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Study of the Process of Potassium Chloride Conversion in the Presence of Diethylamine

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ABSTRACT

The aim of the study is to establish the regularities of the process of obtaining potassium sulfate by sulfuric acid conversion of potassium chloride in the presence of diethylamine. To increase the efficiency of the process, the optimal sequence of feeding the initial components has been determined. The influence of technological factors on the yield and moisture content of the product has been studied. The chemical and mineralogical compositions of the resulting products have established through X-ray phase, microscopic and energy dispersive analyzes. The rheological properties of intermediate solutions and suspensions have been determined.

Keywords: potassium sulfate, potassium chloride, diethyl amine, sulfuric acid, conversion, energy dispersive spectrum, X-ray diffraction pattern

1. Introduction. In the preparation of inorganic salts, amines are widely used [1-7], one of which is diethylamine.

The use of diethylamine to create conditions for the salting out of the resulting inorganic salts, allows you to create an energy-saving technology for the production of various salts [8].

There are no data in the literature on the influence of technological parameters on individual stages of the process of obtaining potassium sulfate by sulfuric acid

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conversion of potassium chloride in the presence of diethylamine.

In the experiments, white crystalline potassium chloride obtained from the flotation potassium chloride of the Dekhkanabad Potash Plant JSC, sulfuric acid with a concentration of 93.5% and diethylamine of Russian production were used as the initial components.

2. Methodology.

The following physicochemical methods of analysis were used in the studies: electron-microscopic, thermoanalytical, and X-ray phase analysis.

The morphology and microstructure of the samples were measured using a SEM - EVO MA 10 scanning electron microscope (Carl Zeiss, Germany); the local elemental composition of the powders was determined using an EDX energy-dispersive elemental analyzer (Oxford Instrument). During sample preparation, the sample was dried and mounted on a microscope stage, over which aluminum foil with a double-sided adhesive was glued. Powder was glued onto this foil, then the object stage was installed in the working chamber of the microscope, from which air was evacuated to create a vacuum. For measurements, an accelerating voltage of 10 kV was applied to the filament. At the same time, the working distance was 8.5 mm. Local elemental analysis was obtained at a scale of 100 μm using the Aztec Energy Advanced software [9-11].

TG-DSCconditions: Thermoanalytical studies of the presented samples were carried out on a Netzsch Simultaneous Analyzer STA 409 PG (Germany) with a K-type thermocouple (Low RG Silver) and aluminum crucibles. All measurements were carried out in an inert nitrogen atmosphere with a nitrogen flow rate of 50 ml / min. The temperature range of measurements was 25-370 °C; the heating rate was 5 k / min. The amount of sample per measurement is 5-10 mg. The measuring system was calibrated with a standard set of substances KNO_3, In, Bi, Sn, Zn [12, 13].

Conditions for X-ray phase analysis: Identification of the samples was carried out on the basis of diffraction patterns that were recorded on a XRD-6100 apparatus (Shimadzu, Japan), computer-controlled.

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CuKα radiation (β filter, Ni, 1.54178, current mode and tube voltage of 30 mA, 30 kV) and a constant detector rotation speed of 4deg / min in increments of 0.02 deg were used. (ω / 2θ coupling), and the scanning angle varied from 4 to 800 [14-16].

3. Research results

Previously, we have determined the sequence of feeding the starting components in the process of obtaining potassium sulfate; water, potassium chloride, diethylamine and sulfuric acid [1,2]. In this work, we studied the mass ratio of the concentration of sulfuric acid, the initial components $Et_2NH{:}H_2SO_4{:}KCl{:}H_2O$ 1:(05-2,0):(0,8-1,2):(1,2-1,4). The process of obtaining potassium sulfate by sulfuric acid conversion of potassium chloride was carried out at a temperature of 70°C and a process duration of 20 minutes (Tables 1-3).

When studying the reaction below, the rate of the starting components was taken as stoichiometric:

$$2(C_2H_5)_2NH + 2KCl + H_2SO_4 \rightarrow K_2SO_4 + 2(C_2H_5)_2NH_2Cl \quad (1)$$

The experiments were carried out in a three-necked glass reactor equipped with a stirring device. After the supply of water, potassium chloride and diethylamine, the calculated amount of sulfuric acid was gradually dosed over a period of 20 minutes. After the dosage, the temperature of the reaction mixture reached 70-73°C, and within 20 minutes the decrease was only 2-4°C. After completion of the reaction process, the reaction mass was cooled to 20°C for 60 minutes. Then, the resulting suspension was filtered under vacuum at a residual pressure of 0.6 at, with recording of the filtration time and washing of the precipitate with a saturated potassium sulfate solution (SPSS), the ratio of SPSS:precipitate is 1:1.

