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A STUDY OF REACTIONS OF LAYER SILICATES WITH MOLTEN AMMONIUM SULPHATE

PART I. REACTIONS OF KAOLINITE, HALLOYSITE, MUSCOVITE AND BIOTITE WITH /NH_4/$_2SO_4$ AT 350°C

A b s t r a c t. At 350°C /NH_4/$_2SO_4$ enters into reaction with the cations of the octahedral sheets of layer silicates, forming sulphates soluble in 5% H_2SO_4 solution. The course of reaction of /NH_4/$_2SO_4$ with kaolinite, halloysite, muscovite and biotite has been studied. It has been found that the reactivity of layer silicates depends on the type of layers and the kind of cations in the octahedral sheet.

INTRODUCTION

Up till now the reactions of layer silicates with molten salts have been the subject of very few papers. Some of them have been concerned with the reactions of micas and montmorillonite with molten potassium and lithium nitrates /White, 1956/. The action of these salts on clay minerals causes the substitution of their interlayer cations for K^+ or Li^+ respectively.

Ammonium sulphate is a salt possessing very specific properties. Heated above 300°C, it melts passing simultaneously into acid ammonium sulphate. Acid ammonium sulphate melt is strongly dissociated and contains hydrogen ions which bring about the decomposition even of chemical resistant substances. This property is utilized by some chemical

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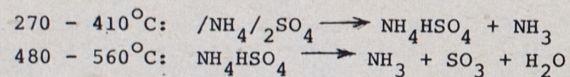
technologies, e.g., in the production of titanium oxide, which is obtained by sintering titanium ore with $/NH_4/_2SO_4$ in order that titanium will combine to form sulphates soluble in aqueous solutions.

The action of molten $/NH_4/_2SO_4$ on minerals is similar to the action of strong acids. Added in an amount of 20 wt.% to kaolin, ammonium sulphate reacts at $300^{\circ}C$ with the titanium and iron minerals. Due to this, the reaction with $/NH_4/_2SO_4$ can be used to remove impurities of this type from kaolins /Badyoczek, 1977/.

The object of this paper was to study the kinetics and mechanism of the reaction of molten $/NH_4/_2SO_4$ with some layer silicates. The investigations were carried out on kaolinites showing various degrees of crystallinity, as well as on halloysite, muscovite and biotite. The action of molten ammonium sulphates on these minerals was expected to be similar to their dissolution in sulphuric acid. Yet, in contradistinction to the reactions in sulphuric acid aqueous solutions, this process does not coincide with the hydrolysis of decomposition products. The action of these salts on the cations occurring in the structure of layer silicates should be selective.

According to Cvetkov and Valašichina /1955/, two endothermic reactions take place during the heating of ammonium sulphate:

$$270 - 410^{\circ}C: \quad /NH_4/_2SO_4 \longrightarrow NH_4HSO_4 + NH_3$$
$$480 - 560^{\circ}C: \quad NH_4HSO_4 \longrightarrow NH_3 + SO_3 + H_2O$$

Later studies of the $/NH_4/_2SO_4 - H_2SO_4$ system /Margulis et al., 1966/ revealed that the thermal decomposition of $/NH_4/_2SO_4$ attended by the evolution of gaseous NH_3 is initiated at $355^{\circ}C$. At this temperature a liquid phase forms whose composition, corresponding to a 33-34 wt.% H_2SO_4 content in the melt, is stable until the decomposition of ammonium sulphate has proceeded to completion. This liquid boils incongruently with the evolution of NH_3, H_2O and SO_3, and its composition changes until an azeotropic mixture forms with the boiling point at $462^{\circ}C$ and the composition corresponding to ammonium pyrosulphate. The system discussed also includes the compound $/NH_4/_3H/SO_4/_2$, which melts incongruently at $225^{\circ}C$. Another compound occurring in this system, NH_4HSO_4, melts congruently at $146^{\circ}C$ and the resulting melt has a composition corresponding to a content of 40% H_2SO_4. This compound forms an eutectic mixture with $/NH_4/_3H/SO_4/_2$ at $109^{\circ}C$.

EXPERIMENTAL

Investigations were carried out on < 20 μm fractions separated from the Maria III washed kaolin, kaolinite clay from Baranów, and halloy-

site from the basaltic weathering crust from Duninów. The fractions had the following mineralogical composition: the Maria III kaolin - 78% kaolinite, 15% quartz, 7% minerals of the mica group; the Baranów clay - 50% kaolinite, 24% quartz, 25% minerals of the mica group, 1% feldspars; the basaltic weathering crust from Duninów - halloysite with an admixture of iron oxides. Kaolinite from the Maria III kaolin shows a high degree of crystallinity, its X-ray crystallinity index $I_{020}/I_{1\bar{1}0}$ /Stoch, Sikora, 1966/ being 0.7. Kaolinite from the Baranów clay, on the other hand, has a disordered structure /X-ray crystallinity index - 1.5/.

Muscovite was obtained from pegmatite from the Boroviany deposit /Czechoslovakia/. Its grain-size was reduced by scraping and grinding, and the sieve fraction < 45 μm was taken for investigations. It contains an insignificant admixture of kaolinite. Biotite was isolated from the Nadziejów granite /Lower Silesia/.

The chemical composition of the samples studied is given in Table 1.

Table 1

Chemical composition of investigated samples, in weight %

Component	Biotite from Nadziejów	Muscovite from Boroviany	Kaolinite Maria III	Clay from Baranów	Halloysite from Duninów
SiO_2	47.81	49.12	n.d.	n.d.	n.d.
Al_2O_3	15.15	21.20	34.31	27.64	30.63
Fe_2O_3	15.97	3.12	0.45	1.45	4.64
TiO_2	2.10	0.24	0.36	1.05	1.10
CaO	1.10	5.62	n.d.	n.d.	n.d.
MgO	7.06	0.72	n.d.	n.d.	n.d.
Na_2O	1.34	4.08	n.d.	n.d.	n.d.
K_2O	8.60	8.04	n.d.	n.d.	n.d.
loss on ignition	1.52	8.20	n.d.	n.d.	n.d.

n.d. - not determined.

To determine the temperatures of reactions taking place in the mixtures, thermal analysis was made with a derivatograph /heating rate $10^{\circ}C/min.$, thermocouples Pt-PtRh 10%, disk platinum crucibles, standard - heated Al_2O_3/.

