

THERMOANALYTICAL STUDIES ON THE PREPARATION OF INDUSTRIAL CRYSTALLINE ALUMINIUM SULPHATE

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Changes in the water content of aluminium sulphate hydrate were investigated gravimetrically at room temperature in air with different relative humidities. The samples conditioned in this way were characterized by thermoanalytical (TG, DTG, DSC) and X-ray diffraction measurements. Industrial aluminium sulphate hydrate obtained by freezing the melt has a partly crystalline structure. After grinding, this material crystallizes during storage. This process requires a humid atmosphere; increasing relative humidity brings about more intensive crystallization.

It was found that the crystallization of aluminium sulphate from the melt is facilitated by a higher water content of the melt.

Our group has been studying solid–liquid transformations for several years. One part of this research programme concerned the crystallization of sorbitol, described in this journal [1]. The present paper gives an account of the behaviour of aluminium sulphate, which (similarly to sorbitol) is quite difficult to crystallize. The goal was to determine the optimum circumstances of this process.

In the literature, 13 neutral aluminium sulphate hydrates and more than 40 basic or acidic salts have been reported. A number of these modifications are of negligible practical importance, and even their existence is often questionable. The formula $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ has traditionally been written for commercial dry alum; however, the latter is partly dehydrated [2]. The stable form with the highest amount of water was reported to contain 17 moles [3, 4] or 16 moles [5–7] of water. Other well-defined crystal hydrates contain 14 moles [4, 7, 8], 12 moles [4, 7, 8], 9 moles [5, 7–11] and 6 moles [5, 12–14] of water. The majority of these hydrates were prepared by thermal decomposition from forms with higher water contents; the new phases were identified by means of thermoanalytical methods and X-ray diffraction.

The data in the above publications show that the problems relating to the dehydration processes and the phases that actually exist have not been completely solved so far.

Technical or commercial grade aluminium sulphate hydrate is available both as lumps or a granular solid containing 17.0–17.5% Al_2O_3 , and also as a solution containing 7.5–8.5% Al_2O_3 . The solid product is usually prepared on cooled stainless steel or rubber belts, by freezing the melt. Some other processes have also been reported, involving granulation, drying in a fluid bed or spray-drying [2, 15–17]. The aluminium sulphate hydrates obtained in these processes are generally amorphous or slightly crystalline.

The crystallization of aluminium sulphate from solution was studied by Namour et al. by means of differential scanning calorimetry [18], but similar investigations on crystallization from melts have not been reported.

Experimental

The aluminium sulphate used in this work was manufactured by the Mosonmagyaróvár Alumina and Synthetic Corundum Works, Hungary, from alumina (obtained by the Bayer process) and sulphuric acid. Samples were taken of the block material frozen from the melt, and of the ground commercial aluminium sulphate with a particle size of < 3 mm. The notation MOTIM refers to these samples. The most important properties of the ground material, determined according to the standard [19] were: Al_2O_3 content 16.5%, insoluble residue 0.04%, Fe content 0.005%, pH of 5% aqueous solution 3.1. The behaviour of the MOTIM samples was compared to that of commercial granular aluminium sulphate manufactured by Boliden Co. (Reymersholmsberken, Helsingborg, Sweden) and to that of the analytical grade Merck (Darmstadt, GFR) reagent.

Samples of about 2 g were placed into atmospheres with different relative humidities (R. H.) at 20° , and the mass change in these samples was determined as a function of time. Atmospheres with R. H. 45, 63, 80 and 92% were maintained in desiccators containing saturated aqueous solutions of potassium carbonate, ammonium carbonate, ammonium sulphate and sodium carbonate, respectively; a dry atmosphere above phosphorus pentoxide was also applied. This conditioning was repeated with samples whose water contents had been decreased to about 9 moles per mole of $\text{Al}_2(\text{SO}_4)_2$ in a drying oven at 128° .