Input parameters were varied at intervals of 50-93% (sulfuric acid concentration) the ratio of the initial components of $Et_2NH{:}H_2SO_4{:}KCl{:}H_2O$ is 1: (05-2.0): (0.8-1.2): (1.2-1.4).

Influence of process parameters on L:S, filtration rate and moisture content of products after washing was determined. Chemical composition of the obtained

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products and mother filtrates was analyzed for chlorine, SO_4 and potassium using chemical methods of analysis [9,10]. Based on the data obtained, the product output relative to potassium was calculated, and the data obtained are shown in Tables 1 and 2.

As the results of the study (Table 1) show, in the studied intervals of variation of the initial components G: T in the suspension after cooling and washing, the humidity of the product fluctuates and the intervals (2.68-4.52): 1 and 12.99-33.18%, respectively. The density of the liquid phase at 20 ° C fluctuates in intervals of 1010-1090 kg/m3 (Table 1).

With an increase in the proportion of sulfuric acid content from 0.23 to 0.91 while maintaining the content of other components, with a proportion equal to 0.61, the exit of potassium sulfate reaches a maximum, its percentage fluctuates in intervals of 60.00-90.00%. The single SO_4 content in the liquid phase reaches more than 5% (Table 2). It can be seen from Tables 1 and 2 that the exit of potassium sulfate reaches 95.83% in condition 7 of the test. Reducing the SO_4 content of the filtrate to 2.94%. The ratios of the initial components Et_2NH:H_2SO_4:KCl:H_2O are 1.00: 0.46: 0.80: 7.23 respectively.

Table 1,2 shows that with a decrease in sulfuric acid concentration, the output of potassium sulfate decreases, and the content of H_2SO_4 in the mother liquor, which increases practically cannot be circulated to the process. In experiment 9, the exit of potassium sulfate does not increase more than 79.31%, however, the SO_4 content in the filtrate is less than 0.3%, which provides a high rate of use of sulfuric acid. And the potassium content is more than 1.5%, it can be separated from the mother liquor. Based on the above, with respect to the output of potassium sulfate, 7,4,11 experiments are optimal, and with respect to the SO^4 content in the mother liquor, 9 and 7 are optimal. The results of the study show that in Table 1, the filtration rate for the solid phase of these samples is 2332.5, 939.5; 5552.7 and 2332.5 kg/m2: h, respectively, 4.7.9 and 11 experiments. That is, the highest filtration rate is observed in the 9th run, with the yield of potassium sulfate reaching 79.31%, and the potassium

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content in the mother liquor is 1.6 and 0.25%, respectively. The results of the experiments show that the granulometric composition of the samples is more than 55% of the fraction, and the crystal size is -0.065 mm (Fig. 1)

Table 1

Influence of process parameters on sulfuric acid conversion of potassium chloride to diethylamine impurities.

