

Fixation of lithium cations in montmorillonite

^aJ. BUJDÁK, ^aH. SLOSIARIKOVÁ, ^bE. NOVÁKOVÁ, and ^bB. ČÍČEL

^a*Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, CS-842 15 Bratislava*

^b*Institute of Inorganic Chemistry, Slovak Academy of Sciences, CS-842 36 Bratislava*

Received 13 February 1990

The method of preparation of montmorillonite with different values of negative residual charge of layers is presented. The change of the negative charge is due to the fixation of lithium cations in the structure. With the fixation of Li^+ the mixed layer materials of the swelling/nonswelling type as well as the local trioctahedral configurations in the octahedral network are formed.

Owing to the temperature the lithium cations are able to migrate from the exchangeable positions in the interlayer spaces of montmorillonite into the layers 2:1 [1–5]. In this process a part of cations is fixed in the layer 2:1, in consequence of which the lowering of the negative residual charge of the layers occurs. The lowering of the negative residual charge is equivalent to the number of fixed lithium cations. This is at the given sample proportional to the heating time of the sample and the used temperature.

Some works [1–4] show that the lithium cations migrate into the vacant octahedral positions and this assumption is supported by formation of local trioctahedral configuration. In [6] it is shown that the lithium cations are bonded to the oxygen atoms of the OH groups which coordinate iron atoms in the octahedral layer, whereby the protons are simultaneously released. *Tettenhorst* [5] concludes that the lithium cations occupy due to the temperature also the hexagonal holes in the SiO_4^- tetrahedral network. His opinion was based on the study of the infrared spectra and the X-ray diffraction patterns of samples saturated with different cations and thermally activated at the temperature of 300 °C during 8 h. On the basis of the study of the infrared spectra of Li as well as other montmorillonite forms activated at different temperatures and time intervals *Calvet* and *Prost* [7] claim that a part of lithium cations migrates into the hexagonal holes and a part into the vacant octahedral positions. The migration of the lithium cations into the 2:1 layers is schematically shown in Fig. 1.

The change of the negative residual charge causes marked changes in the properties of smectites, influences for instance the hydrophobic character,

affects also the ordering of the aliphatic chains of alkylammonium cations sorbed in the interlayer space [8].

The aim of this work is to present the method of preparation of materials with different values of negative residual charge in the 2:1 layer of montmorillonite and to show some changes evoked by fixation of lithium cations in the structure of the modified montmorillonite.

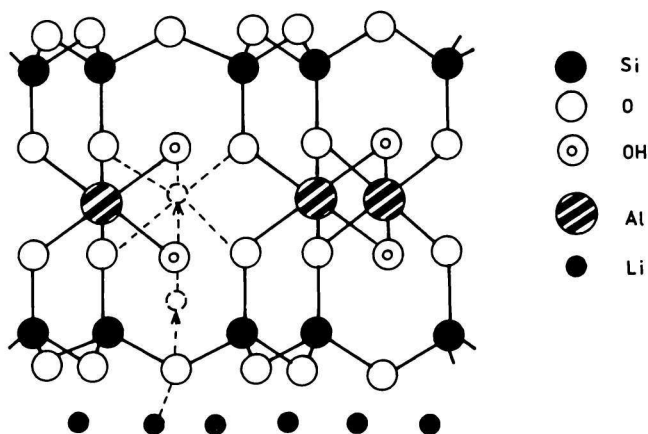


Fig. 1. Migration of Li^+ cations into the layers.

Experimental

The montmorillonite was isolated by sedimentation from the 4% aqueous suspension of bentonite (locality Jelšový Potok, CSFR). The obtained montmorillonite was dried at the temperature of 105–110°C and milled in a vibration mill during 4 h. The purity of the sample was checked by X-ray diffraction method. X-Ray measurements were carried out using an X-ray Philips goniometer PW 1050. The thermal analysis was realized with an OD-102 derivatograph.

