

# Optimal conditions for hydrothermal synthesis of saponite

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*Dedicated to Professor RNDr. J. Masár, CSc., in honour of his 60th birthday*

The products of hydrothermal syntheses in the system of oxides  $\text{SiO}_2\text{—Al}_2\text{O}_3\text{—MgO(MgO—CaO—Na}_2\text{O)—H}_2\text{O}$  in mass amounts 4.4:0.2:3.6:0.2 were studied. Syntheses were performed at temperatures 373, 423, 473, 573, and 608 K during 7, 14, and 21 days. As starting materials amorphous silica with aluminium, magnesium and/or calcium or sodium hydroxides were used. The aim of the study was to find optimal conditions of the synthesis (temperature, pressure, and duration). It was revealed that the temperature 608 K, pressure 13.3 MPa and duration of synthesis 7 days are suitable for formation of the saponite. A badly crystallized saponite is formed even at 373 K and atmospheric pressure.

Исследовались продукты гидротермических синтезов в системе окислов  $\text{SiO}_2\text{—Al}_2\text{O}_3\text{—MgO(MgO—CaO—Na}_2\text{O)—H}_2\text{O}$  в мольных отношениях 4,4:0,2:3,6:0,2. Синтезы проводились при температурах 373, 423, 473, 573 и 608 К. Продолжительность синтеза была 7, 14 или 21 день. В качестве исходных соединений использовались аморфная двуокись кремния и гидроокиси алюминия, магния, кальция и натрия. Целью работы было определение оптимальных условий синтеза (температура, давление и продолжительность синтеза). Обнаружено, что подходящими условиями для данного синтеза являются температура 608 К, давление 13,3 МПа и продолжительность 7 дней, хотя плохо выкристаллизовавшийся сапонит образовывался уже при температуре 373 К и атмосферном давлении.

The mineral saponite with the formula  $[\text{Si}_{7.33}\text{Al}_{0.67}][\text{Mg}_{6.00}(\text{Me}_{0.67}^+) \text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}]$  is trioctahedral smectite in which all octahedral positions are occupied by Mg(II) atoms. According to chemical analysis published in [1], silicon atoms are isomorphously substituted by aluminium atoms in the interval from  $\text{Si}_{7.40}\text{Al}_{0.60}$  to  $\text{Si}_{6.16}\text{Al}_{1.84}$ . Small amounts of aluminium and/or iron atoms can be in the octahedrons.

The study of hydrothermal stability of smectites is described in [2]. The authors investigated the influence of type of lattice substitution, composition, and interlayer cations on thermal stability of smectites. A temperature was changed in the interval from 503 K to 1103 K, while a pressure remained constant — 100 MPa. The upper temperature limit of hydrothermal stability of saponite was found to be 1023 K.

*Iiyama* and *Roy* [3] investigated the conditions of hydrothermal synthesis of the thermally most stable sodium saponite. The formula of the most stable saponite that was formed at the temperature 1123 K and a pressure 100 MPa is  $[\text{Si}_{6.30}\text{Al}_{1.70}][\text{Mg}_{5.40}\text{Al}_{0.60}](\text{Na}_{1.10})\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ .

The hydrothermal stability of saponite at the higher temperature than that of dioctahedral smectites is stated also in [4]. Similarly to [2, 3], the lowest used temperature was 523 K.

During the study of a phase transformation of a mixture of kaolinite with  $\text{MgCO}_3$  and montmorillonite with  $\text{MgCO}_3$  it was found that in these systems saponite is formed only if temperature is higher than 423 K [5].

The aim of our study was to synthesize hydrothermally saponite, to find out the optimal values for temperature and pressure of this synthesis, the influence of type of exchangeable cation and to compare some properties of the synthetic saponite with those of natural minerals described in [6].

## Experimental

The hydrothermal runs were done in autoclaves in which teflon vessels with starting materials in a form of gel were closed. The volume of the starting material used in one run was approximately  $0.1 \text{ dm}^3$ . The autoclaves were heated in a resistance furnace and a temperature was controlled by on-off regulator attached to thermocouple located in the middle among four autoclaves. Temperatures used in this study were 373, 423, 473, 573, and 608 K. Durations of runs were 7 days, 14 days, and 21 days.

Colloidal silica — Aerosil (Degussa), aluminium nitrate (anal. grade), magnesium hydroxide prepared hydrothermally from anal. grade magnesium oxide, calcium hydroxide prepared by reaction of distilled water with oxide prepared by annealing of  $\text{CaC}_2\text{O}_4$  which was precipitated from the solutions of  $\text{H}_2\text{C}_2\text{O}_4$  (anal. grade) and  $\text{CaCl}_2$  (anal. grade) were used as starting materials.

In suspension of colloidal silica in aqueous solution of aluminium nitrate, aluminium hydroxide was precipitated with a weak aqueous solution of ammonia. This precipitate was filtered off and thoroughly washed with water. To this gel-like mixture of  $\text{SiO}_2$  and  $\text{Al}(\text{OH})_3$ , magnesium hydroxide and/or calcium or sodium hydroxides were added. The mass amounts of all components expressed in form of oxides are in Table 1.

