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Evolution of the exchange properties of a K-beidellite submitted to alternate wetting and drying cycles

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Abstract

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Many studies have shown that smectites, particularly under the effect of drying, could be one of the causes of the retrogradation of potassium (K) in the soil. Most of these studies have focused on the fixation of K in montmorillonites with an octahedral charge deficit. However, smectites most often have both tetrahedral and octahedral charge deficits. This led us to study the variation in K exchangeability for a K-beidellite during wetting and drying (WD) treatment. Chemical analysis and X-ray diffraction showed that, the fine fraction of the studied raw clay is a mixed beidellite, where 70% of the charge comes from substitution in the tetrahedral layer. The study in the variation of K exchange capacity for K-beidellite as a function of the number of WD cycles, allowed to show that the amount of fixed K is related both to the number of WD cycles and to the negative charges arising from the substitution in the octahedral sheets.

Keywords: potassium; exchange; beidellite; wetting and drying
Abbreviations: K – potassium, WD – wetting and drying, CEC – cationic exchange capacity

Introduction

Several studies have shown that a fraction of K added to a soil as fertilizer can pass progressively to the non-exchangeable form (Barber, 1995; Zeng and Brown, 2000). This phenomenon, known as "retrogradation", is a subject of great concern. The search for optimization of K fertilizers, with its economic consequences, justifies the interest that agronomists attach to this problem (Barré et al., 2008; Kayser et al., 2012; Zörb et al., 2014; Blanchet et al., 2017). It has appeared that this retention of K in soils may be due to different physicochemical mechanisms, but it is always the phyllite silicates, which are one of the causes for it (Olk et al., 1995; Öborn et al., 2005; Simonsson et al., 2009; Florence et al., 2017). Moreover, the studies on K fixation by montmorillonites reported that alternations of WD remove the swelling properties of these minerals by water and reduce their cationic exchange capacity (CEC) (Mamy and Gaultier, 1979; Eberl et al., 1986; Mikloš and Čičel, 1993; Sardi and Csitari, 1998; Honty et al., 2003). According to these studies, the retention of K would be due to the transformation of clay minerals of this type into structurally close minerals of illite type. It would be useful to see if other swelling clays, with different layer-charge location and present in many soils of the world such as beidellite (Aragoneses and Garcia-González, 1991; Hetzel and Harvey, 1993), can evolve in the same way when K^+ saturates their CEC. On the basis of these considerations, we have studied the evolution of exchange properties of a K-beidellite, with mixed charge deficit, submitted to alternate WD cycles.

Materials and Methods

Preparation of samples

The raw clay used was provided by the National Company of Non Ferrous Mining Products & Useful Substances (ENOF) (Algeria). It was purified by sedimentation. The less than 2 µm fraction was agitated for 4 hours in a chloride solution of the selected cation to saturate its CEC. The quantity of salt is calculated in such a way that it represents ten times the value of the exchange capacity of the clay mass considered. After centrifugation and elimination of the excess solution, we have renewed the operation twice. The solid phase, washed several times until negative test with $AgNO_3$, was then stored in water suspension. We have selected the cations Na^+, K^+ and Ca^{2+}; the samples of clay thus obtained will be denoted as Na-Bed, K-Bed and Ca-Bed, respectively.

WD Procedure

The treatment of samples by a WD cycles was inspired by previous works (Mamy and Gaultier, 1976; Mikloš and Čičel, 1993) and it can be described as follows: sample of clay is immersed in distilled water in a proportion of 50 mL of water per gram of clay. The homogenization of the suspension is assured by stirring for 2 hours and then the suspension is dried at temperature of 60°C for 12 hours. After the first drying, we can say that the mineral has undergone a wetting and drying cycle (1 WD). The choice of this temperature (60°C) is not arbitrary; it takes account of previous work on the study of the evolution of exchange properties of K-montmorillonite as a function of the number of WD cycles at temperatures of 20, 40, 80, 160 and 240°C (Gaultier, 1981). This study showed that the dehydration and not the temperature was the essential factor of the fixation of potassium and the temperature of 40°C is the minimum temperature from which the mineral can be completely dehydrated (Gaultier, 1981; Inoue, 1983).

Methods

The X-ray diffraction analyses were performed on powder and on oriented aggregates at ambient conditions (average temperature around 18°C and relative humidity about 53%), using a Bruker D8 Advance diffractometer operating at 40 kV and 20 mA, equipped with a Cu tube (λ =1.5418 Å). The chemical composition of Na-Bed was determined by X ray fluorescence spectrometry with a Thermo Scientific device.

