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REACTIONS OF MOLTEN $(NH_4)_2SO_4$ WITH SOME SWELLING MINERALS

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Abstract. The mechanism and kinetics of the reaction of molten ammonium sulphate with selected swelling minerals (<4 μm fraction of Krakowiec clay from Machów and <0.3 μm fraction of basaltic weathering crust from Mikołajowice) were determined. Chemical analysis and X-ray investigation showed that the dissolution of beidellite from Mikołajowice was brought to an end within the first hour of reaction, about 40% Al_2O_3, 40% MgO and 50% Fe_2O_3 being extracted from the structure. The destruction of clay minerals from the Krakowiec clay, among which mixed-layer illite (smectite predominated, proceeded at a slower rate. After 10 hours about 50% Al_2O_3, 70% MgO and 100% Fe_2O_3 were extracted. It was found that the <4 μm fraction of the Machów clay activated with ammonium sulphate for one hour possessed good sulphur-bleaching properties.

INTRODUCTION

The mechanism and kinetics of the reaction of molten ammonium sulphate with layer silicates, such as kaolinite, halloysite, muscovite and biotite, were studied by Stoch, Sikora, Budek (1980 a, b). The present authors thought that it might be interesting to investigate the same process for swelling minerals.

The process of dissolution of swelling minerals was studied on the Krakowiec clay from Machów (Tertiary) and the basaltic weathering crust from Mikołajowice (Tertiary). The latter was chosen for investigations because its <0.3 μm fraction contains about 90% of smectite. From the Krakowiec clay the <4 μm fraction was separated. It contains about 65% of mixed-layer illite/ smectite and it can be readily separated in large amounts, which fact is important if it were to be used for the production of bleaching earths.

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MATERIALS

Basaltic weathering crust from Mikołajowice (<0.3 μm fraction)

Chemical analysis of the sample from Mikołajowice gave the following results: 20.34 wt. % Al_2O_3, 12.64 wt. % Fe_2O_3, 2.10 wt. % MgO.

X-ray quantitative investigations have revealed that the <0.3 μm fraction of the weathering crust contains ca 90% of smectite and ca 10% of kaolinite. The position of the 06 line at 1.497 Å indicates that the smectite is dioctahedral.

After deducting 3.44% Fe_2O_3 extractable with sodium dithionite and the constituents entering into the composition of kaolinite from the results of chemical analysis of the <0.3 μm fraction, the structural formula of the smectite was calculated:

$$(Ca^{2+}_{0.24}Na^{+}_{0.03}K^{+}_{0.05})\ (Mg^{2+}_{0.26}Fe^{3+}_{0.57}Al^{3+}_{1.19})\ [Si^{4+}_{3.63}Al^{3+}_{0.37}O_{10}]\ (OH)_2{}^{*}$$

The charge on a layer is —0.57, more than a half of it (—0.37) coming from the tetrahedral sheet, which indicates that the smectite in question is a ferrous beidellite. This statement has been borne out by Greene-Kelly's test (Jackson 1974) and thermal analysis. The dehydroxylation temperature is 540°C, i.e. it is characteristic of smectites of the beidellite-nontronite series.

The cation exchange capacity of the sample is 59 mval/100 g, which also evidennes that the mineral studied is beidellite. According to Marshall (1964), montmorillocites have a cation exchange capacity of about 100 mval/100 g, and beidellites about 70 mval/100 g. The sample studied has a lower capacity than pure beidellite due to the presence of kaolinite.

On the basis of the above data, the smectite occurring in the <0.3 μm fraction of the weathering crust from Mikołajowice can be assigned to the beidellite-nontronite series.

Krakowiec clay from Machów (<4 μm fraction)

X-ray studies have revealed that it is a polymineral sample with the content of dominant clay minerals totalling up to 72%. It is difficult to determine the contents of individual clay minerals because their basal reflections coincide, yielding a broad diffuse reflection in the range of (6—9)° 2θ, CuK_α. It has been estimated (Bahranowski 1980) that about 65 wt. % of the <4 μm fraction is mixed-layer illite/smectite containing about 75% swelling layers. It is accompanied by illite, chlorite and kaolinite. Of non-clay minerals quartz is most abundant (ca 20%). The remaining components are feldspars (ca 5%), calcite, dolomite and siderite (1% each), as well as pyrite (less than 1%).

