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A STUDY OF REACTIONS OF LAYER SILICATES WITH MOLTEN
AMMONIUM SULPHATE

PART II. THE EFFECT OF TEMPERATURE ON REACTIONS OF HALLOYSITE
WITH $\text{NH}_4/2\text{SO}_4$

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Abstract. As the sintering temperature is raised from 250 to 600°C, $\text{NH}_4/3\text{Al}/\text{SO}_4/3$, $\text{NH}_4\text{Al}/\text{SO}_4/2$ and $\text{Al}_2/\text{SO}_4/3$ form successively as the reaction products of halloysite with $\text{NH}_4/2\text{SO}_4$. The extractability of aluminium from the resulting sinters with 5% H_2SO_4 solution varies from 10% at 250°C to nearly 100% at 600°C. The structure of halloysite is progressively destroyed to give a substance of the silica gel type in the final stage of sintering.

INTRODUCTION

Earlier investigations carried out by the authors have shown that molten ammonium sulphate enters into reaction with the cations occupying the octahedral sheet of layer silicates to form sulphates soluble in 5% H_2SO_4 solution.

The present paper aimed to study the effect on temperature on the course of this reactions. Investigations were carried out on halloysite from Duninów, described in Part I of this paper /p. 63/.

EXPERIMENTAL

Thermal curves for ammonium sulphate and its mixtures with halloysite in the proportions of 1:5 and 5:1 were obtained with a deriva-

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tograph. The instrument settings were: heating rate $10^{\circ}/\text{min.}$, thermocouples Pt-PtRh 10%, disk platinum crucibles, standard - sintered Al_2O_3 .

To determine the kind of changes producing peaks on thermal curves, samples were heated to the temperature of the beginning and end of successive peaks on the DTA curve, whereupon the samples were cooled rapidly and their phase composition determined by X-ray method.

Then the mixture with an excess of $\text{NH}_4/2\text{SO}_4$ /1:5/ was held in a muffle furnace at varying temperatures for 0.5 h. The temperature was raised by 50° over the range of 250 – 600°C . The phase composition of sinters and the amount of Al_2O_3 extractable with 5% H_2SO_4 solution were determined.

Infrared absorption spectra of the residue left after the extraction of Al_2O_3 were recorded with a Zeiss UR-10 spectrometer.

RESULTS

Thermal curves for $\text{NH}_4/2\text{SO}_4$ are shown in Figure 1. At 355°C an intense endothermic peak appears on the DTA curve, produced by the melting of this compound and its decomposition into acid sulphates: $\text{NH}_4/3\text{H}/\text{SO}_4/2$ and NH_4HSO_4 . This peak passes into another endothermic peak with a maximum at 430°C , caused by the decomposition of acid sulphates. It corresponds to a substantial weight loss on the TG curve.

The mixture of halloysite with $\text{NH}_4/2\text{SO}_4$ yield more complex thermal curves. When the sulphate is in excess /Fig. 2/, two additional peaks have been recorded, both attended by a weight loss. The two first intense endothermic peaks, produced by the melting and decomposition of ammonium sulphates, obscure the peak associated with the formation of aluminium-ammonium sulphates. At 420°C $\text{NH}_4\text{Al}/\text{SO}_4/2$ was found to be present. This sulphate decomposes to $\text{Al}_2/\text{SO}_4/3$ at 470°C with the evolution of NH_3 , and the latter decomposes completely at 760°C . The X-ray diffraction pattern of a sample heated up to 780°C does not display any lines that would testify to the presence of crystalline phases. The only reflection recorded was a broad band $d = 3.4 - 4.4$ attributed to amorphous silica. For the mixture of halloysite with a deficiency of $\text{NH}_4/2\text{SO}_4$ /Fig. 3/ the following peaks have been recorded: an endothermic peak of dehydration at 60°C , an endothermic peak of dehydroxylation at 535°C , and an exothermic peak at 980°C , all typical of halloysite. The other peaks correspond to those on the curve for the mixture with an excess of $\text{NH}_4/2\text{SO}_4$.

