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THE PROCESS OF EVAPORATION OF SODIUM SULFATE SOLUTION BY LEACHING NATURAL RAW MATERIALS

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ABSTRACT

A specific feature of the chemical composition of the natural mirabilite of the Tumryuk deposit is that the average content of impurity salts of halite, gypsum and epsomite in it is not considered very high. The quality of the product in terms of the content of the main substance and impurity of sodium chloride according to GOST (Government standart) 6318 corresponds to the first grade, and in terms of the amount of impurity of ions Mg^(2+)- to the second grade. The highest demands on the quality of sodium sulfate are imposed by the synthetic detergent industry. This is due to the fact that the micro components introduced into them, which dramatically improve the quality of synthetic detergents, are very sensitive to impurities of some divalent metals, in particular iron, calcium, and zinc.

KEYWORDS: *Sulfate, Dramatically, Impurity, Gypsum*

INTRODUCTION

The process of leaching the natural mirabilite of the Tumryuk deposit with water at temperature not lower than 50℃ were carried out. Under these temperature conditions, the rate of sodium sulfate dissolution will be high compared to 25-35℃. The process of evaporation of sodium sulfate solution which was obtained by leaching natural raw materials with water at 50℃ was studied. The study was carried out at 100℃ under vacuum at a residual pressure of 82,16-86,26 kPa. Evaporation was carried out with constant stirring of solutions and pulps with sedimentNa_2SO_4. According to the obtained data, there is a proportional relationship between the duration of the process and the amount of removed water.

The innovative development of the Republic of Uzbekistan is directly related to the development of priority sectors, in particular, the chemical, biochemical, gas and petrochemical industries in the great levels.

The foundation which has been created in the field in recent years, is able to provide a stable growth dynamics of the potential of the chemical industry for the next 3-5 years. However, the creation of a solid base for the long-term progressive development of all areas of the chemical industry necessitates accelerating the transformation processes of the industry with taking into account the most advanced foreign experience.

Scientific and technological progresses in industries which are using sodium sulfate, as well as the development of new industries, have increased the requirements for the quality of sodium sulfate. The highest demands on the quality of sodium sulfate are imposed by the synthetic detergent industry. This is due to the fact that the micro components introduced into them, which dramatically improve the quality of synthetic detergents, are very sensitive to impurities of some divalent metals, in particular iron, calcium, and zinc. The production of special types of paper for the electrical industry imposes strict requirements on the content of chloride salts in sodium sulfate.

MATERIAL AND METHODS

Sulfate raw materials of the deposit are represented by sodium sulfate in surface brine and intercrystalline brines, bottom sediments of glauberite, astrakhanite and mirabilite. The Kara-Bogaz-Golunikal deposit is considered unique both in terms of raw material reserves and their accumulation, which occurs due to the constant flow of the Caspian water.

Another deposit of sodium sulfate is Lake Kuchuk which is located in the Kulundin flow of the Altai territory. It contains sulphate brine and glassy mirabilite bottom sediments.

Lake Kulundin which is located near Lake Kuchuk, is also of interest for the production of sodium sulfate. The water of this lake contains ≈ 6% salts.

Largely, but currently unexploited deposits include: Djaksi-Klichskoy, which is considered a group of dry salt lakes containing layers of mirabilite, thenardite, gallite and astrakhanite; Lake Ebeyti – is considered surface brine and bottom sediments of mirabilite; Lake Anjbulat is with mirabilite and thenardite.

In Europe, deposits of sodium sulfate in the form of mirabilite or thenardite are found only in Spain and Italy. In Germany, sodium sulfate is obtained by complex processing of the hartsaltz of the Stassfurt deposit.

Glauberite deposits in the Fergana valley and basins among mountains of the TianShan, astrakhanite, thenardite and mirabilite from the Kushkanatauss, Akkala and Tumryuk deposits which are located in Karakalpakistan can be considered as raw materials for the production of sodium sulfate. The reserves of mirabilite at the Akkala deposit alone exceed 2 billion tons.

Existing modern automated production lines set high flowability and uniformity of product granulometric composition as the main condition. This is due to the special requirements for the residual moisture content in sodium sulfate.

Results

The similarity of natural sodium sulfate which is containing raw materials from various deposits of the Earth, leads to some commonality of the technology for producing sodium sulfate. However, the specific features of the production, mineralogical and chemical composition of raw materials in different countries determine the well-known uniqueness of the organization of production in each of them.