№	Norm ratio $Et_2HN:H_2SO_4: KCl: H_2O$				L:S	Humidity	Filtration rate, kg/m^2*h		Density g/cm^3 at temperature 20°C	Relative output%
							Solid phase	Liquid phase		
1	1,00	0,23	1,00	7,23	3,64:1	18,01	714,0	2598,8	**1010**	**60,00**
2	1,00	0,46	1,00	7,23	2,98:1	16,16	4365,5	13013,8	**1090**	**72,87**
3	1,00	0,53	1,00	7,23	2,91:1	16,87	2296,7	6685,6	**1048**	**83,90**
4	1,00	0,610	1,00	7,23	2,68:1	21,86	2332,5	6255,8	**1050**	**90,00**
5	1,00	0,685	1,00	7,23	3,19:1	22,56	4196,2	13392,3	**1070**	**84,02**
6	1,00	0,91	1,00	7,23	3,78:1	17,74	3897,3	14730,8	**1090**	**78,27**
7	1,00	0,46	0,80	7,23	3,03:1	24,49	939,5	2848,3	**1030**	**95,83**
8	1,00	0,46	1,00	7,23	2,98:1	16,16	4365,5	13013,8	**1090**	**72,87**
9	1,00	0,46	1,20	7,23	2,39:1	21,76	5552,7	13271,5	**1035**	**79,31**
10	1,00	0,61	1,00	6,67	2,94:1	27,23	2865,3	8438,9	**1075**	**83,90**
11	1,00	0,61	1,00	7,23	2,68:1	21,86	2332,5	6255,8	**1050**	**90,00**
12	1,00	0,61	1,00	7,78	3,13:1	33,18	2339,9	7325,3	**1053**	**76,55**
13	1,00	0,685	0,80	7,23	3,79:1	20,80	1276,5	4844,8	**1085**	**83,47**
14	1,00	0,685	1,00	7,23	3,19:1	22,56	4196,2	13392,3	**1070**	**84,02**
15	1,00	0,685	1,20	7,23	2,61:1	17,61	5237,2	13680,3	**1070**	**85,44**
16	1,00	0,61	1,00	7,23	3,16:1	12,99	1326,2	4197,3	**1060**	**81,6**
17	1,00	0,61	1,00	7,23	3,33:1	16,24	711,2	2367,6	**1082**	**76,55**
18	1,00	0,61	1,00	7,23	4,52:1	23,72	902,4	4075,2	**1085**	**65,05**
19	1,00	0,61	1,00	7,23	3,51:1	13,37	1344,0	4723,8	**1075**	**81,60**

Concentrate series acid 1-15-93%; 16-85% ;17-73% ;18-57.6% ;19-50%

Process duration-20 min.

Table 2

Chemical composition of the mother liquor

Sample numbers correspond to the numbers in Table 1.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
%		45,68	91,4	106	111,6	137,0	182,7	114,2	91,35	76,13	121,80	121,80	121,80	171,29	137,03	114,19	121,80	121,80	121,80	121,80
Liquid phase , %	**K**	2,08	2,96	1,66	1,00	1,08	1,00	0,58	2,96	1,60	3,20	1,00	1,17	1,04	1,08	1,36	0,83	1,58	1,12	1,75
	Cl	8,86	14,84	12,66	12,41	13,30	12,41	11,97	14,84	14,40	4,43	12,41	12,19	10,64	13,30	13,30	11,52	11,97	9,31	11,52
	SO_4	0,37	4,44	3,17	5,08	8,81	10,45	2,94	4,44	0,25	5,80	5,08	6,19	11,60	8,81	5,88 1.	7,06	8,19	10,78	6,32

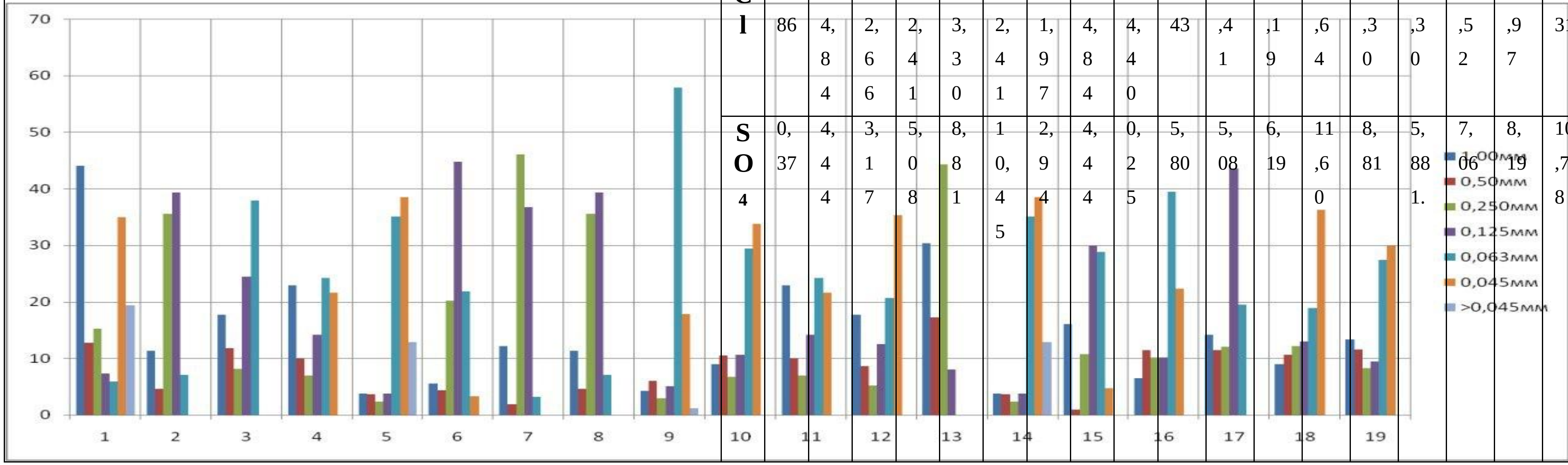

Figure 1. Dependence of conversion process condition on fractional composition of samples.

