

Andrzej WIEWIÓRA \*

## X-RAY, INFRARED AND DTA STUDIES OF EXPANDED KAOLINITES

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**Abstract.** Studies of fine particle size fractions of well-ordered Polish kaolinites, by X-ray, infrared and thermal analysis, distinguish intercalation and superficial sorption of organics on kaolinite particles. X-ray and infrared data provide a very good means of following the rate of intercalation. TG may be used for evaluation of the total amount of potassium acetate in kaolinite samples. It has been shown that the very fine particles with very regularly shaped, thin hexagons, did not absorb KAc between the layers, no matter how long and in which effective intercalation medium they were immersed. This must be taken into account when intercalation of KAc is used for characterisation or classification of kaolinitic material, especially fine grained materials.

### INTRODUCTION

For the last twelve years intercalation of kaolinite by various media has been under consideration by many clay mineralogists in almost every country. Assuming that the bases of the phenomenon are generally known, a review of published data seems unnecessary. No discussion of the effectiveness of the different organic media will be given. During the Clay Conference in Tokyo, it was suggested (Heller 1970), that the fine particles may take up KAc but that X-ray diffraction was not observed from a KAc complex because of considerable disorder generated in these small crystals. So far, lack of a relationship between  $I_{14.1}/I_{7.15}$  intensity ratio and KAc content measured chemically (Bodenheimer et al. 1967) also remained obscure. Main attention will be attached then to the intercalation of fine particles of kaolinite, mostly by KAc. Hydrazine will be used for comparison. An effort will be made to distinguish adsorption and intercalation. The present study may also contribute to the general discussion of the character of cohesion between kaolinite layers.

\* Research Centre of Geological Sciences, Polish Academy of Sciences, Warsaw.

## EXPERIMENTAL DATA

### Material characteristics

In the course of mineralogical studies of Polish primary and sedimentary kaolins, experiments were performed with intercalation of the bulk samples. Kaolinites in sedimentary kaolins, like Maria and Zofia, and primary kaolins like Wyzonowice, Bolesławice and Roztoka, intercalated more than 90 per cent of KAc with two minor exceptions among 30 investigated samples.

Six representative samples of primary and sedimentary kaolins have been carefully divided into seven particle size fractions, namely  $< 0.2$ ,  $0.2-0.5$ ,  $0.5-2.0$ ,  $2-5$ ,  $5-15$ ,  $15-30$ ,  $> 30 \mu\text{m}$  using both standard and flow-type centrifuges. The fractions were X-rayed for mineral composition and crystallinity of kaolinite. In the primary kaolins, mica and quartz appeared to be present in practically all fractions. In the sedimentary kaolins the three finest fractions were essentially free of mineral contamination, apart from minor quantities of quartz. All separated particle size fractions were included into general consideration of the extent of intercalation. However, for studies by X-ray, I. R. and DTA the sedimentary, Maria kaolin was chosen. X-ray diffractograms of the three finest particle fractions of this kaolin, presented in Figure 1, show no remarkable difference in crystallinity of the kaolinite. Especially, crystallinity of  $< 0.2 \mu\text{m}$  particles is not worse than that of the larger particles. Photograph 1 shows that the individual grains represent very thin, but very well developed hexagons.

### Intercalation procedure

To prove that the effect of particle size on intercalation rate (Wiewióra and Brindley 1969) concerns each type of kaolinite, the kaolin fractions were treated with 8 N KAc and separately by 10 M hydrazine.

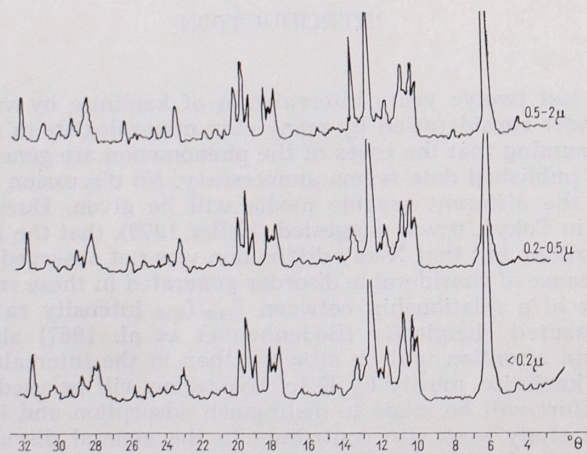


Fig. 1. Diffractograms of  $< 0.2$ ,  $0.2-0.5$ ,  $0.5-2.0 \mu\text{m}$  particle size fractions of Maria kaolinite (untreated)

