Krystyna BŁASZCZAK, Roman PAMPUCH *

STUDY OF THE REACTION SERIES KAOLINITE — METAKAOLIN BY INFRARED SPECTROSCOPY AND ACID DISSOLUTION TECHNIQUE

A b s t r a c t. Chemical and infrared spectrophotometric study of products of thermal decomposition of kaolinite. In light of the present study products of decomposition alter their composition continuously, only the product obtained at lowest temperature may be regarded as „metakaolin", at 500—600°C the „metakaolin" decomposes into free SiO_2 and better crystalline alumina-bearing phase.

INTRODUCTION

Many layer-lattice silicates dissolve in acids, at least partially. Consequently, the technique of acid dissolution has been frequently used in studies of such silicates, like montmorillonite (Osthaus 1954, 1956, Čičel *et al.* 1964), kaolinite (Gastuche, Fripiat 1962), glauconite (Cloos, Gastuche, Croegaert 1960), and ortochlorite (Brindley, Youell 1951).

A rational application of acid dissolution technique is to be expected when the nature of products of thermal decomposition of layer-lattice silicates is investigated. This applies especially to metakaolin, the complex, mainly X-ray amorphous product of dehydroxylation of kaolinite. Some of the components or component phases of metakaolin dissolve in acids very easily what led the earliest workers (Le Chatelier, Mellor) to state that metakaolin is a mixture of amorphous silica and alumina. Later, however, on application of X-ray and electron diffraction, crystalline components or component phases have been found in metakaolin. The occurrence of such crystalline components could explain the topotaxial relations in the kaolinite-mullite reaction series. According to the scheme proposed by Brindley and Nakahira (1959), decomposition of kaolinite brings about a formation of metakaolin whose structure preserves the SiO layer of

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* Academy of Mining and Metallurgy, Institute of Materials Engineering, Cracow (Kraków).

kaolinite together with a transformed AlO layer. Further heating to 980°C brings about a formation of an AlSi-spinel phase which is crystallographically oriented to the original kaolinite network so that some of its oxygen planes remain parallel to the (0001) planes of the kaolinite structure. In order to account for the change of chemical composition these authors postulate a precipitation of free SiO_2 at the stage of formation of the spinel. Further elimination of SiO_2 at higher temperatures accompanies the formation of mullite.

Notwithstanding past and future corrections in the two points of view, there is no doubt that metakaolin is in fact a complex mixture of cyrstalline and non-crystalline components or phases. It is to be expected that disordered components or phases of metakaolin shall be more soluble in acids than the more crystalline ones. Hence, a „purification" of the more crystalline components could be envisaged by preferential dissolution of the more amorphous components in acids. A study of such systems should enable to better understand the nature of the crystalline components. In any event, the study of dissolution of the components of metakaolin in acids should at least enable to discern the components by their different rate of dissolution. This is of interest since our present knowledge of the metakaolin is far from satisfactory. Somewhat better are known the initial changes in the SiO layer of kaolinite after dehydroxylation. According to Pampuch (1966) and Brindley and Gibbon (1968), the SiO layer of kaolinite undergoes an expansion only after dehydroxylation, the SiO_4 tetrahedra of the layer assuming a more open hexagonal packing instead of the di-trigonal present in original kaolinite which is due to constraints imposed on the SiO layer by the AlOOH layer of kaolinite. The further fate of such SiO layers has been never experimentally studied although the elimination of SiO_2 on formation of the AlSi-spinel phase (or γ-alumina phase) means that these layers must, at least partially, polymerize to the three-dimensional SiO_2 lattice on heating to temperatures higher than 500—600°C. Less certain are the changes of the AlOOH layer of kaolinite after dehydroxylation. All concepts presented so far assume that the transformed AlO layer remains in a common lattice with the transformed SiO layer, their separation being implicitely or explicitely admitted at temperatures of formation of the AlSi spinel phase (or γ-alumina). As far as the present authors know, there is only one single previous proposal that postulates a separation of an aluminous phase already at the very begin of formation of metakaolin, i. e. at temperatures 550—650°C (Pampuch, 1966). However, no informations were available at that time about details of the structure of this phase although a six-fold co-ordination of Al's has been supposed in this phase. The models of the AlO layer forming a common lattice with the transformed SiO layer of kaolinite assume without exception a [IV]Al co-ordination (see e.g. Brindley, Nakahira 1959, Tscheischwili, Buessem, Weyl 1939, Iwai, Tagai, Shimamune 1969, Pampuch 1966). Were the formation of a separate Al-bearing phase correct, both [IV]Al and [VI]Al should occur in metakaolin. Recent works by Fripiat and Léonard (1967) as well as by MacKenzie (1969) give a convincing evidence for the fact that Al occurs in metakaolin as [IV]Al as well as [VI]Al. No detailed evaluation of the structures with [IV]Al and [VI]Al has been made, however, by these authors and it remains an open question in what types of structure occur

the [IV]Al and [VI]Al's. Owing to experimental difficulties no detailed study of the nature of X-ray amorphous components or phases of metakaolin has been made so far. At the present status knowledge, a study of the components of metakaolin purified by acid dissolution and the investigation of the course of dissolution of the different components is expected to give more insight into the complex problem of metakaolin and the kaolinite-mullite reaction series. This paper reports results of our studies in which kaolinite decomposed thermally to a different degree has been subjected to action of HCl, and the course of dissolution followed by infrared analyses of the solid residue as well as chemical determination of Al and Si going into solution.

EXPERIMENTAL PART

The study has been made on a 0,5—1 μm fraction of kaolin Sedlec (Czechoslovakia), which is almost a pure kaolinite (Pampuchowa 1965, Konta 1965). The samples were heated in a tube furnace to successively increasing temperatures in the range 450—800°C, the temperature being held at a given temperature level for different periods of time. Each level of temperature was held constant with a precision of ±5°C. The kaolinite heated under such conditions was next placed in amounts of 100 ±0,1 mg in a 250 ml bulb. The solid was then immersed in 100 ml of 2N HCl and the suspension heated at 80°C for periods ranging from 2 to 30 hours. The suspension was at the same time vigorously stirred. After the acid treatment the suspension was cooled quickly and the acid solution and solid residue separated. In the solution a direct determination of Al_2O_3 content was made by means of potentiometric titration while the SiO_2 content was determined directly from another part of the solution spectrophotometrically as yellow α-siliciummolybdenic heteropolyacid. The solid residue of acid treatment were characterised by IR spectra recorded with a UR-10 IR-spectrophotometer in the spectral range between 400 and 3700 cm^{-1}.

DISCUSSION OF RESULTS

The amounts of Al_2O_3 and SiO_2 dissolved in acid after different times of treatment from samples of kaolinite heated before at different temperatures are given in Tables 1 and 2. The fractions of these components in acid solution expressed on basis of their amounts in the solid before acid treatment are given in Figs. 1 and 2 (as α'). These Figures indicate that.