TG and DSC investigations on the original samples and those obtained after conditioning for 125 days were carried out with the Du Pont 990 Thermal Analysis System. In the thermogravimetric measurements, 10–11 samples were heated at a rate of 10 deg/min in static air. For the DSC runs, 2–3 mg samples were put into aluminium pans coated by an oxide layer, and the sample holders were then hermetically sealed. The heating rate was 5 deg/min. Crystalline phases were identified through X-ray diffraction. Cu K_α radiation and a 1 deg/min scanning rate were applied in measurements on an HZG-4/c diffractometer (Zeiss, Jena, DDR).

The effect of the water content on the crystallization process was investigated on a MOTIM aluminium sulphate. Parts of this material were kept in atmospheres with

92% and 0% R. H. to achieve the desired water contents. The samples thus obtained were heated in the DSC cell at a rate of 5 deg/min to 120°, the free cooling curves of the resulting melts were then recorded.

Results and discussion

The water content of industrial MOTIM aluminium sulphate kept in air with different R. H. is plotted in Fig. 1 as a function of time. The sample above phosphorus pentoxide contained water corresponding to about 10 molecules after 125 days, but the mass was still slowly decreasing.

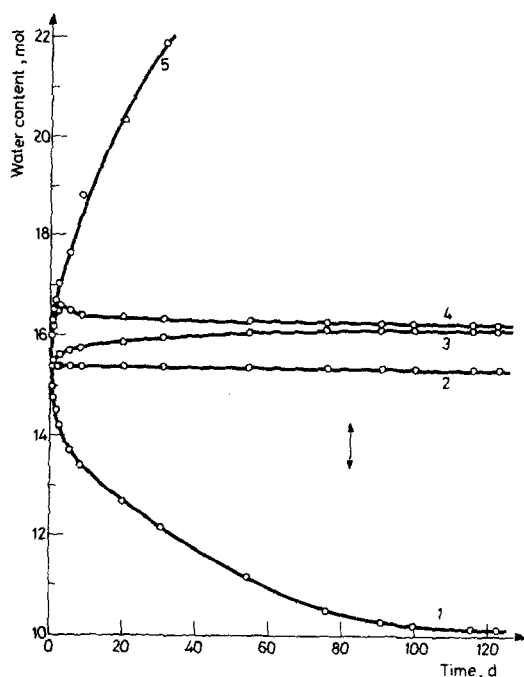


Fig. 1 The water content of aluminium sulphate as a function of time in air with different relative humidities. 1, 0% R. H.; 2, 45% R. H.; 3, 63% R. H.; 4, 80% R. H.; 5, 92% R. H.

In the atmosphere with the highest R. H. the sample took up a large amount of water and liquefied. The mass of the sample kept in an atmosphere with 45% R. H. was constant; those under 63% and 80% R. H. reached a constant level of 16.2 molecules in about 100 days and 16.3 molecules in about 75 days, respectively. The maximum in curve 4 of Fig. 1 is reproducible; it was also observed with the Boliden aluminium sulphate. The composition range specified in the standard for industrial aluminium sulphate [2, 19] is indicated by the double-headed arrow in Fig. 1. It should

be noted that in air with normal R. H. (40–80%) the equilibrium water content is higher than the maximum allowed by the standard.

The TG and DTG curves of the samples after conditioning in atmospheres with different R. H. are shown in Fig. 2. The thermogravimetric characteristics of the starting material were the same as those of the sample kept under 45% R. H. The curves reveal that an increase in the R. H. of the air led to a higher amount of weakly-bound water, and also to a change in the shape of the dehydration steps. The highest dehydration step shifted towards lower temperatures, and the temperature and the shape of the second step were also influenced. These effects are illustrated by the DTG curves of samples treated in atmospheres with 45 and 80% R. H., shown in Fig. 2.

The differences between the TG and DTG curves of the particular samples are too large to be caused simply by the small differences in the amount of weakly-bound water. The explanation was obtained from the DSC and the X-ray diffraction data. The diffraction patterns in Fig. 3 indicate an increase in crystallinity as a result of treatment in atmospheres with higher R. H. The patterns also show that the sole effect is an increase in the intensities of reflections found in the pattern of the starting material (whose diffraction pattern was practically identical with that of the sample kept under 45% R. H.); consequently, no new crystalline phase formed. On the basis of the calculated d values (distances of lattice plane), the crystal structures of the samples were similar to that of alunogen, a natural mineral. Alunogen was reported to contain 17 and 18 molecules of water per $\text{Al}_2(\text{SO}_4)_3$ unit [4, 20], but on exposure to air it probably stabilizes at a level lower than 17 molecules.