Montmorillonite Li form

To the suspension of the isolated natural form of montmorillonite (100 g of sample, 8 dm³ of distilled water) 0.5 dm³ of 10% aqueous solution of lithium chloride was added. The suspension was mixed and kept to sedimentation for 24 h. After this time the solution over the solid phase was separated and a new lithium chloride solution was added. This procedure was five times repeated. The obtained Li form was washed with distilled water

up to a negative reaction to chloride ions, dried at ambient temperature, ground and sifted through a 0.2 mm sieve.

Fixation of lithium cations

The Li-montmorillonite was heated at different temperatures and time intervals given in Table 1. In this way we have prepared 23 samples with a different fixation degree of lithium cations in the montmorillonite structure.

Table 1

The used temperatures and times of heating of Li-montmorillonite

Heating temperature/°C	Heating time/h								
135	1	4	6	15	24				
150	1	2	3	5	10	15	24		
180	1	2	3	5	10	24			
210	1	2	5	24					

The lithium cations in the exchange positions were determined after releasing with a 1 M solution of barium nitrate using a spectrometer AAS 1 (Zeiss). The amount of fixed lithium cations was determined as the difference between their content in the starting Li form and the content of the exchangeable lithium cations in the samples after the thermal treatment. The calcium and magnesium cations in the natural and Li forms were determined by means of the complexometric titration with chelator III after displacing with the solution anilinium chloride [9].

We have synthesized eight samples with different fixation degree of lithium cations, *A* to *I*, whereby the sample *A* represents the original lithium form. The experimental conditions of the preparation are given in Table 2.

Table 2

The experimental conditions at the preparation of samples with different fixation degree of lithium cations in the structure of montmorillonite

Sample	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>	<i>I</i>
Heating temperature/°C	—	135	135	150	150	135	150	180	210
Heating time/h	—	2	4	1	2	24	10	3	24

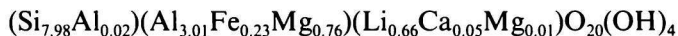
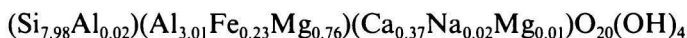
In the given samples we determined the content of exchangeable lithium, calcium, and magnesium cations and calculated the amount of fixed lithium cations, as well as the cation-exchange capacity. Using the ion exchange we further prepared from the samples *A*—*I* the montmorillonite Ca forms with a different negative residual charge in the layers.

Montmorillonite Ca form

To the individual Li form (100 g of samples *A—D*) we added 1 M-CaCl₂ (0.5 dm³). The obtained suspensions were shaken during 3 h and then kept for 24 h. The solution over the solid phase was separated and a new calcium chloride solution was added. This procedure was six times repeated. The Ca form was washed with distilled water up to the negative reaction to the chloride ions and finally with a 50 % aqueous solution of ethanol. The samples were dried, ground so as to pass a 0.2 mm mesh.

Results and discussion

On the basis of the bulk chemical analysis we calculated the crystallochemical formulae of the starting (natural) and the Li form of montmorillonite



From the crystallochemical formula of the natural form it follows that it is practically a Ca form. The second crystallochemical formula shows that the ions Ca²⁺ were practically fully displaced by Li⁺ ions.

At the heating of the Li-montmorillonite a part of the lithium cations migrates into the structure of the montmorillonite, where they are fixed. We denoted the amount of substance of fixed cations as $n(\text{Li}_{\text{fix}})$, the remaining amount in the exchange positions as $n(\text{Li}_{\text{ex}})$. We suppose the validity of the relation

$$n(\text{Li}_{\text{ex}}) + n(\text{Li}_{\text{fix}}) = n(\text{Li}_{\text{ex}}^{\circ})$$

where $n(\text{Li}_{\text{ex}}^{\circ})$ is the amount of substance of the exchangeable lithium cations in