After more than a month of equilibration, the oriented aggregates (smears) were mounted on the diffractometer and basal X-ray reflections registered. Intensity ratio  $I_{(001) \text{ complex}}/I_{(001) \text{ kaolinite}}$  has been used for semi-quantitative evaluation of the extent of penetration of organics between the kaolinite layers.

Coarse grained kaolinites, namely  $> 0.5 \mu\text{m}$  e.s.d., intercalated completely in hydrazine and also completely in KAc, in all samples. The two finest fractions reacted in KAc incompletely:  $0.2-0.5 \mu\text{m}$  material of the primary kaolins reacted nearly — in 90 per cent, in sedimentary ones — in about 80 per cent:  $< 0.2 \mu\text{m}$  material reacted only in 2-8 per cent in both kinds of clay.

In the X-ray experiments, no care has been attached to the possible excess of organics and water. The infrared technique of studying the  $14.1 \text{ \AA}$  KAc complex required that the excess of water together with non-reacted, highly hygroscopic salt, must be removed. This was achieved by washing with small quantity of 2-propanol (5 ml/150 mg of dry clay). The experiments have shown, that washing caused an unwanted but distinct regress of the intercalation process, perhaps due to the lower dielectric constant of 2-propanol, than that of water. Neglecting this, 2-propanol may be used for the removal of the excess of KAc and was used in studying the intercalation of the fine particle size fractions of Maria kaolinite.

### X-ray data

Basal reflections of KAc- and hydrazine-kaolinite complexes, and for comparison 001 reflection of oriented aggregates of kaolinite, are presented in Figures 2 and 3. It is seen that the finest particles ( $< 0.2 \mu\text{m}$  e.s.d.) show very little intercalation. The extent of intercalation increases with the size of kaolinite particles.

When an excess of salt in aggregates in uncontrollable and high, and kaolinite content low, then very high absorption of X-ray by the salt (Fig. 4) simulates a disordering in the fine crystals. In reality the fine particles are not at all amorphous (Figs. 2

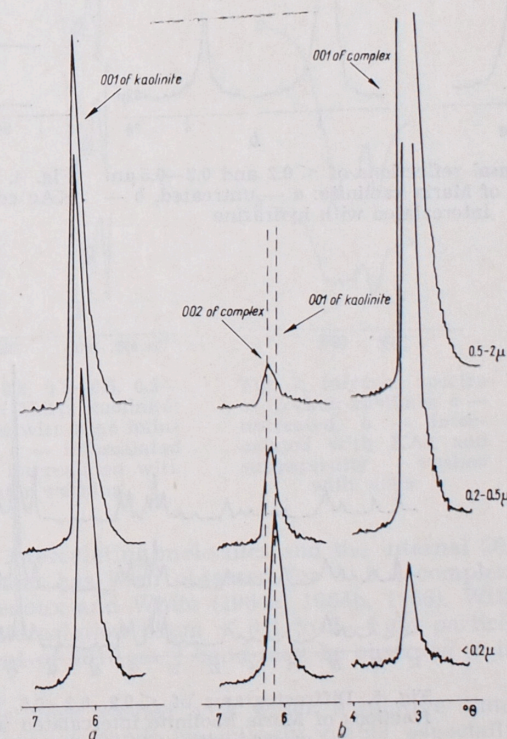


Fig. 2. Basal reflections of  $< 0.2$ ,  $0.2-0.5$ ,  $0.5-2.0 \mu\text{m}$  fractions of Maria kaolinite, a — untreated and b — intercalated with KAc

