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The thermal dissociation of basic aluminium-potassium sulphate in an atmosphere of hydrogen and carbon monoxide

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Abstract

The mechanism and kinetics of the desulphuration of basic aluminium-potassium sulphate in a mixture of H_2 and CO (3:1 by mole) was studied as a function of the pressure of the reducing mixture. The studies provided the temperature region of the process, the nature of all the solid and gaseous intermediate products, as well as the equations and the kinetic parameters describing the rate of desulphuration of the compound. Complex analysis of the obtained results permits the conditions of the process to be determined, i.e. the temperature and the composition of the gas phase, enabling aluminium oxide modifications of required specific properties to be manufactured.

Keywords: Active alumina; Kinetics; Reduction calcination; Synthetic alunite

1. Introduction

Former studies have shown [1–6] that the thermal decomposition of basic aluminium salts under reducing conditions is profitable for two reasons. Firstly, the desulphuration of these salts under such conditions may be carried out at much lower temperatures, which reduces the energy consumption of the process and, in the case of potassium alunite, provides more complete decomposition of the starting material. Secondly, creation of reducing conditions in the reaction zone gives a possibility of obtaining products of better physicochemical properties [7–9].

To undertake the process under technological conditions, it was necessary to investigate the effect of a 3:1 (by mole) mixture of H_2 and CO as a reducing agent. Under industrial conditions such a mixture can be obtained in the process of methane conversion with steam. The results of studies on the decomposition of basic aluminium

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salts in a hydrogen atmosphere or in carbon and water vapour media have shown that the reducing agent only affects the course of the final stage of the decomposition, which is the desulphuration. These results have also enabled both the temperature regions of the desulphuration process and its stoichiometry to be determined. The studies have shown that dissociation is a complex process consisting of many intermediate, often overlapping stages. This complexity results in considerable difficulties in determining the regions of individual reactions and in the study of their rates. This work has been an attempt to determine the effect of a mixture of hydrogen and carbon monoxide on the mechanism and kinetics of decomposition of basic aluminium-potassium sulphate.

2. Experimental

The sample studied was basic aluminium-potassium sulphate, first dehydrated by heating for 1 h at 570°C in air atmosphere (sample P/570/air). The temperature of calcination was attained in a dynamic manner by heating at a rate of 10 K min^{-1}.

Analysis of the samples involved: determination of X-ray diffraction patterns using a HZG-4C diffractometer produced by Carl Zeiss, Jena, using Co Kα radiation; infrared absorption studies with a Specord 75 IR spectrophotometer using KBr tablets; and thermogravimetric studies using a Derivatograph C produced by MOM, Budapest. The kinetic measurements for the desulphuration of the P/570/air sample were carried out in a glass apparatus which provided a controlled gas atmosphere, with a quartz spiral as a weighing element. A 20 mg sample of the material was first degassed for 1 h at 200°C, then it was shifted outside the heating zone of the furnace and the latter was heated to the temperature of measurement. Predetermined amounts of hydrogen and carbon monoxide were then introduced and supplemented with argon to match atmospheric pressure. The sample was then placed again in the heating zone of the furnace, and the loss of mass of the sample was recorded as a function of time. The rate of desulphuration of the sample of basic aluminium-potassium sulphate was measured in three series of experiments carried out at the following partial pressures of H_2 and CO: 133 hPa H_2 and 44 hPa CO, 66 hPa H_2 and 22 hPa CO, and 33 hPa H_2 and 11 hPa CO. The degree of transformation was calculated from the formula

$$\alpha = \Delta m / \Delta m_{\mathrm{max}}$$

where Δm is the loss of sample mass in time t, and Δm_{max} corresponds to the amount of SO_3 bound with aluminium in the sample. In order to identify the intermediate products of desulphuration, more detailed studies were performed on the decomposition of basic aluminium-potassium sulphate at 670°C under partial pressures of 66 hPa H_2 and 22 hPa CO. The kinetic curve obtained under these conditions exhibited a rather long plateau which made it possible to single out individual stages of the process of desulphuration (see the kinetic curve for temperature 670°C in Fig. 7). The initial sample was decomposed under isothermal and isobaric conditions by means of a method applied in kinetic measurements, using the following times of heating: 20 min (P/670/20), 70 min (P/670/70), and 120 min (P/670/120). In all cases the solid decomposition products were subjected to thermogravimetric, X-ray diffraction, and infrared absorption analyses.