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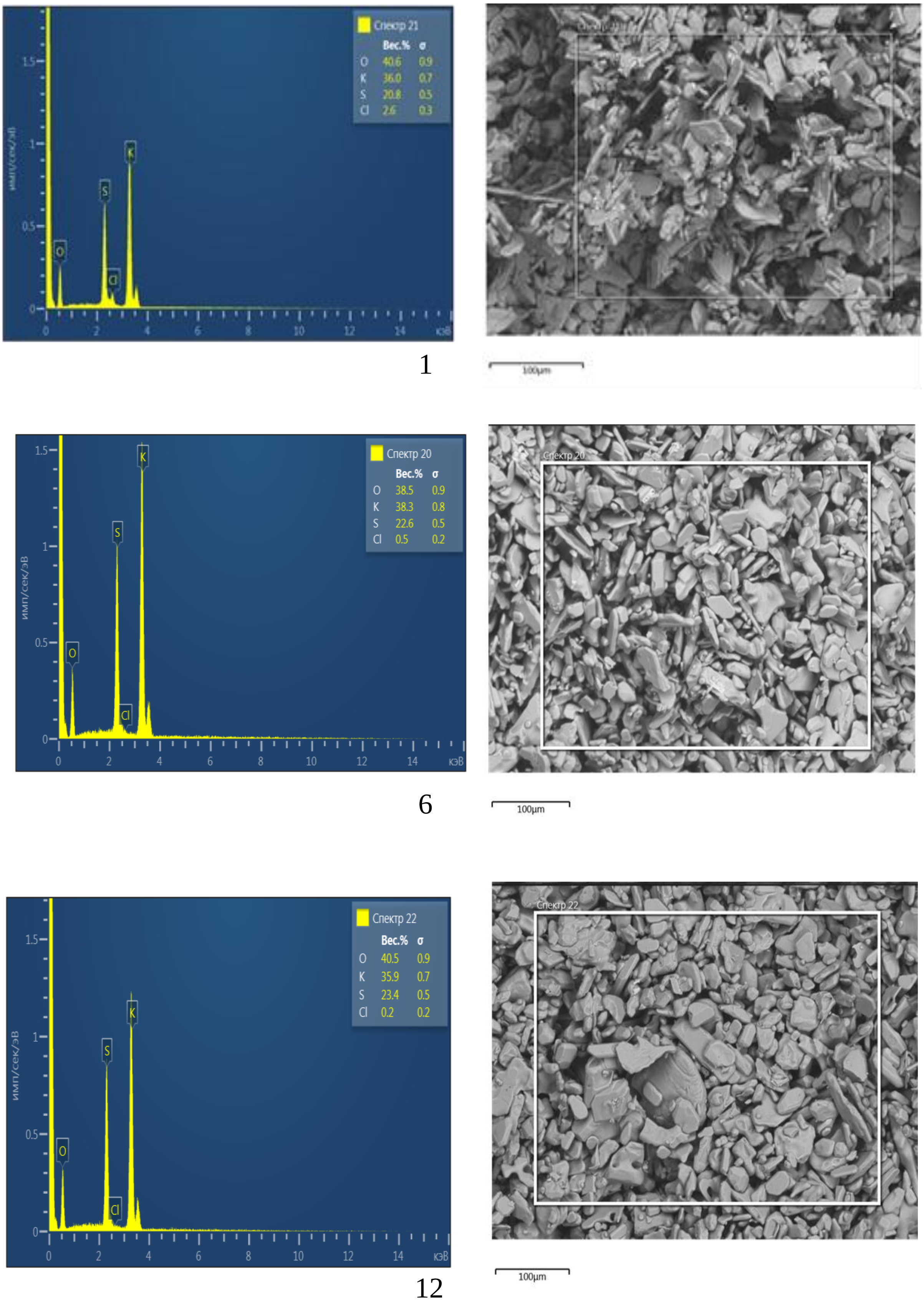

Figure 2. Energy dispersion spectrum of samples

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Sample numbers correspond to Table 1 numbers.

