Research paper

Cation exchange capacity of natural and synthetic hectorite

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ABSTRACT

Cation exchange capacity (CEC) of smectites is a function of both layer charge and lateral layer dimension, the later ones determining their edge surface area. Two trioctahedral smectites similar in layer charge, the Na-saturated hectorite SHCa-1 $< 0.2\,\mu m$ and the synthetic Laponite® RD, were studied differing by morphology and particle size with a proportion due to the edge specific surface area of about 2.0% and 6.9%, respectively, considering single layers. The CEC of the materials was evaluated using the Cu-trien method over the pH range of 6 to 13. For this purpose, the Cu-trien method was evaluated for a use at pH above 10, out of the usual pH range of application. In addition, stability of clays was followed by analysing aqueous concentrations issued from the dissolution of the minerals. The CEC were measured at $83 \pm 1\,cmol(+)\,kg^{-1}$ at pH 7.9 for HtCa-0.2Na and $79 \pm 1\,cmol(+)\,kg^{-1}$ at pH 8.9 for Laponite® RD following the usual Cu-trien procedure without pH adjustment. The CEC ranged from 50 to 150 $cmol(+)\,kg^{-1}$ over the pH range of 6 to 13. The strong CEC increase at $pH > 10$ was correlated to the deprotonation of the silanol edge sites. The larger CEC development observed for Laponite® RD was related to its morphology and larger edge specific surface area. Estimation of the exchangeable cation population following the usual Cu-trien procedure led to an overestimation of Mg^{2+} and Li^+ due to partial clay dissolution at $pH < 10$.

1. Introduction

Natural swellable clay minerals control cation exchange and rheological properties of slurries in industrial processes and geotechnical applications (Christidis, 2013; Harvey and Lagaly, 2013). Laponite® RD, a synthetic trioctahedral smectite resembling hectorite, is widely used as rheological modifier in many applications and studied as model system to understand the rheological behaviour of dispersions of natural smectite (Ramsay, 1986; Mourchid et al., 1995; Willenbacher, 1996; Mourchid and Levitz, 1998; Levitz et al., 2000; Tombácz and Szekeres, 2004; Cummins, 2007; Ruzicka and Zaccarelli, 2011; Au et al., 2015). Laponite® RD is characterized by a monodispersed lateral layer dimension of diameter about 30 nm and a nominal layer charge of 0.35 eq per formula unit (f.u.) caused by substitution of Li^+ for Mg^{2+} in the octahedral sheet (Neumann, 1965; Avery and Ramsay, 1986), while natural smectite are heterogeneous with respect to lateral layer dimension and layer charge distribution ranging from 0.2 to 0.6 per f.u. (Guggenheim et al., 2006). Smectite layers possess a negative layer charge due to substitutions in tetrahedral and/or octahedral sheets that can be measured or derived from structural formula (Lagaly, 1994; Kaufhold, 2006; Emmerich et al., 2009) and a pH-dependent edge

charge due to the oxide-type functional groups at the edge surface (Tournassat et al., 2016). These pH-dependent edge charges and especially the point of zero edge charge at the edge (PZC,edge) is a criteria often used for the interpretation of the rheological behaviour of clay (Tombácz and Szekeres, 2004). The $pH_{PZC,edge}$ of hectorite was reported ranging from 9.15 to 11.15 (Tawari et al., 2001; Tournassat et al., 2004a; Giannakopoulos et al., 2006). This interval is at higher pH than for the dioctahedral smectites (Tournassat et al., 2004a; Tournassat et al., 2016).

The general formula of hectorite is $M_{x/v}^{v+}(Mg_{3-x}Li_x)Si_4O_{10}(OH_{2-y}F_y)$ where M^{v+} denotes the interlayer cation. Commonly, the layer charge (ξ) of trioctahedral smectite ranges from 0.2 to 0.25 per f.u. (Lagaly, 1994; Czímerová et al., 2006) at the lower boundary for smectite. A layer charge of 0.2 to 0.25 per f.u. corresponds to a permanent cation exchange capacity (CEC_p) of 52 to 66 $cmol(+)\,kg^{-1}$ for a Na-saturated hectorite with an equivalent molar mass of about 381 g mol^{-1}.

