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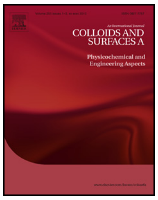

Influence of mineralogical and morphological properties on the cation exchange behavior of dioctahedral smectites

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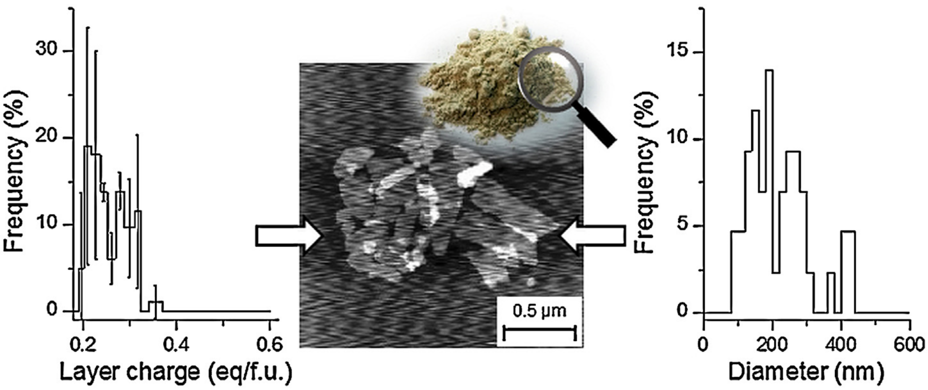
HIGHLIGHTS

- Dioctahedral smectites display structural heterogeneities and variation in size.
- Wyoming smectite is significantly different from other dioctahedral smectites.
- CEC increases with pH similar for natural and reduced charge montmorillonites (RCM).
- RCM are suitable to study edge surface properties of montmorillonites.

GRAPHICAL ABSTRACT



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ABSTRACT

Structure and morphology determine the smectites properties. Thereby, edge sites play a key role for the reactivity and colloidal behavior of the smectite. Even so, the edge surface area represents only 1–3% of the total surface area its contribution is up to 10% of the cation exchange capacity (CEC). Na-saturated dioctahedral smectites <0.2 µm were characterized in detail with respect to their structure (layer charge, octahedral cation distribution, iron content, and layer charge distribution within tetrahedral and octahedral sheets). Furthermore, reduced charge montmorillonite (RCM) of these materials were studied. Particle dimension was estimated from argon adsorption, calculation of specific surface area and direct observation of single layers by atomic force microscopy (AFM), which also revealed morphology and particle size distribution of single layer. CEC was measured both for Na-saturated samples and RCM using the Cu-trien method over a pH range of 4–9. The Wyoming smectite with a mean layer diameter of 277 nm and a low layer charge of 0.26 eq/f.u. differs strongly from the others smectites with a mean layer diameter of about 100 nm and layer charges between 0.30 and 0.37 eq/f.u. Furthermore, the layer stacking

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is much higher for the Wyoming smectite in powder and RCM. Accordingly the edge properties differ between the four smectites. Based on calculation of edge site density and CEC measurements, we showed that the RCM can be used to study the edge site reactivity of the montmorillonites. The increase of CEC above their $pH_{PZC,edge}$ is equal for Na-saturated montmorillonite and RCM. The present study highlights the diversity in structure and morphology and resulting edge properties of four smectites.

1. Introduction

Smectite interfacial interactions with the environment, involving water binding and/or trace element sorption capacity, are mainly responsible for the bentonite properties in widespread applications, such as absorbents, binders in molding sands, or geotechnical barriers in waste repositories [1]. Chemical, mineralogical, and morphological properties of smectites associated with process parameters, such as pH and ionic strength of medium or temperature and pressure, determine their behavior [2]. The most common dioctahedral smectites belong to the montmorillonite–beidellite series with a general formula of $M^{\nu+}_{(x+y)/\nu}(Al, Fe(III))_{2-y}(Mg, Fe(II)_y)(Si_{4-x}Al_x)O_{10}(OH)_2$. Here, $x+y$ is the layer charge resulting from the substitutions within the tetrahedral and octahedral sheets ranging from 0.2 to 0.6 mol/formula unit (f.u.) and $M^{\nu+}$ denotes the interlayer monovalent or divalent cations [3]. Montmorillonites and beidellites are defined by a main layer charge located in the octahedral sheets ($x \ll y$) and in the tetrahedral sheets ($x \gg y$), respectively, with a low iron content. Permanent charge, independent of the pH induced by the layer charge, and variable charges induced by the amphoteric sites (silanols/aluminols) at the edges of the clay particle govern the charge's heterogeneity distribution [4]. It determines the stability and rheological properties of suspensions in particular [5]. The cation exchange capacity (CEC), one of the most important properties of smectite, originates mainly from the layer charge. However, about 10–20% of CEC are due to variable charges depending on the pH and ionic strength of the background electrolyte [6,7]. Distinction of the influence of smectite properties (layer charge, particle size . . .) and medium parameters (pH, ionic strength . . .) on the behavior is a challenge. An extensive database on acid–base potentiometric titration is available to characterize the acid/base properties of clays [8–13]. However, correlation with chemical and/or morphological parameters was restricted to a few samples [14]. Consequently, application of the data obtained to a few reference smectites for, e.g., predictive reactive transport modeling might imply unnecessary uncertainties. In order to assess bentonite performance and predict/control the long-term behavior of bentonites, a fundamental understanding of montmorillonite properties is required and their structure/functionality relation has to be identified.

