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CATION EXCHANGE REACTIONS OF VERMICULITE WITH Cu-TRIETHYLENETETRAMINE AS AFFECTED BY MECHANICAL AND CHEMICAL PRETREATMENT

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Abstract—The cation exchange capacity (CEC) is a characteristic property of expandable clay minerals, such as smectites and vermiculites. The aim of this work was to examine the cation exchange behavior of vermiculite using the Cu-triethylenetetramine (Cu-trien) CEC method and the influence of mechanical and chemical pretreatment, with the ammonium acetate method serving as a reference. The Cu-trien method makes rapid and direct CEC measurements possible. Three different kinds of mill were used to grind a vermiculite sample from Russia, in order to reduce the particle size to <10 µm. The Netzsch CGS 10 dry mill reduced the particle size more effectively than the other grinding methods. Chemical pretreatments were used to remove carbonates, organic matter, Fe oxides, and divalent exchangeable cations from vermiculite samples prior to CEC measurements. Subsamples of ground and chemically pretreated vermiculite samples were saturated with Na, Li, Mg, Ca, and Cu cations to determine the effect of exchangeable cations on measured CEC values. Chemical pretreatment, monovalent cation pretreatment, and 48 h of shaking time were needed to measure vermiculite CEC values effectively using the Cu-trien method.

Key Words—Ammonium Acetate, Cation Exchange Capacity, Cu-triethylenetetramine, Grinding, Vermiculite.

INTRODUCTION

Vermiculites are 2:1 Mg-bearing layer silicates and, unlike smectites, raw vermiculites are often coarse (particle size >20 µm) and contain only small amounts of clay-size particles. Vermiculite is used in many important applications, *e.g.* coatings, lightweight additives, and insulation (Ballard and Rideal, 1983; Konta, 1995; Pérez-Maqueda *et al.*, 2001; Pérez-Rodríquez *et al.*, 2002), some of which require particle-size reduction by mechanical and/or chemical treatments. Mechanical treatment (by grinding or ultrasound) mainly changes the aspect ratio (Wiewióra *et al.* 2003), whereas, chemical treatment changes the thickness (delamination) of the vermiculite stacks (Ballard and Rideal, 1983). Ultrasonic treatment produces delamination along the [001] direction, but also decreases particle size in other directions. Delamination is also produced by other methods such as thermal shock, H_2O_2 treatment, butylammonium intercalation, *etc*. Total delamination of clay mineral particles requires complete interlayer cation exchange.

The effect of ultrasound on natural macroscopic vermiculite flakes was studied by Pérez-Maqueda *et al.* (2001) who reported a practical limit of 40 h of sonication time for the preparation of submicrometer particles. The effect of ultrasound on two natural macroscopic vermiculites with different chemical compositions and layer charges were compared by Pérez-Rodríquez *et al.* (2002), who noted that sonication produced not only delamination in the [001] direction, but also a breaking of particles in the other directions, while the crystalline character was retained. The effect of sonication depends very much on the layer charge of the vermiculite samples. Ojén vermiculite with a rather small layer charge (0.48 eq/f.u., equivalents per formula unit) delaminated to a greater extent than the Santa Ollala vermiculite which has a larger layer charge (0.88 eq/f.u.). The samples formed thin layers and rolled into nanotubes (Pérez-Rodríquez *et al.*, 2002). High- and low-charge vermiculites subjected to ultrasonic treatment (Wiewióra *et al.*, 2003) produced particle separation without damage of the structure and the degree of separation depended on vermiculite layer charge. Jiménez De Haro *et al.* (2004) studied the effects of mechanical treatments (grinding and ultrasonic) and cation type (NH_4^+, K^+, Mg^{2+}, Na^+) on Santa Ollala vermiculite microporosity. Ultrasonic treatment increased the surface area, but little change in microporosity was observed. Grinding increased the surface area and microporosity significantly. The effects of grinding and ultrasonic treatment on vermiculite were examined by Pérez-Maqueda *et al.* (2004). Ultrasonic treatment produced a crystalline material with a drastically reduced particle size (median = 2.4 µm).

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Grinding produced particles (median = 9 µm) with a very wide particle-size distribution, but prolonged grinding of vermiculite reduced long-range order and eventually produced an amorphous product.