Mixed-layer illite/smectite contains about 15% Fe cations and about 15% Mg cations in the octahedral sheet. However, the charge on a layer also comes from the tetrahedral sheet because silica is partly substituted isomorphously by aluminium (Stoch et al. 1977).

The chemical analysis of the <4 μm fraction of the Machów clay gave the following results: 16.24 wt. % Al_2O_3, 4.64 wt. % Fe_2O_3, 2.44 wt. %MgO.

METHODS

The dissolution of swelling minerals was carried out at an excess of ammonium sulphate. Accordingly, 1:5 mixtures of samples with ammonium sulphate were prepared. This ratio was chosen on the basis of the studies of Stoch, Sikora and Budek (1980 a). In order to follow the process of dissolution of smectites, six equal portions were weighed out from the mixture and each was sintered for a different length of time (0.5, 1, 2, 4, 7, 10 hrs.).

The mixtures were placed in the form of thin layers in flat porcelain vessels and heated at 350°C in a resistance furnace. The phase composition of the resulting sinters was controlled by X-ray method using a DRON diffractometer. Then the sinters were heat-treated with 5% H_2SO_4 solution on a water bath at 90°C for 15 minutes to dissolve the soluble reaction products, whereupon the solution was analysed for Al_2O_3, Fe_2O_3 and MgO. The phase composition of the insoluble residue was controlled by X-ray method.

* All iron was determined in the form of Fe^{3+}.

RESULTS

X-RAY INVESTIGATIONS

Basaltic weathering crust from Mikołajowice (<0.3 μm fraction)

X-ray investigations of beidellite sinters with $(NH_4)_2SO_4$ have revealed the presence of sulphates only. This is presumably due to their precipitation at the surface of clay minerals which, for that reason, do not take part in X-ray diffraction.

The sequence of formation of sulphates in the process of sintering of beidellite with ammonium sulphate is shown in Table 1, where the new-formed sulphate phases are listed according to the decreasing intensity of their strongest X-ray lines.

To find out what changes in the structure of beidellite were produced by the action of $(NH_4)_2SO_4$, the residue insoluble in 5% H_2SO_4 solution was subjected to X-ray analysis. The analysis concerned the position, intensity and in some cases, the half--width of the *001* basal reflections yielding information on the structure of smectite

Table 1

Phases formed during the sintering of beidellite from Mikołajowice with $(NH_4)_2SO_4$

Sintering time (h)	Phases
0,5	NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, $(NH_4)_3Al(SO_4)_3$, $(NH_4)_3Fe(SO_4)_3$
1	NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, $NH_4Al(SO_4)_2$, $NH_4Fe(SO_4)_2$, $(NH_4)_3Al(SO_4)_3$, $(NH_4)_3Fe(SO_4)_3$
2	NH_4HSO_4, $NH_4Al(SO_4)_2$, $NH_4Fe(SO_4)_2$, $(NH_4)_3H(SO_4)_2$, $(NH_4/_3Al(SO_4)_3$, $(NH_4)_3Fe(SO_4)_3$
4	$NH_4Al(SO_4)_2$, $NH_4Fe(SO_4)_2$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, $(NH_4)_3Al(SO_4)_3$, $(NH_4)_3Fe(SO_4)_3$
7	$NH_4Al(SO_4)_2$
10	$NH_4Al(SO_4)_2$

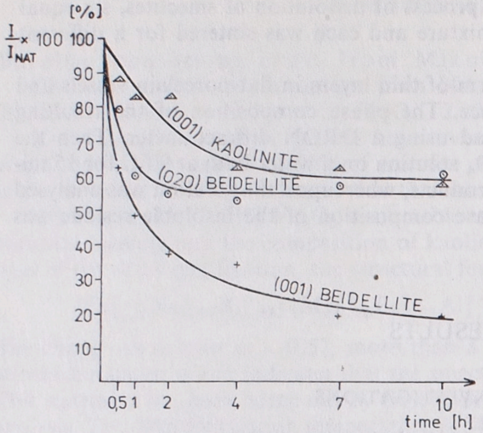

Fig. 1. The reletionship between the intensity of *020* and *001* reflections of clay minerals and the sintering time with $(NH_4)_2SO_4$ (<0.3 μm fraction of basaltic weathering crust from Mikołajowice)

