

MODIFICATION OF THE STRUCTURE OF Ca-MONTMORILLONITE

MODIFIKACE STRUKTURY Ca-MONTMORILLONITU

Lenka FUSOVÁ

*Ing., Institute of environmental engineering, Faculty of Mining and Geology,
VŠB - Technical University of Ostrava
17. listopadu 15/2172, 708 33 Ostrava
tel. (+420) 597 329 381, e-mail: lenka.fusova.hgf@vsb.cz*

Abstract

Clay minerals of the smectite group are distinguished by the presence of different exchangeable cations in the interlayer space. The intercalation of octadecylamine into the interlayer space of montmorillonite in relation to the quantity of added organic substance was investigated and is described in this article. The intercalation was confirmed by powder X-ray diffraction.

Abstrakt

Jílové minerály ze skupiny smektitů se vyznačují přítomností různých výměnných kationtů v mezivrstevním prostoru. V tomto příspěvku byla zkoumána interkalace oktadecylaminu do mezivrstevního prostoru montmorillonitu v závislosti na množství přidané organické látky. Interkalace byla potvrzena RTG difrakcí.

Key words: intercalation; montmorillonite; octadecylamine

1 INTRODUCTION

Organic molecules not only adsorb on surficial exchangeable positions but also intercalate into interlayer space (between 2:1 layers) of the structure of smectite during intensive saturation of smectites. Intercalation into this guest structure can either induce a ion exchange reaction, when organic molecules are intercalated as cations, or are intercalated as neutral organic molecules and the original cations stay partly or completely in the interlayer of the smectite.

The clay minerals of smectite groups occur in the form of very small crystals with frequently defective structure. Theories about their structural constitution come from the hypothesis that their structure is compounded of 2:1 layers, between which are exchangeable hydrated ions. (The 2:1 layer is created when two tetrahedral sheets (with opposite polarity) are connected with one octahedral sheet in the middle - Si.Al.Si.Si.Al.Si-. This latticed structure may lightly expand and bond molecules on the exterior and also interior.) [1]

Water molecules in the interlayer space of smectites and vermiculites can be displaced by many polar organic molecules. Neutral organic ligands can form complexes with the interlayer cations. The interlayer cations can be replaced by various types of organic cations. Alkylammonium ions are widely used in modifying bentonites. The other important group of organic compounds is cationic dyes and cationic complexes. [2]

One of the most significant and widespread minerals of dioctahedral smectite is montmorillonite. It is characterized by no or very small substitution of Al³⁺ for Si⁴⁺ on the tetrahedron position. The charge of the 2:1 layers is produced primarily by octahedron substitution. Variability in chemical composition leads to their division into types: Wyoming, Chambers, Otay, Fe-montmorillonite. Monovalent (especially Na⁺, K⁺) and divalent cations could appear in the interlayer of smectite. These compensate the negative charge of 2:1 layers. [1]

Bentonite is a soft, very fine-grained heterogeneous rock of various colours, composed mostly of clay mineral montmorillonite, which originated mostly by submarine or atmospheric weathering of basic (to a smaller extent also of acid) volcanic rocks (mainly tuffs). Montmorillonite gives to bentonite its typical properties – high sorption capacity, characterized by a high value of cation exchange (the ability to receive certain cations from solutions, and replace them with its own molecules – Mg, and in some cases also Ca and alkalis); internal

swelling after contact with water (some bentonites do not swell, but have a high absorptive capacity as bleaching clays, especially when they are activated); high plasticity and binding ability. Bentonite also contains other clay minerals (kaolinite, illite, beidellite), Fe compounds, quartz, feldspars, volcanic glass, etc., which represent impurities and if possible they are removed during the mineral processing. [3]

Bentonites may be principally divided into:

1. highly swelling Na-bentonites, the so-called Wyoming-type bentonites. Deposits of this raw material are found predominantly in the USA; in the Czech Republic, no Na-bentonite deposits have been found,
2. less swelling potassium, calcium and magnesium bentonites or their combinations. Such bentonites may be industrially enriched with sodium by the so-called activation, the swelling capacities of activated bentonites, however, still do not reach such values as those of Wyoming-type bentonites.

The Czech Republic ranks among the countries with large bentonite deposits, even though, by their properties, the Czech bentonites are similar to each other, being mostly of magnesium-calcium or calcium-magnesium type. [3, 5]

All bentonite deposits in the Czech Republic were formed by clay weathering of volcanic rocks. Bentonite deposits and reserves are almost exclusively concentrated in the area of the Doupovské hory Mountains and the České středohoří Mountains (Kadaň, Podbořany, Karlovy Vary region).

