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HYDROTHERMAL TRANSFORMATION OF KAOLINITE IN AN ALKALINE ENVIRONMENT

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Abstract. Reaction between kaolinite and NaOH solution was investigated. The effect of temperature and stirring on the progress of transformation of this mineral into hydroxysodalite was determined. It is assumed that transformation of kaolinite into hydroxysodalite proceeds mainly through its amorphization and dissolution, with Al^{3+} and Si^{4+} ions passing into solution. These ions crystallize subsequently in the form of hydroxysodalite crystals.

INTRODUCTION

The present paper deals with transformations that kaolinite undergoes in a strongly alkaline environment. The effect of alkaline hydroxide solutions on layer silicates was the subject of several publications (Barrer, Cole, Sticher 1968; Takahashi, Nishimura 1967; Ferrell, Grim 1967; Fijał, Tokarz 1976). Their authors were primarily interested in the kind of products obtained as a result of transformation of kaolinite and similar minerals. Less attention was paid to the conditions under which the process should be conducted, or to the transformation mechanism itself. These particular problems are discussed in this paper.

It is well known that the process of transformation of kaolinite is affected by the temperature and time of reaction, as well as by the kind and concentration of salts which are added in small amounts to initiate and accelerate this process (Barrer, Cole, Villiger 1970). According to Takahashi and Nishimura (1967), the structural transformation kaolinite → → sodalite proceeds through the amorphous stage, whereupon, after a period of nucleation, hydroxysodalite forms from it. The aim of this

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paper was to determine optimum conditions for rapid transformation of kaolinite into hydroxysodalite (further on referred to as sodalite), and to investigate the progress of this process.

EXPERIMENTAL

Investigations were carried out on an almost monomineral kaolinite sample separated by sedimentation from kaolinite clay from the Jegłowa deposit. Its X-ray diffraction patterns show that it contains only an insignificant admixture of illite and montmorillonite. This material was treated with 4 n NaOH solutions.

The effect of temperature and stirring of the suspension during treatment with hot NaOH on the progress of transformation was determined. The reactions were conducted over a temperature range of 70–90°C for 3–100 h, with the ratio of NaOH to untreated kaolinite being constant. Upon completion of each reaction, the obtained products were separated on a filter, washed with distilled water to a pH of 7, and dried at 105°C.

Table 1

List of investigated samples

Sample No	Temperature of reaction, °C	Reaction time, h	Mixing time, h
S-0	initial sample	—	—
S-1	80	25	12
S-2	80	50	25
S-3	80	75	37
S-4	80	100	50
S-5	70	50	5
S-6	90	50	5
S-7	80	50	5
S-9	80	25	4
S-10	80	25	8
S-21	85	3	—
S-22	85	5	—
S-23	85	5	—
S-24	85	10	—
S-25	85	20	—
S-26	85	30	—
S-27	85	50	—
		70	—

The nature of structural changes occurring during the reactions was defined by subjecting the products obtained under different conditions and at different stages to X-ray, infrared spectroscopic and electron microscope studies. A list of samples subjected to such investigations is given in Table 1.

RESULTS

X-ray investigations

X-ray diffraction patterns were obtained with a TUR-M61 diffractometer in a range of 2–22° Θ . The nature of structural changes occurring in kaolinite during treatment with hot NaOH was determined, and secondary minerals forming in this process were identified (Michiejew 1957). Figure 1 shows X-ray diffractograms of samples S-1, S-2, S-3 and S-4. As the reaction is prolonged, the intensity of kaolinite reflections decreases, and after 75 h they disappear altogether (samples S-3 and S-4). Instead, sodalite reflections appear ($d = 6.38, 4.58, 3.68, 3.23, 2.79, 2.60 \text{ \AA}^*$).