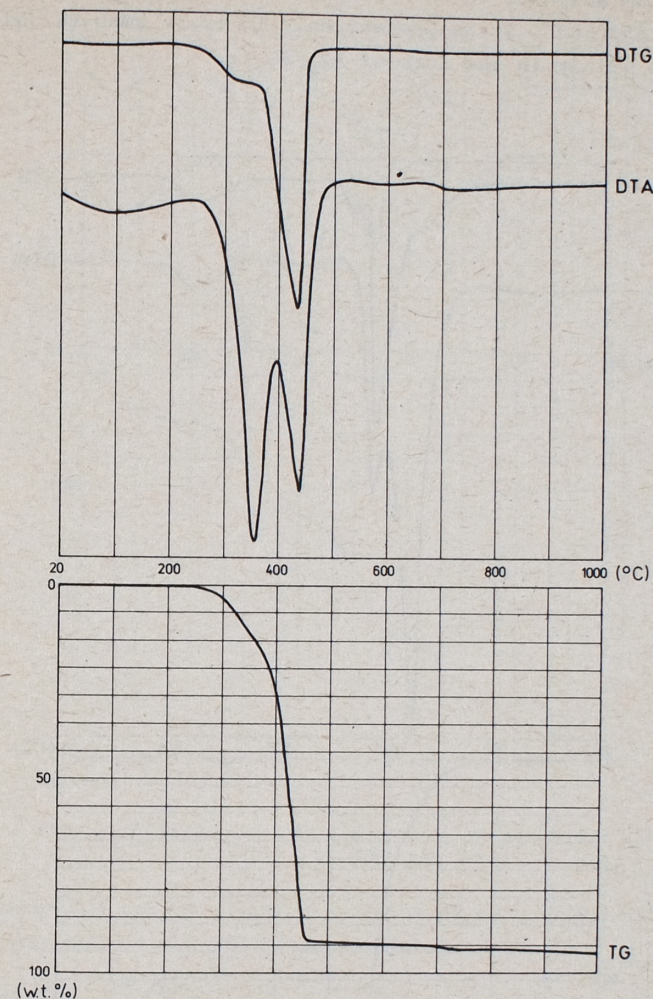


Fig. 1. Thermal curves of $\text{NH}_4/2\text{SO}_4$

Investigations of the mixture of halloysite with an excess of $\text{NH}_4/2\text{SO}_4$, heated in a muffle furnace for 0.5 hour at temperatures raised by 50°C , have revealed that ammonium sulphate first passes into $\text{NH}_4/3\text{H}/\text{SO}_4/2$, which then reacts with aluminium from halloysite to form $\text{NH}_4/3\text{Al}/\text{SO}_4/3$. This aluminium-ammonium sulphate is present in the sinter over a temperature range of 250 – 400°C /Table 1/. At about 300°C $\text{NH}_4/3\text{H}/\text{SO}_4/2$ begins to convert into NH_4HSO_4 ; simultaneously $\text{NH}_4\text{Al}/\text{SO}_4/2$ appears in the sinter. Above 350°C the latter sulphate is virtually the only one to form, whereas $\text{NH}_4/3\text{Al}/\text{SO}_4/3$ disappears. Alu-

minium-ammonium sulphate is the principal component of the sinters up to 500°C. At 550-600°C it is present only in trace amounts while aluminium occurs mainly in the form of $\text{Al}_2/\text{SO}_4/3$.

