

## REVERSIBLE HYDRATION OF Al PILLARED- AND Na-MONTMORILLONITE

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**Abstract:** Adsorption of water by Na montmorillonite (Na MMT) and hydroxy-Al precursor of pillared montmorillonite was measured at constant pressure of water vapour ( $P_{H_2O} = 3.16 \text{ kPa}$ ) after treating the samples at 300 - 900 °C. Na MMT kept its high ability to sorb water even after heating to 600 °C. Al pillared MMT sorbed a significantly lower amount of water after calcination at temperatures higher than 500 °C, when hydrophobic  $Al_2O_3$  pillars were formed in the MMT interlayer space. Contraction/expansion of Al pillared MMT interlayers during calcination was minimal.

**Key words:** montmorillonite, pillared montmorillonite, hydration, thermal analysis, X-ray diffraction.

### Introduction

Hydration of montmorillonite (MMT) is a technologically important adsorption process, where water vapour interacts with the surface of the solid phase. Adsorption processes on MMT are influenced by the distribution of negative layer charge in the structure, by the interlayer cations, specific surface area, defects in the structure, moisture content, etc. (Čičel et al. 1981). The first step of water sorption by dehydrated MMT is the hydration of exchangeable cations occurring on the external surface of the particles, and the hydration of the external surface layers of the MMT structure (Fripiat et al. 1965). The increase of relative water vapour pressure leads to separation of the layers; a spontaneous hydration of the exchangeable interlayer cations begins, after which water molecules start to occupy the spaces between the hydrated exchangeable cations (Norrish 1954). The adsorption proceeds gradually and the interlayer distance increases (Hoffman et al. 1933). According to Low (1961) intensively polarized MMT oxygens form hydrogen bonds with water molecules. These bonds affect the original electron configuration of the oxygen atoms in the water molecules, which form similar bonds with adjacent water molecules. Farmer & Russel (1971) supposed, that water molecules in MMT form chains, which mediate the appropriate connection of charged cations with superficial oxygen atoms. MacEwan (1961) showed the important role of exchangeable cations in the hydration process. The continuous adsorption of water on MMT was described by Roderick et al. (1969). They studied the hydration of  $Ca^{2+}$ -MMT and  $Na^+$ -MMT by checking the  $d_{001}$  parameter.

Partial molar enthalpy, partial molar entropy and free energy of MMT is changed during interlayer water desorption, depending on the amount of adsorbed water (Barshad 1960; Roderick & Demirel 1966; Waksmundzki et al. 1981).

Recent papers on the adsorption characteristics of pillared MMT (Malla et al. 1989; Yamanaka et al. 1990; Malla & Komarneni 1990; Kuykendall & Thomas 1990; Horváth et al. 1991) emphasize the thermal stability and permanent porosity of these

materials. Pillared MMT provides a favourable situation for polar molecules, rather than non-polar, to enter the porous system. MMT layers are kept apart at a constant distance, an expansion or collapse of the structure below 700 - 800 °C was not observed. Most previous studies have described the adsorption and desorption isotherms at a constant temperature, increasing the relative pressure of water vapour (Orchiston 1955; Van Olphen 1965; Roderick & Demirel 1966; Keren & Shainberg 1975; Waksmundzki et al. 1981; Branson & Newman 1983). In the present work we studied dehydration of Na MMT and hydroxy-Al precursor of pillared MMT at 300 - 900 °C, following hydration at room temperature and 3.16 kPa water vapour pressure.

### Experimental

#### Materials

The less than 2  $\mu\text{m}$  fraction of bentonite from Jelšovský Potok (Czechoslovakia) was used in the present work. From this material Na MMT was prepared using standard methods. Hydroxy-Al precursor was prepared by cation-exchange reaction of Na MMT with partially neutralized  $AlCl_3$  solution. Calcination of hydroxy-Al precursor at 500 °C leads to Al pillared MMT (Figueras et al. 1990).

#### Methods

A Derivatograph Q-1500 D (MOM Budapest) was used for calcination and thermal analysis. 150 mg of Na MMT or hydroxy-Al precursor were heated in static air at a heating rate 10 °C  $\text{min}^{-1}$ . TG, DTG, DTA curves are shown in Fig. 1. and Fig. 2.