The reactions of minerals with ammonium sulphate were studied in mixture in which the weight ratio of the mineral to $/NH_4/_2SO_4$ was 1:5 /excess/ or 5:1 /deficiency/. The mixtures were held in a muffle fur-

nace at a temperature of ammonium sulphate decomposition /350°C/ determined from thermal curves. They were placed in the form of thin layers in flat porcelain vessels and heated for various periods of time /0.5 - 10 h./.

The phase composition of sinters obtained by heat treatment of the mixtures was investigated with a DRON 1.5 X-ray diffractometer. The instrument settings used were: CuKα, 40 kV, 20 mA, Ni filter, slits 1; 2; 0.25, time constant 2 sec., goniometer angular speed 2°/min. Then the sinters were hot-treated with 5% H_2SO_4 solution on a water bath at 90°C for 15 minutes to remove the soluble reaction products. The solution was analysed for Al_2O_3, Fe_2O_3, MgO, TiO_2 and alkalies. The insoluble residue was subjected to X-ray investigations and infrared spectroscopic analysis on a UR-10 spectrometer.

REACTION PRODUCTS OF LAYER SILICATES WITH /NH_4/$_2SO_4$

X-ray diffractometry

X-ray investigations have revealed that the heating of kaolinite or halloysite mixtures with /NH_4/$_2SO_4$ in the ratio of 5:1 at 350°C results in the formation of $NH_4Al/SO_4/_2$. Its lines appear in X-ray diffraction patterns of the sinters already after half an hour. Judging by the intensity of X-ray lines, the amount of this compound is insignificant and does not vary even if the heating time is prolonged from 0.5 to 10 hours. Sinters with the Maria III kaolin and the kaolinite clay from Baranów contain preserved kaolinite, quartz and mica besides aluminium-ammonium sulphate. The intensity of their reflections does not change noticeably with the prolongation of the heating time. Halloysite shows a somewhat different behaviour. The lines of $NH_4Al/SO_4/_2$ being formed are less intense but more diffuse. This seems to testify to a vary fine grain-size and/or low degree of crystallinity of the new-forming phase. After 5-hour heating of the halloysite and /NH_4/$_2$SO$_4$ mixture, $Al_2/SO_4/_3$ appears as well. The few reflections it yields are as weak as the $NH_4Al/SO_4/_2$ lines. The heating of the mixture for 7-10 hours leads to the disappearance of $NH_4Al/SO_4/_2$ whilst the intensity of the $Al_2/SO_4/_3$ lines virtually does not change. The intensity of the basal halloysite reflections decreases systematically with the heating time.

In the mixtures of muscovite with a deficiency of ammonium sulphate the only compound being formed is $NH_4Al/SO_4/_2$.

In X-ray diffraction patterns of 5:1 mixtures of biotite and /NH_4/$_2$ SO$_4$ there appear only two very weak MgSO$_4$ lines: 0.366 and 0.355 nm.

In the sinters of muscovite and biotite with /NH_4/$_2SO_4$ no visible changes in the intensity of reflections of these minerals have been noted with the prolonged heating time.

X-ray diffractograms of the residue left after the extraction with 5% H_2SO_4 solution show only lines of the minerals present in the untreated samples. All the sulphates formed during the heating are dissolved.

In the mixtures containing an excess of ammonium sulphate /the weight ratio of the minerals to /NH_4/$_2SO_4$ is 1:5/ the degree of reaction for clay minerals is considerably higher. In X-ray powder patterns of the resulting sinters, the lines of the new-formed compounds are markedly more intense. The heating of these mixtures at 350°C causes the kaolinite and halloysite lines to disappear already after 0.5 hour and intense $NH_4Al/SO_4/_2$ reflections to appear in their place. The prolongation of the heating time results in the formation of $Al_2/SO_4/_3$, the amount of which shows a tendency to increase with the heating time at the cost of $NH_4Al/SO_4/_2$.

In the mixtures of the Maria III kaolin and the Duninów halloysite with /NH_4/$_2SO_4$ the intensity of the $NH_4Al/SO_4/_2$ lines has been found to increase again after a longer period of heating.

The residue left after the extraction of soluble sulphates in 5% H_2SO_4 solution contains only quartz and micas, i.e. the sample components which do not readily enter into reaction with ammonium sulphate. It also displays a broad diffraction line in the angle range of 15-30° which can be attributed to amorphous silica.

Ammonium sulphate, even in excess, little affects muscovite. In the first stage, the only reaction product detectable with X-rays is $NH_4Al/SO_4/_2$. Its ammount increases when the heating time is prolonged to 8 hours. Longer heating /10 h./ reduces the amount of this compound in favour of $Al_2/SO_4/_3$.

The reaction rate of biotite with /NH_4/$_2SO_4$ is more rapid than that of muscovite. After 2-hour heating /NH_4/$_2Fe/SO_4/_3$ lines appear in X-ray diffraction patterns. There also form small amounts of $NH_4Al/SO_4/_2$, $Al_2/SO_4/_3$ and MgSO$_4$, as well as $Fe_2/SO_4/_3$. Biotite lines become very weak. The prolongation of heating time causes a decrease in the content of /NH_4/$_2Fe/SO_4/_3$ and $NH_4Al/SO_4/_2$ and an increase in the content of $Fe_2/SO_4/_3$, $Al_2/SO_4/_3$ and MgSO$_4$.

Infrared absorption spectroscopy

Infrared absorption spectroscopy was employed to trace changes occurring in the structure of minerals of the kaolinite group in respon-

se to their sintering with /NH$_4$/$_2$SO$_4$. Investigations were carried out on the insoluble residue left after treating the sinters with 5% H$_2$SO$_4$ solution. The spectra obtained are presented in Figures 1-4.

In the mixture of kaolinite showing a high degree of crystallinity /Maria III/ with a deficiency of /NH$_4$/$_2$SO$_4$ no pronounced structural changes have been noted /Fig. 1/. The only feature deserving note is a slight reduction in the intensity of the 753 cm^{-1} Si-O-Al absorption band compared with the 800 cm^{-1} quartz band.
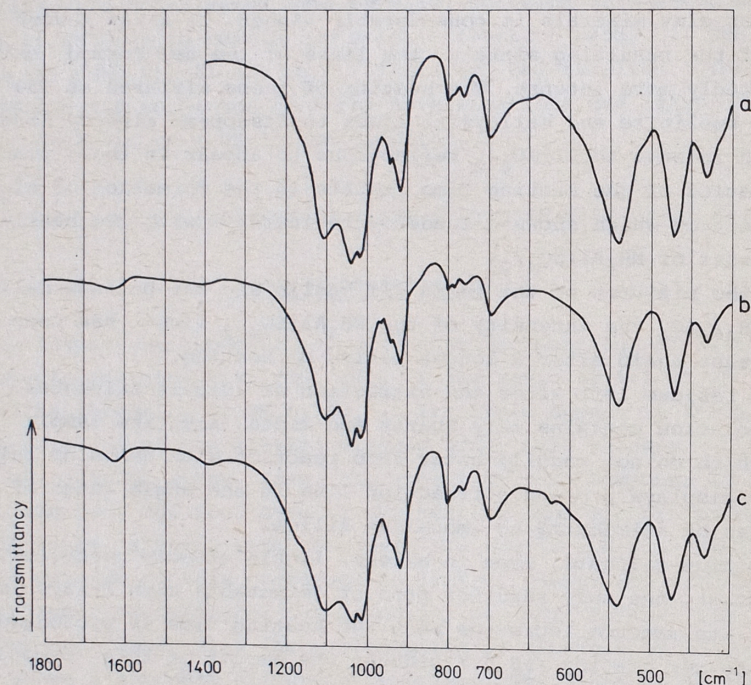