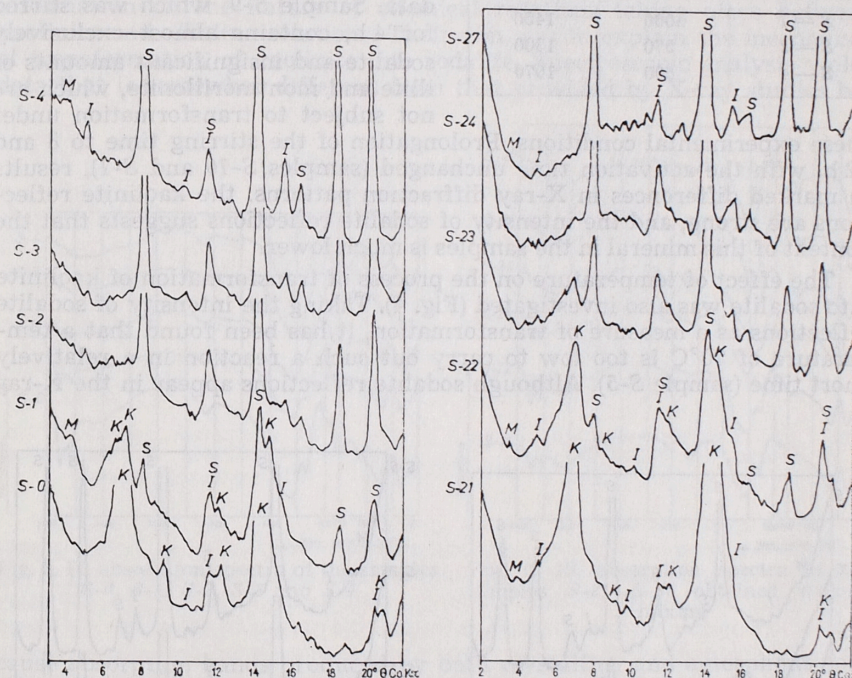


Fig. 1. X-ray diffractograms of untreated kaolinite (sample S-0) and of the samples S-1, S-2, S-3 and S-4, mixed during half time of reaction

Fig. 2. X-ray diffractograms of the samples treated with 4 n NaOH during 3–70 h, without mixing

From X-ray diffraction patterns it is evident that after 100 h (sample S-4) mainly sodalite and a small admixture of illite and montmorillonite are present in the sample. The latter minerals remain unchanged and their content becomes relatively higher because a part of kaolinite dissolves and goes into solution. This observation was confirmed by chemical

* $1 \text{ \AA} = 0.1 \text{ nm}$ (SI system).

analysis of the solution obtained after separation of solid products of transformation (Table 2).

The effect of stirring on the rate of transformation of kaolinite into sodalite was investigated on a series of samples *S-21*—*S-27* (Fig. 2). As the reaction is prolonged, the kaolinite content decreases again, and sodalite appears in its place. The marked absence of kaolinite reflections has already been noted in the X-ray diffraction pattern of a sample activated for 20 h. Also X-ray diffractograms of samples *S-9*, *S-10* and *S-4* (Fig. 3) confirm the previous data. Sample *S-9*, which was stirred for 4 h, contains almost exclusively sodalite and insignificant amounts of illite and montmorillonite, which are not subject to transformation under

these experimental conditions. Prolongation of the stirring time to 8 and 12 h, with the activation time unchanged (samples *S-10* and *S-1*), results in marked differences in X-ray diffraction patterns: the kaolinite reflections are strong, and the intensity of sodalite reflections suggests that the content of this mineral in the samples is much lower.

The effect of temperature on the process of transformation of kaolinite into sodalite was also investigated (Fig. 4). Taking the intensity of sodalite reflections as a measure of transformation, it has been found that a temperature of 70°C is too low to carry out such a reaction in a relatively short time (sample *S-5*). Although sodalite reflections appear in the X-ray

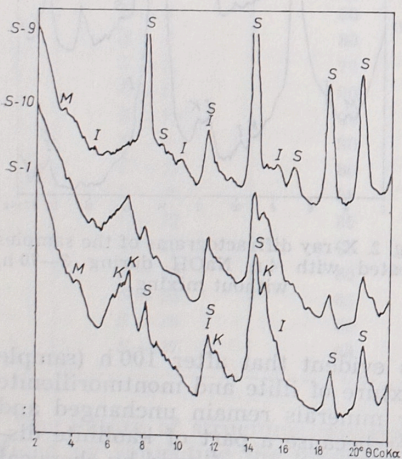


Fig. 3. X-ray diffractograms of the samples *S-9*, *S-10* and *S-1* mixed during 4, 8, and 12 h

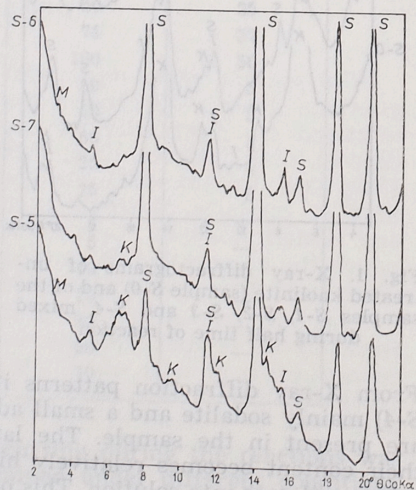


Fig. 4. X-ray diffractograms of the samples obtained at temperatures 70, 80 and 90°C