The same treatment conditions were used for both Na MMT or hydroxy-Al precursor in dehydration-hydration studies. The temperatures of calcination were 300, 400, 500, 600, 700, 800, 900 °C; after achieving the calcination temperature the samples were kept at this temperature for 30 minutes. Then the samples

were weighed and kept in a dessicator above water at room temperature (for the partial water vapour pressure  $P_{H_2O} = 3.16\text{ kPa}$ ) for 24 hours. After that the samples were weighed and heated to the next higher temperature. The changes of the sample weights in the adsorption-desorption processes are given in Fig. 3 and Fig. 4.

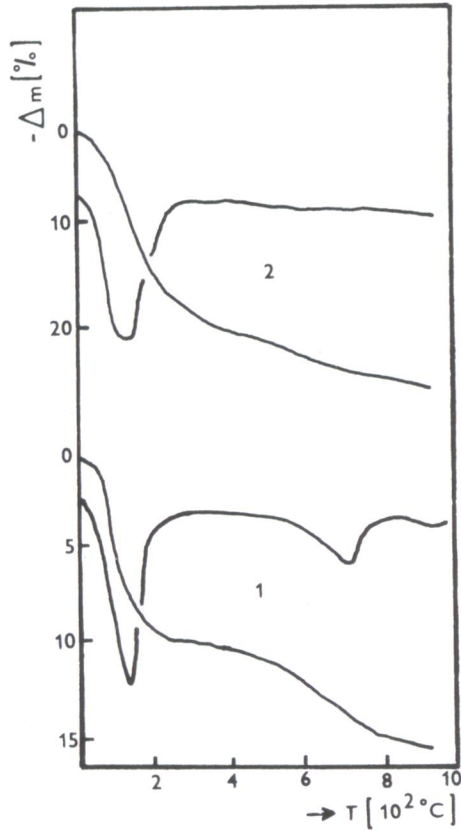


Fig. 1. TG and DTG curves of Na MMT (1) and hydroxy-Al precursor (2).

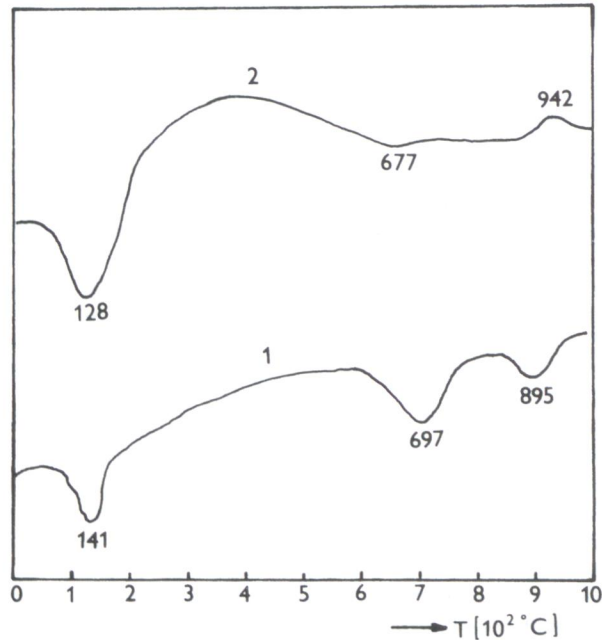


Fig. 2. DTA curves of Na MMT (1) and hydroxy-Al precursor (2).

XRD analysis of dehydrated and hydrated samples was made using separate aliquots of Na MMT or hydroxy-Al precursor treated under the same conditions. Powdered samples were analyzed using a Philips PW 1050 diffractometer and Ni-filtered  $\text{CuK}\alpha$  radiation. The  $d_{001}$  values are given in Fig. 5.