Energy dispersion analysis (Fig.2, Table 3) of the products showed that in experiments 4,6,7 and 11,12,13 products with the lowest chlorine content are obtained, and the formation of potassium sulfate crystals is observed in all versions.

Table 3

Elemental composition of potassium sulfate samples by EDS.

The sample numbers correspond to the numbers of table.1	**Content of elements, %**			
	K	**S**	**O**	**Cl**
1	**35,98**	**20,78**	**40,60**	**2,64**
6	**38,33**	**22,63**	**38,49**	**0,55**
12	**39,25**	**20,48**	**40,13**	**0,13**
13	**36,93**	**23,11**	**39,89**	**0,06**
16	**33,14**	**21,42**	**45,33**	**0,11**
17	**37,58**	**21,17**	**40,77**	**0,49**
18	**39,53**	**22,89**	**38,08**	**0**
19	**35,86**	**23,43**	**40,52**	**0,19**

*** -the sample numbers correspond to the table numbers**

From the radiographs (Fig.3 and Tab.4) it can be seen that the mineralogical composition of the products consists of K_2SO_4, KCl and Et_2NH_4HCl, their content fluctuates in intervals of 75-95; 1-5 and 0-25%, respectively.

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Table 4

Mineralogical composition of reaction products by X-ray phase analysis

The sample numbers correspond to the numbers of table.1	Content of components					
	K_2SO_4		KCl		Et_2NH_2	
	mass. %	Ref.Code	mass. %	Ref.Code	mass. %	Ref.Code
1	78	00-005-0613	-	01-078-3876	-	-
2	95	00-005-0613	-	-	5	01-076-5789
3	80	00-005-0613	4	01-078-3876	16	01-076-5789
4	92	00-005-0613	-	-	8	01-076-5789
5	76	00-005-0613	7	01-078-3876	17	01-076-5789
6	75	00-005-0613	-	-	25	01-076-5789
7	84	00-005-0613	3	01-078-3876	14	01-076-5789
8	95	00-005-0613	-	-	5	01-076-5789
9	76	00-005-0613	-	-	24	01-076-5789
10	86	00-005-0613	2	01-078-3876	12	01-076-5789
11	92	00-005-0613	-	-	8	01-076-5789
12	86	00-005-0613	2	01-078-3876	12	01-076-5789
13	81	00-005-0613	3	01-078-3876	16	01-076-5789
14	76	00-005-0613	7	01-078-3876	17	01-076-5789
15	85	00-005-0613	3	01-078-3876	12	01-076-5789
16	83	00-005-0613	5	01-078-3876	12	01-076-5789
17	86	00-005-0613	-	-	14	01-076-5789
18	78	00-005-0613	-	-	22	01-076-5789
19	85	00-005-0613	4	01-078-3876	11	01-076-5789

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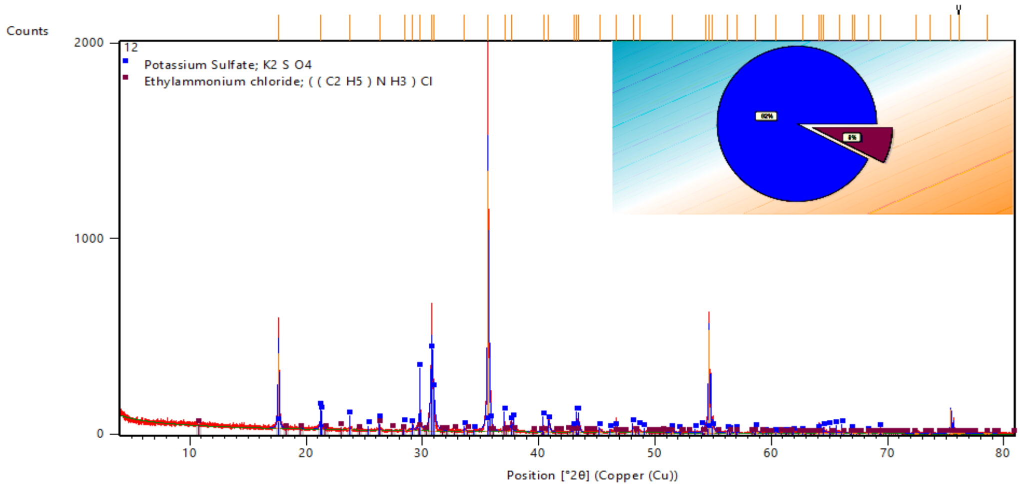