1. The rate of dissolution of SiO_2 and Al_2O_3 in 2N HCl changes with time of acid treatment and slows down remarkably after the first 8 hours of treatment.

2. The amounts of Al_2O_3 and SiO_2 dissolved after the first 8 hours of acid treatment and the amounts of these components dissolved after prolonged treatment (up to 30 h) are different for samples heated before at different temperatures.

The change of the rate of dissolution with time of acid treatment may be due either to the varying rate of diffusion with changing particle size
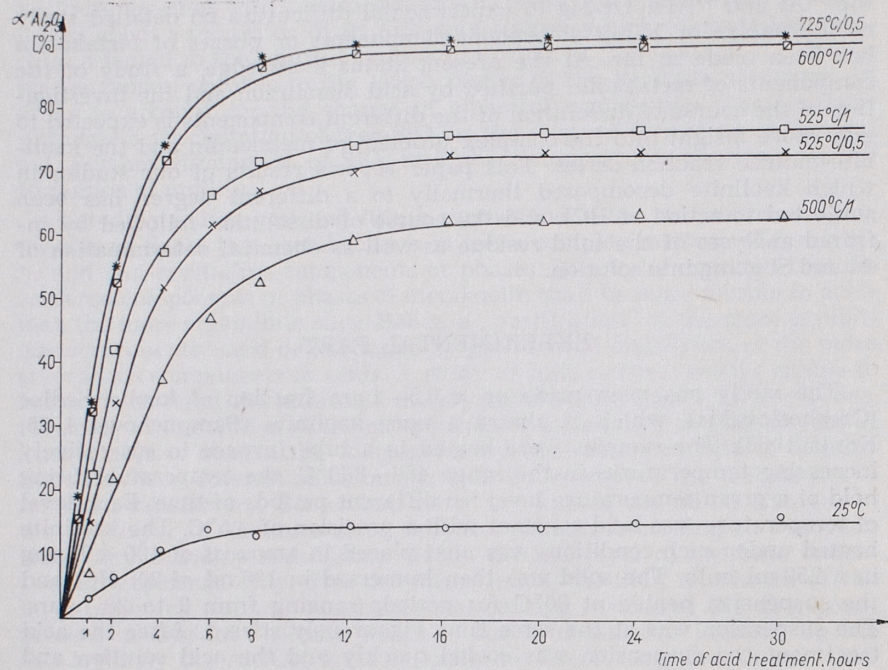
Fig. 1. $\alpha'_{Al_2O_3}$ for acid treated samples of differently heated kaolinite samples. The curves are labelled with the temperatures and hours of heating kaolinite samples prior to acid treatment

and their habit while the dissolution progresses, or to the presence in metakaolin of components and phases of a different crystallinity and solubility. Were the first alternative true then the plot of $1-(1-\alpha_{Al_2O_3})^n$ or $1-(1-\alpha_{SiO_2})^n$ versus time of acid treatment should be a straight line. In the above expresions α — is the fraction of Al_2O_3 or SiO_2 dissolved expressed on basis of their content in dehydroxylated parts of samples of heated kaolinite not subjected to acid treatment; $n = 1/2$ or $1/3$, according to particle shape. The slope of the straight line in this plot depends on acid concentration and temperature of dissolution only. As can be seen from Figures 3 and 4 this is not the case. It can be thus assumed that the two stages of dissolution are due to occurrence of Si and Al in at least two types of structure having a different crystallinity, the amorphous ones being responsible for the greater rate of dissolution. In infrared spectra the different rates of dissolution correspond indeed to two distinct stages of their changes; some of the absorption bands disappearing during the first, some after prolonged times of dissolution only.

As illustrated by Figure 5, after the complete transformation of kaolinite into metakaolin at 600°C, the rate of dissolution of Al_2O_3 from

samples heated before up to this and higher temperatures (800°C) does not change while the rate of SiO_2 dissolution decrease visibly. This indicates that the components or phases of metakaolin which contain Al do not change their degree of order or disorder in the whole range of heating temperatures studied (600—800°C, in some cases 1000°C). The Al--bearing components and phases which form upon decomposition of kaolinite remain thus presumably unchanged up to the temperature of crystallization of the AlSi spinel or $\gamma-Al_2O_3$. On the contrary, the decrease of dissolution rate of SiO_2 can be associated with increasing degree of polymerization of the Si-bearing components or phases of metakaolin. Polymerization of these components or phases is indicated also by the infrared spectra shown in Figure 6. In spectrum of metakaolin formed at the lowest temperatures there appears the Si-O stretch absorption band at 1060 cm⁻¹ which replaces the Si-O stretch absorption bands of the original SiO layer of kaolinite at 1010, 1032, and 1112 cm⁻¹. As ascribed by one of us (Pampuch, 1966, 1970), these changes are due to a change of the symmetry of the SiO layer from the original di-trigonal into an open hexagonal with change of the packing of the SiO_4 tetrahedra. Other absorption bands associated with the transformed SiO layer appear at lower wave numbers but are not specific in so far as they coincide with absorption bands occurring also in spectra of many other silicates having various structures. No absorption bands due to free silica (1080, 800, and 475 cm⁻¹ *) are present in the IR spectrum of such metakaolin
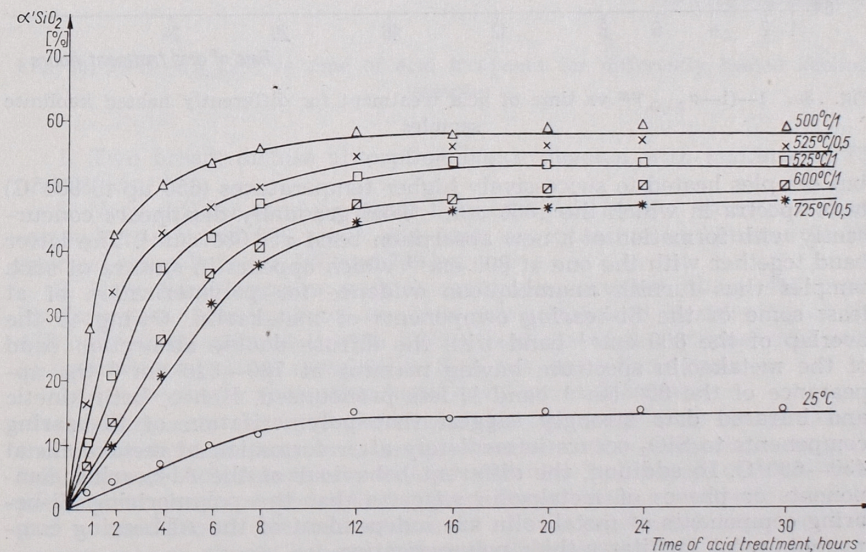

