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STRUCTURAL CHARACTERIZATION OF (Cu^{2+},Na^+)- AND (Cu^{2+},NH_4^+)-EXCHANGED BENTONITES UPON THERMAL TREATMENT

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Abstract—Bentonites are excellent materials for sequestering various metal cations because of the cation fixation ability of the constituent montmorillonite layers, but sometimes, such as in the case of Cu^{2+}, the exact location of cation fixation with respect to the clay layers is difficult to determine. Na-montmorillonite was prepared from the <2 μm fraction of the bentonite Calcigel (from Bavaria, Germany) and exchanged by Cu^{2+} and Na^+ or by Cu^{2+} and NH_4^+ cations. The resulting materials (bi-ionic Cu-Na and Cu-NH_4 samples, respectively, as well as homo-ionic forms with Cu^{2+}, Na^+ and NH_4^+) were heated for 24 h at temperatures of 300 and 450ºC and the structural evolution characterized using X-ray diffraction (XRD) analysis, Fourier Transform Infrared (FTIR) spectroscopy, and differential scanning calorimetry (DSC) analysis.

The XRD patterns showed that the Cu sample and the Cu-Na sample have basal spacings of 12.5 Å. Upon heating at 300 and 450ºC, the layers collapsed to 9.5 Å. In contrast, the d_{001} value in the NH_4 sample and Cu-NH_4 sample decreased to 10.0 Å and 10.2 Å, respectively, during the heat treatment. The Cu^{2+} ions migrated irreversibly into the montmorillonite structure.

For the NH_4 and the Cu-NH_4 samples, DSC analyses show that NH_3 evolved at between 300 and 400ºC though the octahedral sheet was not altered substantially by the H^+ generated. Infrared spectra show that the bands of the Si-O and OH vibrations of all samples were changed upon heating due to the movement of the dehydrated cations into the hexagonal holes of the tetrahedral sheet. Apparently no Cu^{2+} was trapped in the octahedral sheet. In the case of the Cu-NH_4 form, both Cu^{2+} fixation and de-ammonization occurred during the heat treatment. Other than maintaining the basal spacing, no effect of the presence of NH_4^+ on the Cu^{2+} fixation could be found for the montmorillonite studied.

Key Words—Acid Activation, Cu Fixation, De-ammonization, DRIFT, FTIR, Hofmann-Klemen Effect, Montmorillonite, NH_4 Clay.

INTRODUCTION

The interaction of exchangeable heavy-metal cations (such as Cu^{2+}) with the structures of clay minerals is of interest in the field of soil pollution, and in terms of using clays as barriers for waste disposal (Madejová *et al.*, 1999, 2006; Komadel, 2003).

Small cations (such as Li^+, Cu^{2+}) can be fixed in the clay mineral structure by thermal treatment. The movement of the interlayer cations into the structure leads to a loss of the swelling capacity and cation exchange capacity (CEC) of the clay mineral (Hofmann and Klemen, 1950; Greene-Kelly, 1952; Emmerich, 2000; Komadel *et al.*, 2005). If Cu^{2+} is used as the fixing cation, however, the precise location of the fixed Cu^{2+} in the clay mineral structure has yet to be established. Possible locations include the vacant octahedral sites (Mosser *et al.*, 1997; Shaiek *et al.*, 2003; Karmous *et al.*, 2006) or the bottom of the hexagonal cavities of the tetrahedral sheet (Tettenhorst, 1962; Karakassides *et al.*, 1999; Madejová *et al.*, 2006). It could also occupy both sites (McBride and Mortland, 1974; Heller-Kallai and Mosser, 1995; He *et al.*, 2001).

The structural evolution of Cu^{2+}-saturated homo-ionic forms of montmorillonite upon thermal treatment has been studied extensively by different methods, often by infrared (IR) spectroscopy (*e.g.* Madejová *et al.*, 1999). Only a few studies, however, have examined bi-ionic forms with various Cu^{2+} contents (*e.g.* Oueslati *et al.*, 2006).

Another chemical modification of smectites is by acid activation, which is usually carried out by treatment with strong mineral acids. This treatment leads to dissolution of the octahedral sheet followed by a new arrangement of the structure to a framework of amorphous silica (Komadel, 2003). Acid-activated smectites are commonly used as catalysts and sorbents (such as bleaching earth) because of their large surface area and porosity (*e.g.* Chitnis and Sharma, 1997; Kaufhold and Decher, 2003).