3. Results and discussion

The X-ray diffraction pattern, the infrared spectrum, and the TG and DTG curves obtained for the P/570/air sample are shown in Figs. 1 (curve P/570/air), 2 (curve P/570/air), and 3 (curve P/570/air), respectively. The obtained results show that the sample of basic aluminium-potassium sulphate calcinated for 1 h at 570°C was dehydrated with simultaneous destruction of the alunite structure. The positions and heights of the peaks on the X-ray diffraction pattern obtained are characteristic for a well-developed crystallographic form of $KAl(SO_4)_2$.

The results of the measurements of the desulphuration rate of basic aluminium-potassium sulphate obtained in the three series of experiments are presented in Figs. 4, 5, and 6, respectively, for the following pressures of H_2 and CO: 133 hPa H_2 and 44 hPa CO, 66 hPa H_2 and 22 hPa CO, and 33 hPa H_2 and 11 hPa CO.

The results of kinetic measurements carried out at selected constant temperatures under various pressures of the reducing agent are shown in Fig. 7. The shape of the kinetic curves remains basically unchanged, but one can observe a distinct increase of reaction rate with increasing pressure of H_2 and CO. The shape of the kinetic curves (Figs. 4–6) in the upper range of the temperature region studied shows that the desulphuration of the aluminium compounds is accompanied by elimination of sulphur combined with potassium, which is manifested by exceeding a transformation

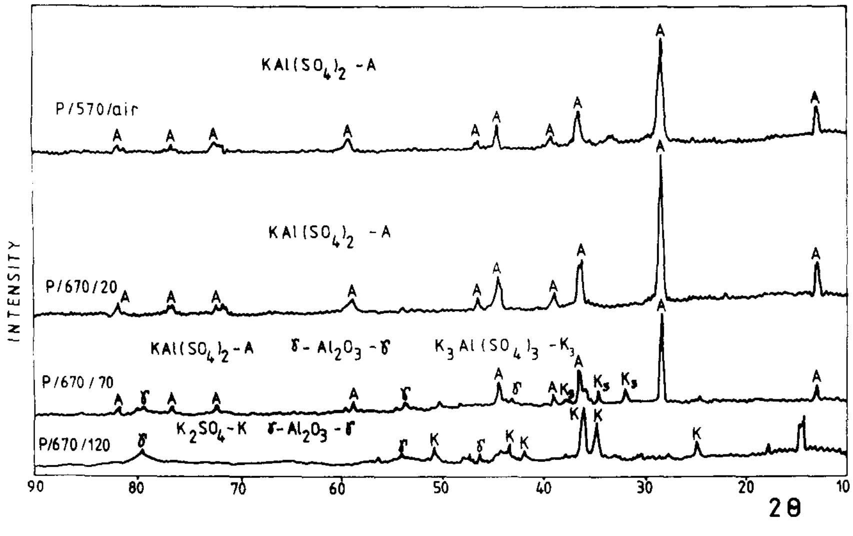

Fig. 1. X-ray diffraction patterns of intermediate products of decomposition of basic aluminium-potassium sulphate in an atmosphere of 66 hPa H_2 + 22 hPa CO.

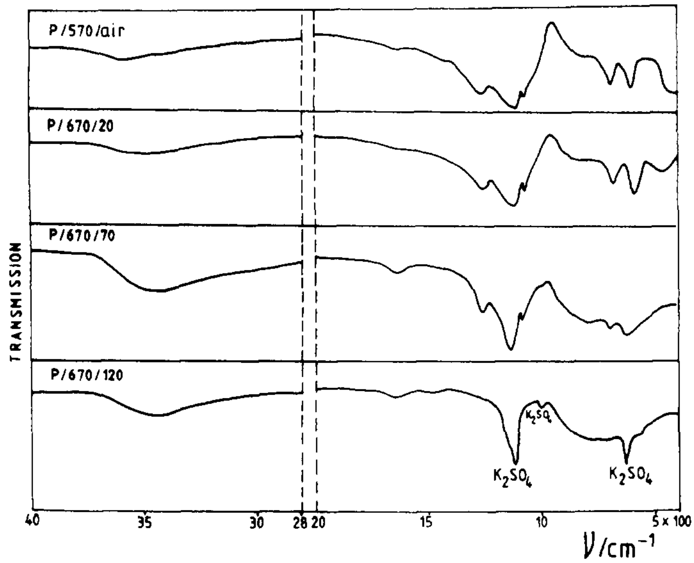

Fig. 2. Infrared spectra of intermediate products of basic aluminium-potassium sulphate decomposition in an atmosphere of 66 hPa H_2 + 22 hPa CO.