The bulk of sodium sulfate produced in the world is obtained according to a two-stage technological scheme with the isolation of mirabilite at the first stage and its processing into a finished product at the second stage by various thermal methods: incongruent melting of mirabilite, melting followed by evaporation of solutions, dissolution with evaporation, and also, spray drying condition, dehydration in furnaces of fluidized layer.

A specific feature of the chemical composition of the natural mirabilite of the Tumryuk deposit is that the average content of impurity salts of halite, gypsum and epsomite in it is not considered very high. This makes it possible to obtain from it anhydrous sodium sulfate without intermediate separation of mirabilite, combining the processes of evaporation and drying. One of the main factors which are determining the quality of sodium sulfate is considered the gypsum content of the product. The content of calcium sulfate in sodium sulfate solutions obtained after leaching of raw materials should not exceed 0,4%. Otherwise, it is impossible to get a quality product from it.

Analysis of the data on the physicochemical properties of the system $Na_2SO_4 - CaSO_4 - H_2$shows that the solubility of calcium sulfate in the presence of sodium sulfate varies differently depending on the temperature and concentration of sodium sulfate in the solution. Below 29℃, gypsum and mirabilite exist as solid phases in the system. The content of calcium sulfate in the eutonic solution reaches 0,33%. An increase in temperature leads to the formation of poorly soluble glauberite $Na_2SO_4 - CaSO_4$, as well as double salts $2Na_2SO_4 \cdot CaSO_4 \cdot 2H_2O$ and $Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$ and decrease in the solubility of calcium sulfate in eutonic solutions. At 35 and 50 in equilibrium eutonic solutions corresponding to the crystallization of sodium sulfate with glauberite, the content of calcium sulfate is $4{,}6 \cdot 10^{-2}$ and $4{,}0 \cdot 10^{-2}$ %, and at 80 – $2{,}5 \cdot 10^{-2}$ %. The solution with high sodium sulfate content forms in this area of the system.

The foregoing indicates the advisability of carrying out the process of leaching the natural mirabilite of the Tumryuk deposit with water at a temperature of at least 50. Under these temperature conditions, on the one hand, the dissolution rate of sodium sulfate will be high compared to 25-35 and on the other hand, due to the low solubility and the rate of dissolution, calcium sulfate does not completely have time to go into solution for a short period of time.

The results of the research of the process of leaching the mirabilite of the Tumryuk deposit with water at 50 at a ratio of S:L 1: 0,37 for 5-6 minutes showed that a solution is formed containing 30,96% Na_2SO_4, 0,27% $MgSO_4$, 0,02 % $CaSO_4$, 0,15% NaCl and 68,41% H_2O.

The duration of cooling to 20 and the change in the concentration of sodium sulfate during cooling of the resulting solution were studied. The solution was cooled with constant stirring with water at an average temperature of 16 (Fig. 1).

It can be seen from Fig. 1 that during the first 7-8 minutes the temperature of the solution drops sharply from 50°C to 31°C and then smoothly decreases to the formation of a solution saturated at 20°C. This is explained by the fact that at the initial stage of the salt crystallization process from the solution does not occur. Upon cooling from 50°C to 20°C a saturated solution is formed only after reaching a temperature of 31°C and from this temperature crystallization of 10-aqueous sodium sulfate begins with further cooling.