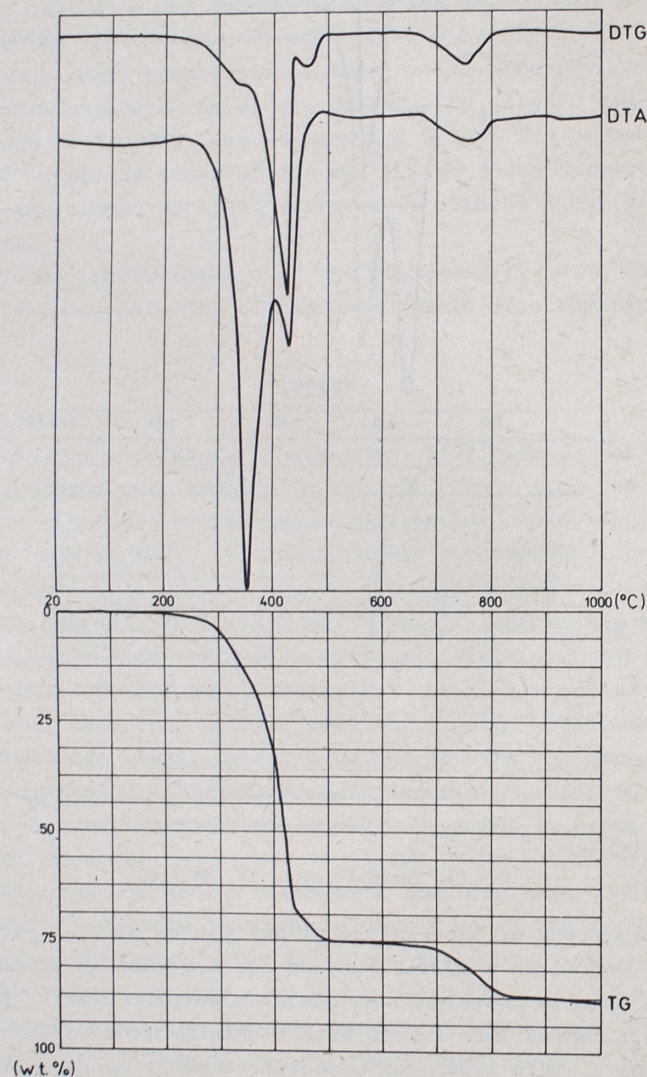


Fig. 2. Thermal curves of the mixture of halloysite with excess of $\text{NH}_4/2\text{SO}_4$ /1:5/

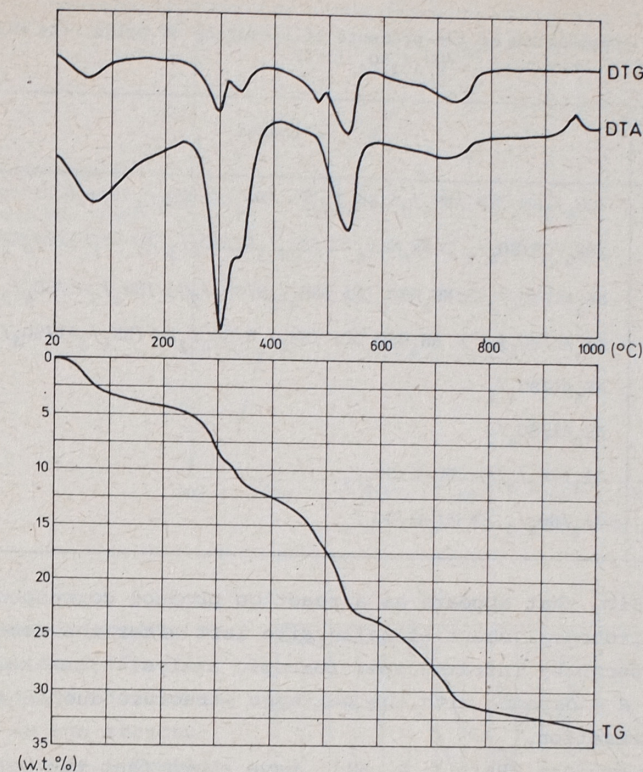


Fig. 3. Thermal curves of the mixture of halloysite with deficiency of $\text{NH}_4/2\text{SO}_4$ /5:1/

The reaction taking place in sinters of halloysite with $\text{NH}_4/2\text{SO}_4$ can be described by the following equations:

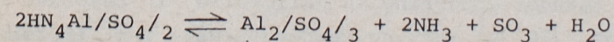
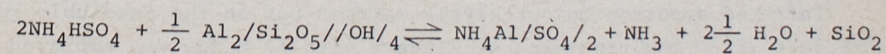
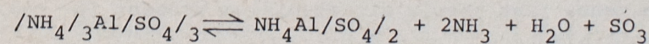
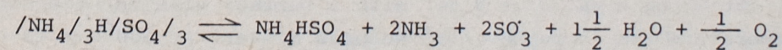
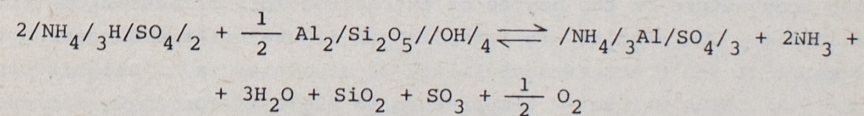
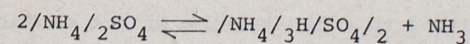


Table 1

Phase composition of the products of sintering of halloysite with $\text{NH}_4/2\text{SO}_4$ /1:5/

Temperature °C	Phases
250	$\text{NH}_4/2\text{SO}_4 \gg \text{NH}_4/3\text{H}/\text{SO}_4/2 \gg \text{NH}_4/\text{Al}/\text{SO}_4/3$
300	$\text{NH}_4/3\text{H}/\text{SO}_4/2 > \text{NH}_4\text{HSO}_4 \approx \text{NH}_4/3\text{Al}/\text{SO}_4/3 \gg \text{NH}_4\text{Al}/\text{SO}_4/2$
350	$\text{NH}_4\text{Al}/\text{SO}_4/2 \approx \text{NH}_4\text{HSO}_4 \gg \text{NH}_4/3\text{H}/\text{SO}_4/2 \approx \text{NH}_4/3\text{Al}/\text{SO}_4/3$
400	$\text{NH}_4\text{Al}/\text{SO}_4/2 > \text{NH}_4\text{HSO}_4 \gg \text{NH}_4/3\text{H}/\text{SO}_4/2 \approx \text{NH}_4/3\text{Al}/\text{SO}_4/3$
450	$\text{NH}_4\text{Al}/\text{SO}_4/2$
500	$\text{NH}_4\text{Al}/\text{SO}_4/2$
550	$\text{Al}_2/\text{SO}_4/3 \gg \text{NH}_4\text{Al}/\text{SO}_4/2$
600	$\text{Al}_2/\text{SO}_4/3 \gg \text{NH}_4\text{Al}/\text{SO}_4/2$

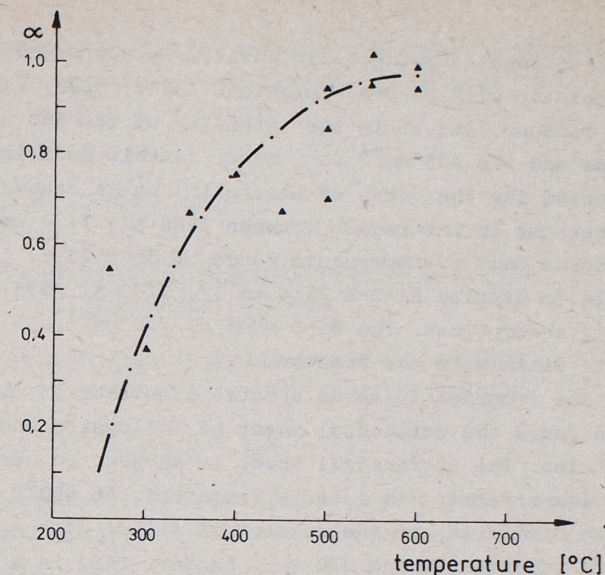
Silica SiO_2 that appears as a reaction product corresponds to the degraded tetrahedral sheet of halloysite left after the removal of aluminium. As shown by infrared spectroscopic analysis [see below], this sheet forms a substance with the gel-type structure due to three-dimensional condensation.

Earlier studies [Part I, p. 61] have shown that the heating of halloysite with an excess of $\text{NH}_4/2\text{SO}_4$ at 350°C results in that the constituent aluminium becomes soluble in 5% H_2SO_4 . This is a consequence of the disturbance of the structure of halloysite caused by the reaction between aluminium and sulphate, and by simultaneous dehydroxylation of halloysite.