Fig. 2. α'_{SiO_2} for acid treated samples of differently heated kaolinite samples

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* The band at 475 cm⁻¹ is not specific in so far as it is common for various silicate structures.
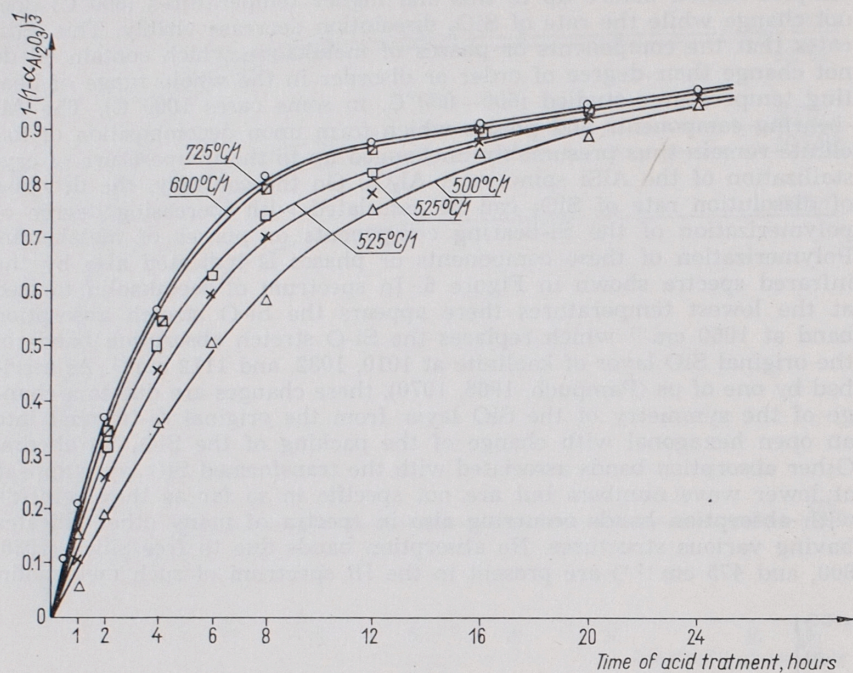
Fig. 3a. $1-(1-\alpha_{Al_2O_3})^{1/2}$ vs time of acid treatment for differently heated kaolinite samples

Fig. 3b, $1-(1-\alpha_{SiO_2})^{1/2}$ vs time of acid treatment for differently heated kaolinite samples

but samples heated to successively higher temperatures (650 up to 800°C) have spectra in which the 1060 cm⁻¹ band gradually disappears concurrently with formation of a new absorption band at 1080 cm⁻¹. The latter band together with the one at 800 cm⁻¹ which appears in spectra of such samples thus furnish unambiquous evidence for polymerization of at least some of the Si-bearing components of metakaolin. Owing to the overlap of the 800 cm⁻¹ band with the diffuse double absorption band of the metakaolin spectrum having maxima at 780—820 cm⁻¹ the appearance of the 800 cm⁻¹ band is less pronounced. Hence, both kinetic and infrared data strongly suggest that polymerization of Si-bearing components to SiO₂ occurs immediately after formation of metakaolin at 450—600°C. In addition, the different behaviour of the Al-bearing components or phases of metakaolin suggests that the polymerizing Si-bearing components of metakaolin are independent of the Al-bearing components what facilitates their polymerization.

Let us now go over to other parts of the metakaolin spectrum. Concurrently with the disappearance of absorption bands associated with the O-H and Al-OH vibrations of the AlOOH layer of kaolinite (3700—3600, 938, 915, 539, and 412 cm⁻¹) new absorption bands are formed in the metakaolin spectrum as shown in Fig. 6:
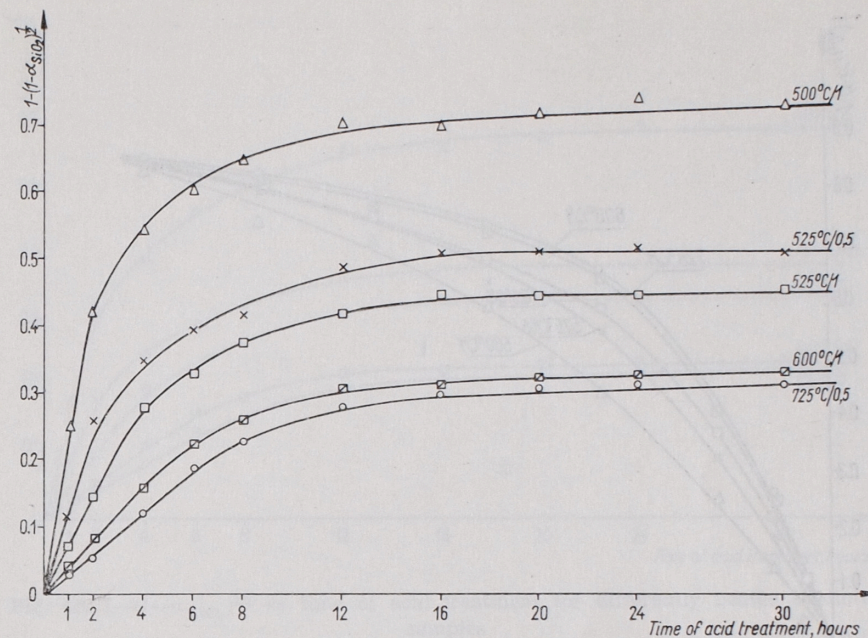
1. Two broad, diffuse absorption bands develop with maxima at 780 and 820 cm⁻¹.

2. Very diffuse band or bands appear which have a broad maximum somewhere around 650 cm⁻¹ and form an intensive background in the spectral range between 500 and 700 cm⁻¹.

3. New band appears with a maximum situated about 450 cm⁻¹. Its formation brings about an asymmetrization and broadening of the 475 cm⁻¹ band associated with Si-O vibrations of the original SiO layer of kaolinite and of the metakaolin. SiO₂ has also a band here.

