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Research paper

The effect of the mineralogical composition of various bentonites on CEC values determined by three different analytical methods

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ABSTRACT

Bentonite is an important source of montmorillonite, but has a complex surface chemistry that results from its unique combination of properties, including thixotropic gel formation with water, high water absorption, high surface area, layered structure and high cation exchange capability, and may contain other crystalline or amorphous substances, such as quartz, cristobalite and feldspar. Montmorillonite is 2:1 layer in which surface charge development caused by isomorphous substitution results in inserting interlayer cations between its layers. The cations are easily exchanged with other cationic species, a property known as the cation exchange capacity (CEC). CEC values of various commercially available bentonites were determined by three different analytical methods to investigate the effect of the mineralogical composition on CEC value. The first CEC analytical method, termed the $BaCl_2/MgSO_4$ method, is to substitute interlayer cations with Ba which is subsequently substituted with Mg and then titrated with EDTA in the presence of ammonia buffer. The second method is an ammonia electrode technique in which after ammoniating bentonites, an ammonia electrode is used to detect dissolved ammonia in the presence of NaOH, and the third is an equilibrium pH method in which all exchangeable metallic cations within the bentonite structure are replaced with acetic acid. Both CEC values obtained by the $BaCl_2/MgSO_4$ method for two different masses of each bentonite were all within ±10% of each other with several exceptions. CEC values obtained by the second and third methods were larger than by the first method, for bentonites that contained heulandite of the zeolite group. Additionally, CEC values found by the equilibrium pH method were higher than those determined by the ammonia electrode method for bentonites containing calcite which can be dissolved in acetic acid solution. Although the equilibrium pH method was the simplest to perform, it may be the least accurate, as the presence of calcite and zeolite-type minerals in bentonite samples can result in artificially high CEC values.

1. Introduction

Smectites are 2:1 clay minerals with negatively charged layers. Montmorillonite is one of the most important members of dioctahedral smectites in which trivalent cations may dominantly occupy the octahedral sheet. Si^{4+}, Al^{3+} and Fe^{3+} are commonly found in tetrahedral sites, and Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+} and Li^{+} generally occupy octahedral sites (Brigatti et al., 2006). Substitution of trivalent cations for Si^{4+} may take place in tetrahedral sites, which leads to a deficiency of positive layer charge (an excess of negative layer charge). Substitution of divalent cations for trivalent cations in octahedral sites results in an excess of negative layer charge, as well (Brigatti et al., 2006; Onal, 2006). Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} which are located in the interlayer space to balance the negative 2:1 layer charge are commonly hydrated and exchangeable. The property of smectites for sorbing cationic species from solution by the exchange between cations balancing the negative layer charge and cations in solution is given as the cation exchange capacity (CEC), and CEC values can be expressed in centimole of positive charge per kilogram of dry clay mineral which is equal to milliequivalent per 100 g clay (meq/100 g) (Brigatti et al., 2006; Uddin, 2008).

There are various methods for determining CEC values. Most of the methods involve the complete exchange of the naturally occurring cations in clay minerals by a cationic species such as ammonium, K, Na, methylene blue, Co(III) hexamine complex, Ba, Ag thiourea complex, Cu(II) ethylenediamine complex or others, followed by the removal of excess species and determination of the amount retained on the clay (Meier and Kahr, 1999). As the determined CEC values are dependent on the method used, limitations to the analytical validity of any one method are inevitable (Dohrmann, 2006). Moreover, certain CEC determination methods are laborious and time-consuming processes that need repeated extractions to accomplish complete exchange (Dohrmann, 2006; Dohrmann and Kaufhold, 2009).

Bentonite is an important source of and is primarily composed of montmorillonite, but has a complex surface chemistry arising from its

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ability to form a thixotropic gel with water, high water absorption, high surface area, layered structure and high cation exchange capability, and may also contain crystalline quartz, cristobalite, feldspar, or other compounds (Uddin, 2008). Therefore, if bentonites are used as received, it is expected that the mineralogical composition will have an effect on the CEC value obtained. The analytical problems that arise with a given CEC determination method are a result of specific interactions between the components of the clay and the exchange solution, which may lead to an increase in or depletion of the index cation concentration (Dohrmann and Kaufhold, 2009).

In this study, three different analytical methods were selected and used to determine CEC values of bentonite samples. The most common methods for CEC determination utilize exchange solutions containing ammonium acetate or barium chloride (Mehlich, 1948; Dohrmann, 2006). As ammonium acetate was noted to be the most aggressive among commonly used leaching solutions (Tucker, 1954; Dohrmann and Kaufhold, 2009), a classical $BaCl_2/MgSO_4$ method (Inglethorpe et al., 1993) was chosen as one of the three different analytical methods. The second method for determining CEC values was an ammonia electrode technique (Borden and Giese, 2001) in which an ammonia electrode was used after ammoniated bentonites were prepared. Finally, a straightforward and simple equilibrium pH method (Jackson, 1962; Aprile and Lorandi, 2012) was selected. CEC values obtained by the three methods were compared one another to investigate how CEC values determined by each method vary with the mineralogical composition.