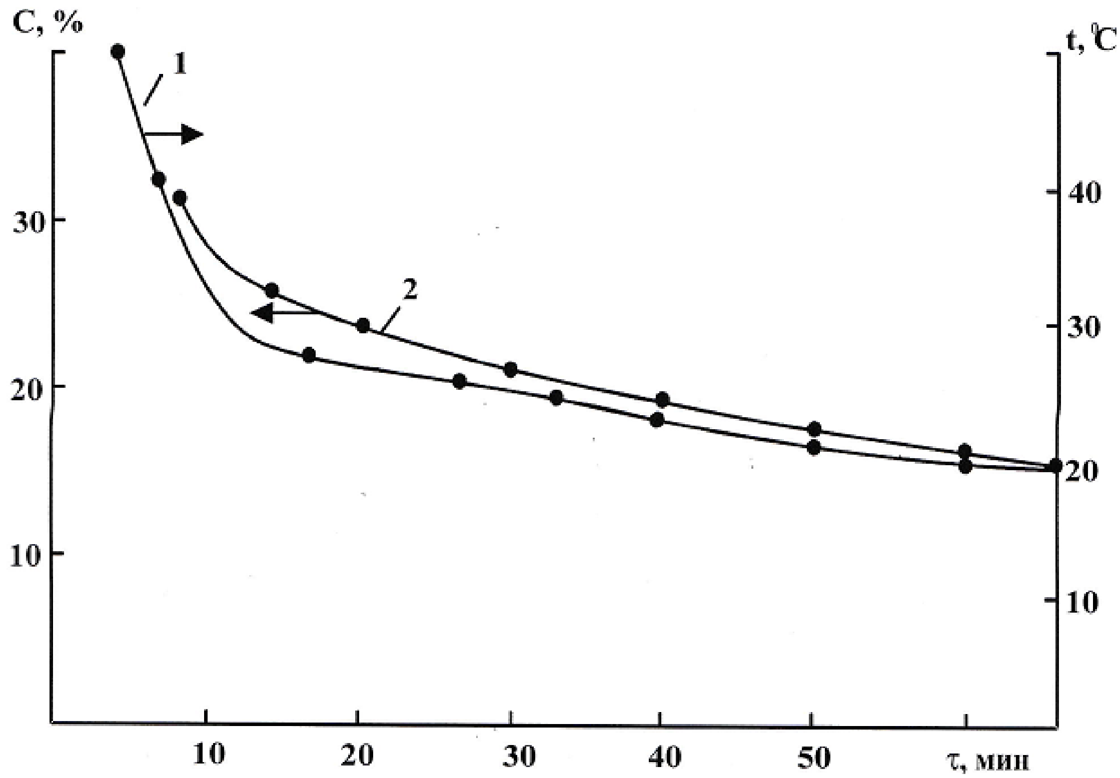

Fig. 1. Dependence of temperature change (1) and sodium sulfate concentration (2) on the duration of cooling up to 20°C

The duration of cooling the solution with the release of 10-aqueous sodium sulfate in the solid phase and the formation of a solution containing 15,92% Na_2SO_4, 0,59% $MgSO_4$, 0,05% $CaSO_4$, 0,33% NaCl and 83,11% H_2O consist of 65-66 minutes. This forms slurry with a precipitate of 10-aqueous sodium sulfate. The ratio of S:L in the pulp is 1:0,87. After filtration, the wet precipitate of 10-aqueous sodium sulfate contains impurities of epsomite, gypsum and halite contained in the solid phase. The 10-aqueous sodium sulfate was washed at the stage of its filtration with chilled water in order to remove them.

In fig.2 is shown the results of tests on washing 10-aqueous sodium sulfate, showing that the use of washing water at a ratio of S: H_2O 1:0,075 is considered sufficient to obtain a product containing the sum of impurities of epsomite, gypsum and sodium chloride less than 0,1%.

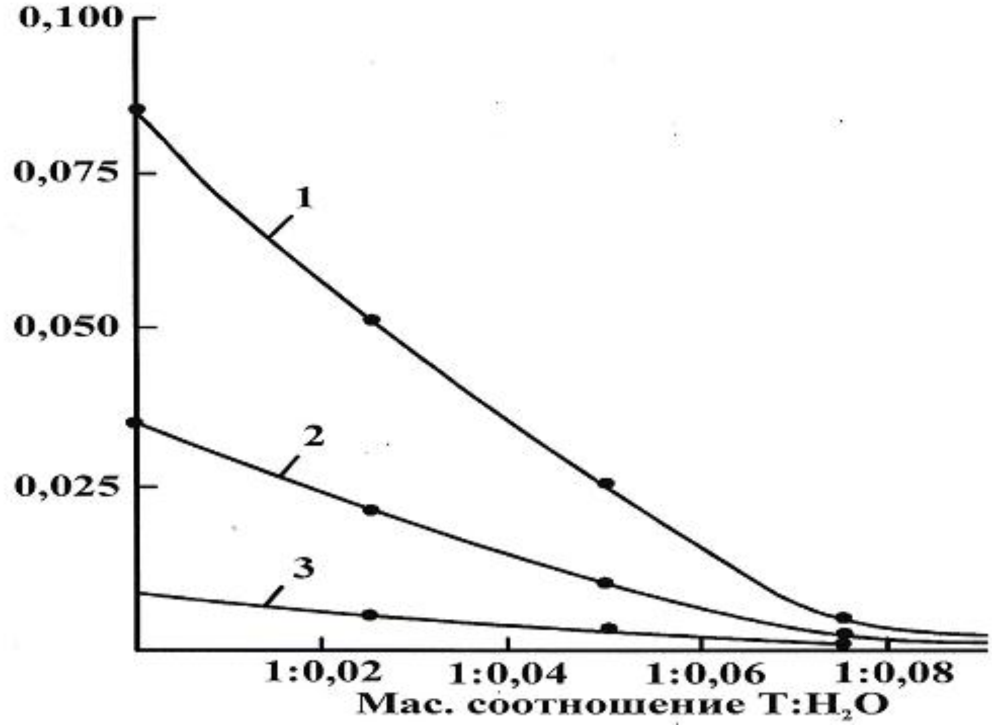

Fig.2. Dependence of the residual content of epsomite (1), halite (2) and gypsum (3) in mirabilite on the ratio S: H_2O when it is washed with water.

