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STUDY OF WATER-REDUCED CHARGE MONTMORILLONITE SYSTEM

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Abstract: The reduced charge montmorillonite (RCM) samples were prepared by heating the exchanged formof lithium at different temperatures for 24 hours. Calcium exchanged forms were used for the study of the interaction with water. The collapse of the interlayer spaces lowered the accessible surface area for the water molecules and decreased the water sorption. Induced acid treatment (after lithium reaction with hydroxyl groups) caused the dissolution of the structure and enhanced specific surface area. The samples with reduced layer charge, but without collapsed interlayers exhibited the highest affinity to water.

Key words: lithium migration, reduced charge montmorillonite, water sorption.

Introduction

After the thermal treatment of lithium saturated montmorillonite, lithium cations move irreversibly towards the negative charge centres in the layers. The migration and following fixation of positive charged cations bring about the lowering of the cation exchange capacity (CEC) (Hofmann & Klemen 1950; Gonzáles García 1950). Hofmann & Klemen (1950) claimed that the cations migrate into the vacant octahedral sites and some authors supported their opinion (Green-Kelly 1953, 1955; Calvet & Prost 1971). On the other hand Tettenhorst (1962) and later others (Luca & Cardile 1988; Luca et al. 1989) considered that cations penetrate into the Si-O network, and bottoms of tetrahedral cavities are the final positions of fixed cations. Glaeser & Mering (1967) discovered that only the octahedral charge is neutralized by lithium migration, which was confirmed by Schultz (1969). Russel & Farmer (1964, 1967) showed the acidic reaction after heating of Li-, Mg- exchanged forms of montmorillonite. Thus migration of small cations seemed to be not so simple as it had been considered earlier. Acidic reaction was caused by the reaction of migrating cations with hydroxyls and following release of protons. Jaynes & Bigham (1987) measured titratable acidity of heated Li-smectites and suggested, that it increased with iron contents.

Relocation of the lithium cations from the interlayer exchange position into the fixed state in the layers has been employed for the preparation of RCMs. The prepared RCMs gave a chance to investigate some properties of the material as a consequence of changes of the layer charge (Brindley & Ertem 1971; Clementz & Mortland 1974; Clementz et al. 1974; Maes et al. 1985).

The amount of water retained on the clay may be used to characterize the mineral. The arrangement and also the amount of water sorbed depends on the balancing cation, surface area and the shape of clay particles and also on density and location of the layer charge. The aim of this work was a study of water sorption on montmorillonite in dependence on the layer charge or the CEC respectively; and investigation of other changes in RCM samples as possible formation of collapsed structure and the changes in the surface area accessible to water.

Experimental

Montmorillonite (M1) was isolated as a 2 *μm* fraction by sedimentation of the 4 % water suspension of Jelšový Potok bentonite (Central Slovakia). The Li-exchanged form was prepared by treatment with lithium chloride solution. The Li saturated montmorillonite was left to dry in air at the room temperature and then pulverized. The RCM samples (M2-M8) were prepared by thermal treatment of the lithium saturated montmorillonite. The time of heating was 24 hours and the temperatures are listed in Tab. 1. After the heating samples M1-M8 were saturated with calcium chloride to prepare calcium exchanged forms.

Table 1: Temperatures used for preparation of RCM samples.

Sample	t (°C)	Sample	t (°C)	Sample	t (°C)	Sample	t (°C)
M1	–	M3	110	M5	130	M7	160
M2	105	M4	120	M6	135	M8	210

A Philips diffractometer model PW 1050 (35 *kV*, 20 *mA*, CuK_{α} radiation, Ni-filter) was used for powder *X*-ray diffraction to identify the samples.

Water sorption was made at 25 °*C* using powdered Ca exchanged forms of samples M1-M8. The samples were kept in a dessicator. The constant pressures of water vapour were fixed by solutions of sulphuric acid, zero pressure by phosphoric oxide. The amount of water sorbed on RCMs was determined by weighing of the samples. Both sorption and desorption curves were measured.

The losses on drying (LD) and ignition (LI) were determined by weighing of heated samples at the temperatures 110 °*C* and 1100 °*C*. The samples were heated several times for 1 hour, untill the weigh of the samples changed.

Results and discussion

The amounts of CaO and Li_2O in RCM samples, CECs, LDs and LIs of RCMs are summarized in Tab. 2. As it was expected, the amount of exchangeable calcium increases and the content of fixed lithium decreases with increasing layer charge. The LD reflects the amount of water sorbed on the external surface and the part of interlayer water, the LI reflects the amount of water in hydroxyl groups (structural water) and the water bound to the exchangeable cations in the interlayer spaces. The lowering of the LI after lithium thermal treatment is connected with the decrease of the amount of the exchangeable cations, but can be affected by the reaction of lithium ions with hydroxyl groups and folowing liberation of protons. The deprotonised hydroxyl groups are stable against the thermal treatment and cannot dehydroxylate (Williams et al. 1991).

