

RESEARCH OF EVAPORATION PROCESS OF MOTHER LIQUOR IN THE PRODUCTION OF POTASSIUM BICARBONATE BY AMINE METHODS

A. N. BOBOKULOV., A. U. ERKAEV., Z. K. TOIROV., D.Z.ESHMETOVA.,
A.KAMBAROV
Tashkent Chemical-Technological Institute, e-mail: kafedranmkt@mail.ru

Abstract. *Prerequisites of the problem.* Currently, the world pays great attention to the production of potassium carbonate (potash) by amine methods. At the same time, there are sufficient proven reserves of potassium-containing raw materials in the world, which, in terms of technological, economic and, most importantly, rational levels of use, provide an opportunity to obtain potash to provide domestic and foreign consumption markets with a point of view available in terms of energy and technological indicators..

In this regard, the development of a method for producing potash based on specific local raw materials is relevant.

Purpose of the work. The purpose of this work is to study the process of separating the residual unreacted part of potassium chloride and diethylamine (DEA) from the mother liquor formed during the production of potassium bicarbonate by amine methods.

Methodology. The experiments were carried out in a glass reactor-evaporator equipped with a stirring device and a condensation system of a laboratory setup for achieving various vacuum pressures at a given degree of evaporation. The resulting one stripped off suspensions were filtered off and the amounts of the solid, liquid phase and condensate in the condensation system were determined depending on the degree of evaporation. As a starting material, the mother liquor was used, formed during the carbonization of potassium chloride in the presence of diethylamine.

Scientific novelty. The process of evaporation of mother liquor was substantiated by theoretical analysis of the three-component systems $KCl-Et_2NH_2Cl-H_2O$ and $KCl-CaCl_2-H_2O$. For the first time, physicochemical studies of the influence of technological parameters on the process of evaporation of mother liquors for the production of potassium bicarbonates, such as temperature, diethylamine rate, process duration and vacuum, have been carried out.

Key words: potassium chloride, diethylamine, evaporation, filtration, parameter, degree, rarefaction, time, process, rate.

Features of work:

- development of a technology for the production of potassium carbonate with circulation of amines based on specific local raw materials;
- evaporation of mother liquors formed during the preparation of potassium bicarbonate, with the release of unreacted potassium chloride in the solid and gas phases, respectively.

Introduction. Prospects for the use of potassium carbonates, especially as chlorine-free potash fertilizers, create certain conditions for organizing their production in Uzbekistan. Currently, there is no production of potassium carbonates in Uzbekistan, although there are deposits of local potassium-containing raw materials in Uzbekistan, which will make it possible to obtain their own potassium carbonate [1-2].

All existing industrial methods for the production of potassium carbonate can be divided into two groups. The first group is the production of potassium carbonate by the electrolysis of potassium chloride solutions followed by the processing of potassium hydroxide into potassium carbonate, which is characterized by the complexity of the process due to the multistage nature, high-energy consumption [3-9] and the high cost of the resulting bicarbonate and potassium carbonate.

The second group of schemes is based on the production of potassium hydrogen carbonate ($KHCO_3$) similar to the ammonia method for producing soda by carbonization of potassium chloride (KCl) in the presence of various aliphatic amines and their salts [10-11].

It is known that in the production of potassium carbonate by the amine method [10], at the first stage in the process of carbonization in the presence of potassium chloride and DEA, potassium bicarbonate is formed in the solid phase and the unreacted part of potassium chloride and DEA remains in the liquid phase, and diethylamine hydrochloride is also formed.

Materials and research methods. The identification of samples of precipitation during evaporation was carried out on the basis of diffraction patterns, which were recorded on an XRD-6100 apparatus (Shimadzu, Japan) controlled by a computer. We used $CuK\alpha$ -radiation (β -filter, Ni, current mode and tube voltage-30 mA, 30 kV) and

a constant detector rotation speed of 4 deg / min with a step of 0.02 deg. ($\omega / 2\theta$ -adhesion), and the scanning angle varied from 4 to 80°C.