Table 2
Al₂O₃ and SiO₂ content in the solution after stopping of the reaction (mg per 10 g of initial kaolinite)

Sample No	Al ₂ O ₃	SiO ₂
<i>S-1</i>	1060	1450
<i>S-2</i>	570	1300
<i>S-4</i>	600	1070

diffraction pattern, their intensity compared with that of kaolinite reflections is low. X-ray diffractograms of samples *S-6* and *S-7* show, on the other hand, that kaolinite underwent complete transformation. The intensity of sodalite reflections in the X-ray diffractogram of sample *S-6* indicates that this sample was transformed more fully than the one activated at 80°C (sample *S-7*).

Infrared spectroscopic investigations

Infrared spectra were obtained with a C. Zeiss UR-10 spectrophotometer using KBr discs technique. The investigations were made to get information on the nature of chemical reactions taking place between kaolinite and alkaline solutions. Their aim was to explain the mechanism of transformation of kaolinite into sodalite. Spectroscopic analysis yields data that is somewhat different from that provided by X-ray studies be-

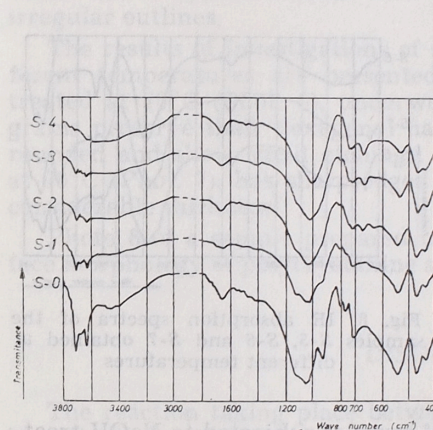


Fig. 5. IR absorption spectra of the samples *S-0*, *S-1*, *S-2*, *S-3* and *S-4*

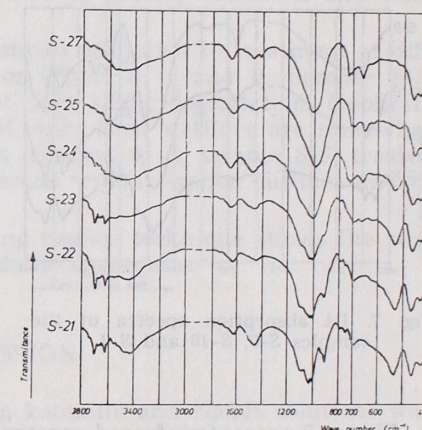


Fig. 6. IR absorption spectra of the samples *S-21*—*S-27* obtained without mixing

cause absorption bands produced by both crystalline and amorphous constituents can be recorded. The spectra obtained were interpreted basing on the data published in Moenke's catalogue (1962).

Infrared spectroscopic analysis made for samples *S-1*—*S-4* (Fig. 5) confirms the data obtained by X-ray method. Treatment of kaolinite with NaOH solution results in a systematic reduction in the intensity of the OH stretching (3600 cm⁻¹) and bending (920 cm⁻¹) absorptions, which testifies to progressive degradation of the structure of the initial kaolinite. Differences have also been noted in the region between 1000 and 1200 cm⁻¹ (ν₃ vibrations of SiO₄ tetrahedra). The 1120 cm⁻¹ absorption band decreases in intensity and becomes slightly broadened towards low wave numbers as the reaction is prolonged. Similarly, the 540 cm⁻¹ band produced by ν₄ vibrations SiO₄ tetrahedra shows a systematic reduction in its intensity. It does not, however, disappear altogether, being present

in sample S-4 treated for 100 h. In the region close to 670 cm^{-1} there appears a new absorption band characteristic of sodalite, with the intensity increasing with the reaction time. In place of a disappearing absorption in the region $750\text{--}820\text{ cm}^{-1}$, a new band attributed to sodalite arises ($700\text{--}750\text{ cm}^{-1}$). Moreover, the intensity ratio between the absorption bands occurring in the region $440\text{--}500\text{ cm}^{-1}$ is changed.