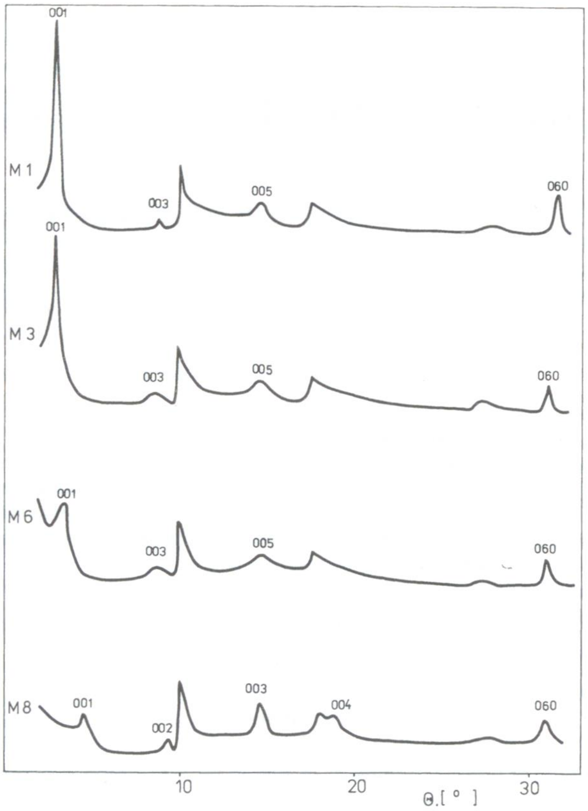

Fig. 1. X-ray diffraction patterns of RCM samples.

Table 2: Composition of RCM samples: the amounts of CaO (%) and Li_2O (%), CEC (*meq/g*), LD, LI (%).

Sample	M1	M2	M3	M4	M5	M6	M7	M8
CaO	3.47	3.33	3.62	2.77	2.37	2.08	1.12	0.54
Li_2O	0.00	0.17	0.20	0.39	0.52	0.65	1.08	1.35
CEC	0.83	0.71	0.65	0.60	0.50	0.46	0.26	0.14
LD	13.67	15.06	15.22	14.87	12.95	11.48	7.49	3.75
LI	9.49	8.48	8.95	8.08	7.32	7.12	6.51	6.25

Fig. 1 shows X-ray diffraction patterns of representative RCMs (M1, M3, M6 and M8). X-ray diffraction proved no impurity in the sample M1. Swelling interlayer spaces of Ca-montmorillonite (M1 - M3) are occupied by two layers of water (d_{001} = 1.55 *nm*). The reduction of the layer charge brings about formation of collapsed interlayers and of a mixed-layer structure with swelling/non-swelling interlayers (sample M6). The highest reduction of the CEC transforms montmorillonite into the non-swelling material (d_{001} = 1.0 *nm*) with pyrophylite-like structure (M8). The samples with a different degree of the charge reduction differ in the proportion of swelling and non-swelling phases and the value of the basal spacing d_{001}. The peaks of d_{002} and d_{004} appeared only in X-ray diffraction pattern of the sample M8, which indicates some arrangement changes of the layers after the collapse of structure. Low increase of d_{060} value can be caused by the formation of local trioctahedral structure after moving of lithium cations into the octahedral sheets.

Sorption of water vapour

Hysteresis water sorption/desorption curves were obtained for all RCMs. Higher amounts of sorbed water were found for desorption than for sorption. This phenomenon is common for the water sorption on montmorillonite and is caused by the vapour condensation on the clay surface. The course of the sorption curves of samples M8 was partly different from others (Fig. 2), because it missed the part concerning the water sorption into the interlayer spaces (low pressures of water vapour).

The relationship between the water sorption and the CEC at different water pressures is shown in Fig. 3. Under the lowest pressure (Fig. 3a) only ions localized at the edges of the layers and on the external surface of clay particles are hydrated. Their amount is not changed after the lithium thermal treatment. This is reflected in practically the same sorption on each sample. At higher pressures (Fig. 3b-d) the exchangeable cations in the interlayer spaces are hydrated and these spaces are gradually filled with water. The increase of the water sorption with the CEC is due to increasing proportion of the expandable layers. In Ca-montmorillonite the amount of exchangeable cations probably does not affect the sorption considerably. In an Li- or Na-montmorillonite a number of water layers in the interlayer spaces strongly depends on the amount of osmotic active cations there. Therefore the water sorption on Li- and Na-RCMs increases with CEC (Calvet & Prost 1971; Sposito et al. 1983). The amount of calcium cations in the interlayer spaces can affect the