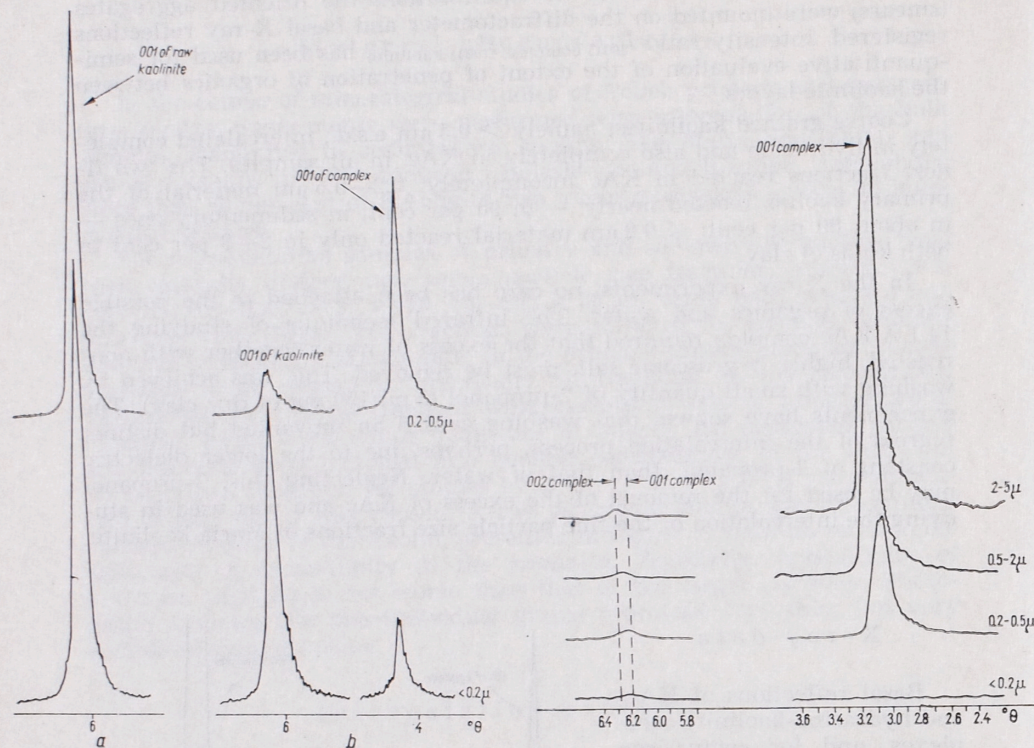


Fig. 3. Basal reflections of  $< 0.2$  and  $0.2-0.5\ \mu\text{m}$  fractions of Maria kaolinite: a — untreated, b — intercalated with hydrazine

Fig. 4. Basal reflections of Maria kaolinites — KAc complexes. An excess of salt is present in aggregates

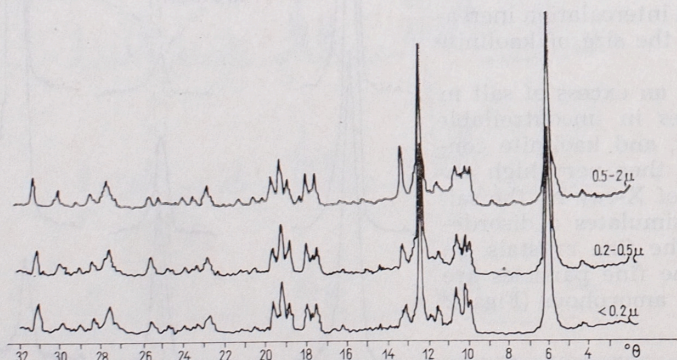


Fig. 5. Diffractograms of  $< 0.2$ ,  $0.2-0.5$ ,  $0.5-2.0\ \mu\text{m}$  particle size fractions of Maria kaolinite intercalated with hydrazine and then washed with water to remove the organics

and 3). In fact, the coarse grains became disordered, and the finest particles showed very little difference in crystallinity, or none (Figs. 5 and 1).

### Infrared data

The infrared spectra of the kaolinite films in nujol, mounted on a KBr window, show four absorption bands at:  $3692$ ,  $3668$ ,  $3648$  and  $3618\ \text{cm}^{-1}$  (a, b, c, d, respectively in Fig. 6), which correspond exactly with those previously reported for well-ordered kaolinite by Pampuch and Błaszczak (1964) and others. Some reduction of the relative intensity of  $3692\ \text{cm}^{-1}$  band may be observed for the coarser particle fractions.