Spectroscopic investigations of samples S-21—S-27 confirm the structural changes revealed by X-ray method (Fig. 6). The 750 , 795 , 920 cm^{-1} bands, as well as absorptions in the region $1000\text{--}1200$ and 3600 cm^{-1} , disappear already after 30 h of activation (sample S-25) whereas after 20 h (sample S-24) absorption bands characteristic of sodalite (670 and 730 cm^{-1}) are visible in the spectra. Moreover, in the spectra of the samples studied absorption bands have been noted close to 1500 cm^{-1} , owing to the presence of unidentifiable carbonates. These carbonates formed probably due to CO_2 sorption from the air during the reaction and failed to be dissolved completely when the samples were washed.

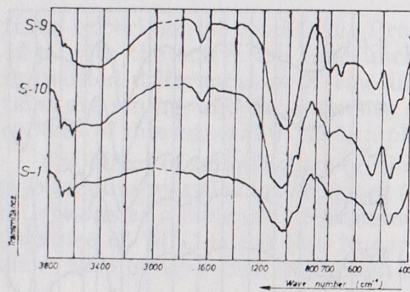


Fig. 7. IR absorption spectra of the samples S-9, S-10 and S-1

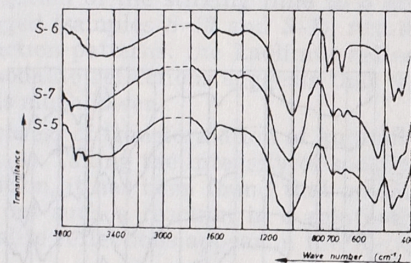


Fig. 8. IR absorption spectra of the samples S-5, S-6 and S-7 obtained at different temperatures

Figure 7 presents infrared spectra of samples subjected to NaOH treatment for the same period of 24 h, but with the stirring time varying from sample to sample (S-9, S-10, S-1). Only the spectrum of samples S-9 stirred for 4 h shows strong absorption bands attributed to sodalite: 670 and $700\text{--}740\text{ cm}^{-1}$. Spectra of the other two samples provide only evidence that amorphization proceeds and that the structure of kaolinite becomes loose, while absorption bands characteristic of sodalite are absent. CO_2 sorption from the air takes place in this case as well, which is shown by the presence of an absorption band close to 1500 cm^{-1} .

Infrared spectroscopic investigations of samples treated at different temperatures provide further evidence that at 90°C well crystallized sodalite can be obtained as the reaction product (Fig. 8). The spectrum of sample S-6 is nearly identical with the standard infrared spectrum of sodalite (Moenke 1962). The 535 cm^{-1} absorption band belonging to kaolinite is still present in the spectrum, but its intensity is insignificant. The spectrum of sample S-5, on the other hand, shows that the sodalite content is very low while kaolinite exhibiting a somewhat loosened structure is still the principal mineral.

Electron micrographs were taken with a Tesla BS 613 electron microscope operated at an accelerating voltage of 100 kV , using both powder and replica technique. The magnification range was $4.700\text{--}55.500\text{ X}$. The aim of these studies was to determine the influence of the processes discussed on the morphology of kaolinite grains, and to investigate the process of amorphization of kaolinite.

Electron micrographs taken for sample S-0 (Photos 1, 2) show flakes and polycrystalline aggregates of kaolinite. Individual kaolinite grains exhibit a distinct hexagonal habit and are sharp-edged. Kaolinite treatment with alkaline solutions for 25 and 100 h (samples S-1 and S-4) induces pronounced changes in the morphology of grains (Photos 3, 4, 5). Photos 3 and 4 reveal that degradation takes place, the marginal zones of grains being most liable to this process. After 100 h treatment (sample S-4) there are virtually no transparent kaolinite grains with a hexagonal habit. There appear instead dark grains of greater thickness and with irregular outlines.

The results of investigations of samples subjected to treatment at different temperatures are presented on Photos 6, 7 and 8. Sample S-5, treated at 70°C (Phot. 6), underwent only slight degradation. Kaolinite grains preserve their hexagonal habit, only their outlines are somewhat rounded and show small etchings. In contrast to it, sample S-6, treated at 90°C (Phot. 7), has sharp-edged grains with irregular outlines and of considerable thickness.

Photo 8 of a sample prepared using replica technique shows the surface morphology of polycrystalline sodalite aggregates.