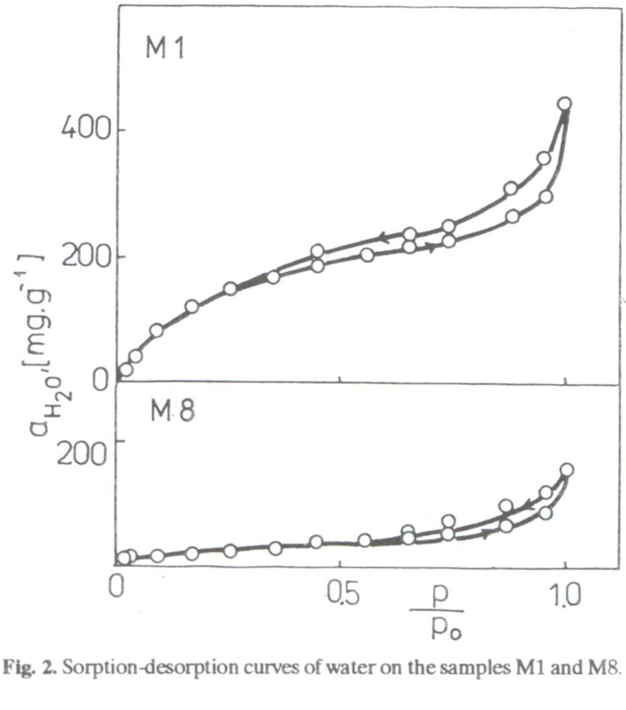

Fig. 2. Sorption-desorption curves of water on the samples M1 and M8.

expandability of the interlayer spaces. There is a constant water amount sorbed on the samples without collapsed interlayers (M1-M3) (Fig. 3b-d). This means that, the number of water layers in the swelling interlayer spaces of calcium RCMs is not significantly affected by the calcium content. The relationships between the water sorption and the CEC at high vapour pressures are shown in Fig. 3e, f. The sorption increases up to the CEC = 0.65 *meq/g* (samples M8-M3) because of the increase of the number of expandable interlayer spaces. Further increase of the CEC does not enhance an affinity to water, but the sorption is lowered. Described courses are confirmed by LDs and DTG measurements (Bujdák & Slosiariková 1992) of samples. Under high water pressures the water molecules fill the spaces between clay particles and the amount of sorbed water is affected by the surface area of the particles and their shape. The samples M2 -M4 have probably higher surface area than the original (lithium untreated) sample M1. The migration of lithium ions into the structure could increase the surface area of the clay. There are two hypotheses:

1 - Migrating cations evoked structural tension and structural defects were formed.

2 - After the reaction of Li cations with hydroxyls, protons were liberated (Russell & Farmer 1964; Farmer & Russell 1967; Jaynes & Bigham 1987) and partially dissolved the structure (induced acid treatment).

The sample M3 exhibits the highest affinity to water under higher pressures of water vapour. This sample was prepared at a relatively low temperature of 110 °*C*, using lithium thermal treatement. As it was claimed that small cation migration is a general phenomenon (Calvet & Prost 1971) also other cations such as Mg or Al which are common in nature could have the same ability as lithium ions. Then the phenomenon of the increase of clay hydrophility after heating in the presence of small cations could have a considerable significance for the chemistry of smectite transformations.

Conclusions

1 - Lithium thermal treatment caused the lowering of the layer charge and the capacity of exchangeable cations.

2 - The heating of Li-montmorillonite at low temperatures enhanced the surface area and the amount of sorbed water was higher than the amount of water sorbed on an original Li-untreated sample. It was probably caused by partial acid dissolution of motmorillonite after the reaction of lithium cations with hydroxyl groups.

3 - The amounts of sorbed water on montmorillonite after the heating at high temperatures decreased with decreasing layer charge due to the formation of collapsed interlayers.

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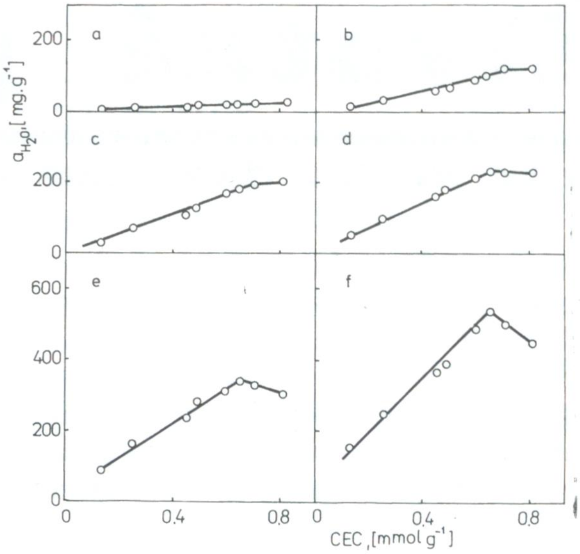

Fig. 3. Relationship between the water sorption and the CEC at constant water pressures: **a** - 0.054, **b** - 0.526, **c** - 1.460, **d** - 2.373, **e** - 2.986, **f** - 3.167 *kPa*.

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