Fig. 1. Infrared spectra of the Maria III kaolin

a – untreated sample, b – after 0.5-hour sintering with a deficiency of /NH$_4$/$_2$SO$_4$ and treatment with 5% H$_2$SO$_4$, c – after 7-hour sintering with a deficiency of /NH$_4$/$_2$SO$_4$ and treatment with 5% H$_2$SO$_4$

Ammonium sulphate added in excess brings about the complete breakdown of the structure of kaolinite /Fig. 2/. A similar behaviour is shown by halloysite sintered with excess /NH$_4$/$_2$SO$_4$ /Fig. 4/. The kaolinite bands disappear already after 0.5 h., and broad bands with peaks at 1100 and 470 cm^{-1}, typical of amorphous or poorly ordered forms of silica, appear in their place. In the spectra of Maria III kaolinite sinters these bands coincide with respective absorption bands produced by a quartz admixture, the characteristic doublet 780 and 800 cm^{-1}

testifying to the presence of the latter. A few other, weak bands /near to 620, 1400 cm^{-1}/ have been attributed to hydrated aluminium-ammonium sulphate, detected with X-rays in the sample.
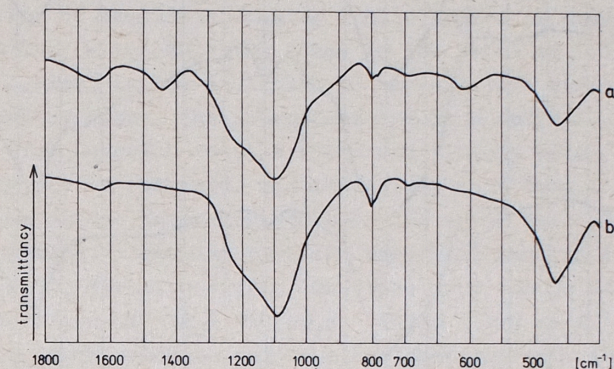

Fig. 2. Infrared spectra of the Maria III kaolin

a – after 0.5-hour sintering with an excess of /NH$_4$/$_2$SO$_4$ and treatment with 5% H$_2$SO$_4$, b – after 5-hour sintering with an excess of /NH$_4$/$_2$SO$_4$ and treatment with 5% H$_2$SO$_4$
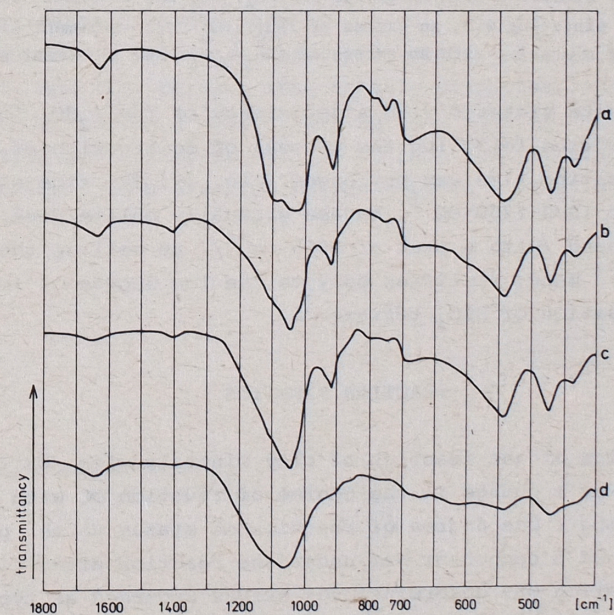

Fig. 3. Infrared spectra of the Duninów halloysite

a – untreated sample, b – after 0.5-hour sintering with a deficiency of /NH$_4$/$_2$SO$_4$ and treatment with 5% H$_2$SO$_4$, c – after 5-hour sintering with a deficiency of /NH$_4$/$_2$SO$_4$ and treatment with 5% H$_2$SO$_4$, d – after 8.5-hour sintering with a deficiency of /NH$_4$/$_2$SO$_4$ and treatment with 5% H$_2$SO$_4$
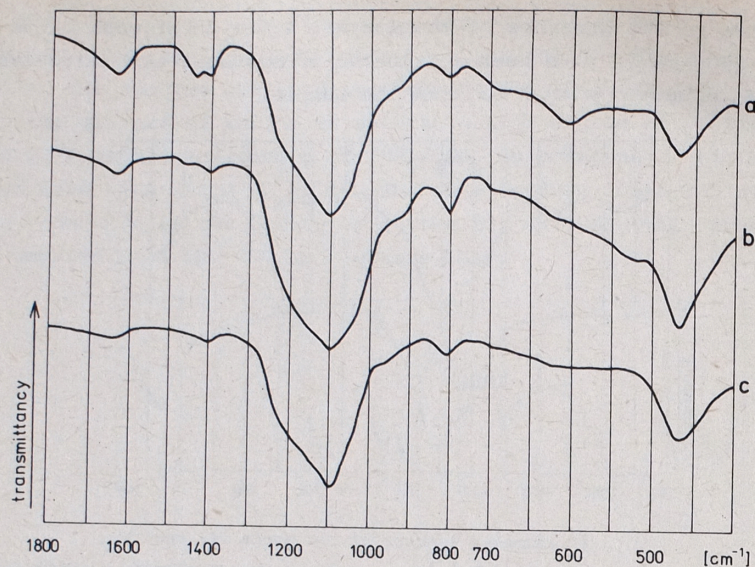
Fig. 4. Infrared spectra of the Duninów halloysite

a - after 0.5-hour sintering with an excess of $/NH_4/_2SO_4$ and treatment with 5% H_2SO_4,
b - after 5-hour sintering with an excess of $/NH_4/_2SO_4$ and treatment with 5% H_2SO_4,
c - after 10-hour sintering with an excess of $/NH_4/_2SO_4$ and treatment with 5% H_2SO_4

In halloysite sintered with a deficiency of $/NH_4/_2SO_4$ infrared spectroscopy permitted following the process of destruction of its structure as the heating time was prolonged /Fig. 3/. The fine structure of bands, e.g. at 1000-1200 cm^{-1}, became gradually obliterated. The position of this band /with a peak at 1065 cm^{-1}/, as well as the absence of the 800 cm^{-1} band, testifies only to the low degree of three-dimensional condensation of SiO_4 tetrahedra.