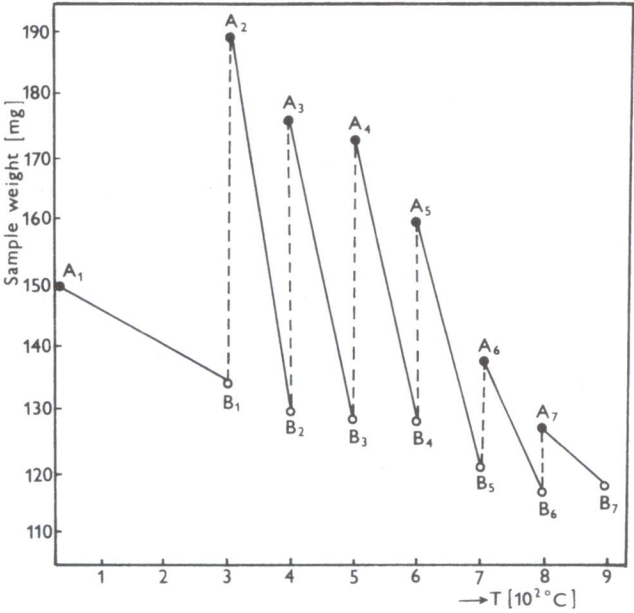


Fig. 3. Dehydration (o) and hydration (●) of Na MMT.

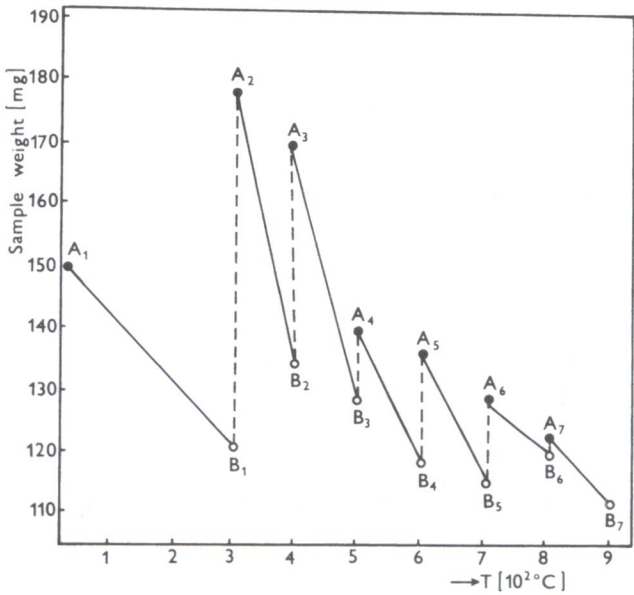


Fig. 4. Dehydration (o) and hydration (●) of hydroxy-Al precursor.



## Results and discussion

Fig. 1 and Fig. 2 show TG, DTG and DTA curves of Na MMT and hydroxy-Al precursor in the temperature range 25 - 1000 °C. Two weight loss steps are recorded in the TG and DTG curves for the Na MMT sample (curve 1, Fig. 1). These are due to dehydration and dehydroxylation of the sample. These two processes can not be distinguished on the TG curve of hydroxy-Al precursor (curve 2, Fig. 1). This curve does not show a dehydroxylation peak.

Similar results were reported by Occelli & Tindwa (1983) on TG analysis of Upton (Wyoming) Na-bentonite and Al pillared bentonite. Different behaviour of Na MMT and hydroxy-Al precursor on heating is shown in the DTA curves (Fig. 2). The high temperature endothermic peak on the Na MMT DTA curve reflects the decomposition of the MMT structure. This peak does not appear on the DTA curve of hydroxy-Al precursor. The exothermic peak at 942 °C on this curve indicates the formation of high-temperature phases.

Differences between Na MMT and hydroxy-Al precursor samples were shown also in the sorption-desorption processes (Fig. 3 and 4). The starting materials were dried at 60 °C for 4 hours. Na MMT lost less water during calcination and then adsorbed more water than Al pillared MMT (500 - 900 °C). The reverse is valid for the hydroxy-Al precursor (300 °C). These processes demonstrate the swelling of Na MMT; a property, which Al pillared MMT does not possess. The total amount of interlayer water lost during dehydration of Na MMT calculated from the TG curve (Fig. 1) was 16.2 mg. 93.5 wt. % of this water

was removed from the sample by the calcination at 300 °C (Fig. 3).