The aim of the present study was to investigate the effect of the presence of NH_4^+ on the fixation of Cu^{2+} during the thermal treatment of Cu-NH_4 montmorillonite at temperatures of 300 and 450ºC: moderate internal acid activation with thermal assistance. If bentonite is saturated with Cu^{2+} and NH_4^+, then following thermal treatment, NH_3 is released in the temperature range from

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300 to 400ºC and protons are generated in the interlayer and on the outer surface, as shown in equation 1 (according to Wright *et al.*, 1972).

$$NH_4^+ \rightarrow H^+ + NH_3\uparrow \quad (1)$$

This moderate acid activation can result in partial alteration of the clay mineral structure. Previously exchangeable Cu^{2+} can be fixed in the structure under these conditions.

Preliminary investigations were carried out by extraction experiments of heated Cu-Ca and Cu-NH_4 bentonites by treating 0.5 g of solid material with 25 mL of 1 M CH_3COONH_4 solution for 2 h (three times). The total amount of Cu^{2+} in both samples was 36 meq/100 g before the extraction experiments. The Cu^{2+} extraction rates of the Cu-Ca and Cu-NH_4 bentonites after thermal treatment at 400ºC were determined to be 27% and 3%, respectively, meaning that the extraction rate of Cu^{2+} is markedly decreased by the presence of NH_4^+ during the thermal treatment, in contrast to an ordinary thermal treatment in the absence of NH_4^+ (Seiffarth and Kaps, 2005).

MATERIALS AND METHODS

The starting material, a Na homo-ionic form of montmorillonite was prepared from the <2 μm fraction of the bentonite 'Calcigel' from the clay deposit in Bavaria (Germany). The chemical compositions of the untreated and purified materials were determined using a C and S analyser and inductively-coupled plasma optical emission spectroscopy (ICP-OES) with an ICP Optima 3000 instrument (Table 1). The chemical pre-treatment of the bentonite to eliminate carbonate, Fe oxide, Al hydroxide, and organic matter was carried out according to Mehra and Jackson (1960), Tributh and Lagaly (1986), and Wolters (2005). The <2 μm fraction was obtained from the purified samples by sedimentation. X-ray diffraction patterns showed that smectite is the dominant mineral in this fine fraction, though impurities of quartz, feldspar, mica, and minor carbonate were identified. The <2 μm samples were saturated with Na^+ by treatment with NaCl and washed free of excess salts, dried at 60ºC, powdered gently in a mortar, and divided into several portions. One portion was mixed with a 0.01 M $CuCl_2$ solution (1 g, 25 mL, 2 h, once) in order to obtain a montmorillonite exchanged with Cu^{2+} and Na^+. Another portion was initially transformed to a Cu homo-ionic form, by treatment with a 0.02 M $CuCl_2$ solution (1 g, 25 mL, 2 h, five times), some of which was mixed subsequently with 0.5 M CH_3COONH_4 solution (1 g, 25 mL, 2 h, once) to produce a montmorillonite exchanged with Cu^{2+} and NH_4^+. In addition, a homo-ionic NH_4^+ form was prepared by treatment with a 1 M CH_3COONH_4 solution (1 g, 25 mL, 2 h, five times). After each step the samples were washed free of excess salts, dried, and powdered as mentioned previously. All solutions were analyzed for Cu^{2+} and Na^+ content, before and after an application, by ICP-OES. The Cu^{2+} content of the resulting Cu-Na and Cu-NH_4 samples was determined to be 30 meq/100 g and 20 meq/100 g, respectively. The total CEC is 60 meq/100 g, measured by the complete treatment with CH_3COONH_4 solutions as well as with $CuCl_2$ solutions.

Five differently exchanged samples, homo-ionic forms with Na^+, Cu^{2+}, NH_4^+, and bi-ionic forms with (Cu^{2+},Na^+) and (Cu^{2+},NH_4^+), were available for investigation. The materials were heated for 24 h at temperatures of 300 and 450ºC (laboratory furnace, corundum vessels, air atmosphere).

The powder XRD patterns were recorded over the range 4–70º2θ using a Seifert 3003 TT diffractometer (CuKα radiation).

Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectra in the 4000–400 cm^{-1} spectral range were obtained on a FTS 175C Biorad infrared spectrometer, using the DuraSampl technique. In addition, diffuse reflectance infrared spectroscopy (DRIFT) was used for detailed measurements in the Si–O stretching region (1300–400 cm^{-1}). Samples of 4 mg were ground slightly with 400 mg of KBr, and the resulting powders poured loosely into the sample cup.

The thermal behavior of the solid samples was studied by DSC using a Setsys 16/18 device (Seteram).

Table 1. Chemical composition (wt.%) of the bentonite Calcigel before and after pre-treatment.

	Raw sample (before pre-treatment)	<2 μm fraction (after pre-treatment)
LOI	17.1	13.4
SiO_2	50.2	55.3
Al_2O_3	17.2	19.0
Fe_2O_3	4.6	5.8
CaO	4.1	0.0
MgO	4.3	3.2
TiO_2	0.26	0.24
MnO	0.04	0.02
K_2O	1.4	0.98
Na_2O	0.33	1.95
P_2O_5	0.1	0.06
SO_3 (sulfate)	0.1	no data
S (sulfide)	0.05	no data
TOC	0.18	no data
TIC	0.82	no data

LOI = loss on ignition
TOC = total organic carbon
TIC = total inorganic carbon

RESULTS AND DISCUSSION

Thermal analyses

The DSC curves of the Cu-Na montmorillonite and Cu-NH_4 montmorilllonite (Figure 1) revealed that heat-

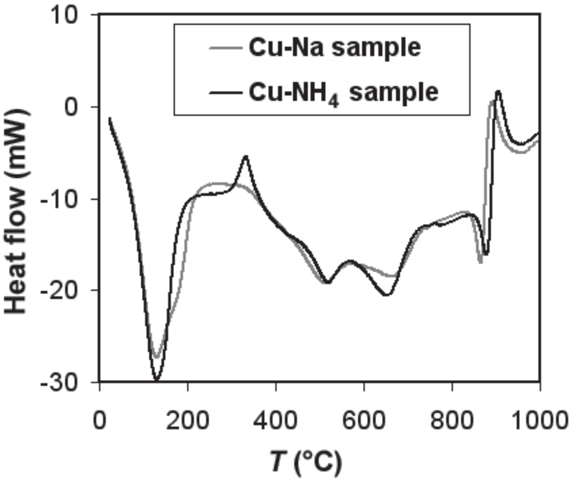

Figure 1. DSC curves of the Cu-Na- and Cu-NH_4-montmorillonites (40 mg, 10 K/min, Pt crucible, air atmosphere).

ing of the Cu-NH_4 sample leads to an exothermic peak between 300 and 400ºC due to the de-ammonization of the NH_4^+, unlike the Cu-Na sample. The exothermic effect probably results from an intracrystalline oxidation of the NH_4^+ upon thermal treatment in an oxidizing atmosphere, according to Barrer (1949), who described this effect for NH_4^+ zeolites. No exothermic effect could be found by DSC in an argon atmosphere.

Dehydroxylation of the montmorillonite investigated occurred in two steps (520−670ºC). Dioctahedral 2:1 clay minerals containing *trans*-vacant and *cis*-vacant varieties in their octahedral sheet (mixed type) have two dehydroxylation peaks (Wolters and Emmerich, 2007). The presence of NH_4^+ in the montmorillonites led to a decrease in the dehydroxylation temperature (*cis*). This is probably caused by the effect of the H^+ generated in the octahedral sheet after the de-ammonization of the NH_4^+.

XRD data

The d_{001} values of the bi-ionic Cu-Na montmorillonite and the Cu-NH_4 montmorillonite at different temperatures (Table 2) indicate that unheated samples have basal spacings of 12.5 Å (Cu-Na) and 12.2 Å (Cu-NH_4). The smaller basal spacing for the Cu-NH_4 form is probably caused by the nature of the NH_4^+ cation that fits into the hexagonal cavities. Upon heating at 300 and 450ºC the layers of the Cu-Na sample collapsed to 9.5 Å, in accordance with previous studies (Mosser *et al.*, 1997; Emmerich, 2000; Shaiek *et al.*, 2003; Karmous *et al.*, 2006) and is caused by the irreversible migration of the Cu^{2+} cations into the montmorillonite structure during the thermal treatment (the 'Hofmann-Klemen effect'). In contrast, the d_{001} value of the Cu-NH_4 sample only decreased to 10.0 Å upon heating. The amount of Cu^{2+} in the Cu-Na form was greater than that of the Cu-NH_4 form. This could be a reason for the different d_{001} values of the samples heated at 300ºC when NH_4^+ was still present in the interlayer. For samples heated at 450ºC, little or no NH_4^+ existed in the interlayer, as confirmed by DSC and FTIR. However, moderate acid activation can lead to partial dissolution of the octahedral sheet so that cations from the structure are present in the interlayer. For instance, the amount of exchangeable Al^{3+} was 12 meq/100 g when 0.1 g of heated NH_4 sample (450ºC) was treated with 25 mL of 0.02 M $CuCl_2$ solution (pH 4.2) for 2 h (three times).