REACTION KINETICS

The kinetics of the reaction of clay minerals with $/NH_4/_2SO_4$ is characterized by a change in the degree of reaction α with the time of its sintering. The degree of reaction α states which part of the inital amount of a component has undergone reaction after time t. The degree of reaction was determined for oxides regarded as typical of the samples studied: Al_2O_3, Fe_2O_3, TiO_2, MgO, K_2O. The ratio of the amount of the oxide which passed into the 5% H_2SO_4-soluble form to its initial content in the sample was taken as a measure of the reaction degree. The reaction degree α for Al_2O_3 was assumed as a measure of the

degree of decomposition of kaolinite and muscovite, and α for MgO as a measure of decomposition of biotite. The α vs. sintering time curves for the minerals studied are shown in Figures 5-7 and 9-11.

Sintering of kaolinite showing a high degree of crystallinity /Maria III kaolin/ with $/NH_4/_2SO_4$ added in the ratio of 5:1 causes 10% of aluminium present in the kaolinite to convert into sulphate /α = 0.1/. It is a maximum amount the introduced ammonium sulphate is able to combine with. The reaction rate is rapid and already after 1 hour all ammonium sulphate is combined. Simultaneously more than a half of iron and titanium oxides accompanying kaolinite enter into reaction. With the prolongation of heating time the amount of TiO_2 in the form soluble in 5% H_2SO_4 diminishes /Fig. 5/. This fact can be accounted for by the decomposition of $/NH_4/_2TiO/SO_4/_2$, which forms as a reaction product of TiO_2 with ammonium sulphate and then converts into $TiOSO_4$ /Badyoczek, 1977/ sparingly soluble in 5% H_2SO_4. After 6-hour sintering the amount of titanium that will go into solution increases again. This may mean that $TiOSO_4$ reverts to $/NH_4/_2/SO_4/_2$. This process is comparable to the disappearance of $Al_2/SO_4/_3$, which reconverts into $NH_4Al/SO_4/_2$ after several hours' heating.

The addition of excess ammonium sulphate results in that nearly all Al_2O_3, Fe_2O_3 and TiO_2 changes into soluble sulphates, and the reaction attains α = 0.9 after 4-hour sintering. The rate of sulphonation of aluminium from kaolinite, as well as of iron and titanium oxides, is almost identical. When ammonium sulphate is in excess, it no longer
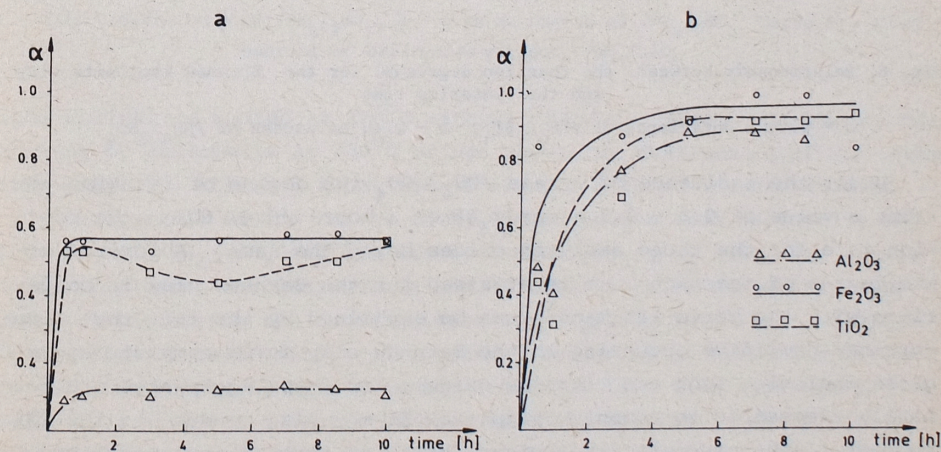

Fig. 5. Relationship between the reaction degree α for the Maria III kaolin and the sintering time

a - with a deficiency of $/NH_4/_2SO_4$, b - with an excess of $/NH_4/_2SO_4$

reacts selectively as it does when it is added to the sample in deficiency.

The Baranów clay, which contains kaolinite with a disordered structure, reacts somewhat differently. Ammonium sulphate added in deficiency enters completely into reaction with aluminium, iron and titanium already within the first hour $/\alpha$ is respectively equal to 0.12, 0.18 and 0.32//Fig. 6a/. When the heating time is longer than 5 hours, additional amounts of Al_2O_3 begin to go into 5% H_2SO_4 solution $/\alpha$ increases/ due to gradual dehydroxylation of kaolinite with a disordered structure. Dehydrated kaolinite is not resistant to the action of sulphuric acid and the constituent aluminium passes into solution.
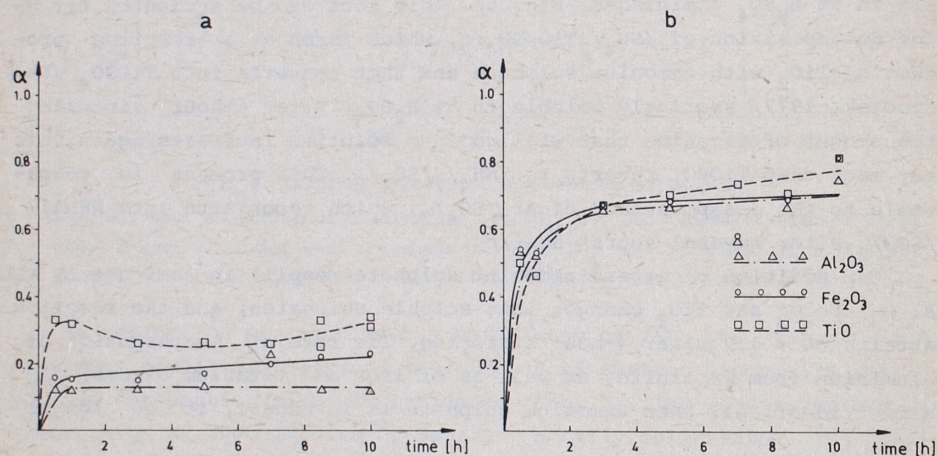