The precipitate of 10-aqueous sodium sulfate was washed twice with cold water, first at a ratio of S: H_2O 1:0,05, and then at 1:0,025. The 10-aqueous sodium sulfate which is containing $4,7·10^{-3}$% epsomite, $6·10^{-4}$% gypsum and $1,9·10^{-3}$% halite, with a moisture content of 12,65% was received.

Drying the wet product allows to obtain 10-aqueous sodium sulfate containing 99,98%Na_2SO_4, $5,210^{-3}$ % $MgSO_4 \cdot 7H_2O$, $6,8·10^{-3}$% $CaSO_4 \cdot 2H_2O$ and $2,210^{-3}$% NaCl. According to GOST 6319 (Government standart), the quality of the product corresponds to medical sodium sulfate - Glauber salt.

$Na_2SO_4 \cdot 10H_2O$ contains 55,9% crystallization water. This increases the cost of its transportation and contributes to its caking. Therefore, 10-aqueous sodium sulfate, in addition to medical purposes, is dehydrated near the places of its extraction by various methods.

In this regard, the process of evaporation of sodium sulfate solution obtained by leaching natural raw materials with water at 50 was studied. The study was carried out at 100 under vacuum at a residual pressure of 82,16-86,26 kPa. Evaporation was carried out with constant stirring of solutions and pulps with sediment Na_2SO_4. According to the obtained data, there is a proportional relationship between the duration of the process and the amount of removed water.

Removal of 34,5% water from the original solution for 15 minutes leads to the formation of slurry with a ratio of L:S 5,1:1. 75% of water is removed from the solution with duration of process 37 minutes. This leads to the release of an even larger amount of sodium sulfate into the solid phase and the formation of a pulp with a ratio of L:S = 1:1. When the duration of the evaporation is more than 52 minutes, complete drying of the initial solution is observed. In this case, drying the solution to residual moisture of 0,32% leads to a product which is containing 98,17%Na_2SO_4, 0,02 Ca^{2+}, 0,17% Mg^{2+} and 0,32% NaCl. The quality of the product in terms of the content of the main substance and impurity of sodium chloride according to GOST (Government standart) 6318 corresponds to the first grade, and in terms of the amount of impurity of ions Mg^{2+}- to the second grade.

The obtained samples of Glauber's salt and sodium sulfate were studied by X-ray phase, IR spectroscopic and thermogravimetric methods of analysis.

DISCUSSION

According to the X-ray phase analysis data, obtained Glauber's salt and sodium sulfate have a crystalline structure (Table 1). On the diffraction pattern of Glauber's salt, diffraction reflections with interplanar distances are distinguished by the highest intensity: 5,51; 4,82; 3,22; 3,11; 2,81 and 2,53 À. For sodium sulfate, reflexes with a d value are considered more intense and characteristic 4,69; 3,91; 3,63; 2,87; 2,71; 1,97; 1,57 and 1,51 À. The obtained data are considered in good agreement with the tabular data for pure mirabilite and sodium sulfate.

The X-ray spectra of the samples $Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4 which were obtained from the natural mirabilite of the Tumryuk deposit are characterized by a doublet at 640-625 and 645-640 cm^{-1} in the region of the deformation vibration of the sulfate ion and the intense band at 1140-1130 cm^{-1}, corresponding to the vibration ν (SO) (Fig.3).