DISCUSSION

The reaction taking place between kaolinite and NaOH solutions was investigated with the aim to determine the effect of suspension stirring and of the reaction temperature on the progress of transformation of kaolinite into sodalite (hydroxysodalite). It has been found that temperature is the main determinant of the transformation rate. This process is also significantly affected by the manner of stirring of the suspension during its reaction with NaOH. Stirring during the initial stage of the reaction, i.e. 3—5 h after its beginning, expedites and accelerates the process of kaolinite transformation because it ensures a better contact between fine kaolinite crystals and NaOH solution. In this way, amorphization and dissolution of kaolinite are accelerated. However, if stirring is prolonged outside this initial stage, the process of transformation is inhibited. This is probably so because stable equilibrium conditions, necessary in the process of formation of hydroxysodalite, must be maintained.

The above studies substantiated the theories of other authors (Takahashi, Nishimura 1967) that the process of kaolinite transformation embraces the stage of amorphization and partial dissolution of kaolinite. This statement is supported both by mineralogical investigations of the reaction products and by chemical analysis of the solutions left after

separation of these products. Although chemical studies suggest that sodalite forms by way of crystallization from the solution (Al_2O_3 and SiO_2 concentration in the solution decreases as the reaction is prolonged), infrared spectroscopic analysis provides evidence that even after a 100 h reaction remains of the amorphized kaolinite structure are present in the transformation products (535 cm^{-1} absorption band). Therefore, it is feasible that the transformation of kaolinite into hydroxysodalite proceeds through the stage of amorphization and dissolution of this mineral, with Al^{3+} and Si^{4+} ions passing into solution. These ions crystallize subsequently in the form of hydroxysodalite crystals. However, basing on the present studies, another possibility cannot be discounted, viz. that of transformation of kaolinite into hydroxysodalite from the amorphous phase. Such course of reaction was suggested by Takahashi and Nishimura (1967), and further data are required to ascertain whether only the first of the processes discussed takes place or the two processes are parallel.

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Marek TOKARZ

Z BADAŃ NAD HYDROTHERMALNYM PRZEobrażeniem KAOLINITU W ŚRODOWISKU ALKALICZNYM

Streszczenie

Przebadano przebieg procesu oddziaływań kaolinitu z roztworami ługu sodowego. Określono wpływ mieszania i temperatury na przebieg procesu przeobrażenia tego minerału w kierunku hydroxysodalitu. Zdaniem autora przeobrażenie kaolinitu w hydroxysodalit przebiega w głównej mierze na drodze amorfizacji i rozpuszczania tego minerału, przy czym do roztworu przechodzą jony Al^{3+} i Si^{4+} , które następnie wykrywalizują w formie kryształów hydroxysodalitu.

OBJAŚNIENIA FIGUR

- Fig. 1. Dyfraktogramy rentgenowskie kaolinitu wyjściowego (próbka S-0) oraz próbek S-1, S-2, S-3 i S-4 mieszanych przez połowę czasu trwania reakcji
- Fig. 2. Dyfraktogramy rentgenowskie próbek traktowanych 4n NaOH w czasie 3—70 h bez mieszania
- Fig. 3. Dyfraktogramy rentgenowskie próbek S-9, S-10 i S-1 mieszanych przez 4, 8 i 12 h
- Fig. 4. Dyfraktogramy rentgenowskie próbek uzyskanych w wyniku reakcji prowadzonych w temperaturze 70, 80 i 90°C
- Fig. 5. Widma absorpcyjne w podczerwieni próbek S-0, S-1, S-2, S-3 i S-4
- Fig. 6. Widma absorpcyjne w podczerwieni próbek S-21—S-27 uzyskanych bez mieszania
- Fig. 7. Widma absorpcyjne w podczerwieni próbek S-9, S-10 i S-1
- Fig. 8. Widma absorpcyjne w podczerwieni próbek S-5, S-6 i S-7 otrzymanych w wyniku reakcji prowadzonej w różnych temperaturach

OBJAŚNIENIA FOTOGRAFII

- Fot. 1. Obraz elektronowy polikrystalicznych agregatów kaolinitu z Jegłowej (próbka S-0). Pow. $\times 98\ 000$
- Fot. 2. Obraz elektronowy heksagonalnych blaszek kaolinitu z Jegłowej (próbka S-0). Pow. $\times 80\ 000$
- Fot. 3. Obraz elektronowy agregatu kaolinitu po 25 h traktowania 4n NaOH (próbka S-1). Pow. $\times 33\ 000$
- Fot. 4. Obraz elektronowy agregatów kaolinitu po 25 h obróbki (próbka S-1). Pow. $\times 110\ 000$
- Fot. 5. Obraz elektronowy agregatów hydroxysodalitu (próbka S-4). Pow. $\times 9400$
- Fot. 6. Obraz elektronowy agregatów kaolinitu traktowanych w temperaturze 70°C (próbka S-5). Pow. $\times 40\ 000$
- Fot. 7. Obraz elektronowy agregatów hydroxysodalitu (próbka S-6). Pow. $\times 21\ 500$
- Fot. 8. Obraz elektronowy (wykonany techniką replik) agregatów hydroxysodalitu (próbka S-6). Pow. $\times 65\ 000$