An indirect way to evaluate the edge surface charges is by cation exchange capacity (CEC) in function of pH where both layer charge and edge surface area have to be considered (Tournassat et al., 2004a; Kaufhold and Dohrmann, 2013; Delavernhe et al., 2015). The reported CEC values for Laponite® (various grades) vary between 47 and 92 cmol

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(+) kg^{-1} in dependence of applied method (data set in supplementary material, Table S1). Unfortunately, the pH associated to these CEC are rarely indicated, excepted in Bergaya and Vayer (1997).
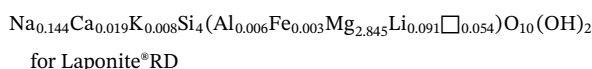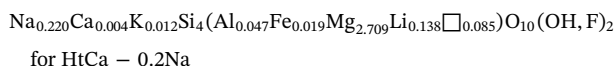
Therefore, the aim of the present study was to evaluate the pH-dependent CEC of trioctahedral smectites using the Cu-trien method. Two materials, the synthetic Laponite® RD and a natural hectorite were selected differing mainly on morphology and particle size.

2. Materials

The natural hectorite SHCa-1 (San Bernardino County California, USA) from the Clay Minerals Society clay repository was used after chemical pre-treatments (carbonate decomposition, iron (hydr)oxides dissolution, organic matter decomposition and homoionic Na saturation) and fractionation < 0.2 μm as detailed in Delavernhe et al. (2015) and Wolters et al. (2009). The Na-saturated hectorite < 0.2 μm was thereafter called HtCa-0.2Na. The synthetic Na-saturated hectorite called Laponite® RD (lot 14-4076 from BYK additives & Instruments and lot 05/4538 from Rockwood Additives Ltd now) was used as supplied.

The methods for the mineralogical and chemical characterization applied to both materials were detailed in Delavernhe et al. (2015). The stoichiometric composition of the materials were calculated based on the assumption of 22 negative charges and the measured layer charge using chemical analysis (Supplementary material, Table S2) according to Köster (1977) after accessory minerals for HtCa-0.2Na and residual chemicals correction for Laponite® RD. The mineralogical characterization of HtCa-0.2Na revealed some residual quartz (SiO_2) and analcime ($Na(AlSi_2O_6) * H_2O$) previously identified in the coarser fractions using X-ray diffraction (XRD) estimated to about $2.2 \pm 0.5\%$ and $0.6 \pm 0.5\%$, respectively, by coupling quantitative analysis done by the Rietveld analysis using AUTOQUAN (Version 2.8,.0; GE Inspection Technologies GmbH, Ahrensburg, Germany) and chemical analysis of the solid. In addition, traces of organic matter, carbonates and sulphates were identified by evolved gas analysis during simultaneous thermal analysis (STA) (Supplementary material, Fig. S1). A mean layer charge of 0.24 ± 0.01 per f.u. was considered (Schnetzer, 2017). For Laponite® RD, about $3.6 \pm 0.3\%$ of amorphous sodium silicate (Na_2SiO_3) was considered in agreement with Thompson and Butterworth (1992) to reach a stoichiometric composition. In addition, STA revealed traces (< 0.1%) of sodium carbonates identified as Trona ($Na_3(CO_3)(HCO_3) * 2\,H_2O$) characterized by the evolved CO_2 at low temperature (Kaufhold et al., 2013; Steudel et al., 2013) and about $0.9 \pm 0.1\%$ sodium sulphates (Na_2SO_4) confirmed by SO_3 content determined by XRF (Supplementary material, Fig. S2). A mean layer charge of 0.19 ± 0.01 per f.u. obtained for a Laponite (unspecified grade) by Czímerová et al. (2006) was used as reference.

The structural formulae of both clay minerals were calculated as follows:

$$Na_{0.220}Ca_{0.004}K_{0.012}Si_4(Al_{0.047}Fe_{0.019}Mg_{2.709}Li_{0.138}\square_{0.085})O_{10}(OH,F)_2$$

for HtCa − 0.2Na

$$Na_{0.144}Ca_{0.019}K_{0.008}Si_4(Al_{0.006}Fe_{0.003}Mg_{2.845}Li_{0.091}\square_{0.054})O_{10}(OH)_2$$

for Laponite®RD

The chemical composition of the synthetic Laponite® RD was corrected considering the presence of Fe, Al, K and Ca as chemicals impurities not incorporated within the clay structure to obtain the typical structural formula according to Neumann (1965) as follows.

$$Na_{0.19}Si_4(Mg_{2.86}Li_{0.09}\square_{0.05})O_{10}(OH)_2 \text{ for Laponite®RD}$$
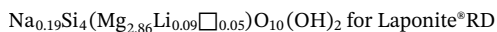
The corresponding CEC_P were 63 ± 2 cmol(+) kg^{-1} for HtCa-0.2Na and 50 ± 2 cmol(+) kg^{-1} for Laponite® RD with a respective molar mass of 384 g mol^{-1} and 383 g mol^{-1}.