Chemical activation of vermiculite was used to prepare a porous silica that was useful as a gas adsorbent, catalyst support, and cracking catalyst (Suquet *et al.*, 1991; Temuujin *et al.*, 2003). Maqueda *et al.* (2007, 2008) used chemical treatment and combined mechanical and chemical treatments to prepare porous material from vermiculite. The porous material is of interest because it has a large specific surface area that can be used to adsorb contaminants or act as a catalyst. Maqueda *et al.* (2007, 2008) reported that grinding destroyed the long-range order of vermiculite, but left an intact local structure near Fe atoms after a grinding time of up to 10 min. Mössbauer spectroscopy showed no Fe(III) in the tetrahedral sheets and grinding did not lead to significant oxidation of structural Fe(II).

The swelling behavior of some vermiculite-organic complexes in water using several alkylammonium compounds was studied by Garret and Walker (1960). Vermiculite cation exchange anomalies were studied by Graf von Reichenbach (1966). High charge-density layer silicates can yield anomalous CEC values because of heterogeneous properties. He found three causes for exchange anomalies. First, exchange positions at the vermiculite surface are not equivalent. Second, exchange equilibrium in the interlayer is partially inhibited. Third, vermiculite has a strong tendency to contract. Ghabru *et al.* (1989) studied the layer-charge and cation-exchange characteristics of vermiculite and determined the CEC by Ca-Mg exchange (Rich, 1961). The layer charge was measured using the alkylammonium method (Lagaly and Weiss, 1969). Lagaly (1982) studied the layer-charge heterogeneity in vermiculites. D'Espinose de la Caillerie and Fripiat (1991) studied the 'dealumination' and the aluminum intercalation of vermiculite. Measured CEC was one characterization technique, which was determined by displacement of exchangeable Na^+ with NH_4^+. Abate and Masini (2005) studied the effects of natural organic matter on the adsorption of Cd^{2+} and Pb^{2+} to vermiculite as a function of ionic medium and pH, but did not measure CEC prior to the experiments. Cu-triethylenetetramine was used (Osman, 2006) to measure the CEC value of vermiculites used in an organo-vermiculite study. A pristine Mg-rich vermiculite sample had a measured CEC of only 30 meq/100 g which increased to 120 meq/100 g after the first Na-exchange step, but this CEC is still too small for vermiculite. Osman (2006) concluded that Cu-trien exchange for Mg^{2+} is too slow and the reaction did not complete within the time frame of the experiment or that not all interlayer Mg^{2+} cations were accessible. In the preparation of organo-vermiculite, interlayer Mg^{2+} must be replaced by Na^+ prior to organic cation exchange. Abollino *et al.* (2008) used the ammonium acetate CEC method in a study of metal-ion adsorption to montmorillonite and vermiculite used to predict metal-ion uptake efficiency from contaminated effluents. Ramírez-Valle *et al.* (2008) studied the influence of interlayer cations (Na^+, Mg^{2+}, Fe^{3+}) on pyrrole/vermiculite interactions and observed pyrrole polymerization in all samples. The polymerization was presumably triggered by structural Fe, but in most cases the pyrrole polymers were deposited externally. The best interlayer pyrrole uptake was observed for Fe^{3+}-intercalated Ojen vermiculite, which has a smaller layer charge than that of the Santa Olalla vermiculite.

One objective of this study was to increase the amount of vermiculite in the clay size (<2 µm) fraction prior to the exchange experiments. Several mills were used to grind vermiculite samples, and particle size and X-ray diffraction (XRD) analyses were used to compare the ground samples. Minimal structural change of the vermiculite was an aim of the grinding procedures. Vermiculite CEC values can be measured using the ammonium acetate method (Mackenzie, 1951; Abollino *et al.*, 2008), but this method includes many exchange steps.

A faster method to determine the CEC was published by Meier and Kahr (1999) using Cu-triethylenetetramine (Cu-trien). The Cu-trien method was used successfully to determine the CEC values of smectites. Hence, the main objective of this research was to evaluate the feasibility of using the Cu-trien method to measure the CEC values of vermiculite.

An important advantage is that the concentration of Cu-trien can be directly measured optically using a spectrometer. Other CEC methods require atomic absorption or emission spectrometry to measure the index cation. The Cu-trien CEC method uses less expensive equipment and minimal sample preparation efforts are needed in comparison to other methods.