Deposits of the Most region at the boundary of the south-eastern margin of the North Bohemian Basin and the České středohoří Mountains represent the second most significant bentonite area of the Czech Republic at present. The Braňany-Černý vrch, Stránce and Střimice deposits belong to the most important ones. [3]

2 INTERCALATION REACTIONS OF 2:1 CLAY MINERALS

The adsorption of neutral molecules on smectites is driven by various chemical interactions: hydrogen bonds, ion-dipole interaction, co-ordination bonds, acid-base reactions, charge-transfer, and van der Waals forces. Polar molecules, such as alcohols, amines, amides, ketones, aldehydes, and nitriles, form intercalation complexes with smectites. Even acids are intercalated. Guest compounds can be intercalated from the vapour, liquid, and solid state. When intercalated from solutions, solvent molecules are generally co-adsorbed in the interlayer space.

Guest molecules may be intercalated in dried clay minerals or may displace the water molecules of hydrated smectites and vermiculites. The displacement of interlayer water molecules depends on the HSAB ('hard and soft acids and bases') character of the interlayer cations and the interacting groups of the guest molecules. Water molecules around hard cations, like Na^+ , Mg^{2+} and Ca^{2+} , are only displaced by $\text{HO}-$ or $\text{O}=\text{C}$ containing compounds but not by amines. In contrast, amines as soft bases displace water molecules from soft interlayer cations like Cu^{2+} and Zn^{2+} . [2]

Intercalation is achieved by three methods:

1. reaction between smectite (solid phase) and a solution in which organic substance is included. This reaction is called "solid-liquid",
2. reaction between smectite (solid phase) and steams of organic substance, which is called "solid-gas",
3. reaction between smectite (solid phase) and organic substance, which is also in solid phase. This is called "solid-solid".

Organic molecules are usually bigger in dimension than the original interlayer material of natural smectite (cations with molecular water) and therefore this process is connected with considerable expansion of the structure of smectite in layers with a perpendicular orientation. The placement of (n)alkyl-ammonium chains in the interlayer can occur in these variants:

1. α -complex – interlayer molecules are deposited such that alkyl chains are approximately parallel with basal plane of 2:1 layers and basal spacing d_{001} is about 13.5 Å,
2. β -complex – one layer of alkyl chains can be inclined to a basal plane of 2:1 layers and the value of basal spacing increase,
3. γ -complex – two layers of alkyl chains in the interlayer, chains are inclined to basal plane of 2:1 layers, another increase of value of basal spacing. [4]

3 EXPERIMENTAL

3.1 Material

A sample of Ca⁺-rich montmorillonite (blue-green colour) was taken from the Braňany – Ārný Vrch locality, Czech Republic, as the host structure for the intercalation. The following crystallochemical formula was calculated from the chemical analysis using a basis of 10 structural O and 2 OH (Tab. 1): (Ca_{0.18}Na_{0.09}K_{0.08})(Al_{0.98}Fe_{0.54}Mg_{0.31}Ti_{0.11})(Si_{3.70}Al_{0.30})O₁₀(OH)₂·7.72H₂O. [4]

3.2 Organic compound

Octadecylamine C₁₈H₃₉N (tech., 90%) was used as an intercalant. Its melting point is 50 – 60 °C, boiling point is 232 °C, flash point is 148 °C and molecular mass is 269.51.

3.3 Methods used for the analysis

The samples were analysed using the X-Ray Fluorescence (XRF) (Spectroscan MAKC GVII, VŠB-Technical University of Ostrava, Research Centre, Czech Republic).

Tab. 1 Chemical composition of bentonite

		Bentonite
Chemical composition (wt. %)	SiO ₂	47.71
	TiO ₂	1.93
	Al ₂ O ₃	13.98
	Fe ₂ O ₃	9.26
	MnO	0.04
	MgO	2.64
	CaO	2.21
	Na ₂ O	0.57
	K ₂ O	0.77
	SO ₃	0.04
	P ₂ O ₅	0.34
	loss of ignition	20.51

The X-ray diffraction (XRD) study was performed using a powder diffractometer (Philips, United Kingdom) – CuK_α radiation. The XRD was operated at 40 kV and 100 mA in a step scan mode. The scanning speed was 0.02°/s. The powder diffraction patterns of the bentonite in an air-dried condition, an ethylene glycol-solvated condition, and after heating to collapse any expandable layers are shown in Fig. 1 and the values of basal spacing are in Tab. 2.