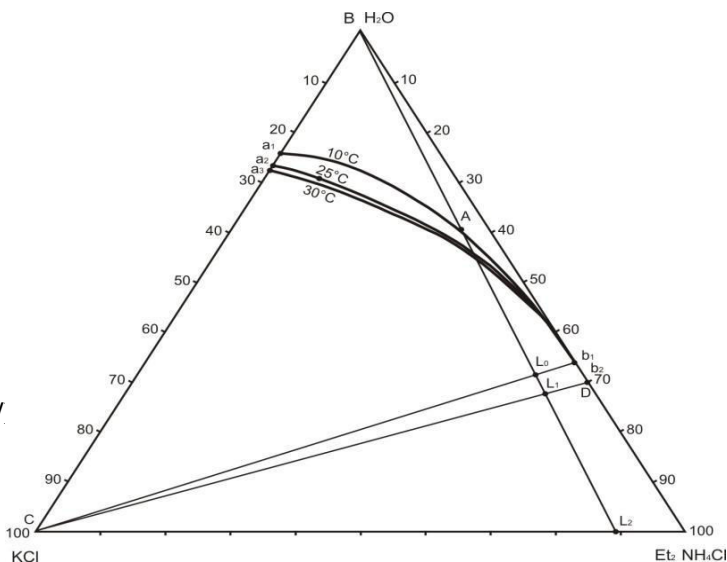
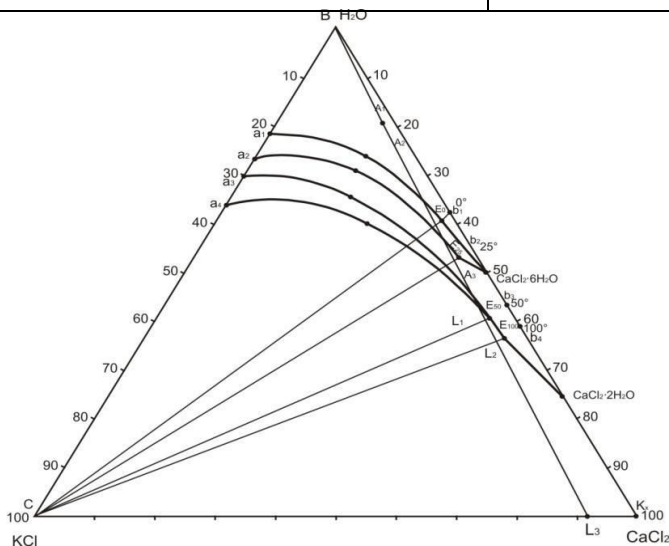
Thermo analytical studies of the presented samples were carried out on a Netzsch Simultaneous Analyzer STA 409 PG device (Germany), with a K-type thermocouple (Low RG Silver) and aluminum crucibles. All dimensions were carried out in an inert nitrogen atmosphere with a nitrogen flow rate of 50 ml / min. The samples were visualized using a computer-controlled microscope (Leica, Germany). The optical system of the Leica DM500 microscope includes a lens, an eyepiece and an illumination device - a condenser with a diaphragm and a light filter and an electric light.

Results and discussion. Experimental data show that potassium chloride is not completely converted into potassium bicarbonate at a conversion rate of no more than 90%. The remainder of potassium chloride from the filtrate can be separated by stripping the original mother liquor of the composition, wt%: H₂O - 41.95, KHCO₃-4.12, Et₂NH₂Cl-34.93, Et₂NH₂HCO₃-20.53, which on the diagrams of solubility Fig. 1) corresponds to figurative point A. The evaporation process proceeds along the beam BL₂. The diagram also shows that the maximum degree of evaporation must be continued up to the point L1, which ensures the maximum precipitation of the potassium chloride residue, which is equal to $m \text{ KCl} / m \text{ liquid} (B2) = L1w2 / L1C$. In the case of continuation of the process of evaporation into a solid phase, a mixture of crystals of potassium chloride and chloride N, N - diethyl ammonium chloride precipitates. After separation of the solid phase, a liquid phase of the composition is formed, mass %: 30.19 H₂O, 69.60 Et₂NH₂Cl, and 0.24 KCl, and the carbonates are almost completely decomposed with the release into the gas phase and further condensation with the formation of bicarbonate N, N - diethyl ammonium.

In the distillation stage, it can be used lime milk with a concentration of 17, 30 and more than 86%. In this case, when using Ca (OH)₂ with a norm of 110% with respect to chlorine. Firstly, it is consumed by the reaction with potassium carbonates and bicarbonates N, N - diethyl ammonium chloride with the formation of calcium carbonate following which N,N - diethyl ammonium with the formation of calcium chloride and diethylamide.

Fig. 1. Theoretical analysis of the stripping process of mother liquors using the KCl-Et₂NH₂Cl-H₂O system

Fig. 2. Theoretical analysis of the evaporation process of the liquid phase formed after the distillation of mother liquors using the KCl-CaCl₂-H₂O solubility diagram.



As a result of these reactions, suspensions with L: T 10.5: 4.01-1 are formed in the system, containing KCl and CaCl₂, the content of which depends on the concentration of Ca(OH)₂ used. The compositions of the liquid phase are plotted on the solubility diagram of the CaCl₂-KCl-H₂O system (Fig. 2), which are located on the figurative points A, A2 and A3. Figurative points A1 and A2 are in the range of unsaturated solutions, and figurative point A3 is in the range of joint crystallization of crystals of potassium chloride and calcium chloride hexahydrate. From these figurative points, a beam of evaporation BL3 was conducted.

The diagram shows that when the pressure is up to the L2 point, even at 100 ° C, an insignificant amount of potassium chloride crystals with the ratio S/L= 0.023 falls out.

The results of the experiments showed that if it is necessary to isolate the residue of potassium chloride from the maw filtrates, it is necessary to carry out the evaporation process of filtrate before distilling diethyl amine in the presence of lime milk.

In the experiments, the evaporation process was carried out in order to reduce the consumption of lime milk and crystallize unreacted KCl with its return to the beginning of the process to increase the potassium chloride utilization factor.

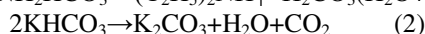
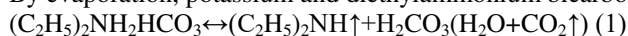
Analysis of the solubility diagram of the KCl-Et₂NH₂Cl-H₂O system showed that to isolate unreacted potassium chloride, the mother liquor from the initial position M is evaporated to point N with removal of 40% moisture relative to the initial mass. When using evaporated DEA, the release rate does not exceed 26.88% relative to the total mass of the original evaporated solution.