EXPERIMENTAL

Material

Because vermiculite samples from Llano and Santa Olalla were not available, a Russian vermiculite sample, obtained from Thermax (Austria), was used in this study. The Russian vermiculite sample contains 84% vermiculite, 14% phlogopite, and 2% calcite. In contrast to smectites, the particle size of the raw Russian vermiculite sample was mostly >63 µm (74%) with only 10% <2 µm, and pretreatments to enrich the <2 µm fraction, *e.g.* grinding, were necessary.

Grinding experiment

The purpose of the grinding experiments was to find a method to increase the <2 µm fraction of vermiculite without affecting the structure. The McCrone mill (McCrone Scientific) and Netzsch PE075 mill use a wet medium and the Fritsch agate mill and Netzsch mill

CGS 10 mill use a dry medium. The agate mill was used in combination with a 63 µm sieve to grind one complete vermiculite sample to <63 µm. The vermiculite sample for the McCrone mill was first ground with the agate mill to obtain <400 µm material. 3 cm^3 of this powder and 10 mL of deionized water were used in the grinding vessel. The suspension was ground in the McCrone mill for 15, 20, and 25 min at 4800 rpm. The Netzsch PE075 mill was used with a rotation speed of 1000 rpm and samples were removed after 20, 40, and 60 min. Several rotation speeds (16,000, 17,000, and 18,000 rpm) were tested in this dry mill for 15 and 30 min.

Chemical pretreatment and separation of the <2 µm fraction of the ground vermiculite

The ground vermiculite material (using Netzsch mill CGS10) was divided into four portions. One portion was treated according to the Tributh and Lagaly (1986) method and was designated 'TL-treated vermiculite.' The TL treatment procedure consisted of three chemical treatments performed in the following order: (1) acetic acid-acetate buffer (AAAB) treatment; (2) dithionite-citrate-bicarbonate (DCB) buffer treatment (Mehra and Jackson, 1960); and (3) H_2O_2 treatment.

Only one of the trio of treatments which make up the TL procedure was applied to the other three vermiculite portions in order to identify the treatment that has the greatest effect on vermiculite-exchange behavior.

After chemical treatment, the excess reagents were removed by washing four times with 1 M NaCl and five times with deionized water. After washing with NaCl and deionized water, the suspensions were transferred into cleaned dialysis tubing (prior to use, the dialysis tubing was cleaned of organic compounds such as glycerin by two treatments with boiling deionized water) and dialyzed until the electrical conductivity was <5 µS/cm.

The <2 µm fraction was separated from one half of the vermiculite suspension by sedimentation. The <2 µm suspension was flocculated with NaCl (300 g) to reduce the volume of a 10 L vermiculite suspension (1% solids). The concentrated vermiculite suspension was placed in dialysis tubing and dialyzed in deionized water until the conductivity was <5 µS/cm. The TL treatment and <2 µm fraction separation yielded a homo-ionic Na^+-vermiculite. To understand the effects of interlayer cations on vermiculite behavior, homo-ionic vermiculite samples were prepared using several different cations. Vermiculite samples were ground using a Netzsch CGS10 mill. The ground Na^+-exchanged vermiculite and Na^+-exchanged <2 µm vermiculite samples were divided into five portions and made homo-ionic with respect to Na, Li, Mg, Ca, or Cu by suspending 10 g of the Na-vermiculite in 500 mL of deionized water and adding one of the respective salts, NaCl, LiCl, $MgCl_2$, $CaCl_2$, or $CuCl_2$ in an amount equal to 20 × CEC. The suspensions were placed on a shaker for 24 h, centrifuged for 15 min at 4500 rpm, and the clear supernatant was replaced with fresh deionized water and NaCl, LiCl, $MgCl_2$, $CaCl_2$, or $CuCl_2$ salt. The procedure was repeated four times. The homo-ionic vermiculite samples were then washed with deionized water, dialyzed, dried at 60ºC, and ground gently (*i.e.* without damaging the material) in an agate mill.