When intercalated with KAc the kaolinites show considerable decrease in intensity of  $3692\ \text{cm}^{-1}$  absorption band; and an additional absorption band appears at  $3610\ \text{cm}^{-1}$  (e in Fig. 6) due to the formation of strong

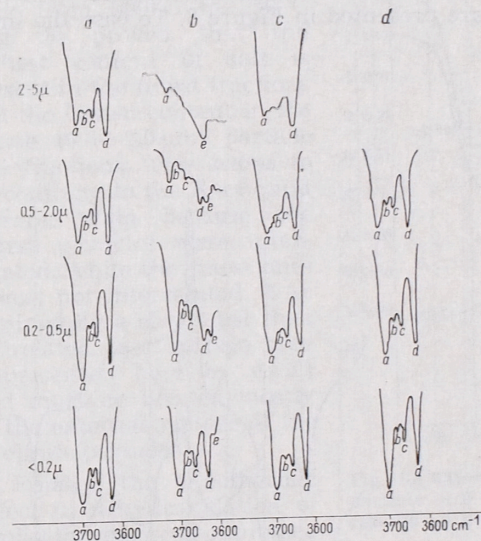


Fig. 6. Infrared spectra of  $< 0.2$ ,  $0.2-0.5$ ,  $0.5-2.0\ \mu\text{m}$  particle size fractions of Maria kaolinite: a — untreated, b — intercalated with KAc followed by 2-propanol treatment, c — intercalated and washed with water, d — intercalated with hydrazine followed by water washing

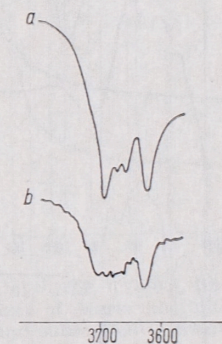


Fig. 7. Infrared spectra of Koekuk kaolinite: a — untreated, b — intercalated with KAc and subsequently washed with water

hydrogen bonds between the intercalating molecules and the internal OH surface. Similar frequency band has been obtained for  $11.5\ \text{\AA}$  complex, when heated at  $110^\circ\text{C}$ , by Ledoux and White (1964a, 1964b, 1966). With increase of the amount of intercalation (from  $< 0.2$  to  $2-5\ \mu\text{m}$  particle size fractions) the enhancement of  $3610\ \text{cm}^{-1}$  band may be observed (e in Fig. 6).

When intercalated samples were washed with water, a relative diminishing of the three high frequency bands was clearly visible, especially

in 2–5  $\mu\text{m}$  sample. This effect was even more effective in a coarse-grained Keokuk kaolinite (Fig. 7), in which high frequency bands were completely missing. Diffractograms of the respective natural and intercalated Keokuk kaolinite were presented by Wiewióra and Brindley (1969).

Spectra of kaolinite intercalated with hydrazine and subsequently washed with water show no difference in comparison to the untreated clay.

### Thermal data

Untreated samples and the KAc intercalated and subsequently washed with 2-propanol ones were also investigated by means of thermal analysis. In each case about 300 mg of the procedured clay were heated in a simultaneous DTA, DTG, and TG thermal equipment — Derivatograph 102 (MOM).

DTA curves of < 0.2, 0.2–0.5, and 0.5–2.0  $\mu\text{m}$  intercalated with KAc and washed with 2-propanol are presented in Figure 8. To ease the inter-