The present investigations aimed to determine the effect of sintering temperature on the degree of extraction α of aluminium from halloysite. The results are presented in Figure 4. At a sintering temperature of 250°C the extractability of aluminium is insignificant ($\alpha = 0.1$). With a rise in temperature to 350°C α for Al_2O_3 increases rapidly, attaining a value of 0.65. With a further rise in the sintering temperature the increase in α becomes slower. At 600°C α is close to unity, which means that nearly all aluminium present in halloysite will go into solution.

Infrared spectroscopic analysis carried out on the insoluble residue left after the treatment of sinters with 5% H_2SO_4 was employed to trace the structural changes occurring in halloysite in response to its sintering with $\text{NH}_4/2\text{SO}_4$ at varying temperatures. The infrared

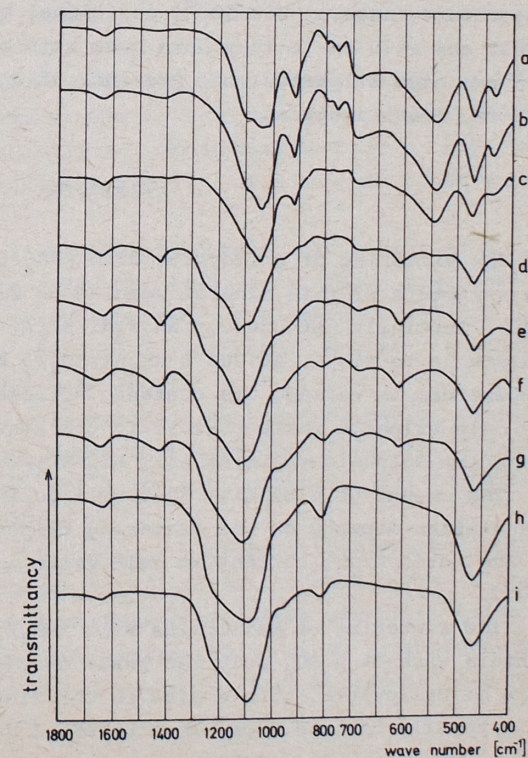
Fig. 4. Relationship between the reaction degree α of Al and the sintering temperature



spectra obtained are shown in Figure 5. At 250°C the spectrum does not disclose any changes in the structure of halloysite. Taking into consideration the facts that $\text{NH}_4/3\text{Al}/\text{SO}_4/3$ already forms at this temperature and the aluminium extractability from the sinter is nearly 10%, it can be presumed that aluminium present at the surface of halloysite grains only enters into reaction with $\text{NH}_4/2\text{SO}_4$ while the structure of this

Fig. 5. Infrared spectra

a - halloysite; b-i - halloysite sintered with $\text{NH}_4/2\text{SO}_4$ /1:5/ at: b - 250°C , c - 300°C , d - 350°C , e - 400°C , f - 450°C , g - 500°C , h - 550°C , i - 600°C , after treating 5% H_2SO_4



mineral remains essentially intact. At 300°C the intensity of bands associated with Al-O-H vibrations /3694, 3629, 918 cm⁻¹/ is considerably reduced, and so is the intensity of the 690 and 539 cm⁻¹ Si-O-Al bands and the 435 cm⁻¹ Si-O band. Certain modifications have also been observed for the group of absorption bands caused by Si-O-Si and Si-O vibrations in the region between 1000 and 1100 cm⁻¹. When the reaction proceeds over a temperature range of 350-500°C, the insoluble residue fails to display Al-O-H /918 cm⁻¹/, Si-O-Al /539 cm⁻¹/ or Si-O /435 cm⁻¹/ absorptions. The Si-O band at 470 cm⁻¹, on the other hand, is still visible in the spectrum.

The recorded infrared spectra show that in the discussed temperature range the octahedral sheet of halloysite undergoes complete destruction. The tetrahedral sheet is subject to certain rearrangements, but its structure is largely preserved. At 550°C the spectrum shows close similarity to the spectra of silica gels /a broad band at 1100 cm⁻¹, intense 810 and 470 cm⁻¹ bands/. This is a result of gradual rearrangement of the defect tetrahedral sheet, left after the removal of the octahedral sheet, towards three-dimensional condensation. In a temperature range of 350-500°C additional bands appear in the spectra at 610 and 1420 cm⁻¹. They have been attributed to incompletely leached ammonium sulphates, the presence of which has also been confirmed by X-ray investigations.