Methods

The CEC values of the untreated and chemically pretreated vermiculite samples were measured using 0.01 M copper triethylenetetramine (Cu-trien) using the method of Meier and Kahr (1999). Prior to the CEC measurements, all vermiculite samples were stored over a saturated solution of $Mg(NO_3)_2$ in a desiccator to equilibrate at a constant relative humidity of 53%. Vermiculite samples (50 mg) were weighed into 50 mL centrifuge tubes that contained 10 mL of deionized water and 5 mL of 0.01 M Cu-trien. The resulting suspensions were shaken for 3 h. However, for some experiments, the shaking time was varied. The suspensions were then centrifuged at 4500 rpm for 10 min and the clear blue supernatant solution was transferred into a cuvette and the Cu-trien concentration of the supernatant measured in a photometer at a wavelength of 580 nm. The CEC measurements were carried out in duplicate and calculated using formula 1, below.

$$m_{\text{dried}}[\text{g}] = m_{\text{net weight}}[\text{g}] \cdot \frac{(100 - w_{\min}[\%])}{100} \qquad (2)$$

$$c_{\text{Cu-trien}}[\text{mmol/L}] = a \cdot Abs \qquad (3)$$

where $c_{\text{Cu-trien}}$ = concentration of copper triethylenetetramine; m_{dried} = mass of dried sample; $m_{\text{net weight}}$ = mass of air dried sample; $w_{\min}$ = water content; a = slope of the calibration curve; and Abs = measured absorbance of the supernatant.

The water contents of the vermiculite samples were required because CEC values are based on dry sample weight. Water contents were measured using simultaneous thermal analysis (STA) with a Netzsch Jupiter STA 449 C instrument connected to a quadrupole mass spectrometer (QMS 403 C, Aeolos, Netzsch) using the experimental parameters of Wolters *et al.* (2009).

The ammonium acetate CEC method described by MacKenzie (1951) and Emmerich (2000) was used as a reference method. Vermiculite samples (60 mg) were weighed into 50 mL centrifuge tubes, 25 to 30 mL of 1 M ammonium acetate solution was added, then the

$$\text{CEC}[\text{meq/100 g}] = \frac{2 \cdot [(0.01\ \text{mol/L} \cdot 5\ \text{mL} - c_{\text{Cu-trien}} \cdot (5\ \text{mL} + 10\ \text{mL}/1000) \cdot 100]}{m_{\text{dried}}[\text{g}]} \qquad (1)$$

suspensions were shaken for 24 h and centrifuged at 4500 rpm for 10 min. The clear supernatant was discarded and replaced with 25 to 30 mL of ammonium acetate solution and the procedure was repeated four times. The vermiculite samples were then washed four times with 25 to 30 mL of ethanol (99.5%). All supernatant solutions were collected in evaporation bowls and dried at 90ºC. The solid residue was prepared for analysis by inductively coupled plasma optical emission spectroscopy. It was redissolved with 3 mL of HNO_3 and deionized water and transferred into a volumetric flask (100 mL) and filled to the mark. The solutions were stored in polyethylene bottles.

The NH_4^+-exchanged vermiculite samples were transferred to Kjeldahl flasks and 30 mL of deionized water and 2 mL of NaOH solution were added before measurement. Interlayer ammonium was displaced by Na^+ and transformed into NH_3. The NH_3 released was transferred to an Erlenmeyer flask by water-vapor distillation. The Erlenmeyer flask contained 2 mL of H_3BO_3 solution and an indicator for titrimetric NH_3 measurement with H_2SO_4. The CEC measurements were performed twice and the water contents of the vermiculite samples were measured by STA. The CEC values were calculated using the following formula:

$$\mathrm{CEC[meq/100\ g]} = \frac{V_{H_2SO_4}[\mathrm{mL}] \cdot n_{H_2SO_4}[\mathrm{mol}] \cdot 100}{m_{\mathrm{dried}}[\mathrm{g}]} \qquad (4)$$

$$V_{H_2SO_4}\ [\mathrm{mL}] = V_{\mathrm{sample}}\ [\mathrm{mL}] - V_{\mathrm{blank}}\ [\mathrm{mL}] \qquad (5)$$

where $V_{H_2SO_4}$ = volume (consumption) of H_2SO_4; $n_{H_2SO_4}$ = the molarity of H_2O_4 (0.0067 mol); m_{dried} = mass of dried sample; V_{sample} = measured volume of H_2SO_4 of the sample used; and V_{blank} = measured volume of H_2SO_4 of the blank sample.