The subsequent rehydration resulted in the sorption of 54.2 mg of water (40.2 wt. % of the previous dehydrated sample). On the next calcination at 400 °C, 30.3 wt. % of hydrated sample was released, and then 34.1 wt. % of dehydrated sample was readsorbed after hydration, etc. Rehydration ability of Na MMT after heating at 400 and 600 °C was decreased moderately. A remarkable decrease in the rehydration ability of Na MMT occurred after heating to 700 °C, when the dehydroxylation reaction and structural disordering begins. The rehydration ability of Na MMT treated above 800 °C is low (Fig. 3).

In contrast to Na MMT, a significant decrease in reversibility of rehydration ability of the hydroxy-Al precursor was observed already after the calcination at 500 °C (Fig. 4). This could be explained by the formation of  $Al_xO_y$  clusters in MMT interlayer. This decrease can be ascribed to the hydrophobic character of  $Al_xO_y$  clusters (Malla et al. 1989) in contrast to Na MMT containing interlayer cations with high hydration energy. This hydrophobicity in Al pillared MMT defended from its higher water sorption. The jump at 700 °C on the sorption-desorption diagram (Fig. 4) is connected with dehydroxylation of Al pillared MMT, after which the water sorption is low.

The hydration-dehydration process was followed by checking the  $d_{001}$  spacings after heating and after water sorption (Fig. 5). The interlayer of Na MMT after 300 °C calcination was contracted. Basal spacings were expanded after the subsequent sorption of water. This cycle was repeated also at higher temperatures up to 800 °C. The primary hydration of the strongly hydrophilic Na cations is supposed to be the driving force of water sorption of Na MMT. The interaction of exchangeable cations and surface oxygen atoms acts against hydration. The ability to sorb water after 800 °C calcination was remarkable. XRD patterns of Na MMT calcined at 900 °C and rehydrated showed no significant difference in the  $d_{001}$  values. While the observed  $d_{001}$  spacings of Na MMT changed remarkably after each dehydration and rehydration up to 800 °C, the value of dehydrated hydroxy-Al precursor decreased from 1.83 nm (25 °C) to 1.79 nm (300 °C). Hydration and dehydration had little effect on interlayer spacings of both hydroxy-Al precursor (25 - 400 °C) and Al pillared MMT (500 - 900 °C). The  $d_{001}$  values in the range 400 - 900 °C were almost constant,  $1.76 \pm 0.02$  nm (Fig. 5). The stable interlayer distance indicates a formation of a porous system in the Al pillared MMT sample. This system is thermally stable up to 900 °C.

## Conclusions

Al pillared montmorillonite is a more thermally stable material than Na montmorillonite, but its sorption ability is lower. The reversible hydration of Na montmorillonite was observed even at 800 °C.

**Acknowledgments:** The authors thank Dr. P. Komadel for stimulating discussion and for help in the article arrangement.

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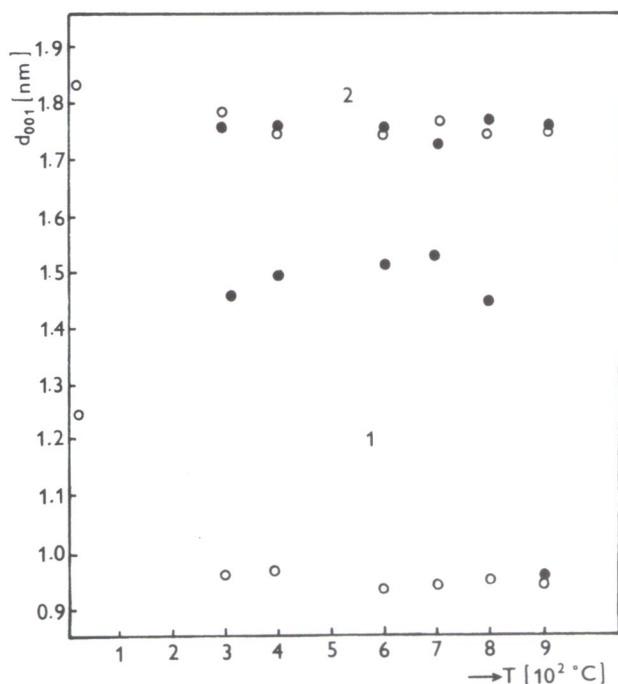


Fig. 5.  $d_{001}$  values after dehydration at given temperature (o) and following hydration at room temperature (●) for Na MMT (1) and hydroxy-Al precursor (2).

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