Марк ТОКАЖ

ИЗ ИССЛЕДОВАНИЙ ГИДРОТЕРМАЛЬНОГО ПРЕОБРАЗОВАНИЯ КАОЛИНИТА В ЩЕЛОЧНОЙ СРЕДЕ

Резюме

Был исследован ход процесса взаимодействий каолинита с растворами натрового щелка. Было определено влияние размешивания и температуры на ход процесса преобразования этого минерала в направлении гидроксисодалита. По мнению автора, преобразование каолинита в гидроксисодалит протекает главным образом из-за аморфизации и растворения этого минерала, при чём в раствор переходят ионы Al^{3+} и Si^{4+} , которые в дальнейшем выкристаллизовываются в форме кристаллов гидроксисодалита.

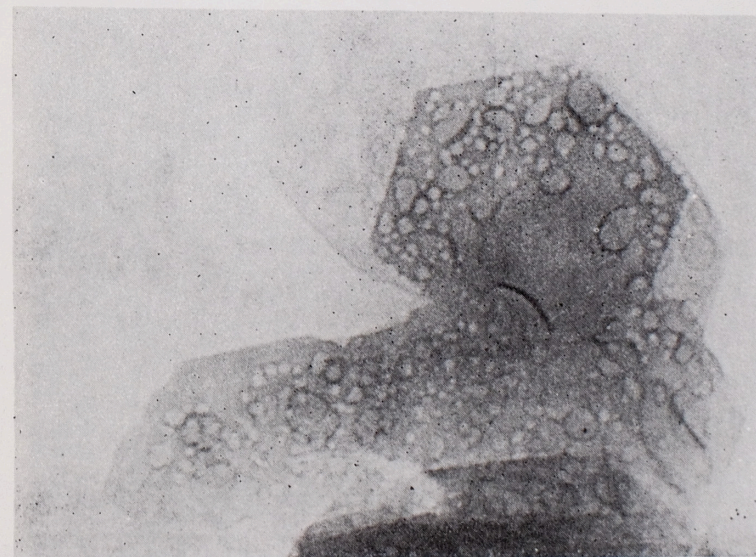
- Фиг. 1. Рентгеновские дифрактограммы исходного каолинита — образец *S-0* и образцов *S-1*, *S-2*, *S-3* и *S-4* размешиванных в течение половины времени реакции
- Фиг. 2. Рентгеновские дифрактограммы образцов подверженных воздействию четырёхнормального NaOH в течение 3—70 h без размешивания
- Фиг. 3. Рентгеновские дифрактограммы образцов *S-9*, *S-10* и *S-1* размешиванных в течение 4, 8 и 12 h
- Фиг. 4. Рентгеновские дифрактограммы образцов полученных вследствие реакций при температурах 70, 80 и 90°
- Фиг. 5. ИК-спектры поглощения образцов *S-0*, *S-1*, *S-2*, *S-3* и *S-4*
- Фиг. 6. ИК-спектры поглощения образцов с *S-21* по *S-27*, полученных без размешивания
- Фиг. 7. ИК-спектры поглощения образцов *S-9*, *S-10* и *S-1*
- Фиг. 8. ИК-спектры поглощения образцов *S-5*, *S-6* и *S-7*, полученных в итоге реакций протекавших в различных температурах

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

- Фото 1. Электронномикроскопный снимок поликристаллических агрегатов каолинита из Егловэй (образец *S-0*). Увеличение $\times 98\ 000$
- Фото 2. Электронномикроскопный снимок гексагональных пластинок каолинита из Егловэй (образец *S-0*). Увеличение $\times 80\ 000$
- Фото 3. Электронномикроскопный снимок агрегата каолинита после 25 час. обработки четырёхнормальным NaOH (образец *S-1*). Увеличение $\times 33\ 000$
- Фото 4. Электронномикроскопный снимок агрегатов каолинита после 25 час. обработки (образец *S-1*). Увеличение $\times 110\ 000$
- Фото 5. Электронномикроскопный снимок агрегатов гидроксисодалита (образец *S-4*). Увеличение $\times 9\ 400$
- Фото 6. Электронномикроскопный снимок агрегатов каолинита подверженных воздействию температуры в 70°C (образец *S-5*). Увеличение $\times 40\ 000$
- Фото 7. Электронномикроскопный снимок агрегатов гидроксисодалита (образец *S-6*). Увеличение $\times 21\ 500$
- Фото 8. Электронномикроскопный снимок (сделанный при помощи техники слепков) агрегатов гидроксисодалита (образец *S-6*). Увеличение $\times 65\ 000$