Cation exchange capacity was measured by the conductometric method (Chiu et al., 1990). The experiments of CEC were repeated at least twice under identical conditions. The reproducibility of the measurements was within limits of 3%.

Results and Discussions

Physicochemical characterization

X-ray diffraction

The detailed mineralogical characterization of clay minerals was obtained by the displacement of the main line corresponding to the (001) plane and under the action of specified treatments (Hofmann and Klemen, 1950; Caillère et al., 1982; Lim and Jackson, 1986; *Campos et al., 2009;* Bouna et al., 2012). The X-ray patterns of the fine fraction Na-Bed, oriented and air-dried, and glycerol-solvated are represented in Figure 1. The Na-Bed sample presents a basal spacing d_{001} similar to that of Na-smectites or Na-vermiculite, to one layer of water (d_{001} = 12.44 Å) (Figure 1a). However the Na-Bed sample, treated with glycerol, shows a basal spacing d_{001} characteristic of smectites and its swelling varies between 17.7 and 18.0 Å (Figure 1b), contrary to the vermiculites which swell to about 14.3 Å after this test. It is thus a smectite. Figure 2 gives the X-ray patterns of the fine fraction Na-Bed after saturated with lithium, heated at 300°C for 24 hours and immersed in glycerol. The results show that the mineral retains its re-expansion power. This characteristic excludes its belonging to the group of montmorillonites whose reticular equidistance is reduced to 10 Å following of the same treatment.

On the X-ray pattern, obtained from air-dried powders of the raw clay (Figure 3), a d_{060} reflection at 1.49 Å is observed. Such peak is characteristic of dioctahedral smectites (Bouna et al., 2012). However, in the vicinity of this peak, another peak appeared at 1.53 Å, is characteristic of trioctahedral smectites such as saponites (Chevalier and Dejou, 1982). Nevertheless, the size of this last peak compared to that of the dioctahedral smectites is small. This suggests that

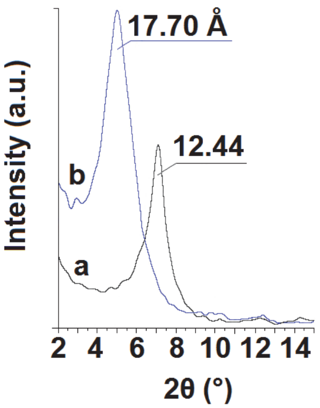

Fig. 1. XRD patterns of air-dried oriented aggregates: (*a*) Na-Bed; (*b*) glycerolated Na-Bed

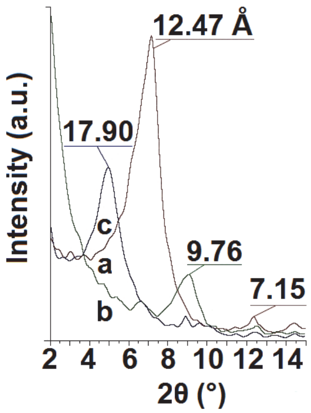

Fig. 2. XRD patterns of air-dried oriented aggregates of Na-Bed: (*a*) after Li^+ saturation, (*b*) followed by heating at 300°C for 24 h, (*c*) glycerolated

the fine fraction Na-Bed is a dioctahedral smectite (beidellite or nontronite) and has a low trioctahedral character. Moreover, the 7.15 and 3.55 Å characteristic lines of kaolinite, and those of illite at 10.03, 5.02 and 3.33 Å (Caillère et al., 1982; Bouna et al., 2012) also appear with low intensity.

Chemical analysis and structural formula determination

The results of the chemical analysis of the Na-Bed clay (Table 1) confirm the conclusions already made; the Si/Al molar ratio = 1.72, proximate to 2, is characteristic of dioctahedral smectites (Bergaya et al., 1986). The quantity of potassium, not exchanged by sodium, is not negligible which is consistent with the presence of illite.

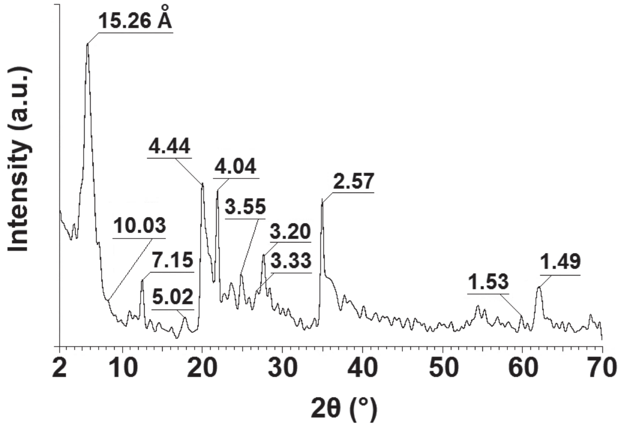

Fig. 3. Powder XRD pattern of the raw clay

Table 1. Chemical analysis of dehydrated Na-smectites: (a) Na-Bed, (b) beidellite of Black Jack Mine (USA) (Weir, 1965; Bouna et al., 2012), (c) beidellite of Unterrupsroth (Germany) (Weir, 1965), (d) nontronite Manito (USA) (Koster et al., 1999), (e) saponite of Vicalvaro (Espagne) (Casal et al., 1997)