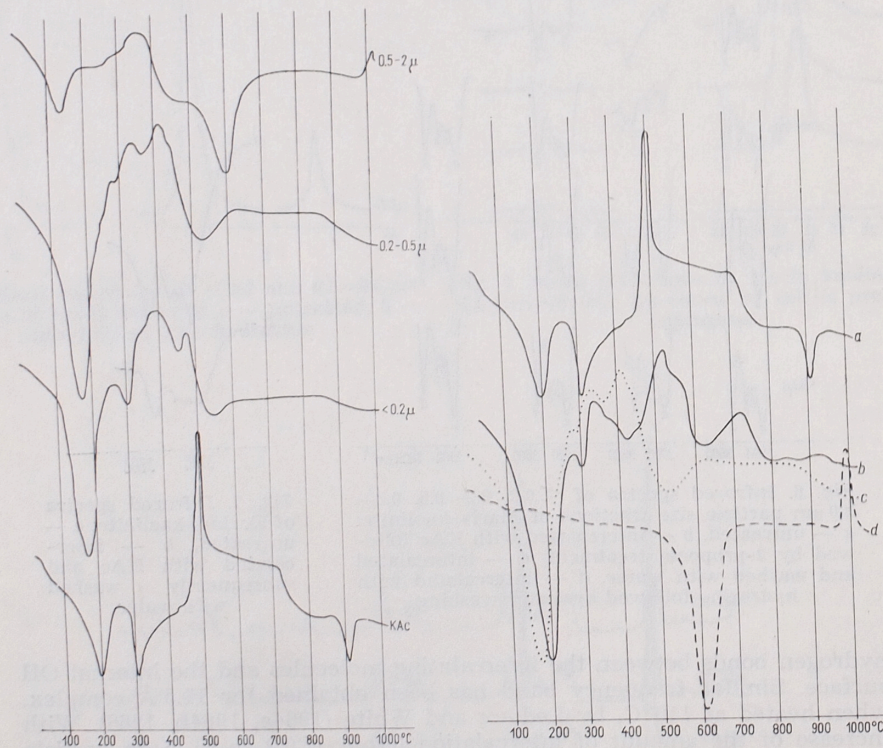


Fig. 8. DTA curves of: KAc (settled on an inert  $\text{Al}_2\text{O}_3$ ) and < 0.2, 0.2–0.5, 0.5–2.0  $\mu\text{m}$  particle size fractions of Maria kaolinite intercalated with KAc

Fig. 9. DTA curves of: a — KAc, b-, c-, d-, of 0.2–0.5  $\mu\text{m}$  Maria kaolinite: b — intercalated with KAc, c — intercalated and subsequently washed with 2-propanol, and d — untreated

pretation of DTA curves, Figure 9 is presented, where: 1 — KAc mixed with an inert  $\text{Al}_2\text{O}_3$ , 2, 3, 4 — 0.2–0.5  $\mu\text{m}$  particle size fractions of Maria kaolinite intercalated with KAc, intercalated and washed with 2-propanol, and untreated respectively, are shown. In Fig. 10, TG curves are presented.

From Figures 8, 9 and 10, it may be seen that the first endothermic effect must be due to salt dehydration. The second endothermic effect (at fixed 300°C) indicates KAc melting. Strong exothermic peak is caused by a deflagration of the salt process.

The low temperature endothermic effect is associated with a weight loss of more than 30 per cent in < 0.2  $\mu\text{m}$ , more than 20 per cent in 0.2–0.5 and less than 5 per cent in 0.5–2 particle size fractions. For the deflagration process, the similar weight loss (Fig. 10), as well as a very distinct shift of the temperature of dehydration from 200°C to 130°C and the temperature of the exothermic peak from 500°C to 350°C (Fig. 8) proved that the highest content of salt is present in the finest fractions and the lowest content in the coarse (0.5–2.0  $\mu\text{m}$ ) particle size fractions. This seems to be contrary to the X-ray and infrared data because the coarse particles were intercalated, while the finest ones almost not intercalated. KAc retained by a clay must then be related to a surface area (represented here by e.s.d.) and must be bonded mostly to the external surface of the kaolinite particles.

Finally, the endothermic effect of dehydroxylation of kaolinite, very well expressed in curve 4 (Fig. 9), is hardly identified in curve 2. It is comparatively much stronger in intercalated 0.5–2.0 than in 0.2–0.5 and in the finest particle size fractions (Fig. 8). Comparing DTA and TG curves (Fig. 8, 19, 10) and X-ray tracing in Fig. 4 one may realize greatly the KAc thinned the content of kaolinite in the fine particle size fractions.