We also studied the influence of technological parameters on the composition of the liquid phase and the evaporation process of mother liquors (MR) formed in the production of potassium bicarbonate at the rate of diethylamine 100 and 145% (Tables 1 and 2). As shown by analyzes, the mother liquor consists of the following components, mass%

Table 1
Chemical composition of liquid phases obtained at different rates of diethylamine

Norm	CO ₃ ⁻² , %	Cl ⁻ , %	K ⁺ , %	HCO ₃ ⁻ , %	Et ₂ NH, %
100	0,71	11,01	2,29	3,24	4,28
145	2,38	11,46	1,51	2,30	5,70

By evaporation, potassium and diethylammonium bicarbonates decompose according to the reactions:



During condensation of steam, diethylammonium bicarbonate can be formed again by the reverse reaction (1). Calculations show that the content of free Et₂NH, taking into account reaction (1), in the samples is 5.25 and 14.45%, respectively.

Table 2
Influence of technological parameters on the process of evaporation of potassium bicarbonate filtrate, formed at the rate of diethylamine 100%

№	T, °C	Residual pressure ΔP, mm. rt. page	Degree of evaporation, %	DEA content in condensate, %	Degree of release of DEA relative to the content in the mother liquor, %	Degree of sedimentation of the solid phase from the mass of the filtrate, %
τ = 15 min						
1	60	739	12,20	7,39	17,18	0
2	90		22,80	14,78	64,21	0
3	60	587	19,00	5,73	20,76	0

4	75		25,56	9,50	46,28	0,03
5	90		28,65	14,03	76,6	0,06
6	60	435	19,97	8,51	32,38	0,03
7	75		27,87	11,55	61,33	0,04
8	90		32,56	12,93	80,19	0,1
9	60	283	27,60	7,48	39,35	0,3
$\tau = 30 \text{ min}$						
10	60	739	15,40	6,65	19,50	0
11	90		39,80	8,87	67,23	2,55
12	60	587	24,10	6,03	27,67	1,10
13	75		31,55	8,32	50,0	1,24
14	90		50,45	7,45	96,43	3,73
15	60	435	29,80	6,43	36,53	2,30
16	75		37,01	9,16	64,57	2,46
17	90		54,62	9,61	100	4,36
18	60	283	40,20	5,53	43,38	2,5

Table 3
Influence of technological parameters on the process of evaporation of potassium bicarbonate filtrate, formed at the rate of diethylamine 145%

No	T, °C	Residual pressure ΔP , mm. rt. Art	Degree of evaporation, %	DEA content in condensate, %	Degree of release of DEA relative to the content in the mother liquor, %	Degree of sedimentation of the solid phase from the mass of the filtrate, %
$\tau = 5 \text{ min}$						
1	60	739	7,1	4,48	2,20	0
2	75		15,3	-	-	0
3	90		21,1	59,58	86,98	0
4	75	587	22,0	12,13	18,47	0
5	60	435	10,4	13,46	9,68	0
6	75		17,7	21,18	25,95	0
7	60	283	11,5	20,43	16,26	0
8	75		32,8	23,68	53,63	0
$\tau = 15 \text{ min}$						
9	60	739	13,40	19,68	18,25	0
10	75		24,40	16,96	28,65	0
11	90		35,40	36,18	88,65	0
12	75	587	28,90	23,58	47,16	0
13	60	435	21,60	24,86	37,16	0
14	75		32,60	27,79	62,70	0,5
15	60	283	28,10	22,48	43,73	0
16	75		40,30	25,98	72,45	3,2
$\tau = 30 \text{ min}$						
17	60	739	16,94	17,52	20,23	0
18	75		26,80	16,70	30,93	0
19	90		41,70	32,58	94,04	0,1
20	75	587	32,45	35,28	79,23	0
21	60	435	33,90	16,57	38,89	0,5
22	75		44,90	21,15	65,73	0,8
$\tau = 45 \text{ min}$						
23	60	739	19,3	-	-	0
24	75		32,9	24,19	55,08	0
25	90		45,4	31,82	100	1,9

26	75	587	36,5	34,96	88,30	2,1
27	60	435	39,5	18,02	49,27	1,2
28	75		61,2	23,53	95,43	3,1

With an increase in temperature and a decrease in the residual pressure ΔP over the system, the degree of evaporation per unit of time increases (Tables 2 and 3). For example, within 15 minutes with a decrease in the residual pressure from 435 to 304 mm Hg, at 60 and 90 ° C the degree of evaporation increases from 12.2 and 22.80 to 19.97 and 32.56%, respectively, when using the first mother liquor. After 30 minutes, these indicators reach 15.40 at 739 mm Hg; 39.80, and at 435 mm Hg - 29.80 and 54.62%.

Under the same conditions of application of the second mother liquor, the degree of evaporation increases by 1.5 - 7.5% as compared to the first mother liquor. This difference increases with decreasing residual pressure in the reactor evaporator (Tables 2 and 3).