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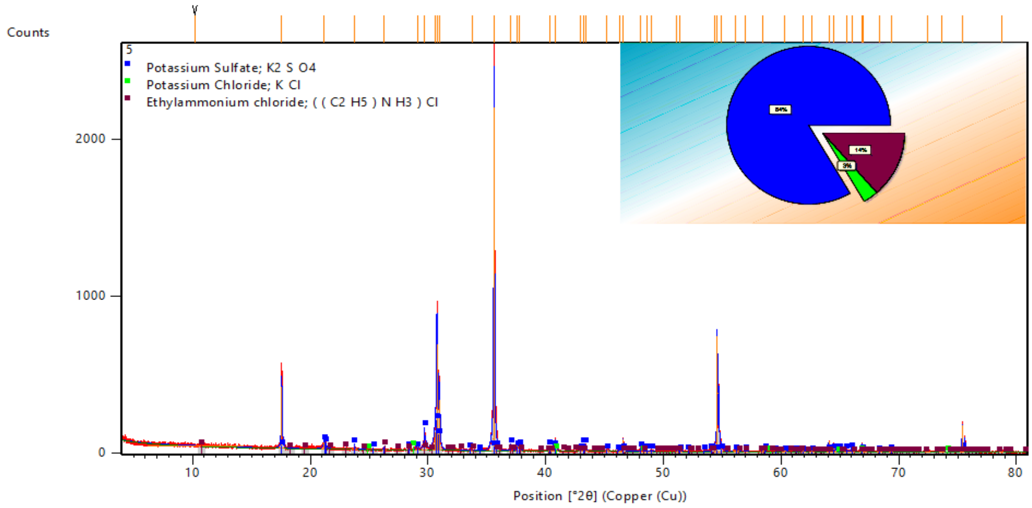

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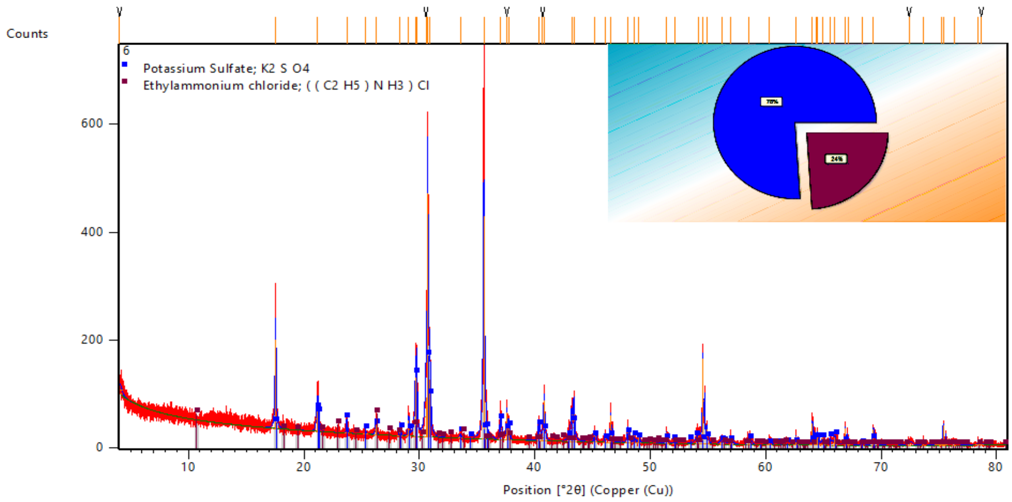

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Figure 3. X-ray patterns of samples.

Sample numbers correspond to table 1 numbers.

4. Conclusion.

Thus, at the studied intervals, the optimal ratio of the initial components $Et_2NH:H_2SO_4:KCL:H_2O$, are 1: (0.46: 0.61): (0.80: 1.20): (7.23-7.78), and the concentration of sulfuric acid is 81-93%, while the exit of potassium sulfate is 79.31-91.8%, contained K and SO_4 in the mother liquor is 1.6: 0.58 and 0.25: 2.94%, respectively.

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