Above phosphorus pentoxide, amorphization of the material predominated, as shown by the appearance of broad bands in the X-ray diffraction patterns.

The maximum in curve 4 of Fig. 1 is related to the formation of a crystalline structure. The highly disordered starting material rapidly takes up water in the humid atmosphere, and at the same time crystallization takes place. The equilibrium water contents of the crystalline phases formed in this process are lower than the amount taken up by the sample. The excess gradually evaporates. This proves that water sorption by the sample precedes crystallization. Similarly, the crystallization is responsible for the shift in the DTG peak relating to the second dehydration step, from 337° to 360° (see Fig. 2).

These conclusions are confirmed by the behaviour of the analytical grade Merck sample as well. The crystallinity of this material (in the original state) is substantially higher than that of the MOTIM samples. Thus, the Merck sample did not exhibit the maximum discussed above, and the second dehydration step of the original material reached its peak at 382° .

The effects of the above phenomena on the technology of aluminium sulphate manufacturing were also investigated. In the process used at the Mosonmagyaróvár Alumina and Synthetic Corundum Works, the molten product of the reaction is frozen in basins with air cooling. The thickness of the material in the basins is about 5 cm. The upper part of Fig. 4 shows the TG curves of samples taken from the top, the centre and the bottom layer immediately after the end of the technological freezing.

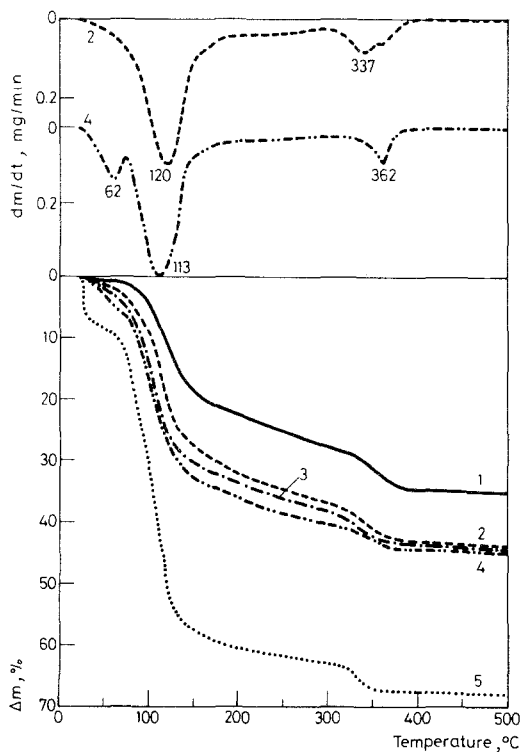


Fig. 2 TG and DTG curves of aluminium sulphate samples conditioned in air with different humidities. R. H. values during conditioning: 1, 0%; 2, 45%; 3, 63%; 4, 80%; 5, 92%

The water contents and the thermal behaviour of the layers are visibly different. A fraction of each layer was ground and subsequently stored in air at room temperature for 3 years. The TG curves of these samples are given in the lower part of Fig. 4. The curves prove that water was taken up by the samples after grinding, with the result that the aluminium oxide contents of the industrial aluminium sulphates were lower than the required standard value. The TG curves also show that the differences between the samples from different layers of the product had almost disappeared by the end of the storage. This levelling-off is explained by the increase in crystallinity of the sulphate and the uptake of an equilibrium amount of water corresponding to the humidity of the surrounding atmosphere. The change in the degree of crystallinity could be detected by means of X-ray diffraction and DSC. Parallel samples from the top layer of an aluminium sulphate block were stored for different durations in closed vessels at room temperature. The DSC curves of these samples are illustrated in Fig. 5. The sample stored for 3 days exhibit several peaks. The first one (above 50°) is assigned to the transition of the amorphous part; an exotherm then indicates crystallization of aluminium sulphate hydrate. The broad endotherm with peak at 101° relates to the melting of a poorly crystalline fraction of the sample. It should be noted