Oxide (wt%)	a	b	c	d	e
SiO_2	60.896	59.300	64.000	51.500	61.167
Al_2O_3	30.001	36.110	29.000	8.967	5.702
Fe_2O_3	2.090	0.500	0.210	35.084	2.032
MgO	2.201	0.100	3.030	0.460	27.023
CaO	0.063	0.020	–	0.034	0.590
K_2O	0.595	0.110	0.050	0.115	0.819
Na_2O	4.087	3.980	3.980	3.664	2.032
MnO	0.015	–	–	–	0.044
TiO_2	0.031	–	–	0.195	0.164
P_2O_5	0.021	–	–	–	–
Total	100.000	100.120	100.270	100.019	99.201

The structural formula established for the dehydrated Na-Bed, out on the basis of 22 oxygen atoms per unit cell, from its chemical composition (Table 1) and following the method of Mauguin described by Caillère et al. (1982), is as follow:

$Ca_{0.008}K_{0.090}Na_{0.942}$ $[Si_{7.242}Al_{0.758}][Al_{3.448}Fe_{0.187}Mg_{0.390}Mn_{0.001}Ti_{0.003}]O_{22}$.

The value of the interfoliar charge of the mineral, close to 1.06, is between 0.40 and 1.20 confirms the smectite predominant in the clay fraction studied (Chevalier and Dejou, 1982). We observe that about 30% of the charge is due to the isomorphous substitutions in the octahedral layer. It also appears from the results reported in Table 1 that the clay fraction studied has iron and magnesium contents much lower than those published for Fe- and Mg-smectites, nontronites and saponites, respectively (Casal et al., 1997; Koster et al., 1999). Similarly, the chemical composition of our clay sample is significantly closer than those of the Black Jake Mine beidellites (Idaho, USA) or Unterrupsroth (Germany) (Weir, 1965), than those of nontronites and saponites. These results therefore bring our clay fraction Na-Bed near to a beidellite.

The fine fraction Na-Bed is therefore a mixed beidellite with dominant tetrahedral charge. It contains small quantities of both kaolinite and illite, and its trioctahedral character is weak.

Evolution of exchange properties

The initial state of the clay materials studied is that which exists before the first drying, that is to say, after the saturation of the exchange capacity of the fraction less than 2 µm of the raw clay with Ca^{2+}, Na^+ or K^+. The measured CEC values are 100, 96 and 93 mEq/100g for Ca-Bed, Na-Bed and K-Bed, respectively.

The results of the experiments relating to the evolution of the CEC of Na-Bed, Ca-Bed and K-Bed samples with the number of WD cycles (Figure 4) indicate, first of all, that the WD cycles have no effect on the variation of the CEC of Na-Bed and Ca-Bed samples. Indeed, all the Na and Ca ions remain exchangeable after 100 WD cycles. This result joins the observation made previously by Calvet and Prost (1971), Mamy and Gaultier (1979) for a Camp Berteaux Na-montmorillonite heated at 250°C during 24 hours and a Wyoming Ca-montmorillonite submitted to alternate WD cycles at 80°C, respectively. Furthermore, Figure 4 shows that during the first WD cycles, the CEC of the K-Bed clay decreases rapidly but, after 40 WD cycles the quantity of K exchangeable reaches a limiting value of about 71 mEq/100g. This behavior has also been observed by other authors on K-montmorillonites, of various origins, submitted to a series of WD cycles (Mamy and Gaultier, 1979; Eberl et al., 1986; Andreoli et al., 1989; Mikloš and Čičel, 1993; Honty et al., 2003). Mamy and Gaultier (1979) and Andreoli et al. (1989) consider K retention to be related to a modification of the superposition order of the elementary layers appearing during WD cycles. When dehydration occurs, the layers get closer and a proportion of them superimpose, which corresponds to a stacking in which the hexagonal cavities of two adjacent layers are facing each other. The initial turbostratic structure evolves into a well ordered one (Mamy and Gaultier, 1979; Andreoli et al., 1989; Reynolds, 1992). This structural rearrangement reduces the interlayer distance, and consequently increases the interaction energy by creating the most possible stable situation, as in illites. This will prevent water accessibility to a part of the interlayer spaces. As a result, a proportion of K^+ passes to the non-exchangeable state. Following these works, several investigators (Altaner and Ylagan, 1997; Honty et al., 2003; Inoue et al., 2005) have attempted to understand the process for the smectite to illite conversion. In many cases the solid-state transformation (SST) mechanism seems to best describe illitization in most bentonites (Altaner and Ylagan, 1997; Drits et al., 1997; Cuadros and Altaner, 1998). Nevertheless, the controversy remains very strong between the different authors for the choice of the mechanism (Meunier et al., 2000; Inoue et al., 2005).