Table 2. d_{001} values (in Å) of the dry-powder samples of bi-ionic Cu-Na and Cu-NH_4 in addition to homo-ionic Cu- and NH_4-montmorillonite at different temperatures.

Starting sample	60ºC	300ºC	450ºC
Cu-Na	12.5	9.5	9.5
Cu-NH_4	12.2	10.2	10.0
Cu	12.5	9.5	9.5
NH_4	12.2	10.0	10.0

The XRD patterns (Table 2) of the homo-ionic Cu and NH_4 forms at different temperatures show, however, features like those of the comparable bi-ionic forms. The basal spacing of the thermally treated NH_4 form (10.0 Å) is greater than for the Cu form (9.5 Å) for treatments at 300ºC as well as at 450ºC. Obviously, the de-ammonization of the NH_4 sample had already begun by 300ºC. However, for clay minerals such as vermiculite with a different octahedral-sheet composition and greater layer charge than for the montmorillonite in the present case, NH_4^+ cations remained in the interlayer after treatments above 450ºC (Poyato *et al.*, 2002; Pérez-Maqueda *et al.*, 2003; Pérez-Rodríguez *et al.*, 2004).

FTIR data

Absorption bands representing vibrational modes in the Si-O stretching, Si-O bending, and O-H bending regions (1300−400 cm^{-1}) were obtained by the DRIFT technique for the bi-ionic Cu-Na and Cu-NH_4 montmorillonites at different temperatures (Figures 2) and for the homo-ionic Na-, Cu-, and NH_4-montmorillonites (Figure 3). The OH- and NH-stretching regions (4000−1400 cm^{-1}) were probed using the FTIR-ATR method (Figure 4).

Si-O vibrations. The broad band at 1050 cm^{-1}, including a shoulder at 1115 cm^{-1}, is assigned to the Si−O stretching vibration in the tetrahedral sheet of the unheated samples (Farmer, 1974). The migration of Cu^{2+} from the interlayer into the hexagonal cavities of the tetrahedral sheet or into vacant octahedral sites affected the Si−O vibrations, in that the Si−O bands in Cu-samples shifted to greater frequencies upon heating, which is consistent with previous studies (Madejová *et al.*, 1999, 2006). Cu-Na and Cu-NH_4 samples showed a shift in the Si−O stretching band to 1058 cm^{-1} and the appearance of a shoulder at 1120 cm^{-1} after heating at

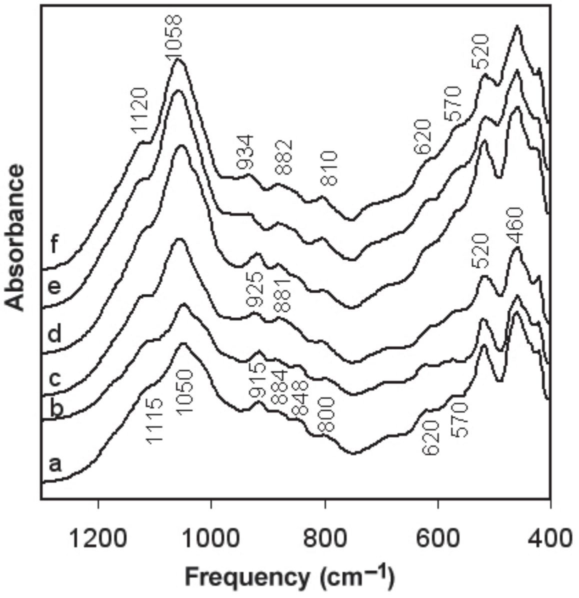

Figure 2. DRIFT spectra of bi-ionic Cu-Na- and Cu-NH_4-montmorillonites at different temperatures: Cu-Na 60ºC (a), Cu-NH_4 60ºC (b), Cu-Na 300ºC (c), Cu-NH_4 300ºC (d), Cu-Na 450ºC (e), and Cu-NH_4 450ºC (f).