along the c-axis, and of the *020* reflection determining the layer structure along the b-axis. During the sintering with ammonium sulphate the *020* reflection of beidellite decreases in intensity by 40% after one hour of reaction, whereupon its intensity is virtually constant. This behaviour suggests that the destruction of the layer structure is brought to an end after the first hour. The intensity of the *001* reflection, on the other hand, decreases systematically during 10 hours of reaction, which points to the progressive reduction in the crystallite dimension in the "*c*" direction. The same inference can be made from the broadening of the *001* reflection, which is particularly pronounced after 4 hours of reaction (Fig. 1).

The effect of sintering at 350°C for 3 hours and of the treatment with H_2SO_4 on the structural changes of smectite was also investigated. The results obtained (Table 2) show that the sintering has not produced any changes in the layer structure of beidellite but sulphuric acid has disarranged it, which is reflected by the reduction in the intensity of the *020* reflection by about 20%. Yet it can be assumed that the action of H_2SO_4 on the structure of smectite sintered with $(NH_4)_2SO_4$ is much weaker, as it reacts mainly with sulphates which dominate in the sinter.

Table 2

The change in the (*020*) reflection intensity after various treatments

Beidellite from Mikołajowice	$\frac{I_{(020)}}{I_{(020)nat.}} \times 100$ (%)
after treatment with 5% H_2SO_4	81
after 3-hour sintering at 350% and treatment with 5% H_2SO_4	87

Krakowiec clay from Machów (<4 μm fraction)

The phase composition of the sinters obtained shows close similarity to that described above for the sample from Mikołajowice, but the sample from Machów has also been found to contain $Al_2(SO_4)_3$ at all the analysed stages of the process (Table 3).

During the sintering carbonates have been dissolved whereas quartz and feldspars have shown poor reactivity. The information on the structural changes in clay minerals (among which mixed-layer I/S predominates) is provided by the intensity

Table 3

Phases formed during the sintering of clay from Machów with $(NH_4)_2SO_4$

Sintering time (h)	Phases
0,5	NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, $(NH_4)_3Al(SO_4)_3$, $(NH_4)_3Fe(SO_4)_3$, $NH_4Al(SO_4)_2$, $NH_4Fe(SO_4)_2$, $Al_2(SO_4)_3$
1	NH_4HSO_4, $NH_4Al(SO_4)_2$, $NH_4Fe(SO_4)_2$, $(NH_4)_3H(SO_4)_2$, $(NH_4)_3Al(SO_4)_3$, $(NH_4)_3Fe(SO_4)_3$, $Al_2(SO_4)_3$
2	$NH_4Al(SO_4)_2$, $NH_4Fe(SO_4)_2$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, $(NH_4)_3Al(SO_4)_3$, $(NH_4)_3Fe(SO_4)_3$, $Al_2(SO_4)_3$
4	$NH_4Al(SO_4)_2$, $NH_4Fe(SO_4)_2$, NH_4HSO_4, $Al_2(SO_4)_3$, $(NH_4)_3H(SO_4)_2$, $(NH_4)_3Al(SO_4)_3$, $(NH_4)_3Fe(SO_4)_3$
7	$NH_4Al(SO_4)_2$, $Al_2(SO_4)_3$
10	$NH_4Al(SO_4)_2$, $Al_2(SO_4)_3$

of the *020* reflection (4.4 Å), common to these minerals. It decreases systematically during 10 hours of the process (Fig. 2), which testifies to the progressing destruction of the layers. Some interesting data are also yielded by the analysis of a broad reflection in the range of (6—9)° 2θ, CuK_{α}. Its intensity is reduced as the reaction progresses, the *001* line of illite becoming more and more pronounced against it. This is due to the slower dissolution of illite compared with mixed-layer illite/smectite (Fig. 3).