The particle size of the vermiculite samples was measured using an Horiba LA-950 laser scattering

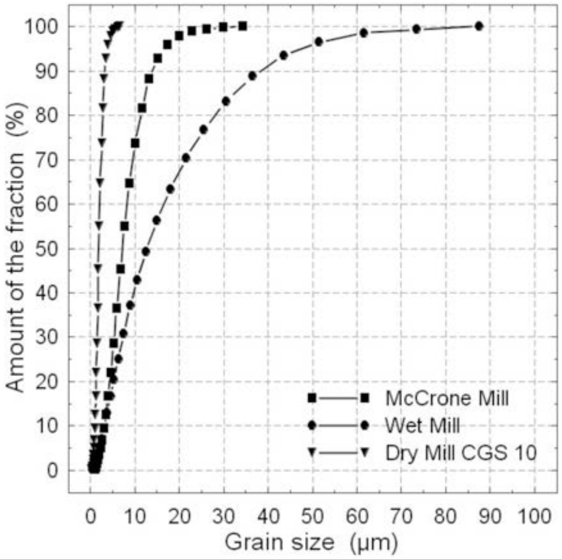

Figure 1. Comparison of the cumulative particle-size curves using the McCrone mill (25 min), the wet mill (60 min) and the dry mill (30 min).

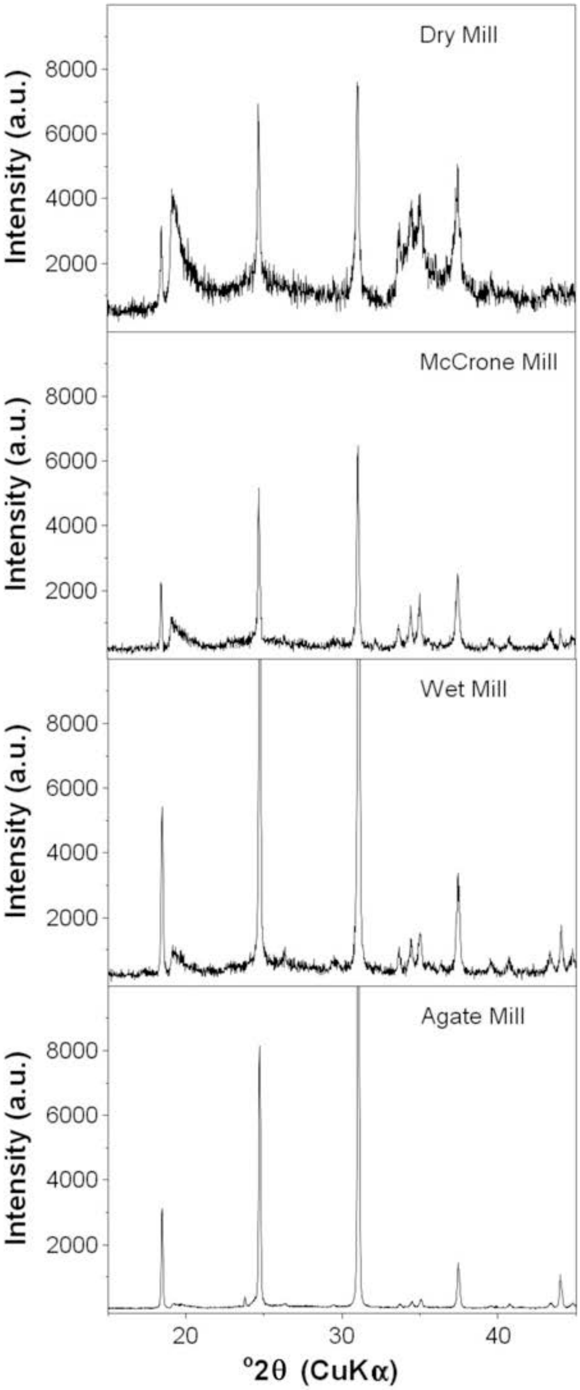

Figure 2. Influence of the grinding procedure on the vermiculite structure. (Note: the XRD pattern of the original material was the same as that after use of the Agate Mill).

particle-size distribution analyzer. The mineral phases and structural changes caused by mechanical treatment were examined using XRD analysis. Powder XRD measurements were performed using a Siemens D5000 diffractometer with a graphite diffracted-beam monochromator and CuKα radiation. The divergence and antiscatter slits were fixed at 1 mm and the detector slit was 0.1 mm. The XRD patterns were recorded from 5 to 80°2θ with a step size of 0.02°2θ and step time of 3 s.