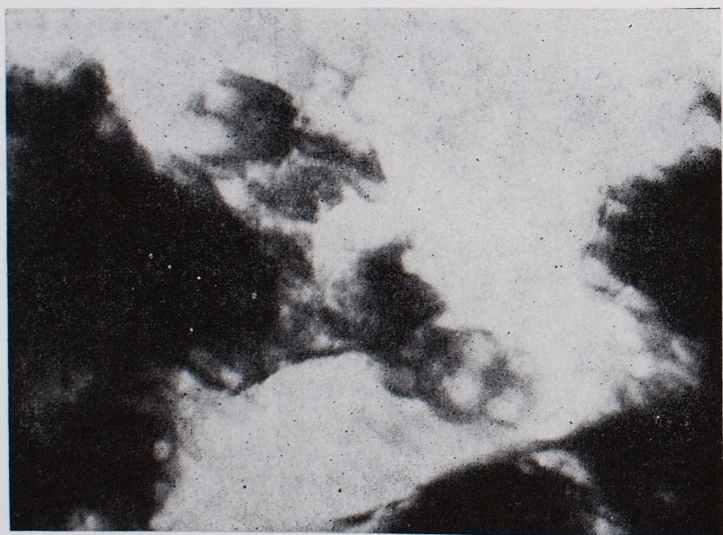
Phot. 1. Electron micrograph of polycrystalline aggregates of kaolinite from Jegłowa (sample *S-0*). Magn. $\times 98\ 000$



Phot. 2. Electron micrograph of hexagonal flakes of kaolinite from Jegłowa (sample *S-0*). Magn. $\times 80\ 000$

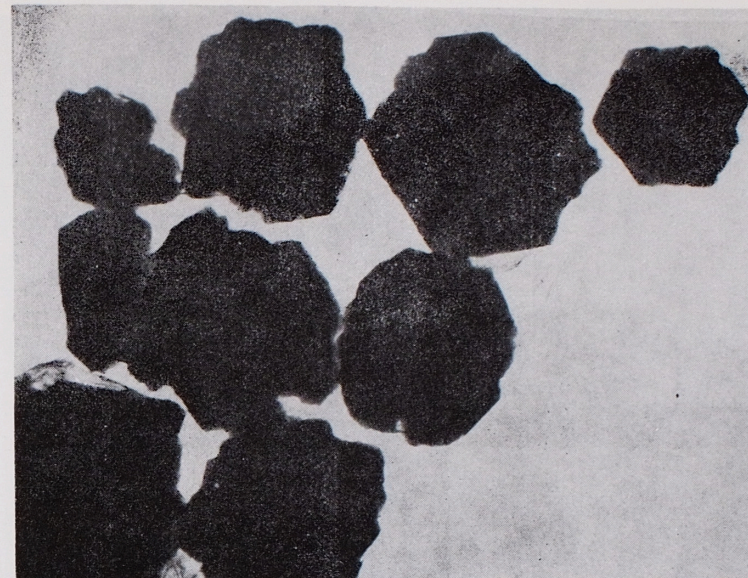


Phot. 3. Electron micrograph of kaolinite aggregates after treating with 4 n NaOH during 25 h (sample S-1). Magn. $\times 33\ 000$