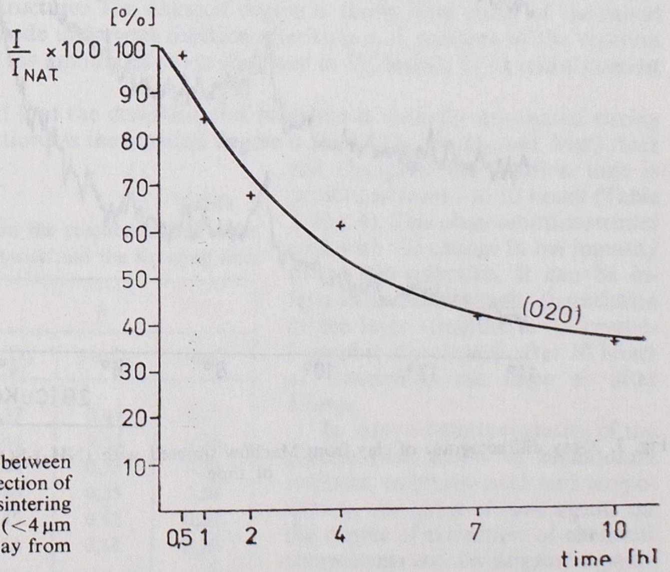

Fig. 2. The relationship between the intensity of *020* reflection of clay minerals and the sintering time with $(NH_4)_2SO_4$ (<4 μm fraction of Krakowiec clay from Machów)

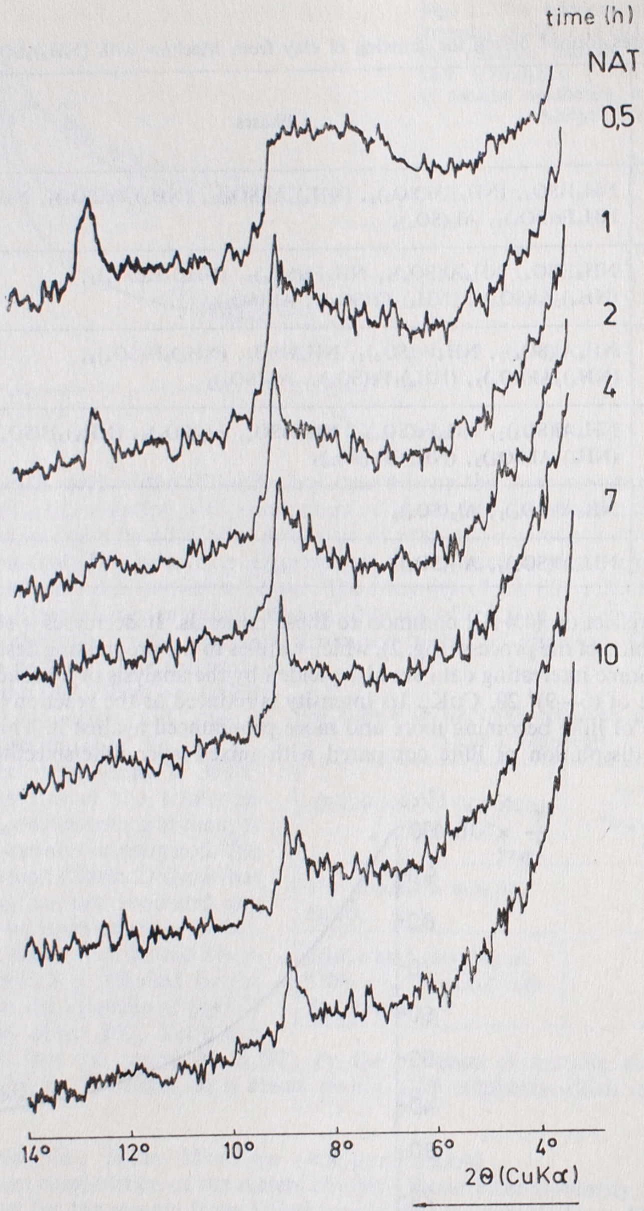

Fig. 3. X-ray diffractogram of clay from Machów sintered with $(NH_4)_2SO_4$ for different lengths of time

Kaolinite present in the sample appears to be non-resistant in the process of sintering with ammonium sulphate, and its *001* reflection disappears within two hours.

Investigations were also carried out to find how the sintering at 350°C and the treatment with 5% H_2SO_4 affects the structure of clay minerals in the sample from Machów. As in the sample from Mikołajowice, the sintering does not produce and changes in their structure while sulphuric acid disarranges it (Table 4).