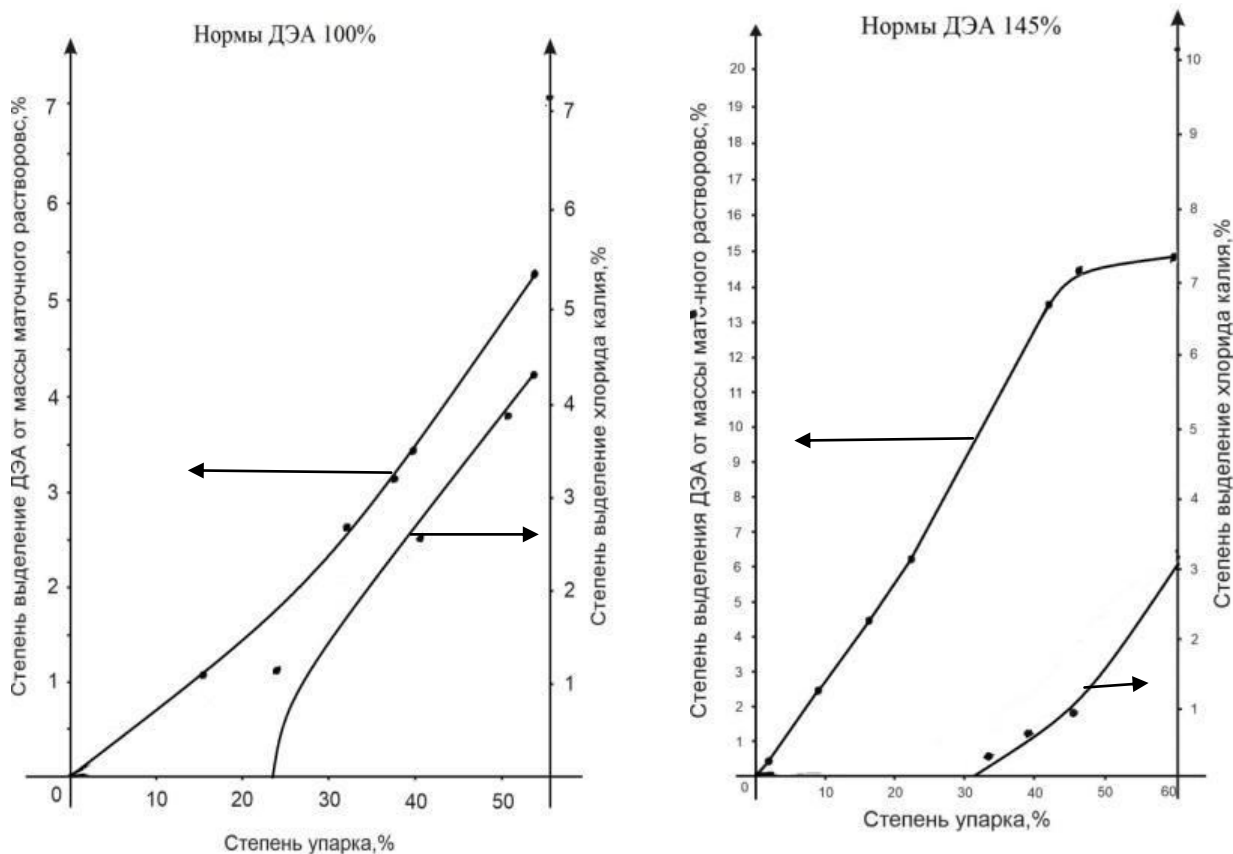


Fig. 3. Influence of evaporation degree on the yield of potassium chloride in the solid phase and DEA in the gas phase at a rate of DEA at the carbonization stage of 100% (a), 145% (b).

The content of DEA in the condensate, depending on the technological parameters, varies in the range of 4.48-59.58%. Separation of solid phase begins at a DEA content of 25.56 and 32.6%. The degree of separation of the solid phase from the initial solutions fluctuates in the range of 0.03-4.36% relative to the mass of the initial solution. (fig. 3)

The unwashed solid phases obtained as a result of evaporation of solutions were identified by X-ray phase, thermal and microscopic methods.