In this way prepared gel that was X-ray amorphous and contained about 95 % of water was homogenized in a ball mill and immediately after that it was put into teflon vessels. Into a space between teflon vessel and autoclave  $5 \text{ cm}^3$  of distilled water were added.

Table 1

Ratios of mass amounts of starting materials

Sample No.	$n(\text{SiO}_2)$ mol	$n(\text{Al}_2\text{O}_3)$ mol	$n(\text{MgO})$ mol	$n(\text{CaO})$ mol	$n(\text{Na}_2\text{O})$ mol
1	4.4	0.2	3.8	—	—
2	4.4	0.2	3.6	0.2	—
3	4.4	0.2	3.7	—	0.1
4	4.4	0.2	3.6	—	0.2

X-Ray diffraction and thermoanalytical techniques (DTA, TG, and DTG) were used for identification of the resulting phases of all 60 runs. The X-ray measurements were done with a Philips vertical diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation. Measurements were performed on a thermoanalyzer Derivatograph OD-102 (MOM, Budapest) up to 1273 K (heating rate  $10 \text{ K min}^{-1}$ , mass of sample 300 mg, reference material  $\alpha\text{-Al}_2\text{O}_3$ , atmosphere static air). Prior to all measurements, the water content of samples was standardized by placing the samples into desiccator above a saturated solution of magnesium nitrate at temperature  $20^\circ\text{C}$  for 5 days.

### Discussion

According to X-ray as well as thermoanalytical measurements, the product of syntheses at temperatures 373 K and 423 K with duration 7 days, 14 days, and 21 days was saponite with not well-ordered structure. However, in several cases in diffraction patterns of these products only lines of magnesium hydroxide occurred.

At a temperature of synthesis 473 K with duration 21 days saponite was the only product of all four runs with different composition of starting materials (Table 1). When duration of syntheses was 7 days and 14 days, except several runs when the only crystalline phase was magnesium hydroxide and one case (sample 4) when magnesium hydroxide and unidentified phase ( $d_{\text{hkl}} = 0.155 \text{ nm}$ ) occurred, saponite was the only crystalline phase at this temperature. As follows from the thermoanalytical measurements (TG curve), in cases when crystalline magnesium hydroxide occurred after the synthesis, its amount varied between 3 and 5%.

At higher temperatures of syntheses, saponite with a well-ordered structure was the only product of all runs regardless of duration of the synthesis and composition of starting materials. The thermoanalytical curves (DTA, TG, and DTG) of these products were typical for saponite and confirmed that the products of syntheses at 573 K and 608 K were monomineral. The maximal rate of mass loss during dehydration was in the temperature interval from 1113 K to 1143 K. The type of exchangeable cation used in this study did not influence significantly temperature of dehydration and dehydroxylation of synthetic sap-

onite. A total relative mass loss (to 1273 K) was also very similar for all four samples with different exchangeable cation and was about 17 %.

While the duration of syntheses at these two highest used temperatures of syntheses had no significant effect on the course of diffraction patterns, the type of exchangeable cation influenced mainly the intensity of basal spacing (001), which increased from sample 1 to sample 4, that is from magnesium, calcium, sodium—magnesium, to sodium (Fig. 1). Other diffraction lines were not influenced so considerably so that diffraction patterns in the range from  $10^\circ$  to  $65^\circ 2\theta$  were nearly the same. The diffraction pattern of sample 4 synthesized at 608 K is in Fig. 2. The interplanar spacings belonging to the five most intensive diffraction lines were  $d_i/\text{nm}$ : 1.21, 0.457, 0.315, 0.255, and 0.1529. According to the interplanar spacing  $d_{001} = 1.21$  nm there is a monomolecular layer of water in the interlayer space of this mineral at relative humidity 55 %. The value of  $d_{060} = 0.1529$  nm confirms that it is a trioctahedral smectite, otherwise it would be only about 0.149 nm.

After a treatment with ethylene glycol the basal spacing (001) of all samples synthesized at 573 K and 608 K increased to 1.73 nm as it is usual in natural smectites.

The observed increase in the intensities of diffraction lines (001) from sample 1 to sample 4 (Fig. 1) can be explained by increasing of the order of structure, mainly along the crystallographic axis  $z$ .

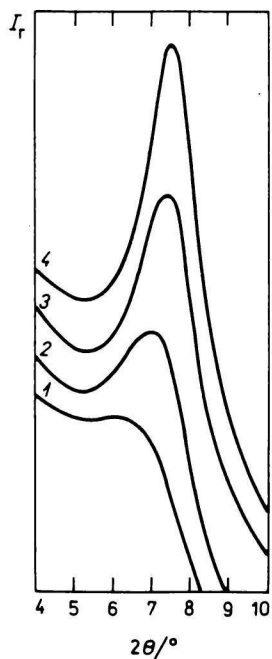


Fig. 1. X-Ray diffraction patterns (001) of samples 1 to 4 (Table 1).