Table 4

The change in the *(020)* reflection intensity after various treatments

Clay from Machów	$\frac{I_{(020)}}{I_{(020)\,nat.}} \times 100$ (%)
after treatment with 5% H_2SO_4	86
after 3-hour sintering at 350°C and treatment with 5% H_2SO_4	84

CHEMICAL ANALYSIS

Basaltic weathering crust from Mikołajowice (<0.3 μm fraction)

The degree of disarrangement of the structure of swelling minerals is also determined by the amount of chemical components extracted in the process of sintering with sulphate.

Kaolinite, which is an admixture in the sample from Mikołajowice, shows low chemical reactivity, so it can be safely assumed that the analysed chemical components (except iron that appears in amorphous form) derive mainly from the structure of beidellite.

The kinetics of the sintering process of beidellite with ammonium sulphate is determined by the change in the reaction degree α in time. The reaction degree for beidellite can be determined through the reaction degree for Al_2O_3, Fe_2O_3 and MgO extracted from its structure. The reaction degree α shows how much of the initial amount of a given oxide undergoes reaction after time *t*. A measure of the reaction degree is the ratio of the amount of oxide dissolved in 5% H_2SO_4 to its initial content in the sample.

It has been found that the dissolution of beidellite is virtually terminated during the first hour of reaction, as the reaction degree α for Al_2O_3, Fe_2O_3 and MgO does not change if the reaction time is prolonged from 1 to 10 hours (Table 5, Fig. 4). This observation correlates well with the change in the intensity of the *020* reflection. It can be inferred therefore that the degradation of the layer structure in the crystallographic direction b after 10 hours of reaction is the same as after 1 hour.

In view of the complexity of the process (the action of ammonium sulphate, sulphuric acid and temperature), the effect of these agents on the degree of extraction of chemical components was investigated separa-

Table 5

The relationship between the reaction degree α for beidellite from Mikołajowice and the sintering time

Sintering time (h)	α		
	Al_2O_3	Fe_2O_3	MgO
0,5	0,37	0,48	0,37
1	0,44	0,54	0,39
2	0,44	0,55	0,39
4	0,45	0,55	0,39
7	0,45	0,52	0,39
10	0,48	0,53	0,39

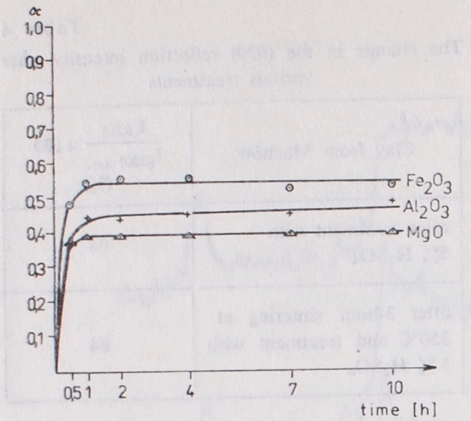

Fig. 4. The relationship between the reaction degree α of the beidellite from Mikołajowice and the sintering time with $(NH_4)_2SO_4$

tely. It appeared that treatment with 5% H_2SO_4 extracts 13% Al_2O_3, 27% Fe_2O_3 and 28% MgO from the sample. The prior heating of the sample at 350°C does not increase these amounts (Table 6). This observation is in accord with X-ray data (changes in the intensity of the *020* reflection).

Krakowiec clay from Machów (<4 μm fraction)

On the basis of the chemical analysis of extraction solutions, the reaction degree was calculated for Al_2O_3, Fe_2O_3 and MgO (Table 7, Fig. 5).