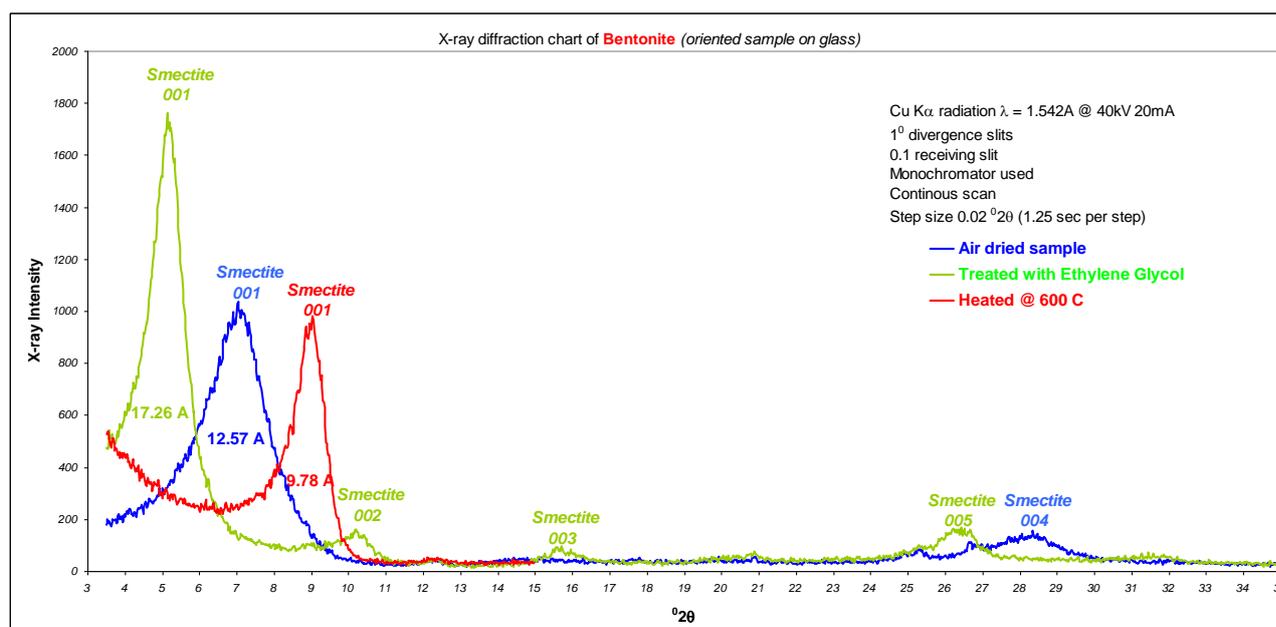


Fig. 1 The X-ray powder diffraction patterns of bentonite

Tab. 2 The values of basal spacing of bentonite

No	d (sample treated with Ethylene Glycol) (Å)	d (air dried sample) (Å)	d (sample heated to 600 °C) (Å)
1	17.26	12.57	9.78
2	8.69	5.98	
3	5.64	4.27	
4	4.26	3.12	
5	3.37		

3.4 Sample preparation

The intercalation of octadecylamine into bentonite was carried out by a reaction in which the bentonite dry powder was mixed with fine octadecylamine flakes. Various conditions were used, with variable amine/clay ratio. Two samples were thus prepared.

Sample I. A blend of 150 g of octadecylamine and 100 g of bentonite (in the molar ratio of MMT:ODA = 1:3) was mixed and baked at 80 °C for 24 hours.

Sample II. A blend of 75 g of octadecylamine and 100 g of bentonite (in the molar ratio of MMT:ODA = 3:2) was mixed and baked at 80 °C for 24 hours.

The XRD patterns of the bentonite and products are shown in Figs 2 and 3.