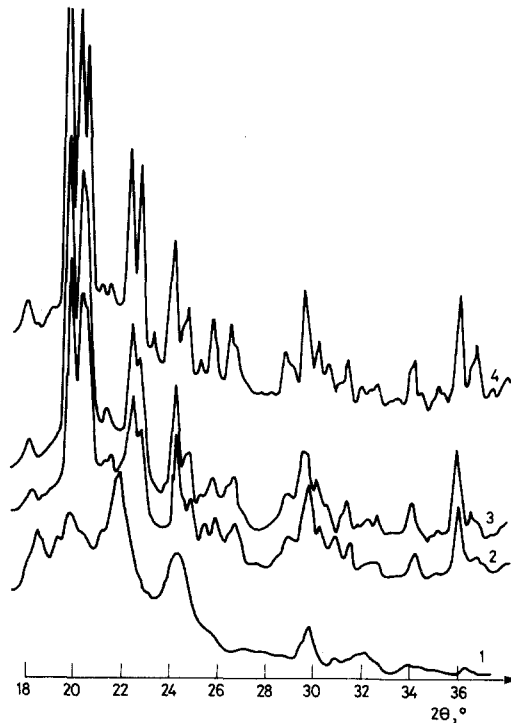


Fig. 3 A characteristic region of the X-ray diffraction patterns of aluminium sulphate samples, after conditioning in air with different humidities. R. H. values during conditioning: 1, 0%; 2, 45%; 3, 63%; 4, 80%

that the mass of sample 1 is about 5 times higher than those of samples 2 and 3. The phase transition of the crystalline fraction is the predominant effect in the curve recorded after 14 months of storage, and the behaviour of the sample stored for 3 years is characteristic of the melting of a totally crystalline material. The extremely slow rate of this process may be attributed to the low partial pressure of water vapour in the vessels, and to the slow diffusion of water into the compact particles of ground aluminium sulphate, which have a small specific surface area. Accordingly, less time was required for the crystallization of MOTIM material ground to finer particles.

Generally speaking, the rate of water sorption and crystallization depends on the morphology of the material. A comparison of the behaviour of the MOTIM samples with that of the granular Boliden product (consisting of particles with a loose texture) confirmed this: the time needed for crystallization of the Boliden samples was substantially less in all the cases (i. e. atmospheres with different R. M.) studied our experiments.

Crystallization experiments were repeated with samples partly dehydrated in a drying oven, in order to decide whether the humidity of the air can cause crystallization of aluminium sulphate with a significantly lower water content. It was found that

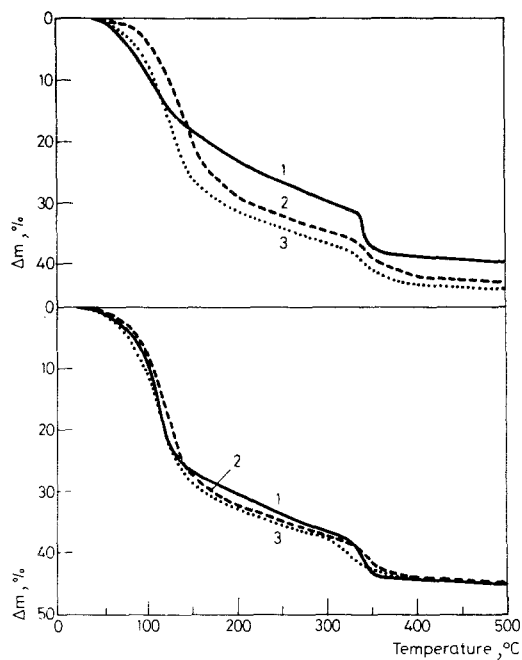


Fig. 4 TG curves of MOTIM aluminium sulphate samples taken from the top (1), centre (2) and bottom (3) layers of the frozen block. The upper curves were recorded immediately after manufacture, the lower ones after storing