In contrast to the sample from Mikołajowice, the amount of aluminium and iron extracted from the clay increases systematically throughout the process. It is interesting to note that all iron but only 50% of aluminium and about 70% of magnesium are extracted during 10 hours. The rate of extraction of the latter is the most rapid so

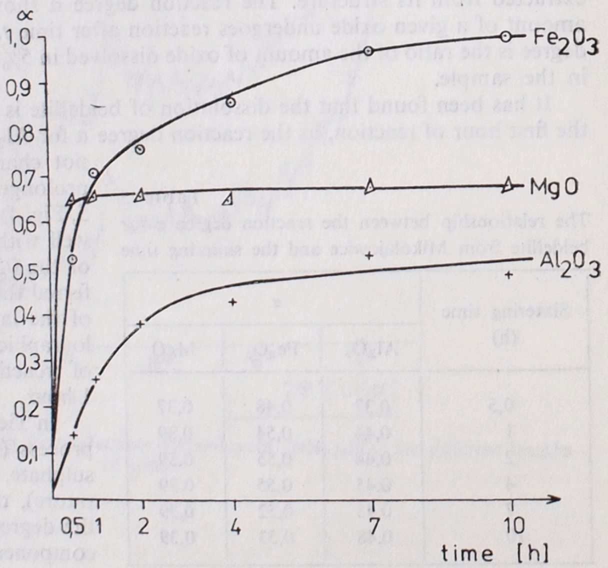

Fig. 5. The relationship between the reaction degree α of clay minerals from Machów and the sintering time with $(NH_4)_2SO_4$

Table 6

The reaction degree α for beidellite from Mikołajowice after various treatments

Beidellite from Mikołajowice	α		
	Al_2O_3	Fe_2O_2	MgO
after treatment with 5% H_2SO_4	0.13	0.27	0.28
after 3-hour sintering at 350°C and treatment with 5% H_2SO_4	0.12	0.26	0.25

Table 7

The relationship between the reaction degree α for clay from Machów and the sintering time

Sintering time (h)	α		
	Al_2O_3	Fe_2O_3	MgO
0,5	0.14	0.52	0.65
1	0.26	0.71	0.66
2	0.38	0.76	0.66
4	0.43	0.86	0.66
7	0.53	0.97	0.68
10	0.49	1.00	0.68

that after half an hour all the amount of magnesium extractable by this method passes into the melt. However, the reaction degree for MgO cannot be regarded as a measure of destruction of the swelling I/S mineral because magnesium partly derives from the dissolution of dolomite.

The effect of heating and treatment with 5% H_2SO_4 on the degree of extraction of the selected components is illustrated in Table 8. These results accord well with X-ray data.

Table 8

The reaction degree α for clay from Machów after various treatments

The clay from Machów	α		
	Al_2O_3	Fe_2O_3	MgO
after treatment with 5% H_2SO_4	0.06	0.30	0.36
after 3-hour sintering at 350°C and treatment with 5% H_2SO_4	0.06	0.29	0.37

The process of sintering of swelling minerals with $(NH_4)_2SO_4$

X-ray investigation and chemical analysis indicate that the dissolution of swelling minerals in ammonium sulphate proceeds in the following way: At the first stage of the process ammonium sulphate decomposes into NH_4HSO_4 and $(NH_4)_3H(SO_4)_2$, and aluminium and iron partly removed from the structure of swelling minerals combine respectively to form $(NH_4)_3Al(SO_4)_3$ and $(NH_4)_3Fe(SO_4)_3$ and then $NH_4Al(SO_4)_2$ and presumably $NH_4Fe(SO_4)_2$. After 7 hours of reaction aluminium-ammonium sulphate has been identified by X-ray method, and in the sinter of the Machów clay also aluminium sulphate.

It is difficult to determine univocally the mechanism of dissolution of swelling minerals in molten $(NH_4)_2SO_4$. There is no doubt that the ammonium ion is accomodated in the interlayer spaces, substituting for calcium. It is not known, however, what agent is responsible for the breaking of bonds in the structure and for the extraction of aluminium, iron and magnesium ions.

In beidellite from Mikołajowice the amount of components removable under these conditions is extracted after one hour, and so the layer destruction is virtually brought to an end within that time. Afterwards the destruction of crystallites along the c-axis only takes place. X-ray analysis has shown that after 10 hours of reaction beidellite still retains its structure, although it is partly destroyed. The structural destruction of mixed-layer I/S in the Machów clay proceeds at a slower rate. Aluminium and iron are removed progressively and the process comes to an end after 7 hours.