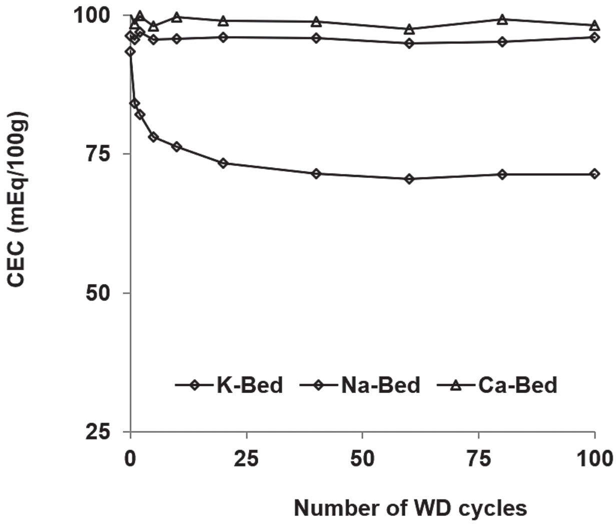

Fig. 4. Evolution of CEC with the number of WD cycles

The calculation of the percentage of non-exchangeable K must take into account the K retained on external surface of mineral, the latter always being considered as exchangeable. For the smectites, the CEC due to external surface is estimated to be about 15% of the total CEC (Ben Hadj-Amara et al., 1987; Čumakov et al., 2000). We can note, after 40 WD cycles, that 28% of interlayer K (79 mEq/100 g) remains fixed on the mineral K-Bed. This proportion of fixed K is close to that of octahedral origin charge. Comparing our results with that found for K-montmorillonite Wyoming with predominantly octahedral charges (Mamy and Gaultier, 1979), where the quantity of K non-exchangeable has reached a value more than 64 mEq/100 g after 100 WD cycles which corresponds to 79% of interlayer K is fixed, we note that the retention of K is stronger for the Wyoming montmorillonite than that for K-Bed. This difference may be related to the heterogeneity in the charges distribution of the sheets of our mineral, a common phenomenon in smectite minerals (Ben Hadj-Amara et al., 1987; Lagaly, 1994; Gier et al., 1998; Ferrage et al., 2007; Ferrage et al., 2010). This heterogeneity is partly attributed to the presence of different types of layers to microstructural scale within of a same crystal. These layers, with a purely tetrahedral charge, others with purely octahedral charge, and all possibilities can exist between these two cases extremes (Lagaly, 1994; Ben Hadj-Amara et al., 1987; Ferrage et al., 2007; Ferrage et al., 2010), may exhibit different behavior towards WD cycles. This suggests that the effect of WD cycles favors the reorganization in the stacking of the octahedral sheets existing in mixed beidellites; this disposition is probably responsible for K fixation. This result joins the observation made previously by Weir (1965), Cuadros and Altaner (1998) and Chittamart et al. (2010), namely, that the beidellite does not fix substantial amount of K and there is no relation between the amount of potassium retained and the tetrahedral charge.