degree of 1. The shape of the kinetic curves enables a distinct separation of the two stages of desulphuration. Elimination of the sulphur oxides combined with potassium takes place at temperatures above 670°C at partial pressures of 33 hPa H_2 + 11 hPa CO, at above 650°C under pressure of 66 hPa H_2 + 22 hPa CO, and at above 630°C under pressure of 133 hPa H_2 + 44 hPa CO under conditions of 2 h thermal decomposition of the compound.

Figs. 1–3 show the results of studies of decomposition products obtained at 670°C for reaction times of 20 min (curves P/670/20), 70 min (curves P/670/70), and 120 min (curves P/670/120).

The X-ray diffraction pattern of the sample P/670/20, shown in Fig. 1, exhibits distinct reflections due to $KAl(SO_4)_2$. Also the shape of the infrared spectrum does not change appreciably with respect to that of the initial sample (curves P/570/air and P/670/20 in Fig. 2). The DTG curve of the sample P/670/20 shown in Fig. 3 exhibits a peak at 820°C, accompanied by a mass loss, due to desulphuration of aluminium. The X-ray diffraction pattern of the sample P/670/70 (Fig. 1) contains, in addition to reflections characteristic for $KAl(SO_4)_2$, also the reflections due to $K_3Al(SO_4)_3$ and γ-Al_2O_3. The presence of reflections due to the latter compound is confirmed by the shape of the infrared spectrum, which contains a distinct large band in the range 400–1000 cm^{-1}, characteristic of γ-Al_2O_3 (curve P/670/70 in Fig. 2). Analysis of the thermogravimetric curves shows that the elimination of sulphur combined with aluminium has not been completed. Complete desulphuration of aluminium compounds may be seen on analysing the shape of the thermogravimetric curves of sample P/670/120 (curve P/670/120 in Fig. 3). This conclusion is confirmed by the results of

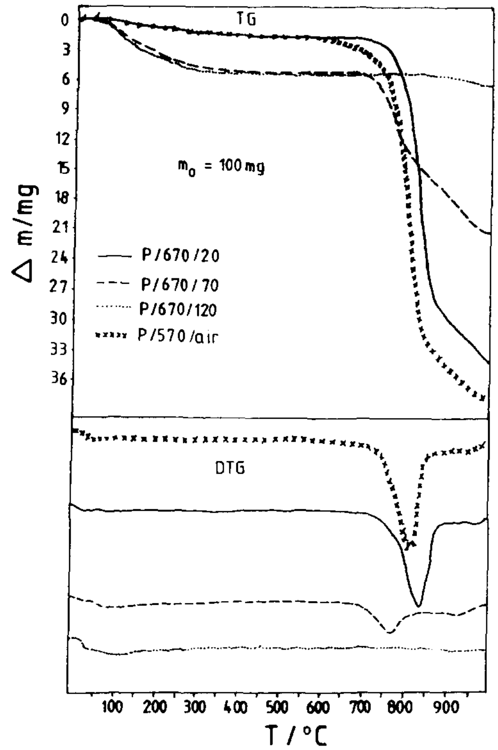

Fig. 3. Thermogravimetric curves of intermediate products of basic aluminium-potassium sulphate decomposition in an atmosphere of 66 hPa H_2 + 22 hPa CO.

X-ray diffraction and infrared absorption analyses. The X-ray diffraction pattern contains no more reflections characteristic for $KAl(SO_4)_2$ or $K_3Al(SO_4)_3$. There are only reflections due to K_2SO_4 and γ-Al_2O_3 (curve P/670/120 in Fig. 1). The infrared absorption spectrum of the sample P/670/120 (Fig. 2) presents three bands at wavenumbers 622, 985, and 1120 cm^{-1}, characteristic for K_2SO_4, and a broad band from 400 to 1000 cm^{-1}, due to Al_2O_3. The shape of the infrared spectrum does not exclude the presence of potassium aluminate in the sample (bands at 620 to 670 cm^{-1} and 800 to 920 cm^{-1}).