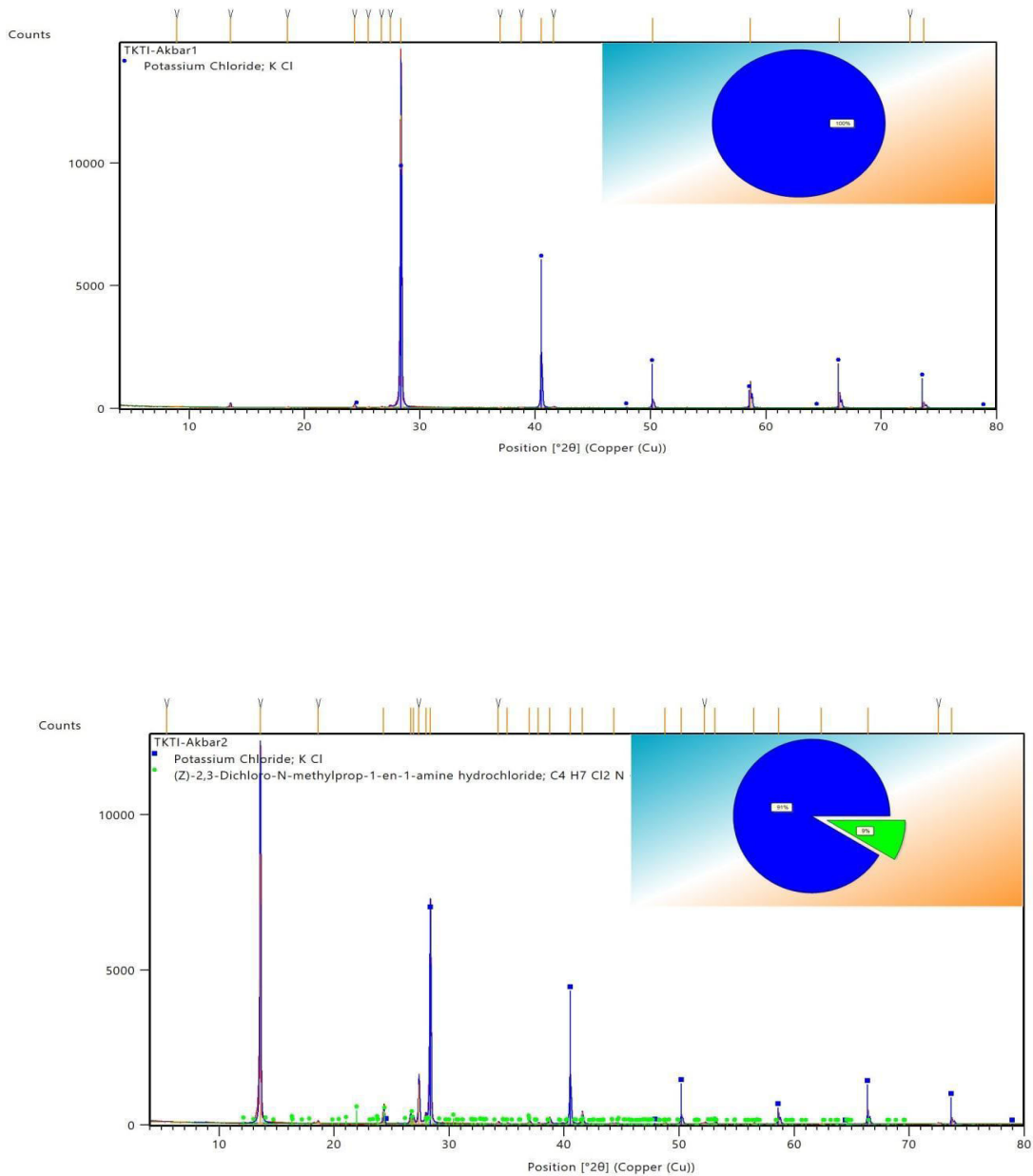
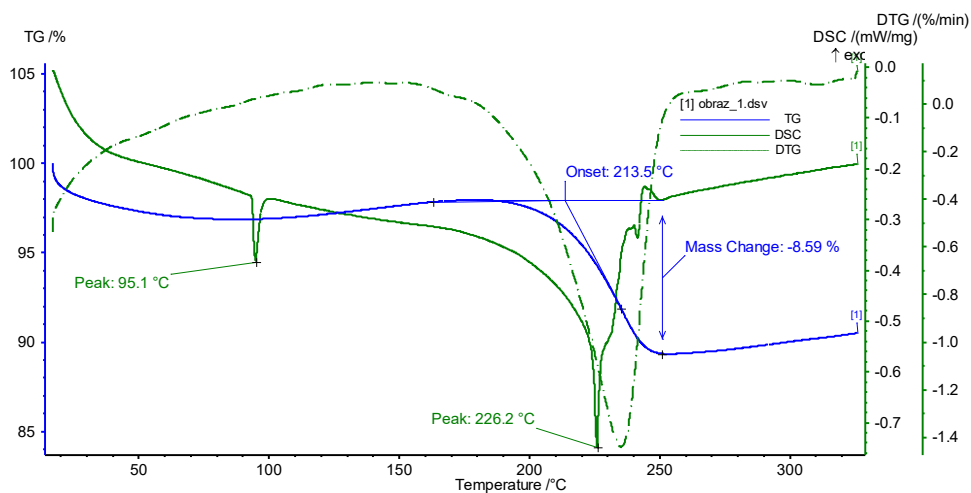


Fig 4. X-ray phase analysis of the solid phase.

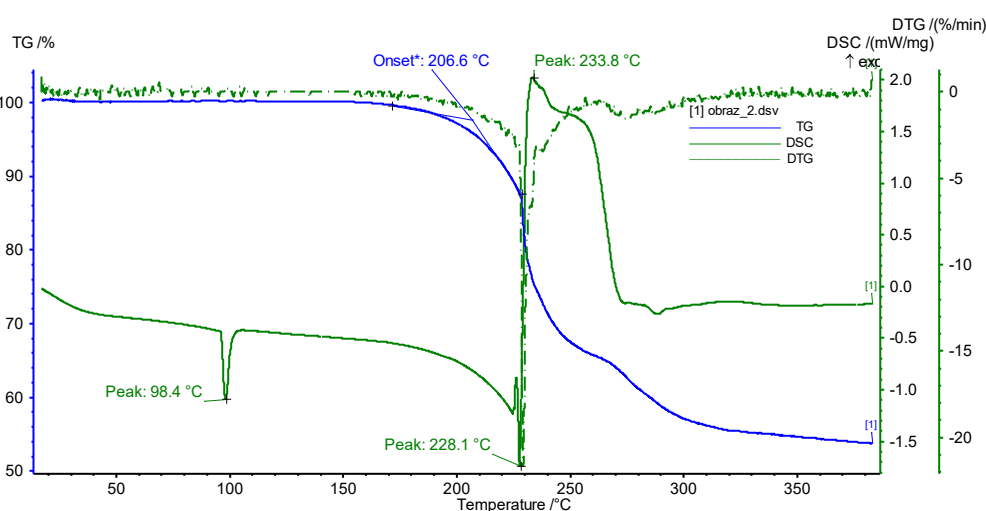
Sample numbers correspond to the numbers in Table