The chemical composition of the natural and pretreated materials was determined using X-ray fluorescence analysis (XRF). The analyses were performed using a MagiXPRO spectrometer (Phillips) equipped with a rhodium X-ray tube (stimulation power: 3.2 kW) using air-dry powdered samples fused with lithium tetraborate (mixing ratio 1:7). The loss on ignition was determined separately at 1000°C (2 h).

The structural formulae were calculated from the chemical compositions of the <2 μm vermiculite fractions using the measured layer-charge values (Köster, 1977; Olis *et al.*, 1990; Lagaly, 1994; Wolters *et al.*, 2009). Vermiculite layer charge was determined according to the empirical, rapid mean-layer-charge estimation method (Olis *et al.*, 1990). Only one alkylammonium chain length (n_c = 12 or 18) was used in this method. For mean layer-charge determination, aqueous solutions of *n*-alkylammonium formiate were used because of the greater solubility, especially of the longer chains (Wolters *et al.*, 2009). Alkylammonium solutions of the n_c = 12 and n_c = 18 formiate salts were prepared according to Lagaly and Weiss (1969) and Wolters *et al.* (2009). A vermiculite clay sample (100 mg) was mixed with 3 mL of 1 M alkylammonium solution and stored at 60°C for 2 weeks. Afterward, the solutions were washed free of excess alkylammonium solution using 16 wash cycles with ethanol. After centrifugation, the samples were dispersed in 3 mL of ethanol along with small amounts of muscovite in order to prepare oriented samples for XRD analysis. The muscovite served as an internal standard. After drying at room temperature, the samples were stored over P_2O_5 in a desiccator. The XRD patterns were recorded from 2 to 12°2θ using a step size of 0.04°2θ and a count time of 8 s per step.

RESULTS AND DISCUSSION

Grinding experiments

The grinding time needed to obtain the best particle-size reduction varied for the different mills. Repeated grinding of the coarse particles (>63 μm) of a 30 g raw vermiculite sample in the agate mill increased the silt fraction (2–63 μm) to 81%, but only increased the <2 μm fraction from 10% to 16%. Particle-size measurements indicated that 15 min using the McCrone mill yielded nearly 83% <20 μm particles. The <20 μm fraction was increased by ~15% with a longer grinding time of 25 min, but almost no increase in the <2 μm fraction was obtained. Thus, in spite of the increase in the <20 μm fraction, the McCrone mill was too time-consuming to significantly increase the <2 μm fraction. Grinding 100 g of vermiculite powder took 2 days with a grinding time of 15 min per sample charge. Grinding in the wet mill for 20 min yielded 40% of <20 μm fraction and 60 min grinding increased the <90 μm fraction to 70%, but the <2 μm fraction was again insufficient for particle-size separation. Vermiculite sample grinding for 15 min at 16,000 rpm in the CGS 10 dry mill reduced all the material to <20 μm and 25% of it to <2 μm. Further grinding in the dry mill reduced the grain size to <10 μm and increased the <2 μm content to nearly 50%. The CGS 10 dry mill effectively produced <2 μm vermiculite and the process was not time-consuming; 5 kg of vermiculite was ground in 1 day. Cumulative particle-size curves (Figure 1) illustrate the effects of the three grinding procedures on vermiculite particle-size reduction. In summary, the McCrone rapidly reduces the particle size of small samples for qualitative and quantitative phase analysis, but does not enrich the <2 μm fraction. The Netzsch wet mill also reduces particle size, but requires significantly more time than the McCrone mill. The dry mill effectively enriches the <2 μm fraction. Powder XRD patterns of the vermiculite

Table 1. Ammonium acetate CEC values (meq/100 g) and exchangeable cations of raw, TL-treated <10 μm, and TL-treated <2 μm vermiculite samples.