TABLE 1 INTERPLANAR DISTANCES AND RELATIVE INTENSITY OF REFLECTIONS IN DIFFRACTOGRAMS OF GLAUBER'S SALT AND SODIUM SULFATE

$Na_2SO_4 \cdot 10H_2O$						Na_2SO_4			
d, À	I/I_1, %	d, À	I/I_1, %	d, À	I/I_1, %	d, À	I/I_1, %	d, À	I/I_1, %
6,31	3,1	3,11	50,1	1,98	7,0	4,69	30,2	1,81	20,2
5,51	100,0	2,81	27,2	1,92	17,2	3,91	100,0	1,58	20,0
4,82	42,2	2,70	10,0	1,80	10,1	3,63	60,1	1,57	30,2
4,34	13,1	2,53	26,9	1,66	10,2	2,87	89,9	1,51	40,1
3,83	27,2	2,45	10,1	1,37	6,9	2,71	90,0	1,35	20,3
3,60	7,0	2,37	7,0	1,31	7,0	2,35	20,1	-	-
3,39	7,1	2,11	20,1	-	-	2,22	19,9	-	-
3,22	50,3	2,03	6,9	-	-	1,97	70,3	-	-

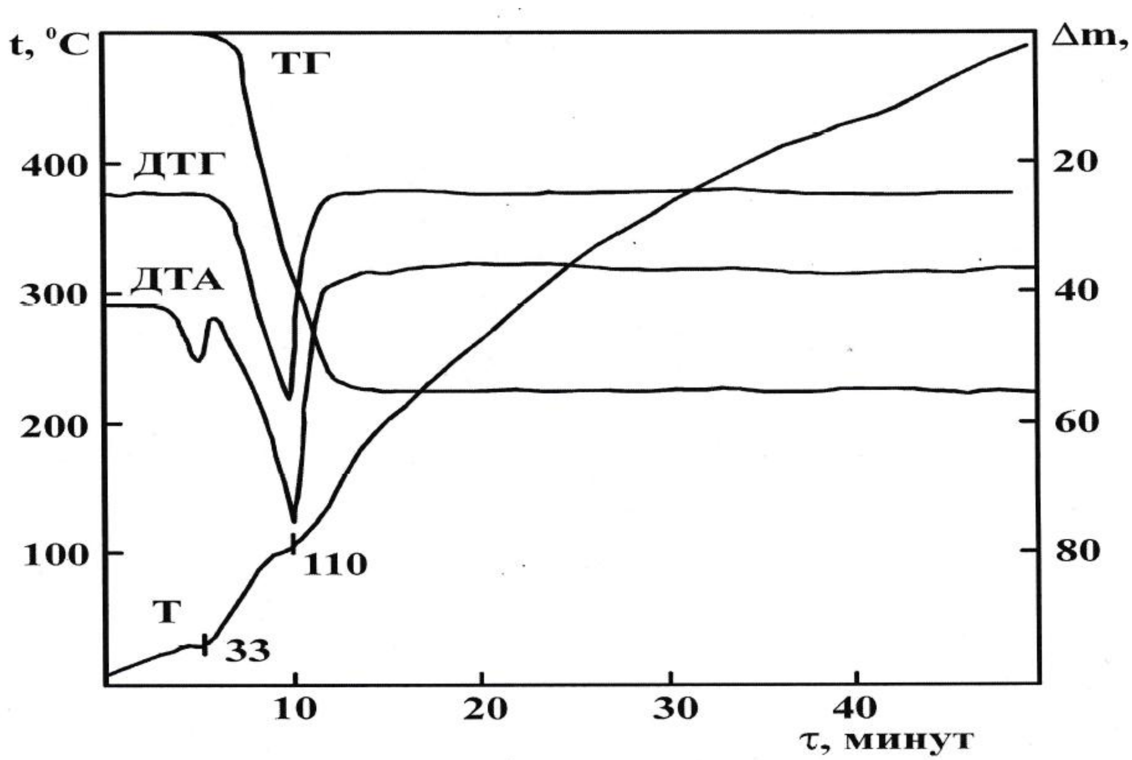

Fig.3. X-ray spectra of samples of Glauber's salt which is containing 99,8% $Na_2SO_4 \cdot 10H_2O$ (1) and sodium sulfate which is containing 98,2% Na_2SO_4 (2).

Deformation vibrations of crystallization water in the X-ray spectrum were found in the frequency range of 1665 cm^{-1}, and its asymmetric and symmetric vibrations at 3470 and 3380 cm^{-1}.

Weak bands which were observed in the frequency range of 3470-3385 and 1670 cm^{-1} correspond to ν (H_2O) and δ (H_2O) which was residual crystallization water present in the composition of dried sodium sulfate.