2. Materials and methods

2.1. Clay materials

For the determination and comparison of CEC values, 12 commercially available and 2 standard bentonites (SWy-2 and STx-1) were used. The commercially available bentonites were labeled in a series from Bent1 to Bent12.

X-ray diffraction (XRD, PHILIPS Expert MPD) analysis was performed to obtain semi-quantitative information on the mineralogical composition of the bentonites. The following parameters were used for the XRD characterization: 2theta ranges of 3 to 65°, a step size of 0.01°, a scan speed of 0.04°/s, a counting time of 1550 s (25.83 min), a slit width of 1/4°, an acceleration voltage and current of 40 kV and 30 mA, respectively, and a time/step of 0.25°. The Siroquent Ver 3.0 software was used for the semi-qualitative analysis.

Differential thermal analyses were carried out on a SDT 2960 simultaneous DTA/TGA apparatus, and ranged from room temperature to 700 or 1000 °C at a heating rate of 10 °C/min under air atmosphere, with calcined α-alumina taken as the reference.

2.2. CEC determination methods

Three different analytical methods were used to determine CEC values for the various bentonites: the equilibrium pH method, the ammonia electrode method and the $BaCl_2/MgSO_4$ method.

In the equilibrium pH method described in the literatures (Jackson, 1962; Aprile and Lorandi, 2012), CEC values of clays can be estimated by replacement with acetic acid. The amount of hydrogen ions removed from the acetic acid solution is determined by measuring the pH change with a pH electrode. Although exchangeable metallic cations in the solution are in equilibrium with the exchanged hydrogen ions, a great excess of acetic acid effectively forces the reaction to completion.

The measurement and calculation of CEC values were performed according to the procedure from Soil Chemical Analysis (Jackson, 1962). A 1 M acetic acid solution was prepared by diluting 57.2 mL of acetic acid to 1 L with deionized water. 25 mL of 1 M acetic acid was added into a conical flask containing a certain amount of clay. The amount of clays which is applicable from pH 2.31 to 2.8 based on the relation of pH of the acetic acid solution to total exchangeable metallic cations extracted from the clay, was used. The suspension was left undisturbed for complete sedimentation of the clay particles, after stirring for 1 h using a mechanical shaker. The pH of the supernatant as well as that of the original acetic acid solution was accurately measured at the same time. The CEC value for each bentonite was measured three times to confirm the reproducibility. The maximum standard deviation was 3.36. The CEC (meq/100 g of clay) values were calculated from the following equation.

$$\mathrm{CEC}(\mathrm{meq\,per\,100\;\,g\,of\,clay}) = (\mathrm{pH\,observed} - \mathrm{pH\,acetic\;acid}) \times 22$$

where, 22 is a conversion factor derived from the curve of Brown (1943).

In the ammonia electrode method (Borden and Giese, 2001), exchangeable cation sites are saturated with ammonium cations. The resulting ammonium-exchanged clay releases the ammonium as dissolved ammonia gas when it is dispersed in an alkaline solution of sodium hydroxide. At the same time, an ammonia electrode can detect the signal from the ammonia dissolved in the solution.

Ammoniation procedure of clays, measurement and calculation of CEC values followed the procedure of Borden and Giese (2001). Bentonite samples were ammoniated with a 1 M ammonium acetate solution adjusted to pH 7.00, for three days. After the supernatant liquid was decanted, the samples were further ammoniated for another three days with a 1 M ammonium acetate solution adjusted to pH 7.00. The ammoniated clays obtained by centrifugation for 10 min at 3000 rpm were washed with a 1 M ammonium acetate solution adjusted to pH 7.00 five times, followed by washing with a 1 M and 0.25 M ammonium chloride solution which is adjusted to pH 7.00, four times and once, respectively. After that, the samples were washed with methanol

Table 1
Semi-quantitative information on the mineralogical composition of bentonites determined by XRD.

Sample number	Montmorillonite	Albite	Quartz	Cristobalite	Calcite	Heulandite	Hornblende	Gypsum	Etc. 1	Etc. 2
Bent1	81.9	6.2	0.8	–	4.4	–	–	–	5.0 (microcline)	1.7 (pyrite)
Bent2	62.8	25.9	4.8	4	2.5	–	–	–	–	–
Bent3	64.7	22.9	4.8	5.7	1.9	–	–	–	–	–
Bent4	56.5	20.4	9	1.4	7.1	5.7	–	–	–	–
Bent5	65.9	12.8	1.7	2.8	–	7.5	9.3	–	–	–
Bent6	57.4	–	42.6	–	–	–	–	–	–	–
Bent7	91.2	–	4	–	–	–	–	3.5	1.3 (biotite)	–
Bent8	58	–	25.2	–	3.2	7.5	–	2.7	–	3.3 (analcite)
Bent9	82.2	–	8.1	–	–	9.6	–	–	–	–
Bent10	79	–	6.6	–	4.3	9.3	–	0.8	–	–
Bent11	–	–	–	–	–	–	–	–	–	–
Bent12	–	–	–	–	–	–	–	–	–	–
STx-1	95–100*	–	1–5*	–	–	–	–	–	–	–
SWy-2	90–100*	–	5–10*	–	–	–	–	–	–	–

* The information was obtained from MSDS.