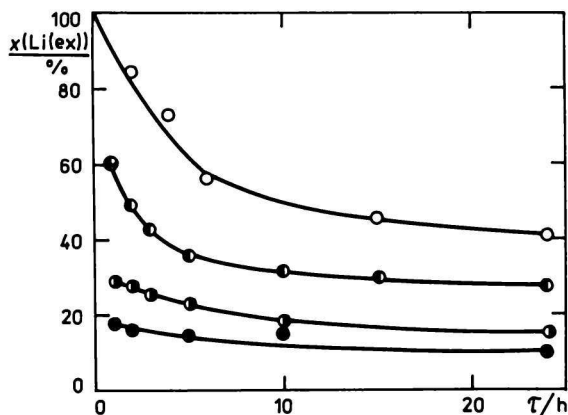


Fig. 2. Dependence of the Li(ex) content on the heating time.

○ 135°C, ● 150°C, ● 180°C, ● 210°C.

the starting Li form. The content of $\text{Li}_{\text{ex}}^{\circ}$ and Li_{ex} has been determined experimentally and Li_{fix} was calculated using the above relation.

Since the negative residual charge is given by the amount of the exchangeable lithium cations, the dependence of the Li_{ex} content on the heating time at the individual temperatures (Fig. 2) was constructed. Fig. 3 shows the dependence of the amount of Li_{ex} on the heating temperature in two very different time intervals (2 and 24 h). The amount of Li_{ex} is given in percentage of the whole content of the lithium cations. From the results it follows that the fixation of the lithium cations in the structure of the given montmorillonite is a function of the temperature and the time of heating of samples. From the dependence shown in Fig. 2 it can be seen that with the increasing heating temperature, so with increasing of the kinetic energy, the interlayer cations are able to overcome the energetic barrier and to pass into the vacant octahedral positions, or into the hexagonal holes in the octahedral network (Fig. 1). From this then follows the lowering of the Li_{ex} content in dependence on the increasing temperature.

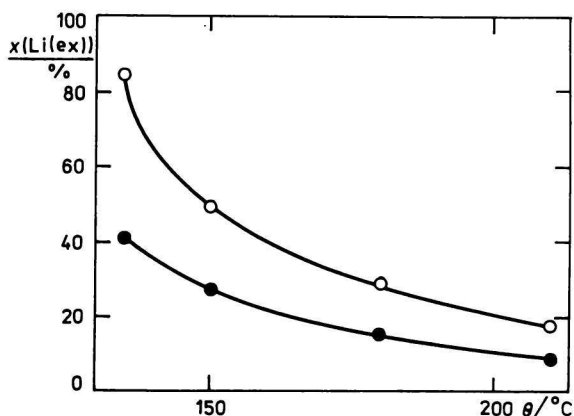


Fig. 3. Dependence of the $\text{Li}(\text{ex})$ content on the heating temperature.

○ 2 h, ● 24 h.

The amounts of the individual exchangeable cations as well as the values of the cation-exchange capacity (CEC) in the samples are given in Table 3.

In Table 4 are summarized the changes in the crystallochemical formula of the samples *A–I* caused by fixation of Li^+ in the structure.

The water content in the samples (Table 5) was determined by evaluation of the TG curves. The mass loss is due to the dehydration process (temperature interval from 20 to 250 °C) as well as the dehydroxylation of the montmorillonite (temperature interval from 500 to 800 °C).

The dependence of the mass loss at the dehydration on the negative residual charge is shown in Fig. 4. The mass loss is related to the mass of the annealed

Table 3

The content of the exchangeable cations and the values of the cation-exchange capacity (CEC) in the samples after the fixation of Li^+ cations in the montmorillonite structure

Sample	$n(\text{Li}^+)^a$	$n(\text{Ca}^{2+})$	$n(\text{Mg}^{2+})$	CEC ^b
	mmol g ⁻¹			mmol g ⁻¹
A	0.888	0.069	0.008	1.042
B	0.635	0.071	0.008	0.794
C	0.609	0.071	0.010	0.771
D	0.559	0.068	0.009	0.715
E	0.513	0.072	0.009	0.673
F	0.426	0.065	0.011	0.579
G	0.381	0.064	0.011	0.533
H	0.249	0.056	0.009	0.379
I	0.073	0.033	0.009	0.158

a) n — amount of substance recalculated to the gram of the sample;

b) the CEC values are related to univalent cations.