Fig. 6. Relationship between the reaction degree α for the Baranów kaolinite clay and the sintering time

a - with a deficiency of $/NH_4/_2SO_4$, b - with an excess of $/NH_4/_2SO_4$

Under the influence of excess $/NH_4/_2SO_4$ the degree of reaction attains a value of 0.6 - 0.7 already after 2 hours /Fig. 6b/, the reaction rate for the three analysed oxides being the same. A lower maximum degree of reaction that is attained for the Baranów clay in comparison with the Maria III kaolin can be explained by the fact that fine-grained kaolinite occurring in the Baranów clay forms compact aggregates enclosing iron and titanium oxides, and these aggregates are not easily accessible to ammonium sulphate. It may also be due to the 25% content of the muscovite-type micas which, as further investigations have revealed, are less reactive to $/NH_4/_2SO_4$ than kaolinite.

The degree of reaction for the Duninów halloysite varies with time in a similar way /Fig. 7/. As a result of prolonged heating with a deficiency of $/NH_4/_2SO_4$, the 5% H_2SO_4 solution leaches the constantly increasing amounts of aluminium from the sinter. This is caused by the progressing dehydroxylation of halloysite as it is held at a temperature of 350°C for longer periods of time. This statement has been substantiated by an additional experiment involving the leaching of Al_2O_3
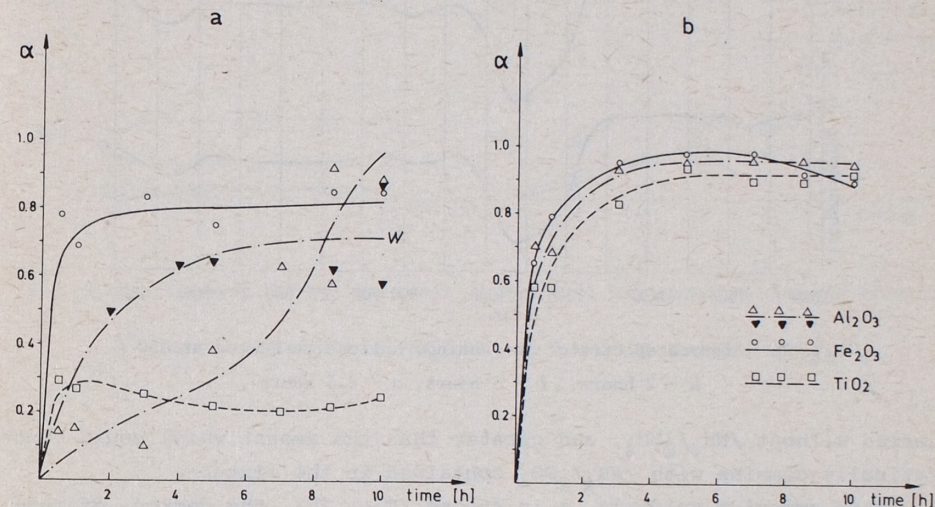

Fig. 7. Relationship between the reaction degree α for the Duninów halloysite and the sintering time

a - with a deficiency of $/NH_4/_2SO_4$, b - with an excess of $/NH_4/_2SO_4$. Curve W - after heating of halloysite without $/NH_4/_2SO_4$

from halloysite heated at 350°C without $/NH_4/_2SO_4$ /Fig. 7a, curve W/. The heating of halloysite at 350°C brings about the destruction of its structure /Fig. 8/, allowing about 60% of aluminium to be leached from it.

A comparison of the curves of Al_2O_3 extraction from halloysite heated without $/NH_4/_2SO_4$ and one sintered with $/NH_4/_2SO_4$ /Fig. 7a/ leads to the following conclusions. In the initial stage of sintering, ammonia evolving during the decomposition of $/NH_4/_2SO_4$ inhibits the dehydroxylation of halloysite. Consequently the amount of aluminium extractable with sulphuric acid from the sinter is less than that extractable from halloysite heated without ammonium sulphate. Yet, reacting with halloysite, ammonium sulphate distorts its structure. As a result of this, the amount of aluminium that will go into solution is greater than could be expected judging by its amount leached from halloysite
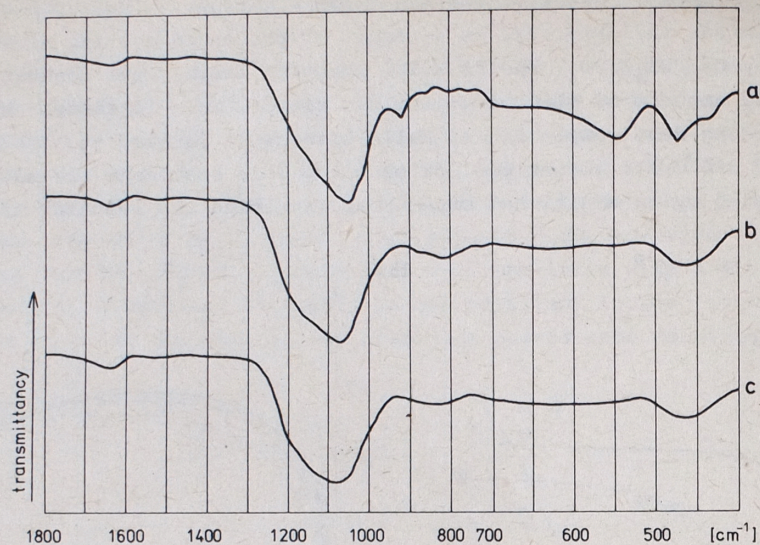
Fig. 8. Infrared spectra of the Duninów halloysite heated at $350^{\circ}C$

a – 2 hours, b – 5 hours, c – 8.5 hours

Fig. 9. Relationship between the reaction degree α for muscovite and the sintering time

a – with a deficiency of $/NH_4/_2SO_4$, b – with an excess of $/NH_4/_2SO_4$

heated without $/NH_4/_2SO_4$, and greater than the amount which could theoretically combine with $/NH_4/_2SO_4$ contained in the mixture.

When ammonium sulphate is in excess /Fig. 7b/, the degree of reaction for halloysite attains a value of 0.9. The reaction rate for aluminium and iron is nearly identical and not much higher than that for titanium.