4. A new single absorption band develops at 565 cm⁻¹.

In contrast to the 1060 cm⁻¹ band, all the bands 1—4 do not change their intensity and position in samples heated to the temperature of crystallization of AlSi spinel or $\gamma - Al_2O_3$ (980°C). This means that the components or phases responsible for these bands remain relatively unchanged in metakaolin. On acid treatment of the pre-heated samples these components or phases behave, however, differently. This is indicated by selective changes in the IR spectra of the solid residues after acid treatment for different periods of time. As shown in figures 7 and 8, the bands 1 and 2 disappear from the spectra already after short times of acid treatment. Their disappearance is linked with formation of new bands due to free SiO₂ (1080 and 800 cm⁻¹). Some part of the SiO₂ for-
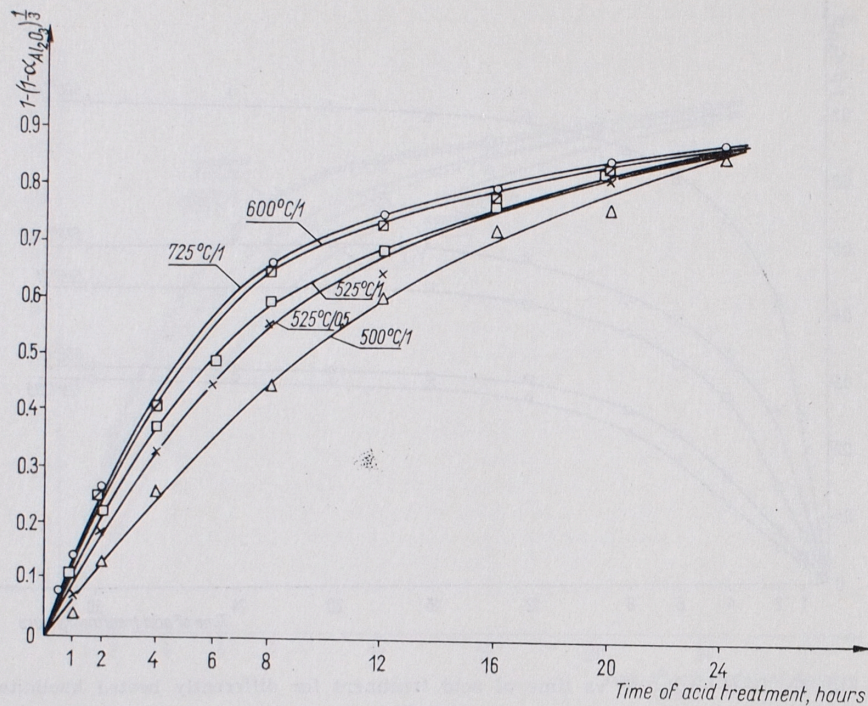
Fig. 4a. $1-(1-\alpha_{Al_2O_3})^{1/3}$ vs time of acid treatment for differently heated kaolinite samples

Fig. 4b. $1-(1-\alpha_{SiO_2})^{1/3}$ vs time of acid treatment for differently heated kaolinite samples
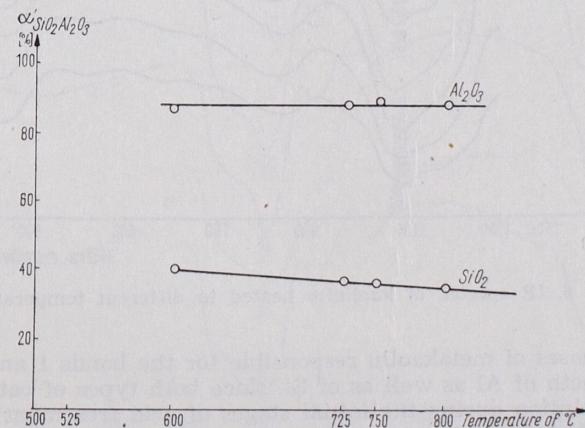
Fig. 5. $\alpha'_{Al_2O_3, SiO_2}$ vs temperature of previous heating of koalinite. The data are given for a constant time of acid treatment (8 hours). R e m a r k s: points for samples contaiining metakaolin only have been included solely in the figure

med is likely to be in a protonated form what is demonstrated by the simultaneous development of bands at 960 and 3400 cm⁻¹, characteristic for silica gel. The rapid elimination of the bands 1 and 2 coincides with the period of acid theatment during which the greatest rate of dissolution of Al and Si in 2N HCl has been observed (see Figs. 1 and 2). All this evidence suggests that the bands 1 and 2 are associated with those components or phases of metakaolin which are amorphous or nearly amorphous and thus more liable to dissolution. To this conclusion points also the observation that in spectra of a metakaolin obtained under very mild conditions (heating at 450°C for 20 h), also under conditions favourable for development of crystallinity, the absorption bands at 780 and 820 cm⁻¹ are more distinct and the background 500—700 cm⁻¹ less diffuse than in spectra of metakaolin obtained at more rapid rates of heating and higher temperatures (upper part of Fig. 9). Hence, the results of acid treatment of the metakaolin obtained under mild conditions substantiate the ease of dissolution of components associated with bands 1 and 2. As shown in lower part of Figure 9, already under very mild conditions of acid treatment (0,1N HCl applied for 4 h) the bands 1 and 2 disappear selectively from the IR spectra of metakaolin. The amorphous compo-
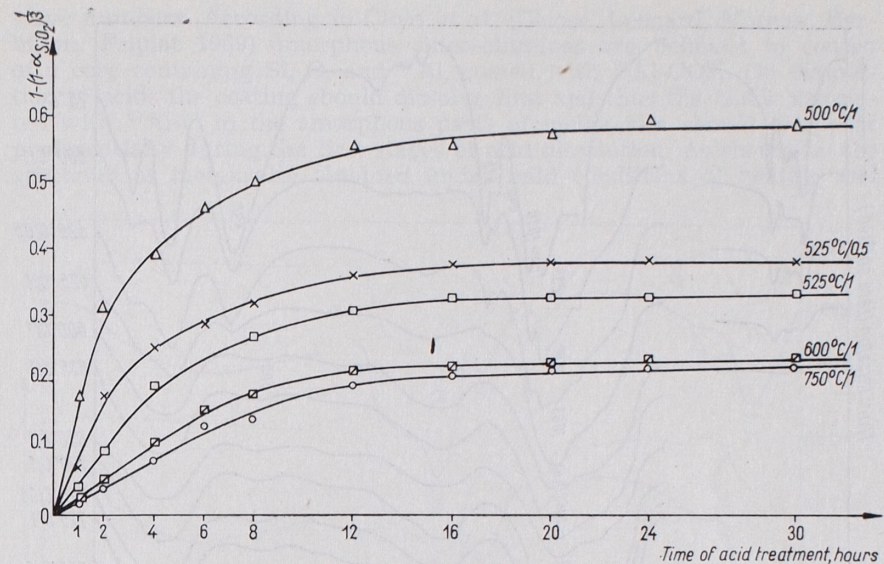
Fig. 6. IR spectra of kaolinite heated to different temperatures
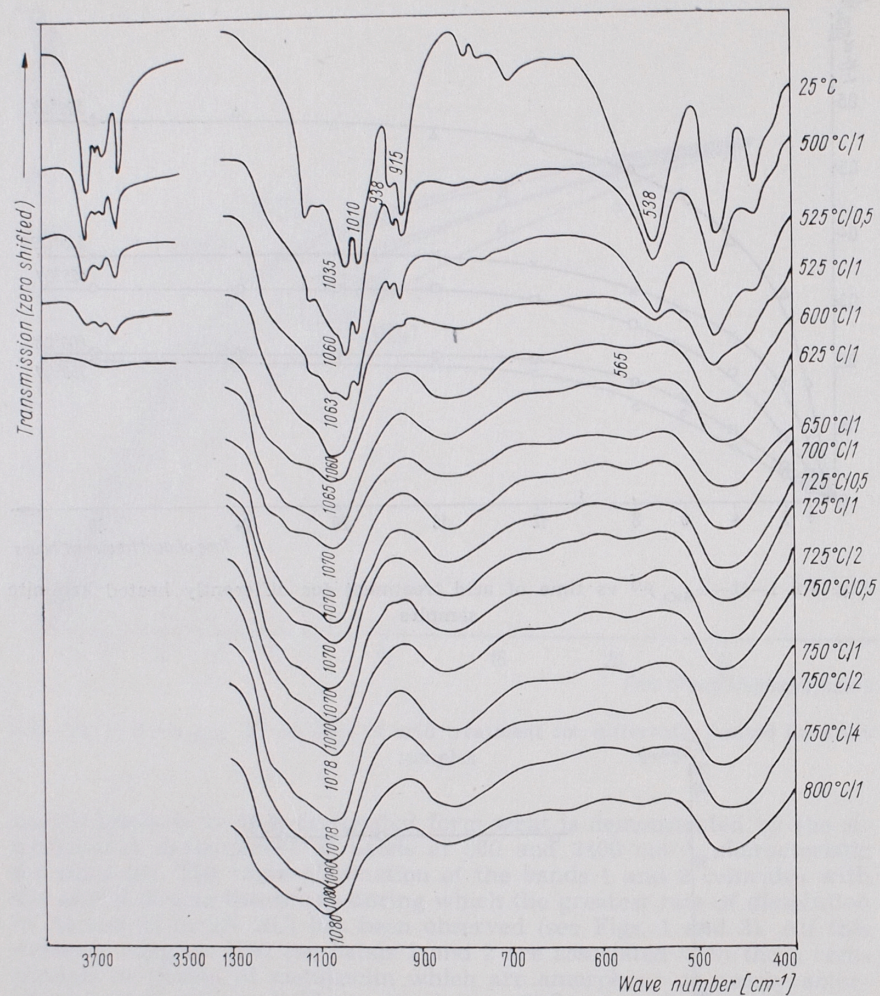
nents or phases of metakaolin responsible for the bands 1 and 2 believed to consist both of Al as well as of Si, since both types of cations go over into acid solution during the initial stages of acid treatment and the de-composition of these components or phases brings about a formation of free SiO_2. The absorption bands at 780 and 820 cm^{-1} are most probably connected with vibrations of groupings containing oxygen and four-fold coordinated aluminium (^{IV}Al), since the ^{IV}Al-O vibrations give rise to characteristic absorption bands in this range (Kolesova 1961, Pampuch 1970), and no silicate is known to give intense absorption bands at these