	Raw vermiculite	TL-treated [#] <10 μm vermiculite	TL-treated[#] <2 μm vermiculite
Na	–	151	157
K	2	0	0
Ca	20	3	4
Mg	98	11	14
Al	33	–	–
Sum of exchanged cations	153	165	175
CEC	159	173	176

[#] Tributh and Lagaly (1986)

samples (Figure 2) indicate increased *hkl* peak intensity, whereas the intensity of the basal reflection (001) decreased slightly as particle size decreased. Primary domains were still present, although particle-length reduction yielded particles with approximately equal length and width. Thus, the smaller vermiculite particles had less preferred orientation (001) than the large particles of raw vermiculite.

Cation exchange reactions

The ammonium acetate CEC values of the raw vermiculite, the TL-treated vermiculite (<10 µm fraction), and the TL-treated vermiculite (<2 µm fraction) samples were 159, 173, and 176 meq/100 g, respectively. The smaller CEC value of the raw vermiculite sample was due to the dilution effect of other mineral phases (*e.g.* phlogopite). The exchangeable cation sums for the vermiculite samples were comparable to the measured CEC values (Table 1). Slightly larger CEC values than cation sums might be explained by excess ammonium that was not removed by washing during the CEC measurements. The ammonium acetate CEC values can serve as a reference data set to evaluate the applicability of Cu-trien for vermiculite CEC measurements. Several experiments were performed to determine the effects of shaking time, temperature, chemical treatment, and interlayer cations on CEC values measured.

Vermiculite CEC values (<10 µm, 53 meq/100 g; <2 µm, 63 meq/100 g) measured using a 3 h shaking time indicated that Cu-trien molecules only replace some of the interlayer cations. The alkylammonium d_{001} value (2.28 nm, $n_c = 12$) and mean layer charge (0.70 eq/f.u.) values of the <2 µm and <10 µm vermiculite samples were equal and indicated that the vermiculite is low-charge, but the $n_c = 18$, $d_{001} = 3.28$ spacing indicated the presence of high-charge domains. Alkylammonium layer-charge measurements of vermiculites require a longer reaction time than smectites. Smectite alkylammonium exchange was completed in 1 week, but >1 month was required for vermiculite. The expectation is, therefore, that Cu-trien exchange of vermiculite would require more time than smectite, and an even longer shaking time failed to produce a remarkable increase in the Cu-trien CEC value (<2 µm vermiculite, CEC = 63 meq/100 g after 28 days) measured.

Table 2. Shaking time and CEC values of TL-treated vermiculite samples measured using Cu-trien.

Shaking time (h)	CEC (meq/100 g) Vermiculite <10 µm	CEC (meq/100 g) Vermiculite <2 µm
3	145	143
6	154	153
24	159	164
48	162	162
72	161	162
96	163	163

Furthermore, the influence of a greater reaction temperature of 60ºC on Cu-trien exchange was tested. The samples were shaken for 24 h then stored at 60ºC for several weeks. To check the thermal stability of the Cu-trien solution and Cu-trien-intercalated clay minerals, the same procedure was applied on a standard smectite sample (Volclay). Measurements indicated that Cu-trien was stable at greater temperatures (60ºC), but again, complete replacement of the exchangeable cations did not occur (vermiculite <2 µm after 28 days: 62 meq/100 g).

Finally, Cu-trien CEC measurements were made on the chemically pre-treated, ground vermiculite samples, TL-treated <10 µm fraction, and on the TL-treated <2 µm fraction. The measured CEC value (Table 2) was now comparable to that determined with ammonium acetate (Table 1). The measurements (Table 2) were repeated with various shaking times (3, 6, 24, 48, 72, and 96 h).

The measured CEC values indicated that shaking times of 24 and 48 h were necessary for complete exchange. This demonstrated that vermiculite CECs can be measured with Cu-trien. The three-step chemical pretreatment of Tributh and Lagaly (1986) yielded homo-ionic, Na-exchanged vermiculite samples. The following experiments were performed to clarify which step of the chemical pretreatment most influenced Cu-trien exchange. The CEC of chemically treated vermiculite samples were measured after 48 h of shaking. The CEC values calculated indicated that all of the chemical treatments enhanced Cu-trien exchange (Table 3). The best result was achieved after TL treatment and one AAAB treatment. The DCB or H_2O_2 treatments yielded only 95.5% exchange, but TL or AAAB treatment

Table 3. CEC values and interlayer compositions per formula unit ($O_{10}(OH)_2$) of chemically-treated <10 µm vermiculite samples measured using Cu-trien and a 48 h shaking time.