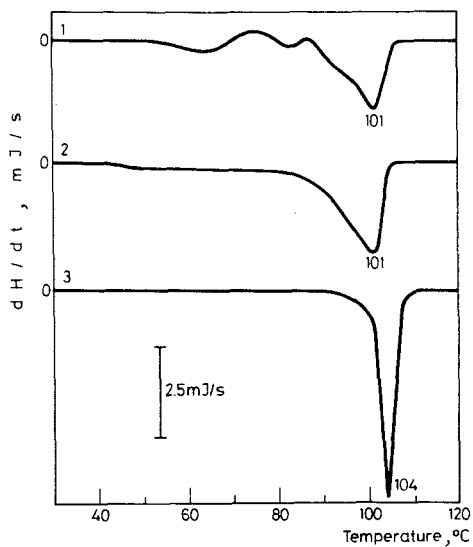


Fig. 5 DSC curves of MOTIM aluminium sulphate samples taken from the top layer after 3 days (1, samples mass 9.83 mg), 14 months (2, 2.05 mg) and 3 years (3, 2.01 mg) of storage

samples dehydrated almost to the composition $\text{Al}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$, which were X-ray amorphous, did crystallize in humid atmospheres, and an increase in R. H. brought about a higher rate of crystallization.

In another series of experiments, aluminium sulphate melts with different water contents were cooled in the DSC cell, and the process of crystallization was followed. The DSC curves in Fig. 6 demonstrate that the crystallization of samples with lower water contents required 40–60° supercooling; moreover, the sulphate containing 12.1 molecules of water did not crystallize at all. On the other hand, the enthalpy changes calculated from the peak areas showed that none of the samples (not even that with 18.4 H_2O) reached the original level of crystallinity. This effect is visible in Fig. 6 too, from a comparison of the crystallization peak with the melting curve at the top of the diagram.

A MOTIM sample conditioned in an atmosphere with 80% R. H. was treated in a series of heating and cooling (melting-crystallizing) cycles in the DSC cell. Subsequent melting curves are illustrated in Fig. 7. The low-temperature region of the curves relating to the fifth and sixth meltings (drawn with a higher sensitivity) indicated the softening of the amorphous fraction. In the subsequent cycles the strength of the water bonding in the solid decreases. Thus, during heating an increasing frac-

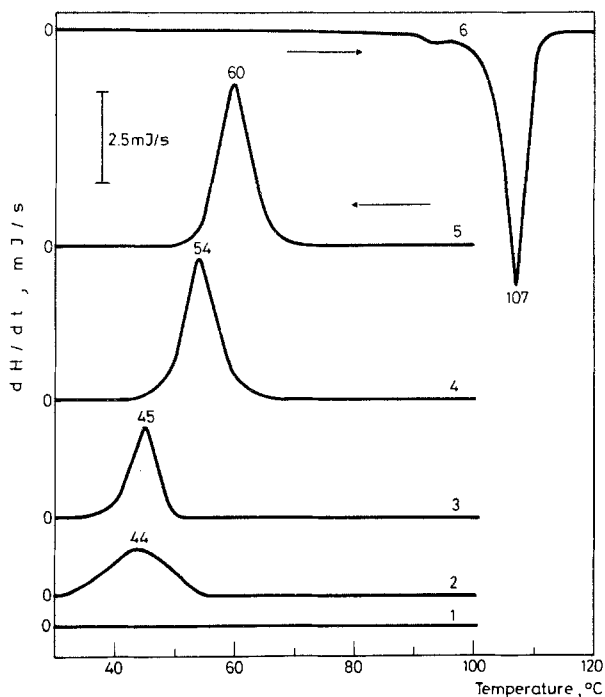


Fig. 6 DSC curves of the crystallization of aluminium sulphate melts with different water contents: 1, 12.1; 2, 14.1; 3, 16.2; 4, 17.6; 5, 18.4 molecules of water per $\text{Al}_2(\text{SO}_4)_3$. The uppermost curve demonstrates the melting of sample 5