300 and 450ºC.

The positions of the Si−O bending vibrations at 620, 520, and 460 cm^{-1} were mainly unchanged. In all samples some decrease in the intensity of the Si−O−Al bands near 620 and 520 cm^{-1} was identified upon heating at 450ºC. Consequently, no substantial alteration of the octahedral sheet occurred due to the H^+ that was generated from the heated NH_4^+, as is often the case for acid-activated montmorillonites (Madejová *et al.*, 1998).

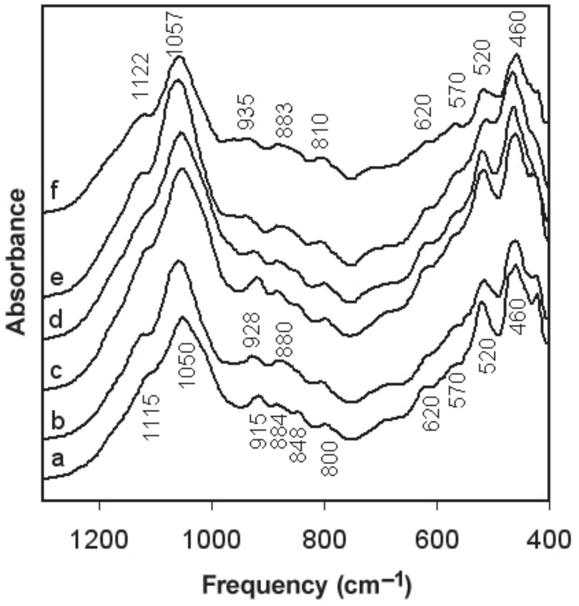

Figure 3. DRIFT spectra of homo-ionic Na-, Cu-, and NH_4-montmorillonites at different temperatures: Na 300ºC (a), Cu 300ºC (b), NH_4 300ºC (c), Na 450ºC (d), Cu 450ºC (e), and NH_4 450ºC (f).

The intensity change and shift to higher frequency of the Si−O−Al band near 700 cm^{-1} may confirm the movement of Cu into the octahedral sites, rather like a mode observed for Cu-muscovite (Friedrich, 2004). However, a discussion about this region in the FTIR spectra (Figure 2) is difficult because of the feldspar admixtures in the samples. Nevertheless, a small shoulder at 500 cm^{-1}, appearing after heating at 450ºC, can be assigned to Si−O vibration of Cu−O−Si also present in the spectrum of chrysocolla, a Cu silicate (Kelm *et al.*, 2001).

OH-bending region. The AlAlOH, AlFeOH, and AlMgOH bands in unheated Cu-Na-, and Cu-NH_4 samples were located at the expected frequencies (Farmer, 1974), at 915, 884, and 848 cm^{-1}. Migration of Cu^{2+} into the hexagonal cavities of the tetrahedral sheet significantly affected the OH-bending vibrations (McBride and Mortland, 1974). Changes in these vibrations upon heating were also consistent with those suggested by Madejová *et al.* (1999, 2006). The AlMgOH band shifted to greater frequencies to overlap with the AlFeOH band, thus broadening the band near 884 cm^{-1}. The AlAlOH band also shifted to a greater frequency, 934 cm^{-1}. No additional changes in the OH-bending vibrations were observed for the Cu-NH_4 sample. No band was observed near 680 cm^{-1} for the CuCuOH-bending vibrations (Kelm, 2001).