The reaction of muscovite with ammonium sulphate proceeds at a slower rate than for kaolinite minerals. When ammonium sulphate is added to muscovite in the proportion of 5:1, the process is soon inhibited, and the degree of reaction α for Al_2O_3 is only 0.25 /Fig. 9a/. The degree of extraction of TiO_2 is 0.1 while these values for Fe_2O_3 and K_2O are even lower.

When $/NH_4/_2SO_4$ is in excess /Fig. 9b/, the degree of reaction for Al_2O_3 can be 0.75, that for K_2O is only 0.25 whereas α for TiO_2 and Fe_2O_3 is even lower.

The reaction of biotite with $/NH_4/_2SO_4$ proceeds at a considerably more rapid rate than that of muscovite. Also the degrees of extration for respective components are less differentiated /Fig. 10a, b/. The cations of the octahedral sheet of biotite, i.e. magnesium, iron, aluminium, and also titanium show a high degree of reaction $/\alpha = 0.8 - 0.9/$ whilst the degree of extraction for the interlayer cations /potassium, sodium/ is considerably lower $/\alpha = 0.6$ and 0.2 resp./.
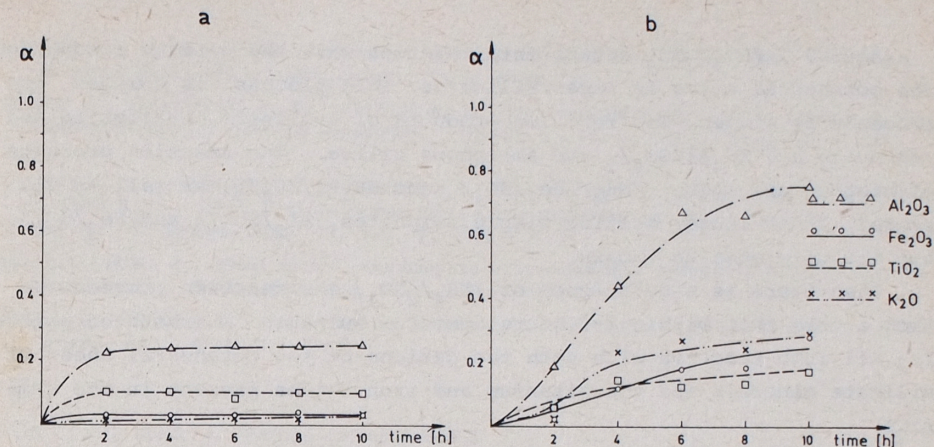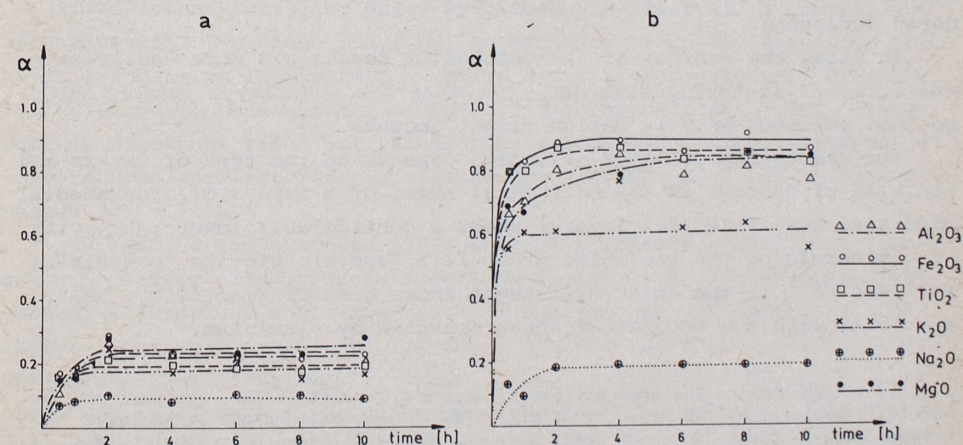

Fig. 10. Relationship between the reaction degree α for biotite and the sintering time

a – with a deficiency of $/NH_4/_2SO_4$, b – with an excess of $/NH_4/_2SO_4$

DISCUSSION

At $350^{\circ}C$ $/NH_4/_2SO_4$ enters into reaction with the cations occupying the octahedral sites in layer silicates. This process is complex and proceeds by stages. The reaction products of kaolinite, halloysite and muscovite are $NH_4Al/SO_4/_2$ and amorphous silica. The reaction products of biotite are $MgSO_4$, $/NH_4/_2Fe_2/SO_4/_3$ and $NH_4Al/SO_4/_2$, as well as silica gel. After longer heating simple sulphates, $Al_2/SO_4/_3$ and $Fe_2/SO_4/_3$, are the only ones to remain.

When there is a deficiency of $/NH_4/_2SO_4$, the reaction proceeds at such a rate that within 1-2 hours ammonium sulphate is exhausted, entering all into reaction with both the cations of the octahedral sheet of silicate minerals and the titanium and iron oxides present in the samples.

When ammonium sulphate is in excess, the layer silicates decompose completely within 1-2 hours. Sintering with ammonium sulphate followed by leaching with 5% H_2SO_4 solution permits the extraction of metals from layer silicates.

If the sintering is carried out with a deficiency of ammonium sulphate, the effect obtained is that of selective extraction of components. Free iron and titanium oxides react more readily than kaolinite with a high degree of crystallinity, and this property can be utilized to decrease their content in kaolins containing such kaolinite. Selectivity of this type has not been displayed by kaolinite with a disordered structure.

In micas the cations of the octahedral sheets are more easily extracted after sintering with $/NH_4/_2SO_4$ than the interlayer cations, which go into solution only in insignificant amounts.

The reactivity of layer silicates depends on the type of layers and the kind of cations in the octahedral sheet of a layer. Of dioctahedral minerals, muscovite /2:1 layers/ shows a considerably lower reactivity than minerals of the kaolinite group /1:1 layers/. Biotite containing Mg^{2+} and Fe^{2+} in the octahedral sheet shows greater reactivity than muscovite with the octahedral sheet occupied by aluminium.

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STUDIUM REAKCJI KRZEMIANÓW WARSTWOWYCH ZE STOPIONYM SIARCZANEM AMONOWYM

CZESC I. REAKCJE KAOLINITU, HALOIZYTU, MUSKOWITU I BIOTYTU Z $/NH_4/_2/SO_4$, W TEMPERATURZE $350^{\circ}C$

S t r e s z c z e n i e

Przedmiotem niniejszej pracy było zbadanie kinetyki i mechanizmu oddziaływania stopionego $/NH_4/_2SO_4$ na niektóre krzemiany warstwowe. Badania wykonano na kaolinitach o różnym stopniu uporządkowania struktury, haloizycie, muskowicie i biotycie, zmieszanych z $/NH_4/_2SO_4$ w stosunkach wagowych: 1:5 i 5:1. Mieszaniny wygrzewano w piecu muflowym, w temperaturze rozkładu siarczanu amonowego /$350^{\circ}C$/ przez różne okresy czasu: 0,5 - 10 h.