Table 4
Mineralogical composition of samples

№	Mineral names	Ref.Code	Content, mass. %.	
			Sample numbers.	
			16	17
*1	Potassium Chloride	01-076-3362	100	
*2	Potassium Chloride	01-076-3361		91
*3	(Z)-2,3-Dichloro-N-methylprop-1-en-1-amine hydrochloride	00-062-1637		9



A



B

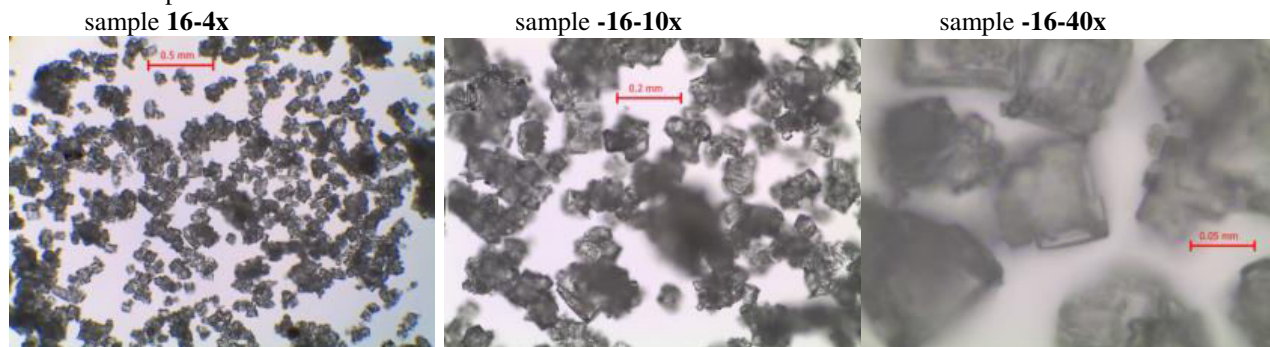
Fig. 5. Thermographs of samples: A- sample16, B- sample17

Sample numbers correspond to the numbers in Table 2

According to X-ray phase analysis (Fig. 3, Table 4), the solid phase of obtained samples contains potassium chloride and a mixture of potassium chloride and diethylamine hydrochloride, characterized by the presence of diffraction maxima on the X-ray diffraction pattern: sample 16 [$d = 3.14601; 2.22447; 1.57284; 1.40700 \text{ \AA}$ (KCl)], sample 17 [$d = 3.65795; 3.25519; 2.22473 \text{ \AA}$ ($(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HCl}$)].

The thermogram in Figure 5A shows that sample 16 does not undergo any changes in the temperature range of 20-94 ° C. At a temperature of 95.1 ° C, melting $(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HCl}$ is observed with energy absorption $\Delta Q = -4.23 \text{ J / g}$. At a temperature of 213.5 ° C, its decomposition begins at a rate of 1.5% / min. The total thermal destruction of the sample was $\Delta m = 8.59\%$. Energy of activation (decomposition) -78 J / g.

Sample 17 (Fig. 5 B) also does not undergo any changes in the temperature range of 20-97 ° C. At a temperature of 98.4 ° C, the melting of the sample $(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HCl}$ with energy absorption $\Delta Q = -29.45 \text{ J / g}$ is observed. At a temperature of 206.6 ° C, the sample begins to decompose at a rate of 20% / min. The total thermal destruction of the sample was $\Delta m = 44.79\%$. These data show that sample B contains $(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HCl}$ 5.21 times more than sample A.



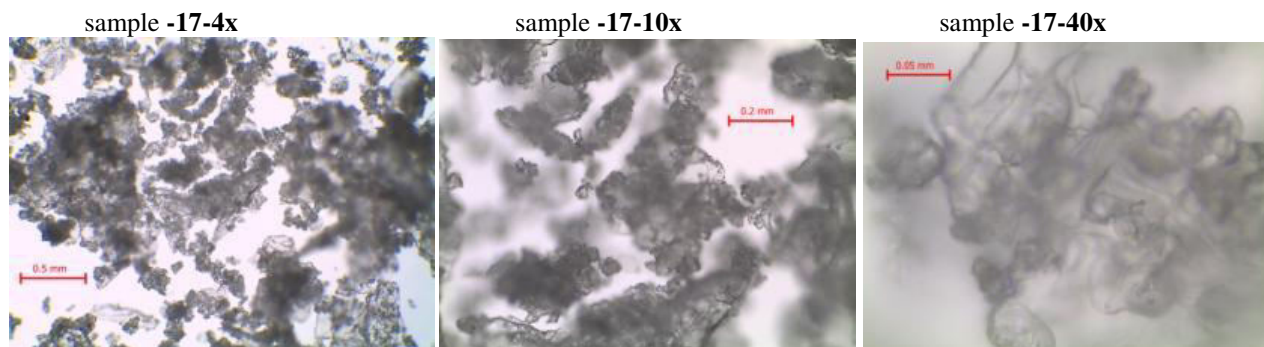


Fig. 6. Microphotograph of obtained samples.
Sample numbers correspond to the numbers in Table 2.