The obtained $Na_2SO_4 \cdot 10H_2O$ has been also studied by thermogravimetric analysis. According to the research results, mirabilite incongruently melts in its own crystallization water, which corresponds to the endothermic effect, is observed on the derivatogram $Na_2SO_4 \cdot 10H_2O$ at 33℃ (Fig.4). This forms a saturated solution with a solid precipitate of sodium sulfate. With further heating, starting from 70℃, water is removed and the solution boils at temperatures above 101-102℃

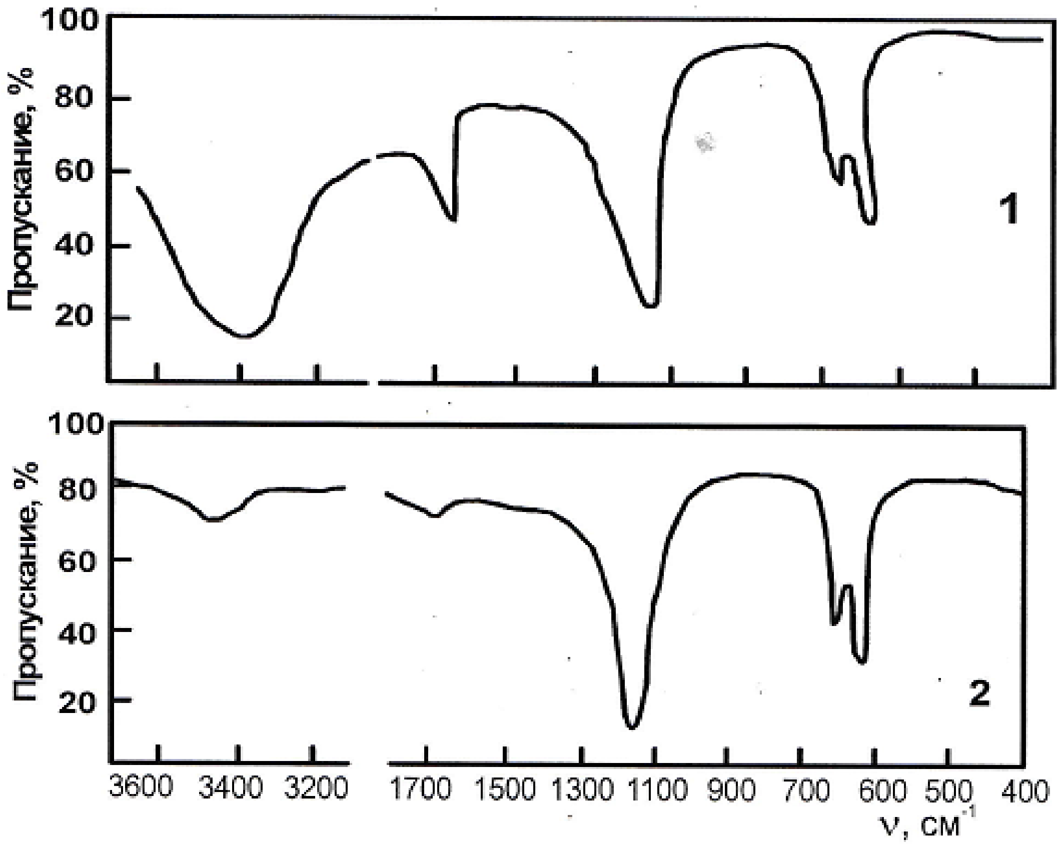

Fig.4. Derivatogram of mirabilite which is containing 99,8% $Na_2SO_4 \cdot 10H_2O$.

Intensive removal of water from the solution is observed in the temperature range 101-103℃ Complete removal of water and the formation of anhydrous sodium sulfate occur when the solution with sodium sulfate precipitate is heated to 200-205℃ On the derivatogram $Na_2SO_4 \cdot 10H_2O$, the process of removal of water corresponds to the endothermic effect at 110℃ According to the S:G derivatogram, the weight loss consists of 55,1%.

CONCLUSION

Thus, the results of the researches which have been carried out, indicate the possibility of obtaining commercial sodium sulfate of the first and second grade from the natural mirabilite of the Tumryuk deposit by leaching the raw material with water at temperatures not lower than 50 ℃ with followed by complete evaporation of the resulting solution. Together with this, it is possible to obtain by stepwise evaporation from the solution about 53% of sodium sulfate in the form of a product of the highest quality, and the remaining 47% in the form of a technical product. In addition, if necessary, it is possible to obtain 10-aqueous sodium sulfate by dissolving the raw material with water, clarifying the liquor by filtration, crystallization, separation of the solid phase, washing and drying it. The quality of the product corresponds to medical sodium sulfate namely, Glauber's salt.

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