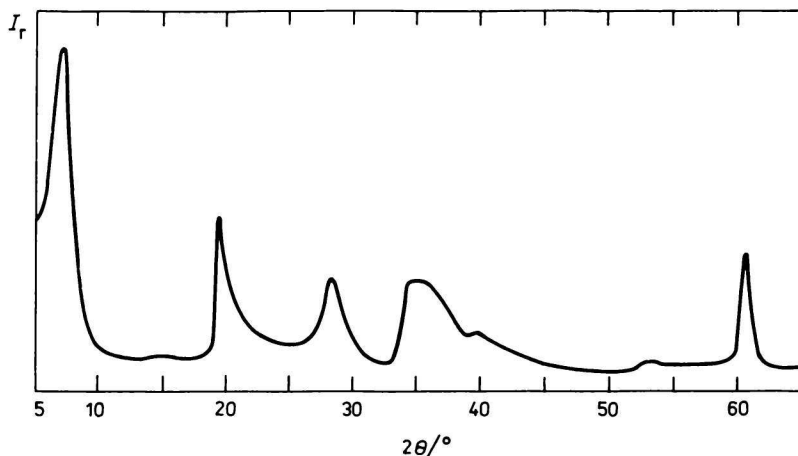


Fig. 2. X-Ray diffraction pattern of Na-saponite (sample 4, Table 1) synthesized at 608 K during 7 days.

All thermoanalytical curves of all products of syntheses at 573 K and 608 K were very similar to those of natural saponites published in [6]. DTA, TG, and DTG curves of synthetic saponite (sample 4) prepared at 608 K are shown in Fig. 3. In the DTA curve there is a strong wide endothermic peak with maximum at 413 K caused by the loss of water bounded in molecular form to the surface of mineral and coordinating exchangeable cations. Another strong but narrow endothermic peak with maximum at 1123 K corresponds to the release of water bounded in the form of OH groups in the structure of mineral. At the same time with dehydroxylation recrystallization occurs so that the exothermic peak is superimposed on the endothermic peak. The maximum of this exothermic peak is at 1108 K.

According to the DTG curve the mass loss occurs in two steps. A maximal rate of the loss of water bounded in a molecular form is at 398 K and a maximal rate of the loss of water bounded in the form of OH groups is at 1123 K. As regards the TG curve, the first mass loss represents 9 % of the mass of sample if we assume that this water is released to 623 K. If we assume that a mass loss in the temperature interval from 723 K to 1273 K is due to the release of water bounded in a form of OH groups this represents 4.8 % of the mass of sample.

The formula of sample 4 for one unit-cell calculated from its composition is  $[\text{Si}_{7.33}\text{Al}_{0.67}][\text{Mg}_{6.00}](\text{Na}_{0.67})\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ . In agreement with this formula two molecules of water formed from four OH groups represent 4.66 %. It is a good agreement with the value we obtained from the TG curve.

If we compare the X-ray diffraction patterns and thermoanalytical curves of all 60 products of hydrothermal syntheses we can assume that the temperature

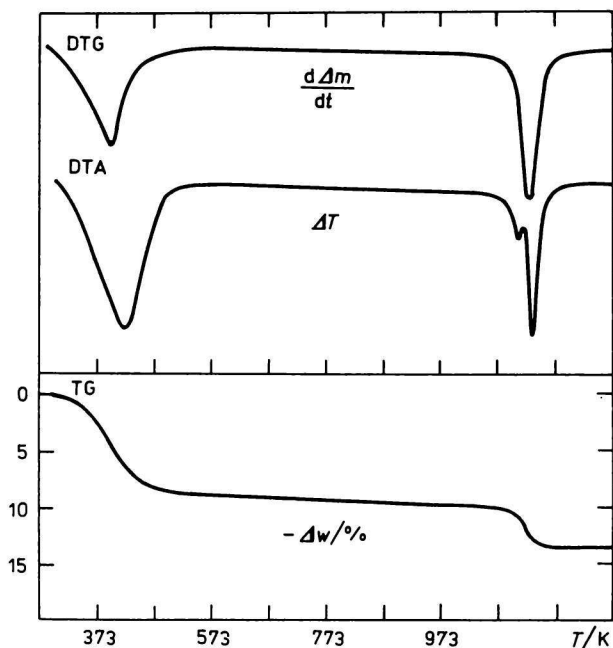


Fig. 3. DTG, DTA, and TG curves of Na-saponite (sample 4, Table 1) synthesized at 608 K during 7 days.

608 K, pressure 13.3 MPa, and duration of synthesis 7 days are suitable conditions for the synthesis of saponite. A product of such synthesis is monomineral and its structure is well ordered.

It is also interesting that while for formation of dioctahedral mineral montmorillonite the temperature of synthesis 373 K is not high enough even if this synthesis runs for many weeks [7, 8], the not well-ordered structure of trioctahedral saponite is formed after 7 days at 373 K (100 °C). It means that trioctahedral smectite saponite is not only hydrothermally more stable than dioctahedral montmorillonite [2—4] but its structure is formed under hydrothermal conditions more easily at lower temperatures.

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