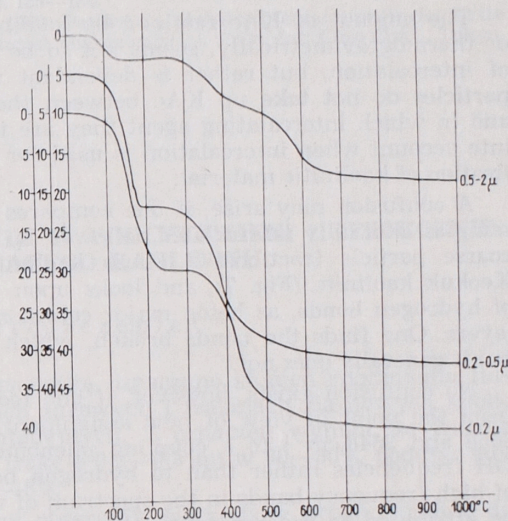


Fig. 10. TG curves of < 0.2, 0.2–0.5, 0.5–2.0  $\mu\text{m}$  particle size fractions of Maria kaolinite intercalated with KAc and subsequently washed with 2-propanol

### DISCUSSION AND CONCLUSIONS

Bradley (1971) in his presidential address to the Mineralogical Society of America stated that attack of a swelling agent on kaolinite minerals „must be looked upon as analogous with the optically observed limited-degree swelling of vermiculite crystals (Walker, 1963) rather than as

a dispersion", which was exactly what Weiss et al. (1970) have observed microscopically.

Contrary to the suggestion that intercalation may cause disorder in the structure of fine kaolinite crystals (Heller, 1970), which according to the present author's conviction may be interpreted in terms of Bradley's dispersion, fine particles stay compact and oppose against letting a swelling agent penetrate between the structural layers.

It seems that nonreactiveness of the finest particles has nothing to do with an order — disorder of any type, contrary to the suggestions of Weiss et al. (1963) and Weiss (1970). The electron micrograph is presented in Photograph 1. If morphology may be related to structure (Bates 1958, 1959; De Souza et al. 1966) then, electron micrograph is consistent with X-ray diffraction picture (Fig. 1), which corresponds to the well ordered triclinic lattice of kaolinite.

The amount of KAc retained by kaolinite, as determined chemically or thermogravimetrically, seems not to be directly related to the extent of intercalation, but rather is dependent upon surface area. Very fine particles do not take up KAc between the layers, no matter how long and in which intercalating agent they are immersed. This must be taken into account when intercalation is used for the characterisation or classification of kaolinitic material.

A confusion may arise, if one compares infrared spectra of untreated samples and fully intercalated followed by water washing ones, like the coarse particle fractions of Maria kaolinite (Fig. 6) or, especially, the Keokuk kaolinite (Fig. 7), and looks upon them from the point of view of hydrogen bonds, as being major cohesion forces between the adjacent layers. One finds the bonds broken, which ought to produce dispersion, but it generally does not.

No confusion exists, however, if one looks upon the infrared spectra from the point of view of new assignment of frequency bands at 3692, 3668 and 3648  $\text{cm}^{-1}$  to a coupling phenomena between almost identical OH frequencies rather than to hydrogen bonds (Cruz et al. 1972). Lack of high frequency bands in the spectrum of washed Keokuk kaolinite may be attributed to the remnants of not completely removed KAc, bonded to OH surfaces of kaolinite. This can effectively prevent the coupling of OH.

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Andrzej WIEWIÓRA

## BADANIA RENTGENOWSKIE, W PODCZERWIENI I TERMICZNIE SPĘCZANIAŁEGO KAOLINITU

### Streszczenie

Półilościową metodą rentgenowską oznaczano stopień spęcznienia (interkalacji) kaolinitu w próbkach surowych i frakcjach ziarnowych kaolinitów pierwotnych i sedimentacyjnych. Z oznaczeń wynika, że frakcje  $< 2 \mu\text{m}$  pęcznią kompletnie, frakcje  $0,2\text{—}0,5 \mu\text{m}$  w 80—90%, podczas gdy frakcje  $< 0,2 \mu\text{m}$  zaledwie w 2—8%.

W widmach w podczerwieni obserwuje się zmiany proporcjonalne do stopnia interkalacji, zwłaszcza spadek intensywności pasma  $3692 \text{cm}^{-1}$ , a pojawienie się pasma  $3610 \text{cm}^{-1}$ . Efekt ten nawyrażniej zaznaczył się we frakcji najgrubszej kaolinitu Maria i w grubokrystalicznym kaolinitie Keokuk.

Na podstawie badań termicznych ustalono, że ilość octanu potasu trwale zawartego w interkalowanych próbkach nie jest proporcjonalna do stopnia interkalacji, lecz do powierzchni rozwiniętej kaolinitu. Świadczą o tym najwyższe zawartości octanu potasu we frakcji najdrobniejszej, a najniższe w najgrubszej.