Table 4

Changes in the crystallochemical formula of the A—I samples caused by fixation of Li^+ in the structure

Sample	Tetr ^a		Oct ^b				Exch ^c		
	Si	Al	Al	Fe	Mg	Li	Li	Ca	Mg
A	7.98	0.02	3.01	0.23	0.76	—	0.66	0.05	0.01
B	7.98	0.02	3.01	0.23	0.76	0.19	0.47	0.05	0.01
C	7.98	0.02	3.01	0.23	0.76	0.21	0.45	0.05	0.01
D	7.98	0.02	3.01	0.23	0.76	0.25	0.41	0.05	0.01
E	7.98	0.02	3.01	0.23	0.76	0.28	0.38	0.05	0.01
F	7.98	0.02	3.01	0.23	0.76	0.35	0.31	0.05	0.01
G	7.98	0.02	3.01	0.23	0.76	0.38	0.28	0.05	0.01
H	7.98	0.02	3.01	0.23	0.76	0.47	0.19	0.05	0.01
I	7.98	0.02	3.01	0.23	0.76	0.61	0.05	0.05	0.01

a) Tetrahedral network; b) octahedral network; c) exchangeable cations.

sample. The negative residual charge is given in percentage of the original negative residual charge.

It is thus obvious that with the increasing fixation of lithium cations into the structure of montmorillonite a marked lowering of the content of water molecules, bonded in the interlayer space, takes place. This results from the decrease

Table 5

Mass losses of samples after thermal dehydration (Δm_1) and dehydroxylation (Δm_2)

Sample	$\frac{\Delta m_1}{\%}$	$\frac{\Delta m_2}{\%}$
Li form	11.3	4.2
<i>A</i>	11.8	4.2
<i>B</i>	6.8	4.2
<i>F</i>	5.3	4.2
<i>H</i>	3.4	4.3
<i>I</i>	2.5	4.3

of the CEC value caused by lowering of the negative residual charge value of montmorillonite. By fixing Li^+ in the structure of montmorillonite the portion of hydrated cations in the interlayer decreases. The mass loss, which accompanies the dehydroxylation, is not expressively influenced by the fixation of the lithium cations.

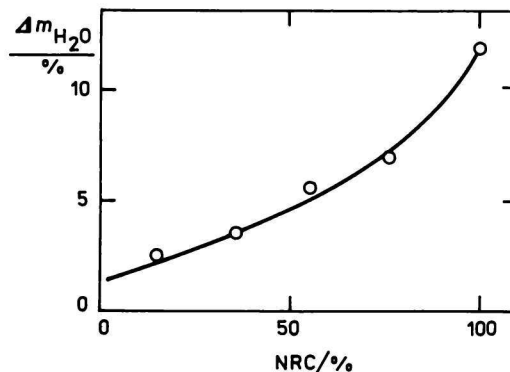


Fig. 4. Dependence of the dehydration mass loss on the negative residual charge (NRC).

The diffraction patterns of the samples used at the construction of Fig. 5 are shown in Fig. 6. The sequence of the diffraction patterns demonstrates the transformation of the Li form of montmorillonite (*A*) passing some stages formed by the mixedlayer structures of the 1.24 nm and 1.0 nm type (*C—H*) up to the practically pure 1.0 nm phase (*I*). Li^+ , bonded in the 2 : 1 layer, compensates locally the unsaturated negative charge. With increasing portion of the fixed Li^+ the 2 : 1 layers lose their negative charge and they behave in the structure like the 2 : 1 layers of pyrophyllite. So originate regions of the coherent dispersion with 1.24/1.0 nm sequences with the different ratio of 2 : 1 layers of

the first and the second type. The changes in the 2 : 1 layer 1.24/1.0 nm ratio are manifested by the 001 diffraction shift and by creation of diffraction with nonrational sequence of the 001 peaks. At the *I* sample we again get a rational sequence of the 001, 002, and 003 peaks for $d(001) = 1.0$ nm. The measured $d(001)$ values as a function of the negative residual charge of Li forms of montmorillonite are shown in Fig. 5.