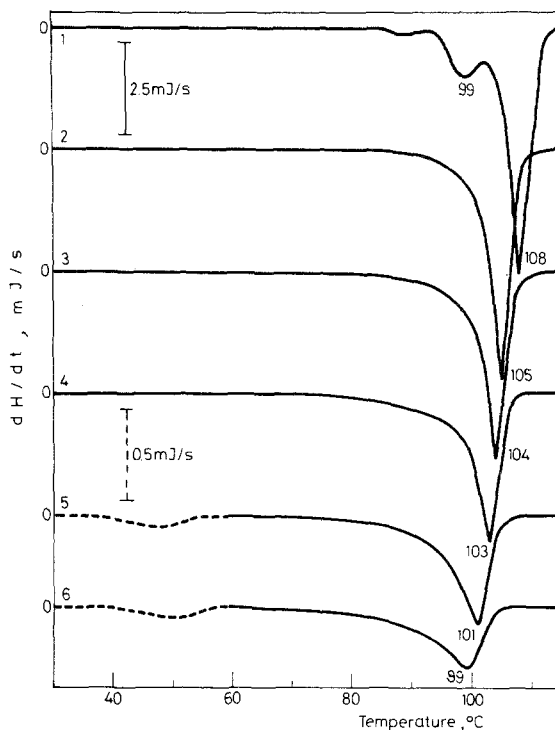


Fig. 7 The behaviour of aluminium sulphate hydrate in repeated melting–freezing cycles. DSC curves of a MOTIM aluminium sulphate sample after conditioning in air with 80% R. H. Serial numbers of subsequent cycles are indicated on the left-hand side

tion of water acts as a solvent, dissolving part of the solid aluminium sulphate. This effect results in lower onset temperatures of the endotherm.

The difference between the behaviour of the material in the DSC experiments and that in technology should also be discussed. The question is why part of the aluminium sulphate crystallized in the DSC cell, while a product amorphous to X-rays was formed in the technological freezing. The reason for this difference is that the order of the structure does not totally cease in the high-viscosity sulphate melt, provided the starting solid is at least partly crystalline. On the freezing of such a melt, a solid with a crystalline fraction is obtained. The melt formed in the industrial process is completely disordered; consequently, its crystallization should be initiated by an external effect (e.g. inoculation).

Conclusions

Storage in contact with a humid atmosphere brings about the crystallization of industrial aluminium sulphate obtained by freezing the melt. Crystallization is in-

tensified by increase of the R. H. of the atmosphere. Depending on the R. H., the water content of samples conditioned at room temperature in air with 45–80% R. H. is in the range 15.4–16.3 molecules of H_2O per $\text{Al}_2(\text{SO}_4)_3$. The crystal structure of conditioned samples is identical with that of alunogen.

In air with 92% R. H. at room temperature, aluminium sulphate liquefies regardless of the crystallinity. Above phosphorus pentoxide, amorphization of the structure was revealed by X-ray diffraction; the evolution of water lasts a very long time (it is detectable even after 125 days). In moist air the material with approximate composition $\text{Al}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$; obtained by thermal dehydration, behaves similar to the frozen industrial product.

A higher water content of the aluminium sulphate melt facilitates crystallization. Considerable supercooling occurs if external effects initiating crystallization are absent. In subsequent melting–freezing cycles the crystallinity decreases.

On the basis of the results discussed here and those of technological experiments, a new process has been developed for the crystallization of aluminium sulphate from the melt [21].