Drobna frakcja ziarnowa ( $< 2 \mu\text{m}$ ) nie dopuszcza octanu potasu między pakiety, co musi być brane pod uwagę przy próbach klasyfikacji materiału kaolinitowego przy zastosowaniu metody interkalacji.

Próbki interkalowane i przemyte wodą wykazują zanik pasm podczerwonych wysokiej częstotliwości. Tłumaczone jest to pozostałością octanu potasu związanego z powierzchnią OH pakietów kaolinitu. W tym świetle przypisanie wspomnianych pasm raczej zjawisku parowania (coupling) grup OH, niż wiązaniom wodorowym (Cruz i inni 1972) wydaje się uzasadnione.

- Fig. 1. Dyfraktogramy rentgenowskie frakcji ziarnowych  $< 0,2$ ,  $0,2-0,5$  i  $0,5-2,0 \mu\text{m}$  kaolinitu Maria (naturalnego)
- Fig. 2. Refleksy podstawowe kaolinitu: *a* — naturalnego i *b* — interkalowanego octanem potasu we frakcjach  $< 0,2$ ;  $0,2-0,5$  i  $0,5-2,0 \mu\text{m}$  kaolinitu Maria
- Fig. 3. Refleksy podstawowe kaolinitu: *a* — naturalnego i *b* — interkalowanego hydrazyną we frakcjach  $< 0,2$  i  $0,2-0,5 \mu\text{m}$  kaolinitu Maria
- Fig. 4. Refleksy podstawowe kaolinitu Maria i jego kompleksu octanowego. W preparatach zachowany jest nadmiar octanu potasu
- Fig. 5. Dyfraktogramy frakcji ziarnowych  $< 0,2$ ;  $0,2-0,5$  i  $0,5-2,0 \mu\text{m}$  kaolinitu Maria po interkalacji kaolinitu hydrazyną i usunięciu jej przez odmywanie wodą
- Fig. 6. Widma w podczerwieni frakcji ziarnowych  $< 0,2$ ;  $0,2-0,5$  i  $0,5-2,0 \mu\text{m}$  kaolinitu Maria: *a* — naturalnych, *b* — interkalowanych octanem potasu i przemytych 2-propanolem, *c* — interkalowanych i przemytych wodą, *d* — interkalowanych hydrazyną i przemytych wodą
- Fig. 7. Widma w podczerwieni kaolinitu Keokuk: *a* — naturalnego, *b* — interkalowanego octanem potasu i następnie przemytego wodą
- Fig. 8. Krzywe DTA: octanu potasu (osadzonego na obojętnym  $\text{Al}_2\text{O}_3$ ) oraz frakcji ziarnowych  $< 0,2$ ;  $0,2-0,5$  i  $0,5-2,0 \mu\text{m}$  kaolinitu Maria interkalowanych octanem potasu
- Fig. 9. Krzywe DTA: *a* — octanu potasu, *b*, *c*, *d* —  $0,2-0,5 \mu\text{m}$  odpowiednio: kaolinitu Maria, *b* — interkalowanego octanem potasu, *c* — interkalowanego i następnie przemytego 2-propanolem oraz *d* — naturalnego
- Fig. 10. Krzywe TG frakcji ziarnowych:  $< 0,2$ ;  $0,2-0,5$  i  $0,5-2,0 \mu\text{m}$  kaolinitu Maria interkalowanych octanem potasu i następnie przemytych 2-propanolem

Анджей ВЕВЮРА

## ИССЛЕДОВАНИЕ НАБУХШЕГО КАОЛИНИТА РЕНТГЕНОВСКИМ, ИК-СПЕКТРАЛЬНЫМ И ТЕРМИЧЕСКИМ МЕТОДАМИ

### Резюме

Полуколичественным рентгеновским анализом определялась степень набухания каолинита в сырых образцах и гранулометрических фракциях первичных и седиментационных каолинитов. Анализы показали, что фракции более  $2 \mu\text{m}$  набухают полностью, фракции  $0,2-0,5 \mu\text{m}$  на  $80-90\%$ , а фракции менее  $0,2 \mu\text{m}$  всего на  $2-8\%$ .