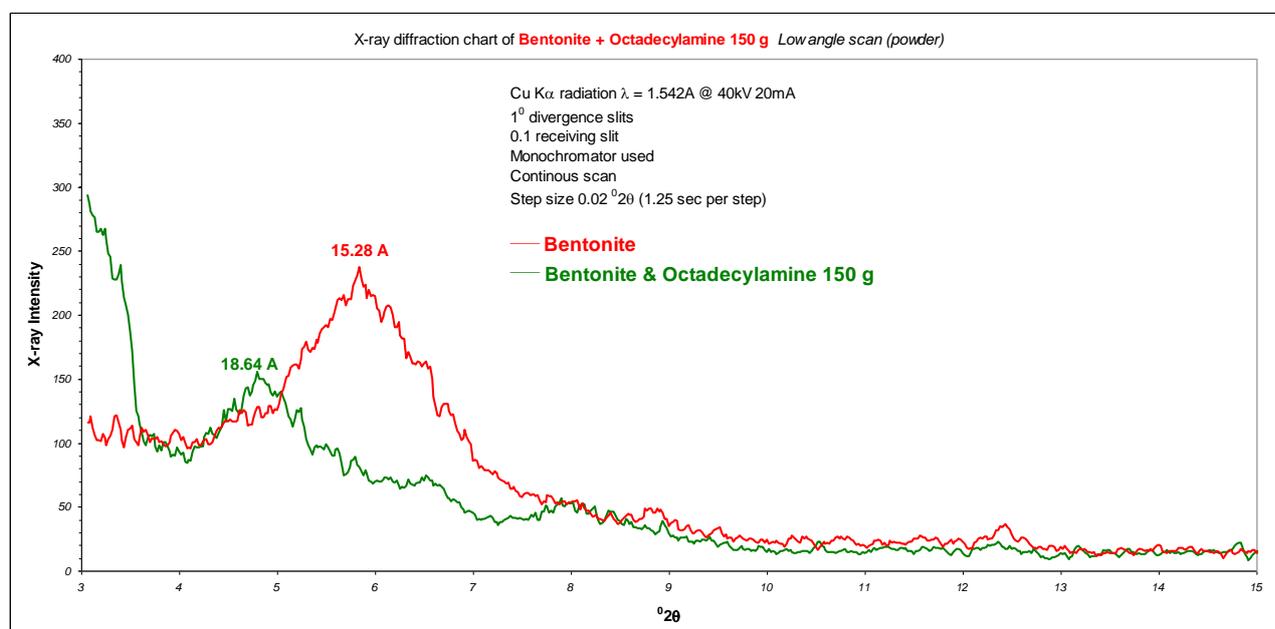


Fig. 2 The X-ray powder diffraction patterns of bentonite and bentonite intercalated with ODA in the molar ratio of MMT:ODA = 1:3. The values (in Å units) refer to the basal spacing of the samples.

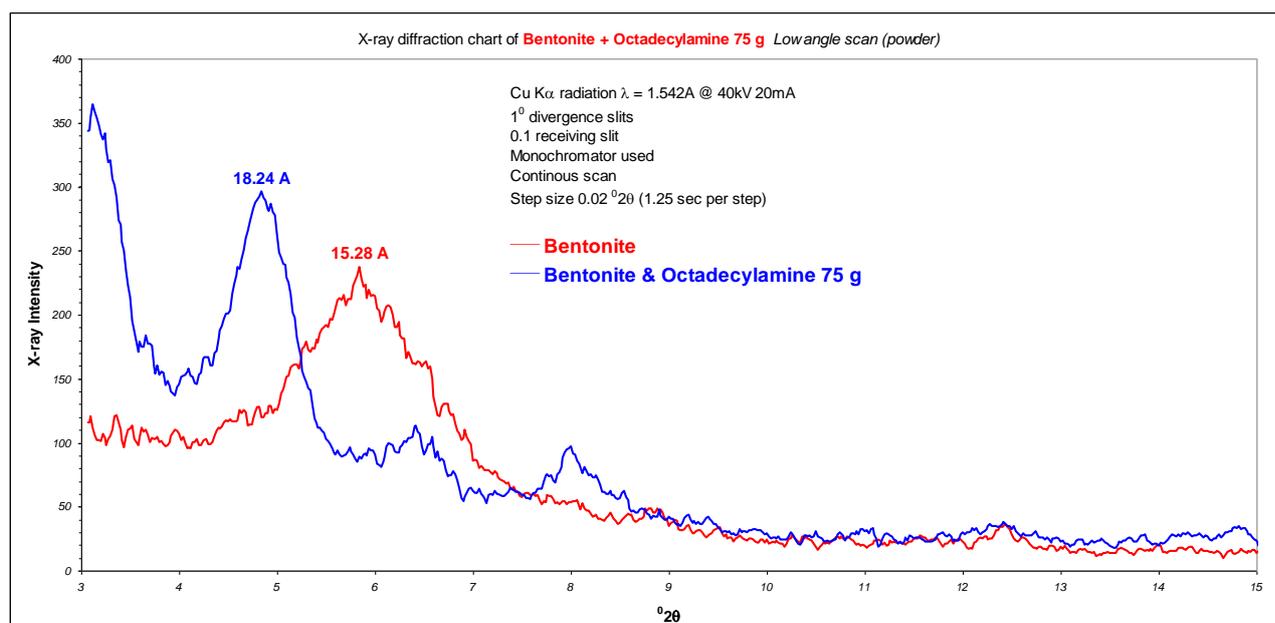


Fig. 3 The X-ray powder diffraction patterns of bentonite and bentonite intercalated with ODA in the ratio of MMT:ODA = 3:2. The values (in Å units) refer to the basal spacing of the samples.