The results of the studies confirm that the desulphuration of basic aluminium-postassium sulphate proceeds in two stages, and the decomposition scheme is similar to that obtained for its decomposition in hydrogen [1].

The first step of the decomposition consists of the elimination of sulphur bound with aluminium. This step leads to formation of γ-Al_2O_3 and K_2SO_4 in the solid reaction products. In the second step, potassium sulphate is desulphurized with the simultaneous formation of potassium aluminate in the solid phase.

The treatment of the desulphuration kinetics has been limited to only the first step of the reaction, which is the removal of sulphur combined with aluminium. In the treatment of the results of kinetic studies, the choice of the function g(α) optimal for

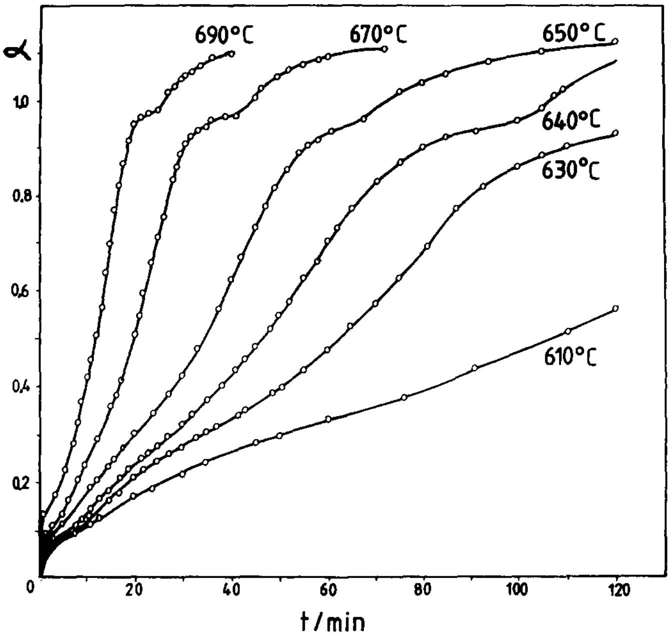

Fig. 4. Kinetic curves of desulphuration of basic aluminium-potassium sulphate in an atmosphere of $3H_2 + CO$ (133 hPa H_2 + 44 hPa CO).

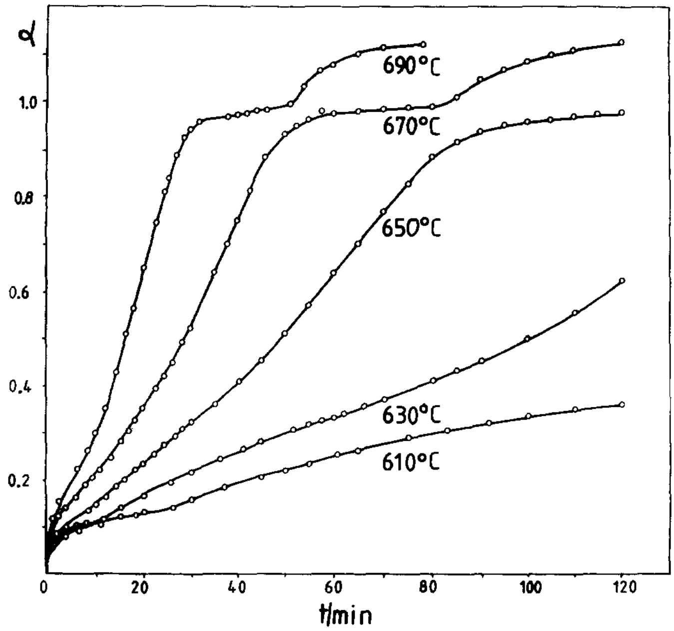

Fig. 5. Kinetic curves of desulphuration of basic aluminium-potassium sulphate in an atmosphere of $3H_2 + CO$ (66 hPa H_2 + 22 hPa CO).