DISCUSSION

The sintering of halloysite with /NH₄/₂SO₄ makes aluminium from the structure of this mineral combine to form sulphates soluble in 5% H₂SO₄. Initially, at 250°C, /NH₄/₃Al/SO₄/₃ forms and persists in the sinters up to 400°C. At 300°C NH₄Al/SO₄/₂ begins to appear. As the temperature is raised, its content increases and at 450-500°C it is the only sulphate phase present in the sinter. Above 500°C aluminium-ammonium sulphate converts into Al₂/SO₄/₃.

The amount of aluminium that will go into 5% H₂SO₄ solution from the sinters depends on the sintering temperature. It increases from 10% of the total Al₂O₃ content in halloysite at 250°C to nearly 100% at 600°C.

The sintering of halloysite with /NH₄/₂SO₄ and the treatment of sinters with 5% H₂SO₄ solution leads to the destruction of the structure of halloysite. With a rise in the sintering temperature aluminium is gradually removed from the octahedral sheet and the tetrahedral

sheet undergoes rearrangement towards three-dimensional condensation. As a result of these processes, a structure of the silica gel type forms at a temperature higher than 500°C.

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STUDIUM REAKCJI KRZEMIANOW WARSTWOWYCH ZE STOPIONYM SIARCZANEM AMONOWYM

CZESC II. WPŁYW TEMPERATURY NA REAKCJE HALOIZYTU Z /NH₄/₂SO₄

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

Wykonano na derywatografie badania termiczne siarczanu amonowego /fig. 1/ oraz mieszanin haloizytu z siarczanem amonowym o proporcjach 1:5 i 5:1 /fig. 2 i 3/. W celu ustalenia rodzaju przemian, którym towarzyszą efekty cieplne na krzywych termicznych, ogrzewanie prowadzono do temperatury początku i końca kolejnych efektów na krzywej DTA i po szybkim ostudzeniu próbki, rentgenograficznie określano skład fazowy.

Mieszanie z nadmiarem /NH₄/₂SO₄ /1:5/ wygrzewano z kolei w piecu muflowym w temperaturach 250-600°C. Określano skład fazowy spieków oraz ilość Al₂O₃ dającego się wyekstrahować 5-procentowym roztworem H₂SO₄.

Prześledzono zmiany zachodzące w strukturze haloizytu pod wpływem spiekania z /NH₄/₂SO₄ i traktowania H₂SO₄, na podstawie badań spektroskopowych w podczerwieni.

W zakresie temperatur 250-400°C produktem reakcji jest /NH₄/₃Al/SO₄/₃. W 300°C pojawia się także NH₄Al/SO₄/₂, którego zawartość w spieku wzrasta wraz ze wzrostem temperatury. W zakresie 450-500°C jest on jedyną fazą siarczanową stwierdzoną w spieku. Powyżej temperatury 500°C NH₄Al/SO₄/₂ przechodzi w Al₂/SO₄/₃.

Ilość glinu jaką można przeprowadzić do 5-procentowego roztworu H₂SO₄ ze spieków, zależy od temperatury spiekania /fig. 4/. Wzrasta ona od 10% całkowitej zawartości Al₂O₃ w haloizycie, dla temperatury 250°C, do prawie 100% w 600°C.

Spiekanie haloizytu z /NH₄/₂SO₄, a następnie traktowanie spieków roztworem H₂SO₄ prowadzi do destrukcji struktury haloizytu. W miarę wzrostu temperatury spiekania następuje stopniowe usuwanie glinu z warstwy oktaedrycznej, a warstwa tetraedryczna ulega przebudowie w kierunku trójwymiarowej kondensacji, w wyniku czego w temperaturze powyżej 500°C powstaje struktura typu gelu krzemionkowego /fig. 5/.