Evolution of hydration properties

Figure 5 shows the evolution of different X-ray diffractograms obtained from powder and under the same experimental conditions, on samples of sodic clay (Na-Bed), calcic (Ca-Bed) and potassic (K-Bed) submitted to WD cycles at 60°C. These analyses do not reveal significant structural changes affecting the hydration properties of Na and Ca-clays after WD treatment (Figures 5a, 5b, 5c and 5d). Indeed, the X-ray diffractograms obtained are not significantly different; the average basal spacing d_{001} of Na-Bed and Ca-Bed samples of the order of 12.5 and 15 Å respectively do not evolve. These results agree with previous results (Mamy and Gaultier, 1979). Furthermore, for the sample K-Bed (Figures 5e, 5f, 5g and 5h), we notice that interfoliar distance decreases with increasing number of WD cycles. It falls from 12.20 Å at 0 WD to 11.36 Å at 60 WD, which corresponds to the existence of interstratified layers 10 – 12.20 Å (Andreoli et al., 1989). Which suggests, in agreement with several previous observations (Čičel and Machajdik, 1981; Andreoli et al., 1989; Mikloš and Čičel, 1993; Gier et al., 1998), that the number of sheets containing a layer of water (d_{001} = 12.20 Å), decreases in favor to the number of dehydrated sheets (d_{001} = 10 Å), which reduces the ability of the clay material to swell in water. A proportion of interfoliar spaces therefore become inaccessible to water; non-exchangeable K is located in these spaces. We also note that the evolution of the hydration status of our potassium mineral seems to stabilize after about 60 WD cycles (Figures 5g and 5h), which is also in acceptable agreement with results previously obtained (Figure 4). It also appears, from X-ray diffraction patterns of K-Bed samples submitted to a series of alternating WD cycles without treatment (Figures 5e, 5f, 5g and 5h) and after solvation in ethylene glycol (Figure 6), an increase in intensity of characteristics reflexions of the illites, corresponding to the first-, second- and third-order (d_{001} = 10, d_{002} = 4,96 and d_{003} = 3,34 Å). Such effects have been reported by other authors (Čičel and Machajdik, 1981; Andreoli et al., 1989; Mikloš and Čičel, 1993; Cuadros and Altaner, 1998; Honty et al., 2003). These observations seem to confirm the existence of a fraction of the mineral K-Bed that undergoes, as the number of WD cycles increases, a structural reorganization causing closing of layers. These layers phase, that have properties nearby to those of illites, is responsible for the retrogradation of K.

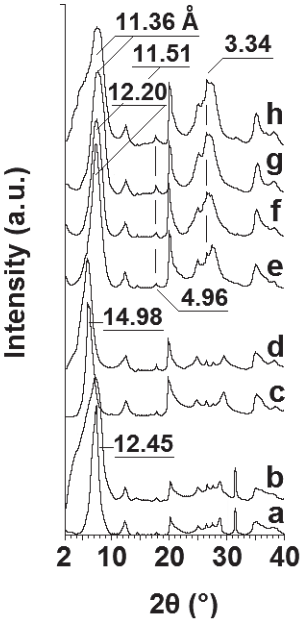

Fig. 5. XRD patterns of samples after WD treatment: (*a*) and (*b*) Na-Bed (at 0 and 100 WD), (*c*) and (*d*) Ca-Bed (at 0 and 100 WD), (*e*), (*f*), (*g*) and (h) K-Bed (at 0, 40, 60 and 100 WD, respectively)

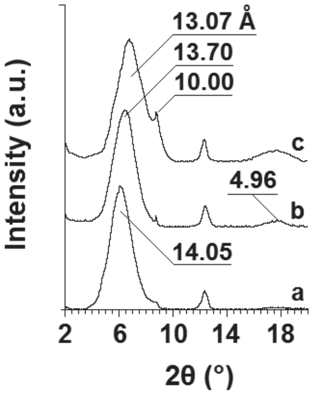

Fig. 6. XRD patterns of air-dried oriented aggregates of K-Bed after WD treatment and solvation in ethylene glycol: (*a*) 0 WD, (*b*) 40 WD and (*c*) 100 WD

Conclusions

A sequence of 100 cycles of wetting and drying has been performed on a K-beidellite with mixed charge deficit. They have allowed highlighting that the penetration of potassium into the interlayer spaces is accompanied by a reduction of exchangeable potassium. The proportion of potassium retained compared to the total quantity of interlamellar potassium is close to that of the octahedral origin charge.

The study of hydration properties of mineral studied using X-ray diffraction has shown that interlamellar spacing decreases with the increasing of WD cycles. All the observed spacing values correspond to interstratified states in which the number of non expanded layers gradually increases. These layers, having properties closer to those of illites, are probably responsible for the irreversible fixation of potassium. However, this rearrangement of the structure, caused by a series of WD cycles, is more limited for our mineral. Indeed, the evolution of hydration status for our sample stabilizes at an interlamellar spacing of 11.36 Å after 60 WD cycles against 10.20 Å for Wyoming montmorillonite after 100 WD cycles. Based on these findings, we can say that the same phenomena of potassium fixation associated with structural reorganization as those observed in montmorillonites find themselves but with a lower intensity. These differences could be related to the location of the layer charge. This is an important point for potassium dynamic in soils rich in clay minerals of this type.

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