В ИК-спектрах наблюдаются изменения пропорциональные степени набухания, особенно снижение интенсивности линии  $3692 \text{ см}^{-1}$  и появление полосы  $3610 \text{ см}^{-1}$ . Этот эффект наиболее четко проявился в самой крупной фракции каолинита Мария и крупнокристаллическом каолините Кеокук.

Термическими анализами определено, что количество ацетата калия, прочно связанного в испытуемых образцах, не пропорциональна степени набухания, а пропорциональна развернутой поверхности каолинита. Об этом свидетельствует самое высокое содержание ацетата калия в самой мелкой фракции и самое низкое содержание в наиболее крупной фракции.

Мелкая гранулометрическая фракция ( $< 0,2 \mu\text{m}$ ) не пропускает ацетата калия в межпакетные пространства, что следует учитывать при оценке каолинитового материала с применением метода набухания.

Образцы набухшие и промытые водой показывают затухание ИК-спектров высокой частоты. Это объясняется остатком ацетата калия, связанного с поверхностью ОН пакетов каолинита. Следовательно, более обоснован взгляд, что упомянутые линии связаны с испарением комплексов ОН, а не с водородными связями (Криз и др., 1972).

### ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Рентгеновские дифрактограммы гранулометрических фракций  $< 0,2$ ,  $0,2-0,5$  и  $0,5-2,0 \mu\text{m}$  каолинита Мария
- Фиг. 2. Основные рефлексы каолинита: *a* — естественного, *b* — набухшего под действием ацетата калия, во фракциях  $< 0,2$ ,  $0,2-0,5$  и  $0,5-2,0 \mu\text{m}$  (каолинит Мария)
- Фиг. 3. Основные рефлексы естественного (*a*) и обработанного гидразином (*b*) каолинита Мария, во фракциях  $< 0,2$ ,  $0,2-0,5 \mu\text{m}$
- Фиг. 4. Основные рефлексы каолинита Мария и его ацетатного комплекса. В препаратах удерживался избыток ацетата калия
- Фиг. 5. Дифрактограммы гранулометрических фракций  $< 0,2$ ,  $0,2-0,5$  и  $0,5-2,0 \mu\text{m}$  каолинита Мария после обработки гидразином и удаления гидразина путем промывки водой
- Фиг. 6. ИК-спектры поглощения гранулометрических фракций  $< 0,2$ ,  $0,2-0,5$  и  $0,5-2,0 \mu\text{m}$  каолинита Мария: *a* — в естественном виде, *b* — обработанных ацетатом калия и промытых пропанолом, *c* — обработанных ацетатом калия и промытых водой, *d* — обработанных гидразином и промытых водой
- Фиг. 7. ИК-спектры каолинита Кеокук: *a* — в естественном виде, *b* — обработанного ацетатом калия и промытого водой
- Фиг. 8. Кривые ДТА: ацетата калия (осажденного на нейтральном  $\text{Al}_2\text{O}_3$ ), и гранулометрических фракций  $< 0,2$ ,  $0,2-0,5$  и  $0,5-2,0 \mu\text{m}$  каолинита Мария, обработанных ацетатом калия
- Фиг. 9. Кривые ДТА: *a* — ацетата калия, *b*, *c*, *d* — фракции  $0,2-0,5 \mu\text{m}$  каолинита Мария, соответственно: *b* — обработанного ацетатом калия, *c* — обработанного и промытого пропанолом, *d* — естественного
- Фиг. 10. Кривые TG гранулометрических фракций  $< 0,2$ ,  $0,2-0,5$  и  $0,5-2,0 \mu\text{m}$  каолинита Мария, обработанных ацетатом калия и промытых пропанолом

## PLATE I (PLANSZA I, ТАБЛИЦА I)

Phot. 1. Electron micrograph of  $< 0.2 \mu\text{m}$  particle size fraction of Maria kaolinite.  
 $\times 50\,000$   
Mikrofotografia elektronowa frakcji ziarnowej  $0.2 \mu\text{m}$  kaolinitu Maria.  
 $\times 50\,000$   
Электронная микрофотография гранулометрической фракции  $< 0.2 \mu\text{m}$  каолинита Марья.  $\times 50\,000$