$/NH_4/_2SO_4$ w temperaturze $350^{\circ}C$ wchodzi w reakcję z kationami tworzącymi warstwę oktaedryczną krzemianów warstwowych. Proces ten jest złożony i przebiega w kilku etapach. Produktem reakcji kaolinitu, haloizytu i muskowitu jest $/NH_4/Al/SO_4/_2$ oraz bezpostaciowa krzemionka. Produktami reakcji biotytu są: $MgSO_4$, $/NH_4/_2Fe_2/SO_4/_3$ i $NH_4Al/SO_4/_2$, a także gel krzemionkowy. Po dłuższym wygrzewaniu siarczany podwójne przechodzą w siarczany proste: $Al_2/SO_4/_3$ i $Fe_2/SO_4/_3$. Przy niedomiarze $/NH_4/_2SO_4$ szybkość reakcji jest taka, że w ciągu 1 - 2 h następuje wyczerpanie siarczanu amonowego, który w całości wchodzi w reakcję z kationami warstwy oktaedrycznej minerałów krzemianowych oraz tlenkami tytanu i żelaza, zawartymi w próbkach.

Wobec nadmiaru /NH$_4$/$_2$SO$_4$ w ciągu 1 - 2 h następuje całkowity rozkład krzemianów warstwowych. Spiekanie z siarczanem amonowym, a następnie ługowanie spieków roztworem 5-procentowym H$_2$SO$_4$ pozwala ekstrahować metale z krzemianów warstwowych.

Gdy spiekanie prowadzi się z niedomiarem /NH$_4$/$_2$SO$_4$, wówczas można uzyskać efekt selektywnej ekstrakcji składników. Wolne tlenki żelaza i tytanu szybciej wchodzą w reakcję niż kaolinit o wysokim stopniu uporządkowania struktury, co można wykorzystać do zmniejszenia ich zawartości w kaolinach zawierających taki kaolinit. Selektywności tego typu nie stwierdzono w przypadku kaolinitu o gorzej uporządkowanej strukturze.

Z mik, po spiekaniu z /NH$_4$/$_2$SO$_4$, znacznie łatwiej ekstrahują się kationy warstw oktaedrycznych niż kationy międzypakietowe. Te drugie tylko w niewielkim stopniu przechodzą do roztworu.

Reaktywność krzemianów warstwowych zależy od typu pakietów oraz rodzaju kationów w warstwie oktaedrycznej pakietu. Spośród minerałów dioktaedrycznych muskowit /pakiety 2:1/ wykazuje znacznie mniejszą reaktywność niż minerały grupy kaolinitu /pakiety 1:1/. Z kolei biotyt zawierający w warstwie oktaedrycznej magnez i żelazo wykazuje większą reaktywność niż muskowit o warstwie oktaedrycznej obsadzonej przez glin.

OBJAŚNIENIA DO FIGUR

Fig. 1. Widma w podczerwieni kaolinu Maria III

a - próbka wyjściowa, b - po 0,5-godzinnym spiekaniu z niedomiarem /NH$_4$/$_2$SO$_4$ i obróbce 5-procentowym H$_2$SO$_4$, c - po 7-godzinnym spiekaniu z niedomiarem /NH$_4$/$_2$SO$_4$ i obróbce 5-procentowym H$_2$SO$_4$

Fig. 2. Widma w podczerwieni kaolinu Maria III

a - po 0,5-godzinnym spiekaniu z nadmiarem /HN$_4$/$_2$SO$_4$ i obróbce 5-procentowym H$_2$SO$_4$, b - po 5-godzinnym spiekaniu z nadmiarem /NH$_4$/$_2$SO$_4$ i obróbce 5-procentowym H$_2$SO$_4$

Fig. 3. Widma w podczerwieni haloizytu z Duninowa

a - próbka wyjściowa, b - po 0,5-godzinnym spiekaniu z niedomiarem /NH$_4$/$_2$SO$_4$ i obróbce 5-procentowym H$_2$SO$_4$, c - po 5-godzinnym spiekaniu z niedomiarem /NH$_4$/$_2$SO$_4$ i obróbce 5-procentowym H$_2$SO$_4$, d - po 8,5-godzinnym spiekaniu z niedomiarem /NH$_4$/$_2$SO$_4$ i obróbce 5-procentowym H$_2$SO$_4$

Fig. 4. Widma w podczerwieni haloizytu z Duninowa

a - po 0,5-godzinnym spiekaniu z nadmiarem /NH$_4$/$_2$SO$_4$ i obróbce 5-procentowym H$_2$SO$_4$, b - po 5-godzinnym spiekaniu z nadmiarem /NH$_4$/$_2$SO$_4$ i obróbce 5-procentowym H$_2$SO$_4$, c - po 10-godzinnym spiekaniu z nadmiarem /NH$_4$/$_2$SO$_4$ i obróbce 5-procentowym H$_2$SO$_4$

Fig. 5. Zależność stopnia reakcji α kaolinu Maria III od czasu spiekania

a - z niedomiarem /NH$_4$/$_2$SO$_4$, b - z nadmiarem /NH$_4$/$_2$SO$_4$

Fig. 6. Zależność stopnia reakcji α gliny kaolinitowej z Baranowa od czasu spiekania

a - z niedomiarem /NH$_4$/$_2$SO$_4$, b - z nadmiarem /NH$_4$/$_2$SO$_4$

Fig. 7. Zależność stopnia reakcji α haloizytu z Duninowa od czasu spiekania

a - z niedomiarem /NH$_4$/$_2$SO$_4$, b - z nadmiarem /NH$_4$/$_2$SO$_4$. Krzywa W - po ogrzewaniu haloizytu bez /NH$_4$/$_2$SO$_4$