According to microscopic analysis, sample A is potassium chloride corresponding to cubic crystals with a length of 0.2 to 3 μm , and sample B is cylindrical crystals, on the surface of which the smallest particles are located, the spreading mass related to $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HCl}$.

As it was noted, that during evaporation and distillation process of DEA from mother liquors, the system gradually concentrates and in the end, depending on the degree of evaporation, a thick suspension is formed.

To determine the state of the system, the sequence of processes, selection of equipment and control of

№	Degree of evaporation, %	Elasticity, mm.Hg				n^{20} ,	Electro conductivity at 20°C, $\mu\text{S/cm}$
		740	588	436	284		
1	0	82,0	78,0	72,0	63,0	1,409	61,59
2	10	83,0	78,5	73,0	63,5	1,413	58,45

technology, it is necessary to study the influence of L: S, and the temperature on the viscosity, density, refractive index and electrical conductivity of the reaction system, as well as the sedimentation rate and suspension filtration. (Table 5-6 and Figure 7-9).

Increasing in concentration and decreasing in temperature, the viscosity of the system increases. The influence of temperature on the process increases when it decreases to 18 ° C and increases the concentration of DEA over 40%. Drawing the viscosity line (Figure 7) for 26.5 cP (d21-d11), obtaining an orthogonal projection (d2-d1) shows that to maintain the viscosity value of 26.5 cP with an increase in the degree of evaporation to 10.20.30% the system temperature must be at least 12,15,16 ° C, respectively.

The data (Table 5) show that decreasing the residual pressure in the vaporization apparatus from 740 to 284 mm Hg, the boiling point of the solution decreases from 83.0, 85.0 ° C to 63.5 and 67.0 ° C, respectively at a concentration of 10.0-45.0%. The light refractive indexes and electrical conductivity of the samples, depending on the degree of evaporation, fluctuate in the ranges 1.409-1.433 and 61.59-27.12 $\mu\text{S/cm}$, respectively. Increasing in the degree of evaporation from 10 to 45%, the light refractive index increases by 0.020, and the electrical conductivity, on the contrary, decreases by 34.47 $\mu\text{S/cm}$.

Table 5
Physicochemical properties of evaporated mother liquors

3	20	83,5	79,0	73,5	64,0	1,416	54,84
4	30	84,0	80,0	74,0	65,0	1,422	47,63
5	40	84,5	81,0	74,5	66,0	1,427	36,66
6	45	85,0	82,0	75,0	67,0	1,433	27,12

The filtration rate is strongly influenced by W: S and the temperature of the filtration process (Table 6). With an increase in W: T at a temperature of 60 ° C, the filtration rate decreases by 2.40; 5.20 times at W: T = 4: 1 and 8: 1, respectively, than at W: T = 2: 1. This tendency intensifies with a decrease in the process temperature to 20 ° C, which the filtration rate decreases by 2.70, 7.15 times, respectively. During evaporation the sludge is formed with W: T more than 20: 1 and at a temperature of 80-90 ° C. Based on the foregoing, W: T must be reduced to no more than 8: 1, and in connection with, we studied the kinetics of the decantation process (Fig. 7).

Table 6
Influence of L: T and temperature on the filterability of evaporated mother liquors

№	L:S	Filtration rate at 20°C, kg/m ² s		Filtration rate at 20°C, kg/m ² s	
		Liquid, phase	Solid, phase	Liquid, phase	Solid, phase
1	1:0	-	-	-	-
2	16:1	856,59	63,29	3234	202
3	8:1	1047,54	156,18	3483	435
4	4:1	1263,31	414,28	3773	944
5	2:1	2134,22	1116,97	4578	2264

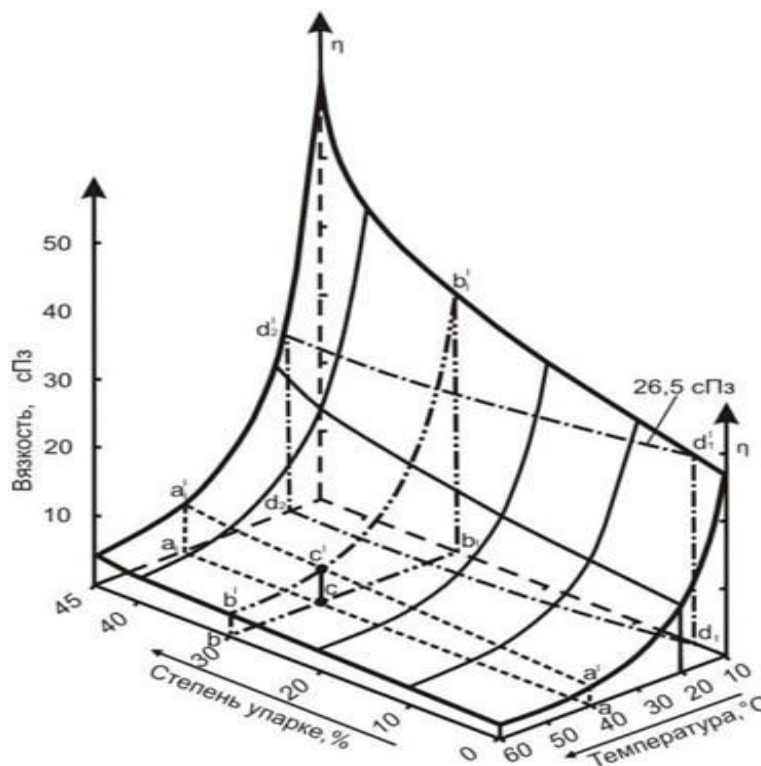


Fig. 7. Change in the viscosity of mother liquors depending on the degree of evaporation and temperature