Fig. 1. Krzywe termiczne NH_4/SO_4 Fig. 2. Krzywe termiczne mieszaniny haloizytu z nadmiarem NH_4/SO_4 /1:5/Fig. 3. Krzywe termiczne mieszaniny haloizytu z niedomiarem NH_4/SO_4 /5:1/Fig. 4. Krzywa zależności stopnia reakcji α glinu od temperatury spiekania

Fig. 5. Widma w podczerwieni

a - haloizytu; $b-i$ - produktów spiekania haloizytu z NH_4/SO_4 /1:5/ w temperaturach: b - 250°C, c - 300°C, d - 350°C, e - 400°C, f - 450°C, g - 500°C, h - 550°C, i - 600°C, po obróbce 5-procentowym H_2SO_4

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ИЗУЧЕНИЕ РЕАКЦИИ СЛОЕВЫХ СИЛИКАТОВ СО СПЛАВЛЕННЫМ

СУЛЬФАТОМ АММОНИЯ

ЧАСТЬ II. ВЛИЯНИЕ ТЕМПЕРАТУРЫ НА РЕАКЦИИ ГАЛЛУАЗИТА С NH_4/SO_4

Резюме

Были проведены термические исследования на дериватографе сульфата аммония /фиг. 1/ а также смеси галлуазита с сульфатом аммония в пропорциях 1:5 и 5:1 /фиг. 2 и 3/. Для определения рода преобразований, которым сопутствуют тепловые эффекты на термических кривых, обогревание производилось до температуры начала и конца очередных эффектов на кривой ДТА и после быстрого охлаждения пробы, фазовый состав определяется рентгенографическим методом.

Смесь с избытком NH_4/SO_4 /1:5/ в свою очередь выгревалась в муфельной печи при температуре 250-600°C. Был определён фазовый состав спеков, а также количество Al_2O_3 , дающееся выэкстрагировать 5%-ым раствором

Были прослежены изменения выступающие в структуре галлуазита под действием спекания с NH_4/SO_4 и обработки раствором H_2SO_4 на основании ик-спектрографических исследований. В диапазоне температур 250-400°C продуктом реакции является $\text{NH}_4/\text{Al}/\text{SO}_4/3$. При 300°C появляется также $\text{NH}_4 \text{ Al}/\text{SO}_4/2$, содержание которого увеличивается с повышением температуры. В диапазоне 450-500°C он является единственной обнаруженной в спеке сульфатной фазой. При температуре свыше 500°C $\text{NH}_4 \text{ Al}/\text{SO}_4/2$ переходит в $\text{Al}_2/\text{SO}_4/3$.

Количество алюминия, которое можно перенести из спеков в 5%-ый раствор H_2SO_4 , зависит от температуры спекания /фиг. 4/. Оно возрастает

от 10% полного содержания Al_2O_3 в галлуазите при температуре 250°C до почти 100% при температуре 600°C.

Спекание галлуазита с NH_4/SO_4 и последующая обработка раствором H_2SO_4 ведёт к разрушению структуры галлуазита. По мере роста температуры спекания происходит постепенное удаление алюминия из октаэдрического слоя, тетраэдрический слой перестраивается в направлении трёхразмерной конденсации в результате чего при температуре свыше 500°C образуется структура типа силикагеля /фиг. 5/.

ОБЪЯСНЕНИЕ ФИГУР

Фиг. 1. Термические кривые NH_4/SO_4 Фиг. 2. Термические кривые смеси галлуазита с избытком NH_4/SO_4 /1:5/Фиг. 3. Термические кривые смеси галлуазита с недостатком NH_4/SO_4 /5:1/Фиг. 4. Кривая зависимости степени реакции α алюминия от температуры спекания

Фиг. 5. Ик-спектры

a - галлуазита, $b-i$ - продуктов спекания галлуазита с NH_4/SO_4 /1:5/ в температурах: b - 250°C, c - 300°C, d - 350°C, e - 400°C, f - 450°C, g - 500°C, h - 550°C, i - 600°C, после обработки 5%-ым раствором H_2SO_4