OH-stretching region. The OH-stretching band at 3400 cm^{-1} from FTIR-ATR spectra of the Cu-Na-montmorillonite and Cu-NH_4-montmorillonite at different temperatures (Figure 4) arose from the hydration shell of the interlayer cations and significantly decreased in intensity upon heating. This is in accord with the thermal development of the OH-deformation band at 1635 cm^{-1}. The band at 3622 cm^{-1}, corresponding to the vibrations of the octahedral hydroxyl groups (Farmer, 1974), shifted to greater frequency upon heating at 300 and 450ºC, ranging from 3633 cm^{-1} to 3640 cm^{-1} depending on the sample. This shift to greater frequency is evidence for a decrease in layer charge due to the movement of Cu^{2+} into the structure. A similar shift to greater frequency was also observed for heated Ni-montmorillonites (Pálková *et al.*, 2003). This may suggest the occurrence of Cu−OH vibrations, indicating an octahedral environment for the fixed Cu^{2+} in the heated sample (Mosser *et al.*, 1997; Madejová *et al.*, 1999). Wright *et al.* (1972) observed the appearance of a shoulder at 3670 cm^{-1} for homo-ionic NH_4-forms of diocthedral clays after thermal activation, resulting from the change of the interlayer cation ($NH_4^+ \rightarrow H^+$). However, this feature was absent in the current

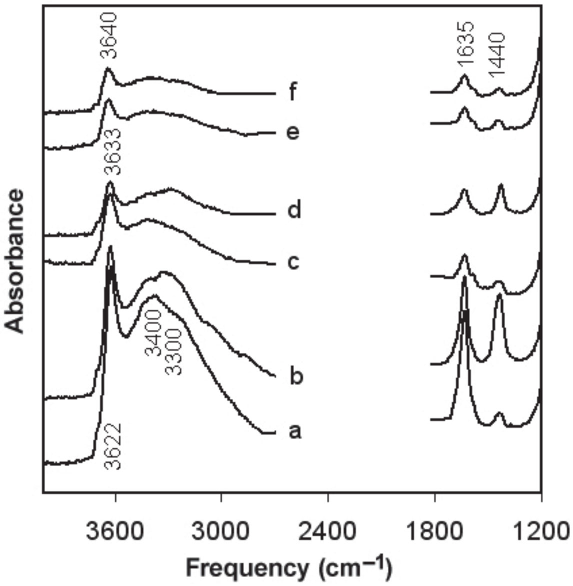

Figure 4. FTIR-ATR spectra of bi-ionic Cu-Na-montmorillonite and Cu-NH_4-montmorillonite at different temperatures: Cu-Na 60ºC (a), Cu-NH_4 60ºC (b), Cu-Na 300ºC (c), Cu-NH_4 300ºC (d), Cu-Na 450ºC (e), and Cu-NH_4 450ºC (f).

experiments for bi-ionic Cu-NH_4- or for homo-ionic NH_4-forms of montmorillonite. This may be because of the relatively small CEC of 60 meq/100 g for the starting material. The possibility that some Cu^{2+} was trapped in vacant sites in the octahedral sheet of Cu-NH_4 and Cu-Na samples cannot, however, be ruled out.

NH vibrations. The FTIR spectra of the unheated Cu-NH_4 sample showed a broad NH band near 3300 cm^{-1} and another near 1440 cm^{-1} (Mortland *et al.*, 1963). These bands decreased significantly in intensity after thermal treatment, mirroring the de-ammonization of the interlayer NH_4^+. The small band near 1440 cm^{-1} appearing in the spectrum of the Cu-Na sample probably corresponds to a minor carbonate admixture in the material.

CONCLUSIONS

Bentonite, a clay containing primarily montmorillonite, has wide potential for environmental application. The purpose of this study was to investigate the migration of Cu^{2+} in montmorillonite under moderate, acid, and thermal conditions concerning the fixation of heavy metal cations to bentonite.

(1) The dehydrated Cu^{2+} cations migrated into the montmorillonite structure with increasing temperature so that the Cu^{2+} was mainly trapped in the hexagonal cavities of the tetrahedral sheet in accordance with previous studies (*e.g.* Madejová *et al.*, 1999, 2006). The possibility remains, however, that some Cu^{2+} was trapped in vacant sites in the octahedral sheet after the heat treatment of the Cu-Na and Cu-NH_4 forms.

(2) In the case of the homo-ionic NH_4 and bi-ionic Cu-NH_4 forms, the structure of the montmorillonite was not substantially altered by the presence of NH_4^+ and heating ($NH_4^+ \rightarrow H^+$), contrary to usual acid activation with strong mineral acids.

(3) De-ammonization certainly led to a decrease in the basal spacing of montmorillonite, but the d_{001} values did not decrease to <10 Å as was the case for the heated Cu form and Cu-Na sample.

(4) No other effects of the presence of NH_4^+ on the Cu^{2+} fixation in the montmorillonite studied here were observed.

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