wave numbers. According to Cloos et al. (Cloose, Leonard, Moreau, Her-billon, Fripiat 1969) amorphous silico-aluminas are believed to consist of a core containing Si, O, and ^{IV}Al, coated with ^{VI}Al-OOH. On dissolu-tion in acids the coating should dissolve first and thus the bands associa-ted with ^{VI}Al-O in the amorphous parts of metakaolin should disappear preferentially during the first stages of acid dissolution. As shown by the spectrum of metakaolin obtained under mild conditions of heating and
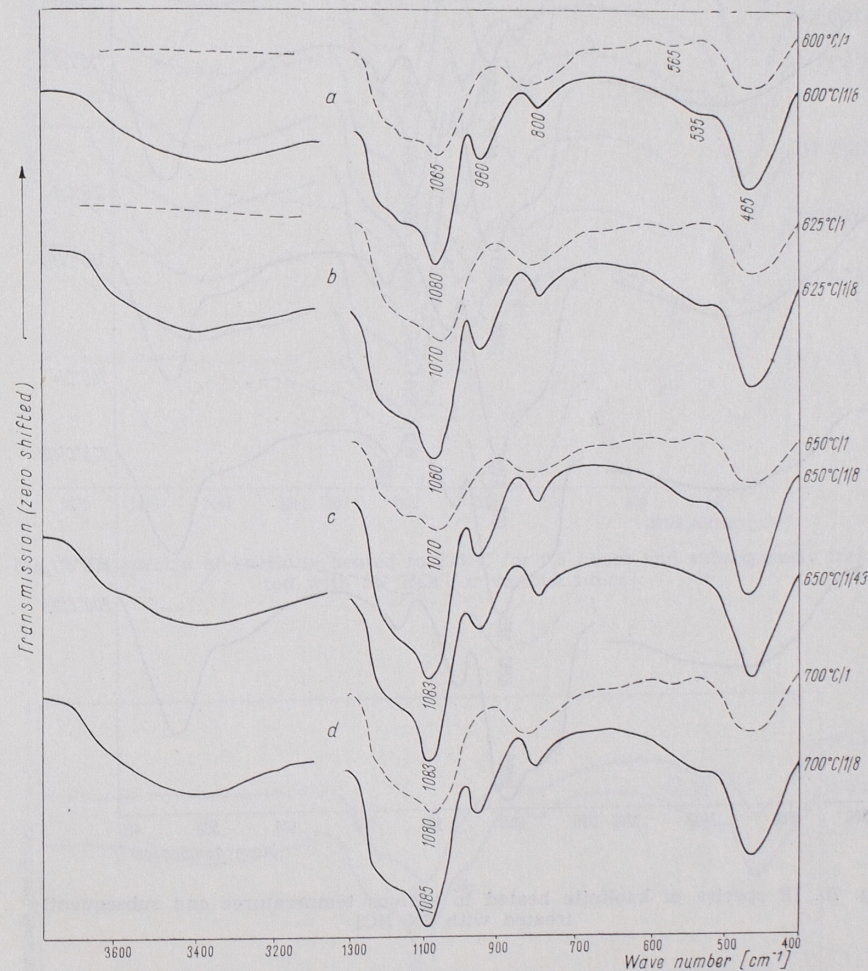