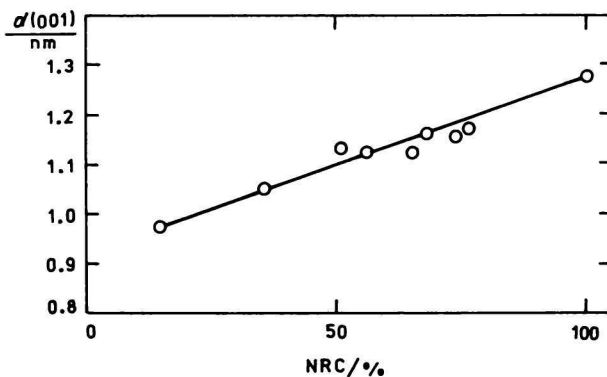


Fig. 5. Dependence of the $d(001)$ values on the negative residual charge (NRC) of the Li-montmorillonite.

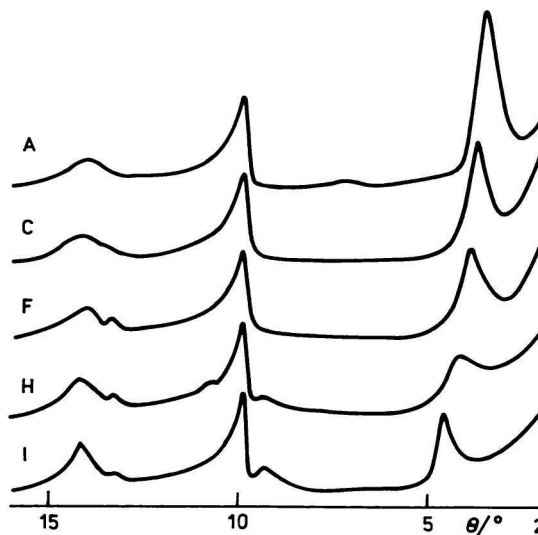


Fig. 6. Diffraction patterns of the *A*–*I* samples.

The measured $d(060)$ values change from the 0.1494 nm value for the *A* sample to 0.1501 nm for the *I* sample. It is due to the increase of the portion of

the local trioctahedral configurations at the formation of the integral $d(060)$ value for the whole sample.

Conclusion

By saturation of the montmorillonite with Li^+ ion and its fixation in the 2 : 1 layer it is possible to prepare materials with a very different negative residual charge, whereby the chemical composition of the natural materials does not practically change. By Li^+ fixation mixedlayer materials of the swelling/non-swelling type and local trioctahedral configurations come into existence in the octahedral network.

References

1. Hoffmann, U. and Klemen, R., *Z. Anorg. Allg. Chem.* 262, 95 (1950).
2. Green-Kelly, R., *Miner. Mag.* 30, 604 (1955).
3. Green-Kelly, R., *Clay Miner. Bull.* 2, 52 (1953).
4. White, J. L., *Clays Clay Miner.* 4, 133 (1956).
5. Tettenhorst, R., *Am. Mineral.* 47, 769 (1962).
6. Russell, J. D., *Clay Miner.* 14, 127 (1979).
7. Calvet, R. and Prost, R., *Clays Clay Miner.* 19, 175 (1971).
8. Lagaly, G., *Clay Miner.* 16, 1 (1981).
9. Mocik, S., Slosiariková, H., and Konvalinová, M., *Chem. Zvesti* 27, 344 (1973).

Translated by V. Daněk