Bleaching properties of samples activated with $(NH_4)_2SO_4$

In view of the fact that the Machów clay activated by various methods appeared to have good bleaching properties (Stoch et al. 1977; Stoch, Bahranowski, Gątarz 1979; Stoch et al. 1979), it seemed advisable to check whether the method of activation with ammonium sulphate could find application in the production of bleaching earths. To this end, the degree of sulphur bleaching was determined, using the <4 μm fraction of clay from Machów and the <0.3 μm fraction of beidellite from Mikołajowice, both activated with ammonium sulphate*. The activation method and the results of sulphur bleaching are given in Table 9.

Table 9

Bleaching properties of the <4 μm fraction of clay from Machów and beidellite from Mikołajowice obtained by different activation methods

Sample	Consumption of earth in (%)	Degree of bleaching of sulphur in (%)
Clay from Machów (<4 μm fraction) after 15' activation with 5% H_2SO_4	0,5	67,6
Clay from Machów (<4 μm fraction) after 1-h. sintering with $(NH_4)_2SO_4$	0,5	79,5
Clay from Machów (<4 μm fraction) after 7-h sintering with $(NH_4)_2SO_4$	0,5	68,8
Beidellite from Mikołajowice (<0,3 μm fraction) after 1-h sintering with $(NH_4)_2SO_4$	0,5	67,3

Under laboratory conditions, clay from Machów activated with ammonium sulphate for 1 hour bleaches sulphur in the same degree as the bleaching earths used now in Poland for that purpose. The latter, however, are obtained by activation with sulphuric acid, which method is cheaper and easier to use on an industrial scale than activation with ammonium sulphate.

The prolongation of the activation of clay from Machów with sulphate to 7 hours decreased the degree of sulphur bleaching by about 10%. A similar degree was obtained using beidellite from Mikołajowice activated for 1 hour. This is probably due to the fact that is spite of different activation time, the two samples show a similar degree of disarrangement of the structure of clay minerals. This statement has been borne out by X-ray and chemical investigations.

* The degree of sulphur bleaching was determined at the Research and Development Centre of Sulphur Industry in Machów near Tarnobrzeg.

CONCLUSIONS

During the sintering of swelling minerals with ammonium sulphate the interlayer cations of smectites are substituted by ammonium ion. The cations of octahedral sheets of clay minerals are removed, and aluminium and iron sulphates form.

The dissolution of beidellite from Mikołajowice proceeds in a different way than the dissolution of clay minerals from the Krakowiec clay from Machów. During the first hour 40% Al_2O_3, 40% MgO and 50% Fe_2O_3 are extracted from the structure of beidellite. The prolongation of reaction time does not bring about any further changes. The destruction of clay minerals from the Krakowiec clay is a progressive process. After 10 hours of reaction about 50% Al_2O_3, 70% MgO and 100% Fe_2O_3 are extracted. It is feasible that the different grain size composition of the samples is responsible for their different behaviour. The very fine grain size of beidellite from Mikołajowice results in that its surface available for reaction is very large and the reaction equilibrium is soon attained. In spite of this different kinetics of the process, the reaction degree for aluminium is the same in both samples whereas the reaction degree for iron is different.

The <4 μm fraction of the Krakowiec clay from Machów activated with ammonium sulphate for 1 hour shows good sulphur-bleaching properties.

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DZIAŁANIE STOPIONEGO $(NH_4)_2SO_4$ NA WYBRANE MINERAŁY PĘCZNIEJĄCE

Streszczenie

Określono mechanizm i kinetykę reakcji stopionego siarczanu amonowego z wybranymi minerałami pęczniejącymi (frakcja <4 μm iłu krakowieckiego z Machowa i frakcja <0,3 μm zwietrzeliny bazaltowej z Mikołajowic). W ciągu 1 godziny reakcji ze struktury beidellitu z Mikołajowic ekstrahuje się około 40% Al_2O_3, 40% MgO i 50% Fe_2O_3. Wydłużanie czasu reakcji nie powoduje dalszych zmian w strukturze beidellitu co potwierdzają badania rentgenograficzne. Natomiast destrukcja minerałów ilastych z iłu krakowieckiego z Machowa (wśród których przeważa minerał pęczniejący I/S) postępuje stopniowo. Po 1 godzinie reakcji ekstrahuje się 25% Al_2O_3, 65% MgO i 70% Fe_2O_3, a po 10 godzinach około 50% Al_2O_3, 70% MgO i 100% Fe_2O_3.