Fig. 8. Widma w podczerwieni haloizytu z Duninowa prażonego w temperaturze 350°C

a - 2 h, b - 5 h, c - 8,5 h

Fig. 9. Zależność stopnia reakcji α muskowitu, od czasu spiekania

a - z niedomiarem /NH$_4$/$_2$SO$_4$, b - z nadmiarem /NH$_4$/$_2$SO$_4$

Fig. 10. Zależność stopnia reakcji α biotytu, od czasu spiekania

a - z niedomiarem /NH$_4$/$_2$SO$_4$, b - z nadmiarem /NH$_4$/$_2$SO$_4$

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ИССЛЕДОВАНИЕ РЕАКЦИЙ СЛОЕВЫХ СИЛИКАТОВ СО СПЛАВЛЕННЫМ

СУЛЬФАТОМ АММОНИЯ

ЧАСТЬ I. РЕАКЦИИ КАОЛИНИТА, ГАЛЛУАЗИТА, МУСКОВИТА И БИОТИТА

С /NH$_4$/$_2$SO$_4$ ПРИ ТЕМПЕРАТУРЕ 350° С

Р е з ю м е

Предметом представленной работы было исследование кинетики и механизма действия сплавленного /NH$_4$/$_2$SO$_4$ на некоторые слоевые силикаты. Исследования проводились на каолинитах с разной степенью упорядочения структуры, галлуазите, мусковите и биотите, смешанных с /NH$_4$/$_2$SO$_4$ в весовом отношении: 1 : 5 и 5 : 1. Смеси выгревались в муфельной печи, при температуре разложения сульфата аммония /350°С/ разное время: 0,5 - 10 часов.

/NH$_4$/$_2$SO$_4$ при температуре 350°С вступает в реакцию с катионами, образующими октаэдрический слой слоевых силикатов. Это сложный процесс, проходящий в нескольких этапах. Продуктом реакции каолинита, галлуазита и мусковита является /NH$_4$/Al/SO$_4$/$_2$ и аморфный кремнозём. Продуктами реакции биотита являются: MgSO$_4$, /NH$_4$/$_2$Fe$_2$/SO$_4$/$_3$ и NH$_4$Al/SO$_4$/$_2$, а также силикагель. После продолжительного обогревания двойные сульфаты переходят в простые сульфаты: Al$_2$/SO$_4$/$_3$ и Fe$_2$/SO$_4$/$_3$. При недостатке /NH$_4$/$_2$SO$_4$ скорость реакции такова, что в течении 1 - 2 часов происходит исчерпыва-

сиз сульфата аммония, который полностью входит в реакцию с катионами октаэдрического слоя кремнезёмных минералов, а также окислами титана и железа, находящимися в пробах.

В связи с избытком $/NH_4/_2SO_4$ в течение 1 - 2 часов происходит полное разложение слоевых силикатов. Спекание с сульфатом аммония и последующее выщелачивание спеков раствором 5% H_2SO_4 даёт возможность извлечь металлы из слоевых силикатов.

Если спекание ведётся с недостатком $/NH_4/_2SO_4$ можно получить эффект селективной экстракции компонентов. Свободные окислы железа и титана вступают в реакцию быстрее, чем каолинит с высокой степенью упорядочения структуры, что можно использовать с целью уменьшения их содержания в каолинах, содержащих такой каолинит. Такого рода селективность не была обнаружена в случае каолинита с худшей степенью упорядочения структуры.

Из слюд, после спекания с $/NH_4/_2SO_4$ значительно лучше экстрагируются катионы октаэдрического слоя, чем межпакетные катионы. Те другие только в незначительной степени переходят в раствор.

Реактивность слоевых силикатов зависит от типа пакетов и рода катионов в октаэдрическом слое пакета. Среди диоктаэдрических минералов мусковит /пакеты 2:1/ обладает значительно меньшей реактивностью, чем минералы группы каолинита /пакеты 1:1/. В свою очередь биотит, содержащий в октаэдрическом слое магний и железо, обладает большей реактивностью, чем мусковит с октаэдрическим слоем, заполненным алюминием.

ОБЪЯСНЕНИЕ ФИГУР

Фиг. 1. Ик-спектры каолина Мария III

    a - исходная проба,

    b - после 0,5 часового спекания с недостатком $/NH_4/_2SO_4$ и обработки 5% раствором H_2SO_4,

    c - после 7 часового спекания с недостатком $/NH_4/_2SO_4$ и обработки 5% раствором H_2SO_4,

Фиг. 2. Ик-спектры каолина Мария III

    a - после 0,5 час. спекания с избытком $/NH_4/_2SO_4$ и обработки 5% раствором H_2SO_4,

    b - после 5 час. спекания с избытком $/NH_4/_2SO_4$ и обработки 5% раствором H_2SO_4,

Фиг 3. Ик-спектры галлуазита из Дунинова

    a - исходная проба,

    b - после 0,5 час. спекания с недостатком $/NH_4/_2SO_4$ и обработки 5% раствором H_2SO_4,

    c - после 5 час. спекания с недостатком $/NH_4/_2SO_4$ и обработки 5% раствором H_2SO_4,

    d - после 8,5 час. спекания с недостатком $/NH_4/_2SO_4$ и обработки 5% H_2SO_4

Фиг. 4. Ик-спектры галлуазита из Дунинова

    a - после 0,5 час. спекания с избытком $/NH_4/_2SO_4$ и обработки 5% H_2SO_4

    b - после 5 час. спекания с избытком $/NH_4/_2SO_4$ и обработки 5%-ым H_2SO_4

    c - после 10 час. спекания с избытком $/NH_4/_2SO_4$ и обработки 5%-ым H_2SO_4

Фиг. 5. Зависимость степени реакции $\propto$ каолина Мария III от времени спекания

    a - с недостатком $/NH_4/_2SO_4$,

    b - с избытком $/NH_4/_2SO_4$

Фиг. 6. Зависимость степени реакции $\propto$ каолинитовой глины из Баранова от времени спекания

    a - с недостатком $/NH_4/_2SO_4$,

    b - с избытком $/NH_4/_2SO_4$

Фиг. 7. Зависимость степени реакции $\propto$ галлуазита из Дунинова от времени спекания

    a - с недостатком $/NH_4/_2SO_4$,

    b - с избытком $/NH_4/_2SO_4$. Кривая W - после спекания галлуазита без $/NH_4/_2SO_4$

Фиг. 8. Ик-спектры галлуазита из Дунинова прокаленного при температуре 350°C

    a - 2 часа,

    b - 5 часов,

    c - 8,5 часа

Фиг. 9. Зависимость степени реакции $\propto$ мусковита от времени спекания

    a - с недостатком $/NH_4/_2SO_4$,

    b - с избытком $/NH_4/_2SO_4$

Фиг. 10. Зависимость степени реакции $\propto$ биотита от времени спекания

    a - с недостатком $/NH_4/_2SO_4$,

    b - с избытком $/NH_4/_2SO_4$