Fig. 7a. IR spectra of kaolinite heated to various temperatures and subsequently treated with 2N HCl. R e m a r k s: the spectra are coded as follows: temperature of heating of kaolinite/time of heating (hours) /time of acid dissolution of heated samples (hours). Dashed lines- heated samples, solid lines- heated and subse- quen-tly treated samples
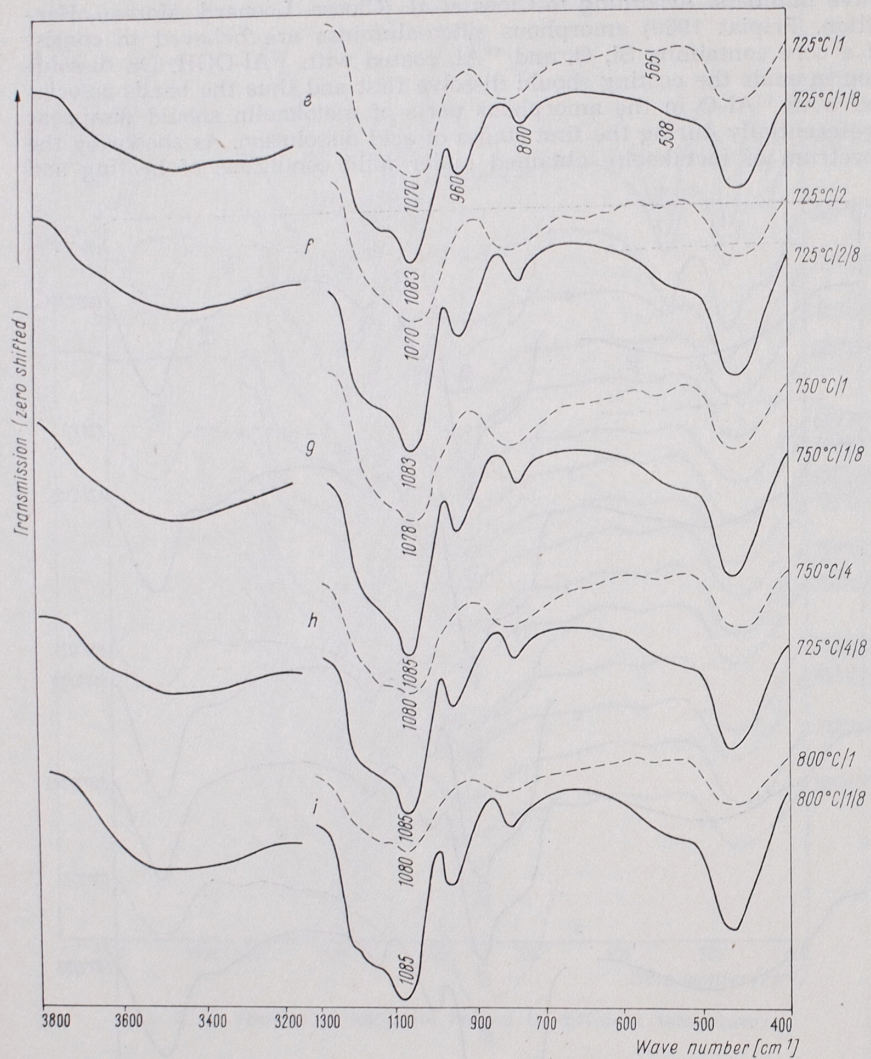
Fig. 7b. IR spectra of kaolinite heated to various temperatures and subsequently treated with 2N HCl

Fig. 8. IR spectra of kaolinite heated to 725°C for 0,5 hours and subsequently treated with 2N HCl for various times
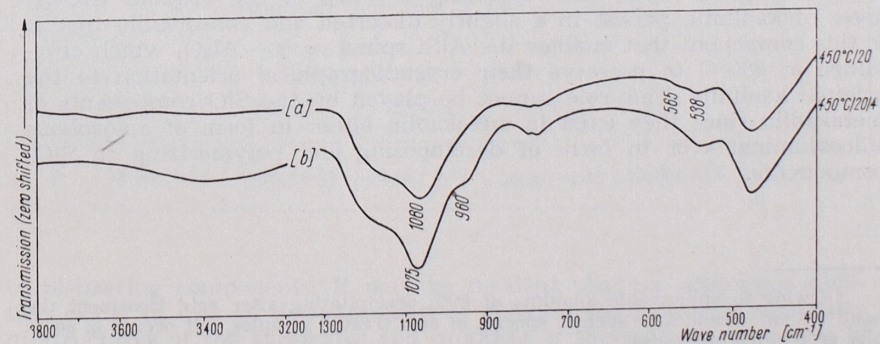
Fig. 9. IR spectrum of kaolinite heated at 450°C for 20 hours (a), and the same kaolinite treated subsequently with 0.1 N HCl for 4 hours (b)

treated afterwards with 0,1 N HCl (lower part of Fig. 9) the band or bands 2 disappear from the spectrum while the bands 1 show nearly no changes. Thus we believe that the intense background between 500 and 700 cm^{-1} may be ascribed to vibrations of the ^{VI}Al-O and more complex types in amorphous structures containing ^{VI}Al. The bands 3 and 4 (565

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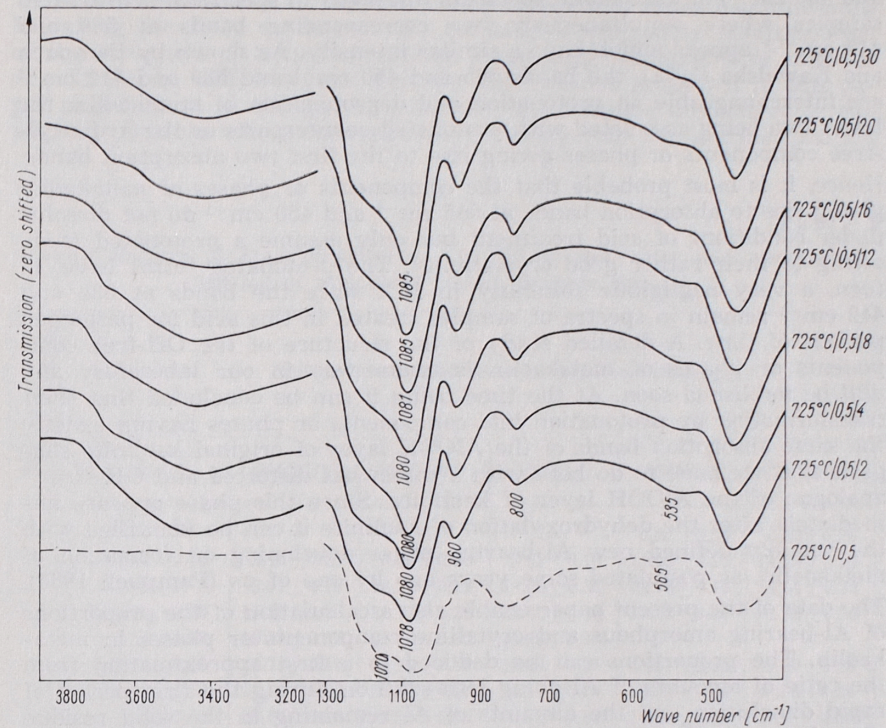and 450 cm^{-1}) of metakaolin spectrum disappear in spectra of acid treated samples where simultaneously two corresponding bands at 539 and 412 cm^{-1}* appear which have a similar intensity. As shown by Pampuch and Kawalska (1971), the bands 565 and 450 cm^{-1} and 539 and 412 cm^{-1} are interchangeable on protonation and deprotonation of metakaolin, the latter two being associated with protonated counterparts or the hydroxyl-free components or phases giving rise to the first two absorption bands.