Można przypuszczać, że różne zachowanie próbek jest spowodowane ich różnym uziarnieniem. Bardzo drobne uziarnienie próbki z Mikołajowic sprawia, że powierzchnia reakcji beidellitu ze stopionym siarczanem jest bardzo duża i równowaga reakcji ustala się szybko. Pomimo tak różnej kinetyki procesu stopień reakcji glinu jest taki sam, natomiast stopień reakcji żelaza jest różny w obu próbkach.

Frakcja <4 μm iłu krakowieckiego z Machowa aktywowana w ciągu 1 godziny siarczanem amonowym wykazała dobre właściwości odbarwiające siarkę.

OBJAŚNIENIE FIGUR

Fig. 1. Zależność intensywności refleksów *020* i *001* minerałów ilastych od czasu spiekania z $(NH_4)_2SO_4$ (frakcja <0,3 (μm zwietrzeliny bazaltowej z Mikołajowic)

Fig. 2. Zależność intensywności refleksu *020* minerałów ilastych od czasu spiekania z $(NH_4)_2SO_4$ (frakcja <4 μm iłu krakowieckiego z Machowa).

Fig. 3. Dyfraktogramy próbek iłu z Machowa spiekanych z $(NH_4)_2SO_4$ przez różne okresy czasu.

Fig. 4. Zależność stopnia reakcji α beidellitu z Mikołajowic od czasu spiekania z $(NH_4)_2SO_4$.

Fig. 5. Zależność stopnia reakcji α minerałów ilastych iłu z Machowa od czasu spiekania z $(NH_4)_2SO_4$,

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ДЕЙСТВИЕ СПЛАВЛЕННОГО $(NH_4)_2SO_4$ НА НЕКОТОРЫЕ ВСПУЧИВАЮЩИЕСЯ МИНЕРАЛЫ

Резюме

Установлены механизм и кинетика реакций сплавленного сульфата аммония с избранными вспучивающимися минералами (фракция < 4 мкм краковецкой глины из Махува и фракция < 0,3 мкм базальтовой коры выветривания из Миколаёвиц). В течении 1-го часа реакции из структуры бейделлита из Миколаёвиц экстрагируется около 40% Al_2O_3, 40% MgO и 50% Fe_2O_3. Растяжение времени реакции не вызывает дальнейших изменений в структуре бейделлита, что подтверждается рентгенографическими исследованиями. Разрушение глинистых минералов краковецких глин из Махува (среди которых преобладает вспучивающийся минерал И/С) происходит постепенно. После 1-го часа реакции экстрагируется 25% Al_2O_3, 65% MgO и 70% Fe_2O_3, а после 10-ти часов — около 50% Al_2O_3, 70% MgO и 100% Fe_2O_3.

Надо полагать, что разное поведение образцов вызвано их различной гранулометрией. Большая мелкозернистость образца из Миколаёвиц является причиной тому, что поверхность реагирования бейделлита со сплавленным сульфатом очень больша и равновесие реакции быстро устанавливается. Несмотря на так различную кинетику процесса, степень реакции алюминия такая же сама, степень же реакции железа в обоих образцах различна.

Фракция < 4 мкм краковецкой глины из Махува, активированная в течении 1-го часа сернокислым аммонием, показала хорошие сероосбесцвечивающие свойства.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Зависимость интенсивности отражений от плоскостей *020* и *001* глинистых минералов от времени спекания с $(NH_4)_2SO_4$ (фракция <0,3 мкм базальтовой коры выветривания из Миколаёвиц)

Фиг. 2. Зависимость интенсивности отражения от плоскости *020* глинистых минералов от времени спекания с $(NH_4)_2SO_4$ (фракция <4 мкм краковецкой глины из Махува)

Фиг. 3. Дифрактограммы образцов глин из Махува, спекаемых с $(NH_4)_2SO_4$ в разных промежутках времени

Фиг. 4. Зависимость степени реакции α бейделлита из Миколаёвиц от времени спекания с $(NH_4)_2SO_4$

Фиг. 5. Зависимость степени реакции α глинистых минералов глины из Махува от времени спекания с $(NH_4)_2SO_4$