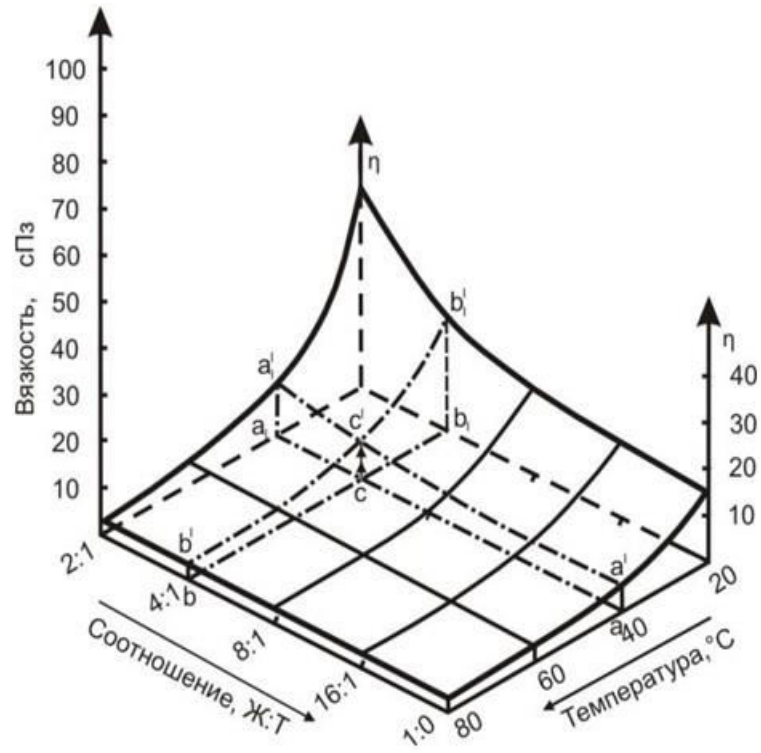


Fig. 8. Changes in the viscosity of 30% evaporated mother liquor depending on the temperature and the ratio of W: T.

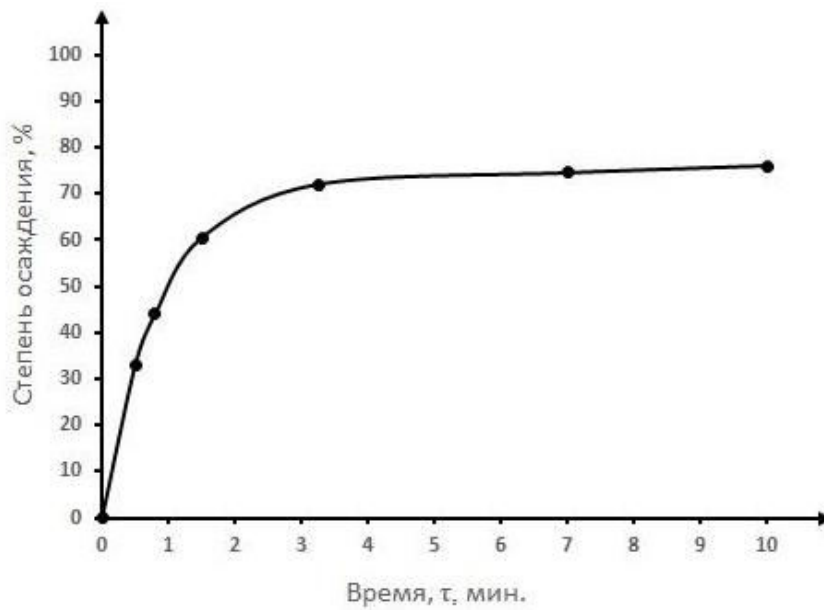


Fig. 9. Kinetics of sedimentation formed during the concentration of mother liquors.

Within 3 minutes, the degree of suspension clarification reaches more than 70% and 75% with a decrease in L: S from 9: 1 to 13: 1, respectively (Fig. 8).

In this way, the mother liquor after the evaporation process, before serving for filtration, maintains for 10-15 minutes and the resulting thick mass with W: T no more than 8: 1 is moved to the filtration stage with a filtration rate at least 435 kg / m² * h.

Conclusion. A theoretical analysis of the systems KCl + Et₂NH₂Cl-H₂O, KCl-CaCl₂-H₂O and a comparative analysis of the processes of evaporation of the filtrates formed after carbonization and distillation have been carried out. It has been proven that from a technological and economic point of view, it is effective to evaporate the filtrate formed after carbonation. The data obtained make it possible to consider the following technological parameters of DEA distillation with lime milk to be optimal: concentration and norm of lime milk - 34 and 130%, respectively. Process temperature - not less than 95 ° C due to heating with hot water vapor, process duration - 40 min. At the same time, the degree of DEA regeneration is at least 95%.

According to their rheological properties, suspensions and solutions are formed in the system, which can be pumped without difficulty using existing devices.

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