Hence, it is most probable that the components or phases of metakaolin giving rise to absorption bands at 565 cm^{-1} and 450 cm^{-1} do not dissolve under conditions of acid treatment but only assume a protonated from, owing to their rather good crystallinity. The protonated forms have, in turn, a very negligibile solubility in HCl since the bands at 539 and 412 cm^{-1} remain in spectra of samples treated in this acid for prolonged periods of time. A detailed study of the structure of the OH-free components or phases of metakaolin is under way in our laboratory and will be published soon. At the time being it can be concluded that their transformation by protonation into components or phases having exactly the same absorption bands of the AlOOH layer of original kaolinite suggests that we have to do here with a somewhat distorted and OH-free ** analogue of the AlOOH layer of kaolinite. Since this phase appears immediately after the dehydroxylation of kaolinite it can be identified with the vaquely defined new Al-bearing phase developing on formation of metakaolin, as postulated some years ago by one of us (Pampuch 1966).

The data of the present paper enable also a calculation of the proportions of Al-bearing amorphous and crytalline components or phases in metakaolin. The proportions can be deduced to a first approximation from the ratio of amounts of Al going into solution during the first period of rapid dissolution and the amounts of Al remaining in the solid residue after long periods of acid treatment. According to Table 1 and 2 85 to 87% of Al initially present in kaolinite dissolves in 2N HCl in the first stage of acid teatment. This may indicate that 85—87% the original AlOOH layer of kaolinite transforms on decomposition, together with the appropriate part of the SiO layer of kaolinite, into an amorphous silico-aluminous phase while the remaining 13—15% of the original AlOOH layer of kaolinite persist in a slightly distorted and conceivable that it is this component that enables the AlSi spinel or $\gamma - Al_2O_3$ which crystallize at 980°C to preserve their crystallographical orientation to the original kaolinite. This role cannot be played by the SiO components of metakaolin since they exist in metakaolin either in form of amorphous silicoaluminates or in form of decomposing and polymerizing to SiO$_2$ components.

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* Owing to appreciable amounts of SiO$_2$ precipitating after acid treatment the band 412 cm^{-1} cannot be seen in spectra of acid treated samples, but occurs in samples protonated otherwise.

** Although no traces of OH grups appear in spectra of metakaolin, there are enough reasons to believe that some amounts of protons remain in metakaolin and probably in the components or phases discussed here.

A better evaluation of the mechanizm of reaction series kaolinite-mullite along the lines envisaged will be feasible only after determination of the structure of better crystalline Al-bearing component of metakaolin. It can be said, however, that the observations presented in this paper might cause to change the point of view assumed implicitly or explicitly hitherto where the structure-retaining role was ascribed mainly

Average amounts of Al$_2$O$_3$ dissolved in 2 N HCl at 80°C after acid treatment of 100 mg of previously heated kaolinite samples

Time of acid treat- ment (hours)	Temperature and time of previous heating					
	25°C	500°C/1	525°C/0.5	525°C/1	600°C/1	725°C/0.5
1/2	—	—	—	—	6.65±0.26	8.20±0.26
1	1.01±0.16	2.76±0.26	6.05±0.16	8.93±0.16	14.05±0.16	14.76±0.26
2	2.20±0.18	8.91±0.16	14.11±0.16	17.60±0.32	22.73±0.16	24.04±0.32
4	3.81±0.26	15.33±0.26	21.71±0.26	24.25±0.16	31.32±0.26	32.38±0.16
6	5.10±0.16	19.78±0.32	25.89±0.32	28.00±0.32	—	—
8	4.79±0.32	21.70±0.16	28.22±0.16	30.24±0.26	37.91±0.32	38.40±0.16
12	5.45±0.26	24.54±0.32	29.45±0.16	31.37±0.16	38.81±0.26	39.30±0.26
16	5.40±0.32	25.67±0.26	30.54±0.32	32.01±0.16	39.15±0.32	39.61±0.32
20	5.40±0.16	25.88±0.32	30.76±0.26	32.24±0.32	39.38±0.16	39.82±0.26
24	5.81±0.26	26.19±0.16	30.92±0.16	32.40±0.26	39.49±0.16	39.90±0.16
30	6.19±0.16	26.30±0.26	31.00±0.16	32.50±0.32	39.60±0.26	40.00±0.16

Time of acid treat- ment (hours)	Temperature and time of previous heating				
	725°C/1	725°C/2	725°C/4	750°C/1	800°C/1
8	38.72±0.16	38.84±0.26	38.95±0.16	39.05±0.32	39.38±0.26

to Si-bearing components. It may be recalled, that an analogous situation exsist in case of decomposition of calcium silicates. The continuity of structures of the substrates and products of thermal decomposition is ensured there by the CaO and not by the SiO lattice. In case of calcium silicates this is not surprising since the force constants of Ca-O bonds are higher than of the Si-O bonds in these compounds (Pampuch 1971).

Table 2

Average amounts of SiO₂ dissolved in 2 N HCl at 80°C after acid treatment of 100 mg of previously heated kaolinite samples

Time of acid treatment (hours)	Temperature and time of previous heating					
	25°C	500°C/1	525°C/0.5	525°C/1	600°C/1	725°C/0.5
1	1.79±0.22	14.02±0.36	8.21±0.50	5.19±0.64	3.30±0.18	2.20±0.07
2	3.02±0.07	21.31±0.36	11.03±0.44	10.51±0.36	7.10±0.36	4.90±0.30
4	4.41±0.30	24.72±0.14	21.81±0.36	19.23±0.62	13.91±0.36	10.80±0.36
6	5.20±0.44	27.11±0.64	23.90±0.64	21.91±0.30	19.51±0.14	16.81±0.14
8	6.75±0.20	28.19±0.56	25.62±0.14	24.19±0.60	22.01±0.58	20.01±0.14
12	6.40±0.36	29.41±0.56	28.09±0.36	26.58±0.20	25.01±0.48	23.71±0.30
16	6.80±0.44	29.29±0.36	28.91±0.30	27.80±0.30	25.61±0.48	25.01±0.14
20	7.02±0.44	29.71±0.36	29.02±0.36	27.71±0.20	26.51±0.36	25.81±0.36
24	7.30±0.14	30.12±0.64	29.29±0.44	27.79±0.56	26.81±0.60	26.01±0.30
30	7.28±0.20	30.00±0.50	29.00±0.20	28.28±0.30	27.01±0.44	26.31±0.14