References

- 1 J. Szatisz, S. Gál, L. Fodor and E. Pungor, *J. Thermal Anal.*, 12 (1977) 351.
- 2 Kirk–Othmer Encyclopedia of Chemical Technology, 3th ed., vol. 2, Wiley-Interscience, New York, 1978, p. 245.
- 3 N. O. Smith and P. N. Wals, *J. Am. Chem. Soc.*, 76 (1954) 2054.
- 4 I. Náray-Szabó, *Acta Chim. Acad. Sci. Hung.*, 60 (1969) 27.
- 5 D. Taylor and H. Basset, *J. Chem. Soc.*, 4431 (1952).
- 6 V. D. Gorbunov and J. G. Druzlinin, *Techn. Nauk.*, 4 (9) (1962) 93.
- 7 P. Barret and R. Thiard, *Compt. Rend. Acad. Sci. Fr.*, 260 (1965) 2823 and 261 (1965) 2367.
- 8 G. Wattle-Marion and R. Thiard, *Compt. Rend. Acad. Sci. Fr.*, 261 (1965) 4105.
- 9 J. L. Henry and G. B. King, *J. Am. Chem. Soc.*, 71 (1949) 1142.
- 10 S. Bretsznajder and Z. Rojkowski, *Bull. Acad. Polonaise Sci.*, 17 (1969) 133.
- 11 A. B. Gancy, *Thermochim. Acta*, 54 (1982) 105.
- 12 E. B. Gitis, E. F. Dubrava, V. F. Annapol'ski, N. M. Pausenko and E. N. Gur, *Zh. Prikl. Khim.*, 46 (1973) 1838.
- 13 T. Sato, F. Ozawa, H. Teroda and J. Ikoma, *Proc. 5th Int. Conf. Therm. Anal.*, ed. H. Chihara, Kagaku Gijutsu-Sha Tokio, 1977, p. 269.
- 14 T. Sato, F. Ozawa and S. Ikoma, *J. Appl. Chem. Biotechnol.*, 28 (1978) 811.
- 15 Encyclopedia of Chemical Processing and Design, eds: J. J. McKetta and W. A. Cunningham, Marcel Dekker, Inc. New York and Basel, 1977, vol. 3., p. 120.
- 16 Ullmanns Encyklopädie der Technischen Chemie, Band 7, Verlag Chemie, Weinheim, 1974, p. 333.
- 17 A. A. Zapol'ski, L. A. Bander and Yu. I. Khvastuklin, *Khim. Technol., Vody*, 2 (1980) 454.
- 18 S. V. Naumor, A. P. Mozhaev, Y. D. Tretyakov and N. D. Topor, *Zh. Fiz. Khim.*, 56 (1982) 232.
- 19 Hungarian Standard, No. 1013-78.
- 20 P. Cesbron and J. Sadrzadeh, *Bull. Soc. Franc. Min. Crist.*, 96 (1973) 385.
- 21 Application for Hung. Patent, Filing No.: 3963/81.

Zusammenfassung – Veränderungen des Wassergehalts von Aluminiumsulfat-Hydrat bei Zimmertemperatur in Luft unterschiedlicher relativer Feuchtigkeit wurden gravimetrisch untersucht. Die auf diese Weise konditionierten Proben wurden durch thermoanalytische (TG, DTG, DSC) und röntgendiffraktometrische Messungen charakterisiert. Durch Erstarren der Schmelze erhaltenes industrielles Aluminiumsulfat-Hydrat ist teilweise kristallin. Nach dem Mahlen kristallisiert dieses Material während der Lagerung. Dieser Prozeß erfordert eine feuchte Atmosphäre, wobei sich der Kristallisationsgrad mit steigender relativer Feuchtigkeit erhöht. Es wurde festgestellt, daß die Kristallisation des Aluminiumsulfats durch einen höheren Wassergehalt der Schmelze gefördert wird.

Резюме – Изменение содержания воды в гидрате сульфата алюминия было исследовано гравиметрически при комнатной температуре в атмосфере воздуха с различной относительной влажностью. Полученные таким путем образцы были охарактеризованы методом ТГ, ДТГ, ДСК и методом дифракции рентгеновских лучей. Технический гидрат сульфата алюминия, полученный замораживанием расплава, имел частично кристаллическую структуру. После измельчения вещество при хранении кристаллизуется. Процесс кристаллизации требует влажной атмосферы, причем увеличение относительной влажности вызывает более интенсивную кристаллизацию. Найдено, что кристаллизация сульфата алюминия из расплава ускоряется при более высоком содержании воды в замесе.