Tab. 3 The values of basal spacing of the bentonite intercalated with ODA

No	d (MMT:ODA = 1:3) (Å)	d (MMT:ODA = 3:2) (Å)
1	37.28 (calc)	36.48 (calc)
2	18.64	18.24
3	13.64	13.76
4	11.11	11.13

4 RESULTS AND DISCUSSION

Fig. 1 shows that this smectite has got a regular structure. The basal spacings of higher degrees reached low intensity so they faded in the background. They are distinct only for bentonite treated with ethylene glycol.

The values of basal spacing are determined in diffractograms in Figs 2 and 3 and Tab. 3. The value of basal spacing of bentonite is different in accordance to the air-dried sample, probably thanks to the change in moisture. By the solid-solid reaction of ODA with bentonite at the molar ratio of MMT:ODA = 1:3, basal spacing was changed to 18.64 Å and at the molar ratio of MMT:ODA = 3:2, it was changed to 18.24 Å. The achieved maximal value of basal spacing of intercalated bentonite has a probable value of second degree. After calculation, the first values are 37.28 Å and 36.48 Å; these values correspond to one layer of molecules of ODA intercalated into the interlayer. Different amounts of organic compound did not have a noticeable impact on the results.

In comparison to [6], octadecylamine was used to intercalate a fraction of natural Mg-vermiculite with the same low-temperature melting procedure. Mixtures of Mg-vermiculite fractions and powdered ODA in the molar ratios of 2:1, 1:1, 1:2 and 1:6 were heated to prepare intercalated samples. From the XRD patterns, it is evident that the basal spacing increased from 14.35 Å (untreated Mg-vermiculite) to 58.4 Å (intercalated with ODA in the molar ratio of 1:6). The intercalation occurred more markedly and the intercalated sample would have a different arrangement of molecules ODA in the interlayer space.

Intercalation of octadecylamine into Na montmorillonite was investigated in [7]. Three samples were prepared: 1) 75 g of ODA and 100 g of montmorillonite, mixed and annealed under vacuum at 80 °C for 6 h; 2) 150 g of ODA and 100 g of montmorillonite, mixed and annealed under vacuum at 80 °C for 6 h; 3) 150 g of ODA and 100 g of montmorillonite, mixed and annealed in vacuum at 150 °C for 6 h. The basal spacing *d* values obtained from the diffraction data for the samples are 32.6 Å (sample 1), 53 Å (sample 2) and 58 Å (sample 3). The intercalation of samples 2 and 3 increased the interlayer space more noticeably.

5 CONCLUSIONS

Octadecylamine was intercalated into the interlayer space of the bentonite, varying the amine/clay ratio in the reaction medium. The intercalated ODA formed amino complexes in the interlayer spaces of montmorillonite.

The XRD patterns of samples intercalated with molar ratios of MMT:ODA = 1:3 and MMT:ODA = 3:2 are very similar. The first basal reflections are about 37 Å. These calculated values are in accordance with the one-layer arrangement of ODA molecules intercalated into the interlayer space.

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RESUMÉ

Minerály ze skupiny smektitů se vyznačují přítomností různých výměnných kationtů v mezivrstvi. Tyto kationty jsou u přírodních smektitů obklopené různým počtem molekul vody. Pro průmyslové využití těchto minerálů je mnohdy nutné převedení minerálu do monoiontové podoby. Tento proces je doprovázen změnou fyzikálních a strukturních vlastností smektitů. Kromě vzájemné výměny kationtů je možné do mezivrstvi vpravit organické molekuly a připravit tak strukturu s předem definovanými rozměry, kterou je možno využít pro selektivní sorpci některých látek. Interkalace je doprovázena zvýšením mezirovinné vzdálenosti a tím i celkovým zvětšením povrchu smektitu.

Při reakci bentonitu s oktadecylaminem došlo ke zvýšení mezirovinné vzdálenosti. Dupočítaná hodnota bazální difrakce prvního řádu odpovídá vytvoření jedné vrstvy molekul ODA interkalovaných do mezivrstevního prostoru. Rozdílná množství organické látky neměla na průběh procesu pozorovatelný vliv.