Treatment	CEC (meq/100 g)	– Interlayer cations (mol p.f.u.) – Na^+	K^+	Ca^{2+}	Mg^{2+}
Tributh and Lagaly (3 step)	163	0.68	–	0.01	–
Acetic acid-acetate buffer	160	0.71	–	0.01	–
Dithionite-citrate buffer	141	0.64	–	0.03	–
H_2O_2	142	0.62	–	0.03	–

Table 4. Interlayer composition p.f.u. ($O_{10}(OH)_2$) of homo-ionic, TL-treated <2 µm vermiculite samples measured using XRF.

TL-treated <2 µm vermiculite	Interlayer cations (mol p.f.u.) Na^+	K^+	Ca^{2+}	Mg^{2+}	Cu^{2+}
Homo-ionic exchanged with					
Na^+	0.68	–	0.01	–	–
Li^+	0.66	0.01	0.02	–	–
Ca^{2+}	–	–	0.35	–	–
Mg^{2+}	–	–	0.01	0.34	–
Cu^{2+}	–	–	–	–	0.36

yielded 98.5% homo-ionic Na exchange (Table 3). Small differences in the amounts of divalent cations in largely monovalent-cation vermiculite samples hindered Cu-trien exchange and indicated that interlayer composition affected exchange behavior. Chemical compositions of the homo-ionic, TL-treated <2 µm vermiculite samples were, therefore, measured (Table 4) and indicated that interlayer cation exchange for the homo-ionic vermiculite samples was only 95 to 97% after 48 h of shaking. The CEC measurements indicated that Cu-trien replaced only a fraction of the raw vermiculite exchangeable cations and the measured CEC values of the monovalent (Na, Li) vermiculites were greater than the divalent (Mg, Ca) vermiculites (Table 5). Chemical pretreatment combined with monovalent cation (Na, Li) exchange permitted complete Cu-trien exchange. Divalent cations, such as Ca, Mg, and Cu, hindered Cu-trien exchange. Although Cu-trien is a divalent cation, it is larger than the divalent interlayer cations (Mg, Ca) in the raw vermiculite. Therefore, both interlayer cation composition and Cu-trien molecular size affected exchange. The Cu-trien complex covers a surface area of 0.83 nm^2 (0.42 per charge) per molecule and a size exclusion effect is not expected for clay minerals with layer charges <0.56 eq/f.u. (Amman *et al.*, 2005). The area of the Cu-trien complex was compared with the equivalent area of vermiculite (= $ab/2\xi$ where a and b are lattice constants and ξ is the layer charge in eq/mol p.f.u.; Amman *et al.*, 2005). The vermiculite had an equivalent area in eq/mol p.f.u. of 0.36 nm^2. This value was remarkably smaller than the area per charge of the Cu-trien complex, but after pretreatment the Cu-trien complex could be intercalated and the CEC value determined.

Table 5. CEC values of homo-ionic vermiculite samples measured using Cu-trien and a 48 h of shaking.

Cation	CEC (meq/100 g) Raw vermiculite	TL-treated <2 µm vermiculite
Na^+	88	164
Li^+	87	161
Ca^{2+}	55	71
Mg^{2+}	54	71
Cu^{2+}	24	47

CONCLUSIONS

For vermiculite with larger particle size, the Netzsch CGS 10 dry mill reduced the particle size most effectively. The CEC with Cu-trien on raw material yielded values which were too small (53 meq/100 g compared to 159 meq/100 g with ammonium acetate). Thus, chemical pretreatment was necessary. Chemical analyses and measured CEC values of homo-ionic vermiculite samples indicated that divalent cations (Mg, Ca, and Cu) inhibit (47 to 71 meq/100 g CEC) complete cation exchange by Cu-trien. Complete vermiculite interlayer Cu-trien exchange (161 to 164 meq/100 g CEC) took 48 h. Hence, acetic acid/acetate pretreatment, monovalent cation pretreatment, and 48 h of shaking time are needed to measure vermiculite CEC values effectively using the Cu-trien method.

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