the particles because the stacking of platelets does not alter these values. This correlation confirms the effectiveness of the interpretation of the gas adsorption experiments lowest pressure domains as the adsorption on lateral surfaces.

The lateral surface area has important implications in the calculation of specific sorption site density on clay material. The relevance of the lateral surface area value (8 m$^2$/g) was tested subsequently with sorption data found in the literature. Based on those results, we show that one essential parameter for the calculation of particle edge-site density is the mean perimeter to area ratio value. This parameter can be obtained by microscopic techniques but the measurement is tedious. The good correlation between the AFM results and the DIS-method results confirms that the latter procedure offers a quick and reliable alternative method for the measurement of the lateral surface area. AFM experiments can be further conducted to constrain the dispersion around the DIS value and the anisotropy of suspended particles.

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INTRODUCTION

Sorption mechanisms on clay surfaces have been studied for decades: inorganic cation exchange on the interlayer and basal surfaces (e.g., Sposito 1981), specific pH dependent sorption of inorganic cations and anions on the edges (e.g., Sposito 1984), sorption of organic hydrophobic molecules on the interlayer and basal surfaces (e.g., Schwarzenbach et al. 1993; Titiloye and Skipper 2000), and binding of organic matter on the edges (e.g., Claret et al. 2002). Edge-sorption mechanisms are related to the acid-base properties of the clay edges, whereas sorption on the interlayer and basal planes are related to the permanent charge generated by the clay structure (cation exchange) or to the presence of hydrophobic patches on these planes (hydrophobic adsorption).

It appeared in the past twenty years that two types of reaction are necessary to explain ion adsorption on clay surfaces.

The first one is a cation-exchange mechanism that occurs on the interlayer and basal planes (Fig. 1), as described by Sposito (1981). It originates from the presence of a permanent negative structural charge in the alumino-silicate layer created by isomorphous substitutions in the lattice. The quantity of exchange sites ($s_0$) can be derived from the structural formula, and is compensated by “exchangeable cations” that generally form outer-sphere complexes with siloxane cavities (Sposito 1981, 1984). The second type of reaction is the pH-dependent, specific sorption on the clay edges (e.g., Fletcher and Sposito 1989; Avena et al. 1990; Charlet et al. 1993; Wanner et al. 1994; Zachara and Smith 1994; Baeyens and Bradbury 1997; Bradbury and Baeyens 1997). On these clay edges, the proton surface charge ($s_n$) depends on physico-chemical solution parameters (pH, ionic strength) that control the protonation state of the surface (e.g., Fletcher and Sposito 1989; Avena et al. 1990; Charlet et al. 1993; Wanner et al. 1994; Zachara and Smith 1994; Baeyens and Bradbury 1997; Bradbury and Baeyens