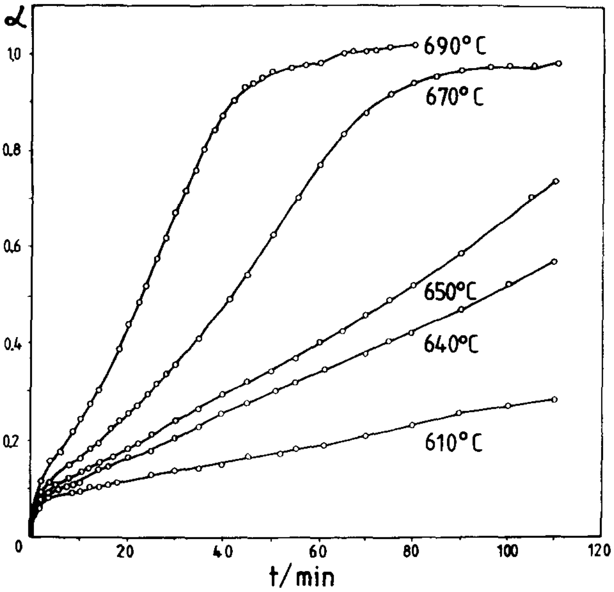

Fig. 6. Kinetic curves of desulphuration of basic aluminium-potassium sulphate in an atmosphere of $3H_2 + CO$ (33 hPa H_2 + 11 hPa CO).

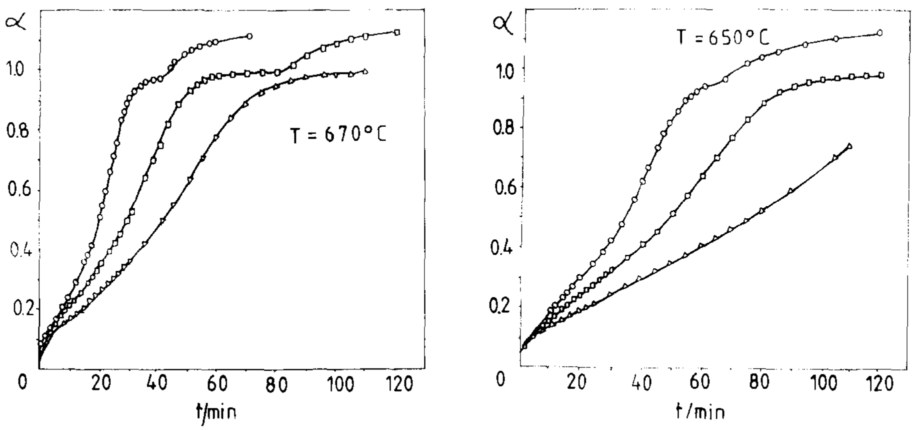

Fig. 7. Isothermal desulphuration of basic aluminium-potassium sulphate as a function of pressure of $3H_2 + CO$ mixture: ○, 133 hPa H_2 + 44 hPa CO; □, 66 hPa H_2 + 22 hPa CO; ▽, 33 hPa H_2 + 11 hPa CO.

description of the experimental results was effected in two ways: by a method based on utilization of statistical criteria [10]; and by a method of comparing the shape of experimental curves representing the transformation degree as a function of reduced time with that of theoretical curves drawn for individual forms of $g(\alpha)$ [11].

Analysis of the relationships between the transformation degree and reduced time, shown as examples in Fig. 8a and b shows that the kinetic curves obtained in individual