Therefore, the aim of our study is to provide a sound characterization of the mineralogical properties in conjunction with morphological parameters as a basis for further research into the structure functionality of montmorillonite, including the trace element sorption properties, colloidal stability, and hydration behavior of technical bentonites.

2. Materials and methods

2.1. Materials origin

Four blended bentonites with a high dioctahedral smectite content [15–17] were selected: Calcigel® (Bavaria, Germany) [18,19] and Volclay® (Wyoming, USA) [20,21] formed by diagenetic alteration of volcanic ash, together with the Cabo de Gata bentonite (Almería, Spain) kindly supplied by ENRESA [22–24] and the bentonite P provided by Süd-Chemie AG (Germany) which were formed by hydrothermal alteration of pyroclastic rocks. The first three bentonites were characterized extensively as potential reference buffer/backfill materials in the context of a geotechnical barrier reported as Calcigel or Montigel [6,25,26], MX-80 [25–27], and Febex [13,28], respectively, just to mention a few references.

2.2. Material pre-treatment

Chemical treatments to separate the fraction <0.2 μm from the bulk bentonite were applied to reduce the cementing interactions of carbonates, iron (hydr)oxides, and organic materials [29,30]. Sets of 100 or 200 g of raw bentonite were purified according to the procedure detailed in Wolters et al. [15]: Carbonates were decomposed by an acetic acid-acetate buffer treatment [29]; iron (hydr)oxides as well as aluminum and manganese (hydr)oxides were dissolved by a buffered dithionite-citrate solution [31]; organic matters were decomposed by the addition of hydrogen peroxide [29]; and a 1 M sodium chloride solution for repeated washing to remove excess reactants was used. The Na-exchanged dispersions of the purified bentonites were dialyzed to remove chloride and surplus cations until the solutions reached a conductivity of 5 μS/cm. For this purpose, a cellulose hydrate Nadir®-dialysis tubing of average pore size of 25–30 Å was used. Then, a sequential fractionation was carried out according to Stokes' equivalent sphere diameter [32,33]. First, dispersions were passed through a 63 μm sieve to collect the sand fraction. Then, the clay fraction <2 μm was separated from the silt fraction 2–63 μm by successive gravitational sedimentation. The silt fractions 2–6.3, 6.3–20 μm, and then the remaining fraction 20–63 μm were obtained by several successive gravitational sedimentations. The clay fractions <0.2, 0.2–0.6 μm, and then the remaining fraction 0.6–2 μm were obtained by several successive centrifugal sedimentations from the <2 μm dispersion after 25 min at 4347 *g*-force and 10 min at 1206 *g*-force, respectively, at 20 °C (Heraeus Multifuge 3SR). All fractions were oven-dried at 60 °C and were gently ground in an agate mortar. The <0.2 μm fractions were stored at a relative humidity of 53% over $Mg(NO_3)_2$, the other fractions were stored in sealed containers for further investigations.

Subsamples <0.2 μm were Li-saturated by three exchanges with LiCl solution equivalent to 20-fold the CEC of the samples according to the homo-ionic exchange process described in Steudel and Emmerich [17]. Then, Li-saturated samples were heated at 300 °C for 24 h to obtain reduced-charge montmorillonites (RCM) according to the Hofmann–Klemen effect [34,35].

In the following sections, the notations B*X*-M0.2Na and B*X*-M0.2Li-300 are used for Na-saturated materials <0.2 μm and for RCM materials, respectively, with *X* = C, V, S, or P for Calcigel®, Volclay®, the Cabo de Gata, and the P bentonites.

2.3. Mineralogical and chemical characterization

Mineralogical identification was accomplished by X-ray diffraction (XRD) (Siemens D5000 diffractometer, Cu Kα radiation, scintillation detector, detector slits of 0.1 mm, divergence and antiscatter slits of 0.6 mm) using randomly oriented powders and