Time of acid treatment (hours)	Temperature and time of previous heating				
	725°C/1	725°C/2	725°C/4	750°C/1	800°C/1
	20.01±0.14	19.78±0.35	19.50±0.50	19.33±0.14	18.90±0.14

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Krystyna BŁASZCZAK, Roman PAMPUCH

BADANIA SERII REAKCJI KAOLINIT — METAKAOLIN METODAMI SPEKTROFOTOMETRII W PODCZERWIENI I ROZPUSZCZANIA KWASOWEGO

Streszczenie

W pracy powiązano badania spektrofotometryczne w podczerwieni struktury produktów odbudowy kwasowej ogrzewanego kaolinitu z analizą chemiczną odbudowującego ośrodka kwasowego.

Doświadczenia przeprowadzono na frakcji 0,5—1 μm kaolinitu podanego procesowi dehydroksylacji w temperaturze 450—800°C, przy różnych czasach ogrzewania w danej temperaturze. Na tak przygotowane próbki działano kwasem solnym w temperaturze 80±0,1°C od 0,5 do 30 godzin a następnie rozdzielano ilościowo. Roztwory badano bezpośrednio na zawartość Al₂O₃ (met. miareczkowania potencjometrycznego) i SiO₂ (met. spektrofotometryczną oznaczania żółto zabarwionej formy α-heteropolikwasu krzemomolibdenowego). Odbudowane produkty rozkładu termicznego kaolinitu badano metodą spektrofotometrii absorpcyjnej w podczerwieni.

Systematyczne badania w podczerwieni odbudowy kwasowej kaolinitu potwierdziły w pełni selektywność rozpuszczania ogrzewanego minerału. Pozwoliły one dokładniej zinterpretować widmo absorpcyjne w podczerwieni metakaolinu, w szczególności przypisać pasma związane z drganiami glinotlenowych faz lub części metakaolinu. Stwierdzono, że budowa metakaolinu zmienia się wraz z postępem reakcji rozkładu; zmiany polegają na stopniowym uniezależnianiu się części krzemo- i glinotlenowych oraz występowaniu ich w dwóch typach struktur — krystalicznej i amorficznej. Wykazano bezpośrednio, że w miarę postępu reakcji rozkładu metakaolinu zwiększa się udział spolimeryzowanej krzemionki oraz wysunięto wnioski o występowaniu glinu w koordynacji tetra- i oktaedrycznej.

Кристина БЛАЩАК, Роман ПАМПУХ

ИССЛЕДОВАНИЕ СЕРИИ РЕАКЦИЙ КАОЛИНИТ — МЕТАКАОЛИН МЕТОДАМИ ИНФРАКРАСНОЙ СПЕКТРОФОТОМЕТРИИ И КИСЛОТНОГО РАСТВОРЕНИЯ

Резюме

В работе сопоставлены инфракрасные спокрофотометрические исследования структуры продуктов кислотного восстановления нагретого каолинита с химическим анализом восстанавливающей кислотной среды.

Исследовалась фракция 0,5-1 μm каолинита, подверженного процессу дегидроксилирования в области температур 450—800°C, с разной продолжительностью нагревания при данной температуре. Подготовленные таким способом образцы обрабатывались соляной кислотой при температуре 80±0,1°C в течение от 0,5 до 30 часов, а затем производилось количественное разделение. В растворах непосредственно определялось содержание Al_2O_3 (методом потенциометрического титрования) и SiO_2 (методом спектрофотометрического определения желтоокрашенной формы кремнемолибденовой α-гетерополикислоты). Восстановленные продукты термического распада каолинита исследовались методом инфракрасной спектрофотометрии поглощения.

Систематические исследования продуктов кислотного восстановления каолинита полностью подтвердили селективное растворение нагретого минерала. Они дали возможность более детально изучить ИК-спектр поглощения метакаолина, в частности определить линии, связанные с колебаниями алюмокислородных фаз или части метакаолина. Констатировано, что структура метакаолина изменяется по ходу реакции распада. Изменение состоит в постепенном обособлении кремнекислородных и алюмокислородных частей и образовании ими двух типов структур — кристаллической и аморфной. Непосредственно доказано, что с развитием реакции распада метакаолина возрастает количество полимеризированного кремнезёма. Высказывается взгляд о наличии тетраэдрической и октаэдрической координаций алюминия.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. $\alpha'_{Al_2O_3}$, обработанных кислотой и различно нагретых каолинитовых образцов. Кривые показывают температуру и время нагревания образцов каолинита до обработки кислотой

Фиг. 2. α'_{SiO_2}, обработанных кислотой и различно нагретых каолинитовых образцов

Фиг. 3a. $1-(1-\alpha_{Al_2O_3})^{1/2}$ в зависимости от времени обработки кислотой различно нагретых каолинитовых образцов

Фиг. 3b. $1-(1-\alpha_{SiO_2})^{1/2}$ в зависимости от времени обработки кислотой различно нагретых каолинитовых образцов

Фиг. 4a. $1-(1-\alpha_{Al_2O_3})^{1/3}$ в зависимости от времени обработки кислотой различно нагретых каолинитовых образцов

Фиг. 4b. $1-(1-\alpha_{SiO_2})^{1/3}$ в зависимости от времени обработки кислотой различно нагретых каолинитовых образцов

Фиг. 5. $\alpha'_{Al_2O_3, SiO_2}$ в зависимости от температуры предварительного нагревания каолинита. Данные представлены для постоянного времени обработки кислотой (8 часов).
Примечание: на рисунке показаны точки для образцов, содержащих единственно метакаолин

Фиг. 6. ИК-спектры каолинита, нагретого в разных температурах

Фиг. 7a. ИК-спектры каолинита, нагретого в разных температурах и потом обработанного кислотой 2N HCl
Примечание: спектры обозначены следующим образом: температура нагревания каолинита — время нагревания, часы — время обработки кислотой нагретых образцов, часы. Пунктирная линия — нагретые образцы, сплошные линии — нагретые и обработанные кислотой образцы

Фиг. 7b. ИК-спектры каолинита, нагретого в разной температуре и потом обработанного 2N HCl

Фиг. 8. ИК-спектры каолинита, нагретого до 725°C в течение 0,5 часа и потом обработанного кислотой в язное время

Фиг. 9. ИК-спектр каолинита, нагретого в температуре 450°C в течение 20 часов (*a*); тот же каолинит, обработанный 0,1 N HCl в течение 4 часов (*b*)