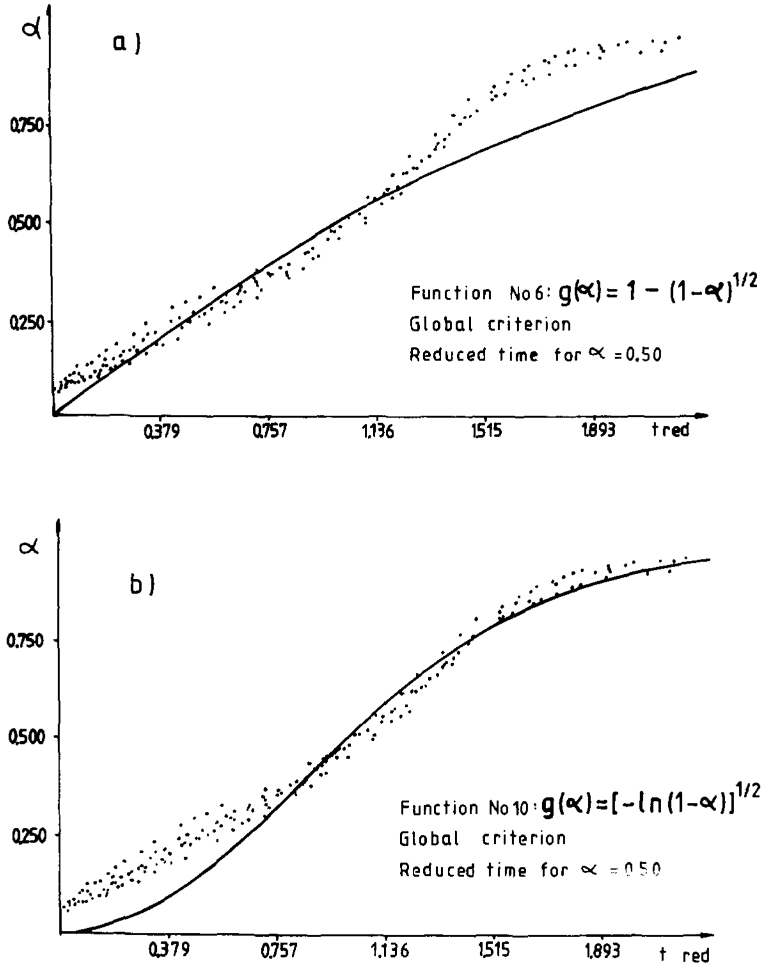

Fig. 8. Relationship between transformation degree and reduced time for the process of desulphuration of basic aluminium-potassium sulphate in an atmosphere of 133 hPa H_2 + 44 hPa CO.

experimental series are affinely transformable, which may be accounted for by the isokinetic nature of the process within the temperature range studied. It is impossible, however, to describe them by means of a single kinetic equation valid within the whole range of transformation degree. A complete kinetic analysis shows that up to a transformation degree of 0.5 the kinetic curves are most satisfactorily described by the function $g(\alpha) = 1 - (1 - \alpha)^{1/2}$, and above the transformation degree of 0.5 by the function $g(\alpha) = [-\ln(1 - \alpha)]^{1/2}$.

The kinetic parameters identified with the aid of the above functions for description of experimental data are collected in Table 1.

Table 1
Kinetic parameters for the first stage of desulphuration of basic aluminium-potassium sulphate in an atmosphere of hydrogen and carbon monoxide
$\alpha < 0.5$; $g(\alpha) = 1 - (1 - \alpha)^{1/2}$
Model 2: $g(\alpha) = a + Kt$; constant weights

Composition of the mixture	A/min^{-1}	E/(kJ mol^{-1})
133 hPa H_2 + 44hPa CO	2.2×10^8	186
66 hPa H_2 + 22 hPa CO	16.0×10^8	204
33 hPa H_2 + 11 hPa CO	10.7×10^8	204

$\alpha > 0.5$; $g(\alpha) = [-\ln(1 - \alpha)]^{1/2}$
Model 1: $g(\alpha) = kt$; constant weights

Composition of the mixture	A/min^{-1}	E/(kJ mol^{-1})
133 hPa H_2 + 44 hPa CO	2.72×10^{10}	212.7
66 hPa H_2 + 22 hPa CO	1.92×10^{10}	213.5
33 hPa H_2 + 11 hPa CO	1.30×10^{10}	213.5

4. Conclusions

Taking into account the studies of the steps and the kinetics of decomposition of basic aluminium-potassium sulphate in the atmosphere of hydrogen and carbon monoxide, one may conclude that desulphuration of the salt is a complex process which proceeds through many intermediate stages.

Nevertheless, complex analysis of the results makes it possible to determine the conditions of realization of the process, i.e. the temperature range, and the composition and pressure of reducing atmosphere, necessary for obtaining low-temperature modifications of aluminium oxide.

The release of the sulphur oxides combined with aluminium takes place at 670°C at partial pressures of 33 hPa H_2 + 11 hPa CO, at 650°C under pressure of 66 hPa H_2 + 22 hPa CO, at 630°C under pressure of 133 hPa H_2 + 44 hPa CO under conditions of a two-hour thermal decomposition of the compound.

In these conditions, the decomposition product of alunite is a mixture of γ-Al_2O_3 and K_2SO_4, from which potassium sulphate can be washed to obtain active aluminium oxide.

Acknowledgements

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