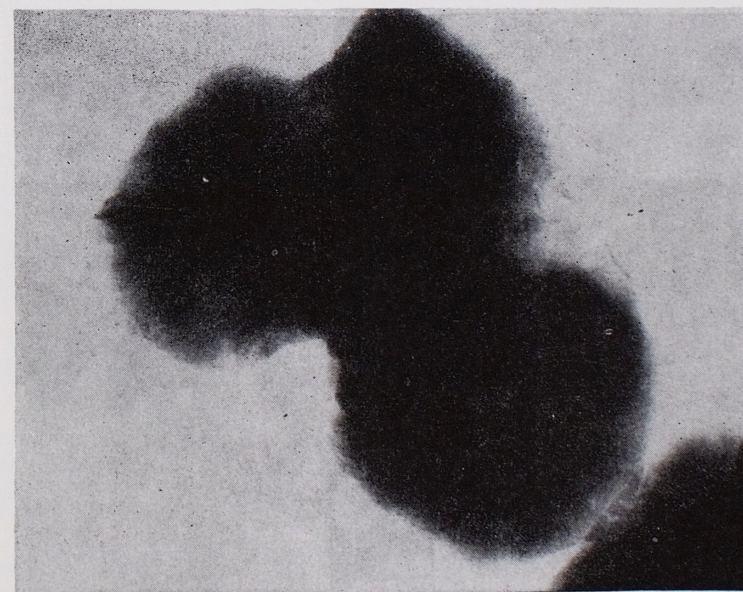


Phot. 4. Electron micrograph of kaolinite aggregates after treating with 4 n NaOH during 25 h (sample S-1). Magn. $\times 110\ 000$

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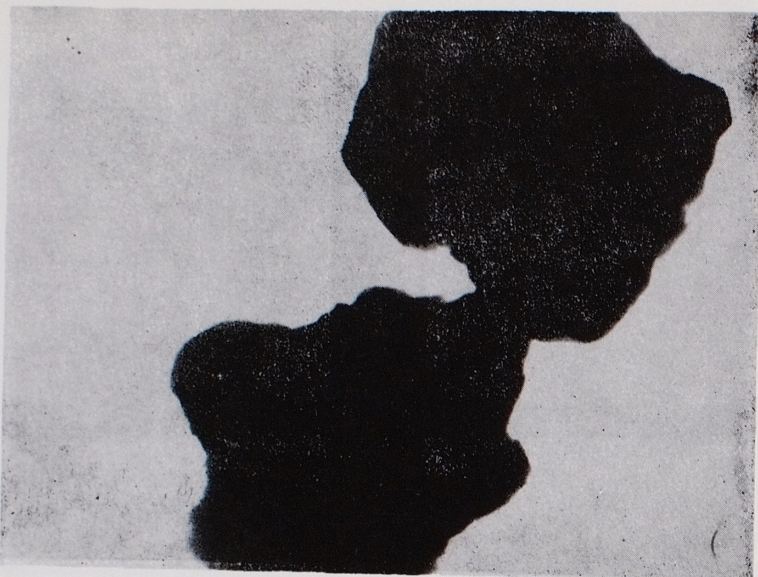


Phot. 5. Electron micrograph of hydroxysodalite aggregates (sample S-4). Magn. $\times 9400$

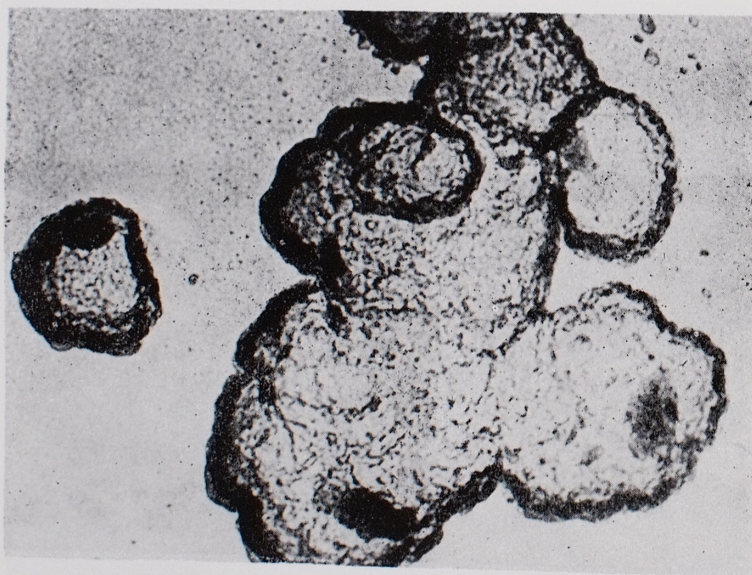


Phot. 6. Electron micrograph of kaolinite aggregates treated at 70°C (sample S-5). Magn. $\times 40\ 000$

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Phot. 7. Electron micrograph of hydroxysodalite aggregates (sample S-6). Magn. $\times 21\,500$



Phot. 8. Electron micrograph (replica) of hydroxysodalite aggregates (sample S-6). Magn. $\times 65\,000$

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