The natural and synthetic hectorite differed strongly in term of morphology and particle size distribution. The natural hectorite was composed of particles of lath-like shape as observed by AFM by Schlegel et al. (1999) and references herein, with a mean particle length of 220 nm and a mean particle width of 60 nm within the fraction < 2 μm (Bosbach et al., 2000). These values were considered consistent with the < 0.2 μm fraction given that it contributes to 98 wt% of the < 2 μm fraction according to the Stokes' equivalent sphere diameter. The Laponite® RD was described as small particles equivalent to disk of diameter ranging from 18.4 nm to 30 nm (Avery and Ramsay, 1986; Gantenbein et al., 2011). An AFM study revised the morphology of the Laponite® RD as an elliptical shape with a mean particle length of 24 ± 6.9 nm and a mean particle width of 16.8 ± 4.9 nm (Balnois et al., 2003). An equivalent diameter of 28 nm was considered in the following.

Based on the geometrical properties, the specific edge surface area ($a_{s,edge}$) and the specific basal surface area ($a_{s,basal}$) of single particles were calculated using the perimeter/basal area ratio ($R_{P/A}$ in nm^{-1}) as follows: $a_{s,edge} = R_{P/A} / \rho_s * 10^6$ (m^2 g^{-1}) and $a_{s,basal} = 2 / (\rho_s * h) * 10^6$ (m^2 g^{-1}) with a thickness (h) of 0.96 nm and a specific density (ρ_s) of 2700 kg m^{-3}. $a_{s,edge}$ was estimated to about 14.8 m^2 g^{-1} and 52.9 m^2 g^{-1} for HtCa-0.2Na and Laponite® RD, respectively. The contribution of $a_{s,edge}$ to the total specific surface area was estimated to about 2.0% and 6.9% for HtCa-0.2Na and Laponite® RD, respectively.

High purity reagents (p.a.) obtained from Merck KGaA (Darmstadt, Germany) and Sigma-Aldrich Chemie GmbH (Steinhein, Germany) and ultrapure water (Milli-Q®) were used for the experiments.

3. Methods

CEC of the materials as a function of pH was measured using the copper triethylenetetramine (Cu-trien) method (Meier and Kahr, 1999). The use of the Cu-trien method to quantify the CEC of clays and clay minerals was recommend over a pH ranging between 5 and 10 where the absorbance of Cu-trien solution is quasi-constant according to Meier and Kahr (1999) after Cheng (1962). Cu-trien method for pH < 5 was discussed for pH-dependent behaviour of dioctahedral smectites (Kaufhold and Dohrmann, 2013; Delavernhe et al., 2015; Stanjek and Künkel, 2016). However, as the pH-dependent behaviour of trioctahedral smectites was relevant for pH > 10, the aqueous speciation of Cu-trien and the Cu-trien method for CEC were first re-evaluated.

3.1. Aqueous speciation of Cu-trien as a function of pH

The formation and protonation properties of the Cu-trien complex, as well as the protonation behaviour of the quadridentate polyamine triethylenetetramine, were thoroughly studied either by potentiometric measurement or UV–Vis spectrophotometry as shown by the numerous studies listed on the NIST Standard reference Database (Martell et al., 2004) or on the IUPAC Stability Constant Database (IUPAC, 2005) or even on the Joint Expert Speciation System thermodynamic database (May and Murray, 2001). Different models were developed for the species distribution of the Cu-trien complex as a function of pH as discussed in Nurchi et al. (2013). Thereafter, only the 1:1 complexes, i.e. $[Cu(trien)]^{2+}$, $[Cu(trien)H]^{3+}$, and $[Cu(trien)OH]^{+}$, were considered. The contribution of the 1:2 complexes identified by Laurie and Sarkar (1977) under excess of trien were considered negligible under the present conditions.

A Cu-trien solution of ratio 1:1 of concentration of 0.01 M was prepared using a 0.1 M copper sulphate solution and a triethylenetetramine solution (purity ≥ 97%). The solution was stored under dark condition at room temperature (21.5 ± 0.5 °C). Absorbance spectra of $3.33 * 10^{-3}$ mol L^{-1} Cu-trien solution (concentration used for the CEC measurements after dilution) were measured over the wavelength range of 400 to 1000 nm at different pH after 72 h (Fig. 1 A) (Cary 5000 UV-VIS-NIR Spectrometer, Agilent Technologies, Santa Clara, CA, USA) using a quartz cuvette (SUPRASIL®, Hellma Analytics, Müllheim, Germany) with a path length (l) of 1 cm. The pH of the initial Cu-trien