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STUDY OF OBTAINING POTASSIUM HYDROXIDE BY ELECTROCHEMICAL METHOD ON THE BASES OF FLOTATION AND HALLURGIC POTASSIUM CHLORIDE

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Abstract. To substantiate the process of obtaining potassium chloride, the compositions of white crystalline and flotation potassium chloride were studied. Studies have been carried out on the purification of the initial solution from impurities of oxides of two and trivalent metals, in particular, calcium and magnesium, which adversely affect the electrolysis process. The degree of purification when purifying a solution from calcium and magnesium ions increases with an increase in the rate of potassium hydroxide and carbonate to calcium and magnesium ions from 100 to 122%. In the case of using white crystalline potassium chloride, the degree of purification from calcium increases and in the case of flotation potassium chloride, it increases less intensively. X-ray phase analysis determined that the resulting sediments consist mainly of calcium carbonate and magnesium hydroxide. To obtain potassium hydroxide by electrolysis methods under given conditions, with an increase in the duration of the flow of the initial solutions (with an increase in the time of supply to the electrolyzer), in fact, this increase in the electrolysis time of the concentration of potassium hydroxide increased.

Keywords: *Potassium chloride, potassium hydroxide, electrolysis, anode, cathode, electrode, chlorine, production.*

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1. Introduction

In industry, potassium hydroxide is obtained by electrolysis of potassium chloride. The main feature of this technology for the production of potassium hydroxide is the fact that similar electrolysis plants can produce both caustic potash (KOH) and caustic soda (NaOH) (Samadiy *et al*., 2023). It allows manufacturers to switch over to the production of potassium hydroxide instead of caustic soda without significant investments, which production is not so profitable and marketing has become more complicated in recent years. In case of changes in the market, electrolyzers can easily be changed to the production of a previously produced product (Bazinet, 2020, Samadiy *et al*., 2022).

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Potassium hydroxide is an almost universal chemical compound.

One of the most important applications of potassium hydroxide is the production of soft soaps. Mixtures of potassium and sodium soaps are used to produce liquid soaps, detergents, shampoos, shaving creams, bleaches and some pharmaceuticals (Panda, 2011).

Caustic soda is produced in Uzbekistan by electrolysis of an aqueous solution of sodium chloride. In the same way, potassium hydroxide can be obtained from a purified aqueous solution of flotation and halurgic potassium chloride.

In this regard, we conducted research in order, if it is necessary, to partially or completely convert the production (Sanli *et al*., 2008) of caustic soda to the production of potassium hydroxide (Turakulov, 2020).

2. Experimental part

For the experiments, a laboratory electrolysis flowing unit with an ion-exchange membrane was used. A stainless steel sheet of type AISI 304 (08X18H10) was used as the cathode and an anode cell ORTA with 1 dm^2 was used for the anode. The distance between the electrodes is 15-16 mm and the volume of the electrolyzer is 0,3 l. Two separating funnels with a volume of 1 liter were used to supply the initial solutions of potassium chloride and hydroxide, which were connected to the device with a heat-resistant transparent hose. It is placed 50 cm above the apparatus for the gravity supply of initial solutions and the creation of hydraulic resistance to the release of hydrogen and chlorine through the pressure tank of the initial solutions. To obtain the reaction of the product, the outlet pipe of the apparatus was connected using hoses to two flasks located 50 cm below the apparatus (Spackman *et al*., 1958).

For experiments, 28,488 and 27,0 % solutions of potassium hydroxide and KCl were used, respectively. Chemical methods were used to determine the concentration of solutions before and after the process.

The electrolysis was carried out under the following conditions: the passing time of 600 ml solution through the electrolyzer was 20, 26, 33, 40 and 50 minutes. The current density and temperature of the solutions were 5 A/dm^2 and 55°C, respectively. In the selected sample, the content of OH^-, CO_2 was determined by the known methods of analytical chemistry (Zhukov *et al*., 2001; Policy, 2012; Schwarzenbach & Flashka, 1970) the content of calcium ions by the trilonometric method (Bykova, 1968). Potassium ions by flame photometry (Abate & Kibret, 2016) and chlorine-ion Mohr's method (Zolotov, 2018).

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 (Bousfield, 1992).

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. 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 (Nabity *et al*., 2006; Echlin, 2011; Otsuka & Kinoshita, 2010; Newman, 2011).

3. Results and discussion

It is known that during the production of potassium chloride at the Dekhkanabad potash plant by the flotation method, a product with the following contents, (wt. %) is obtained: KCl – 95,0; NaCl – 2,16; insoluble residue (i.r.) – 2,38.

Potassium chloride obtained by the halurgic method has the following contents, (wt. %): KCl- 99,02; NaCl-0,75.

For the physicochemical explanation of the process to obtain the potassium hydroxide, we studied the physicochemical properties of white crystalline and flotation potassium chloride.

Figure 1 shows the energy dispersive spectra of the initial potassium chloride samples.

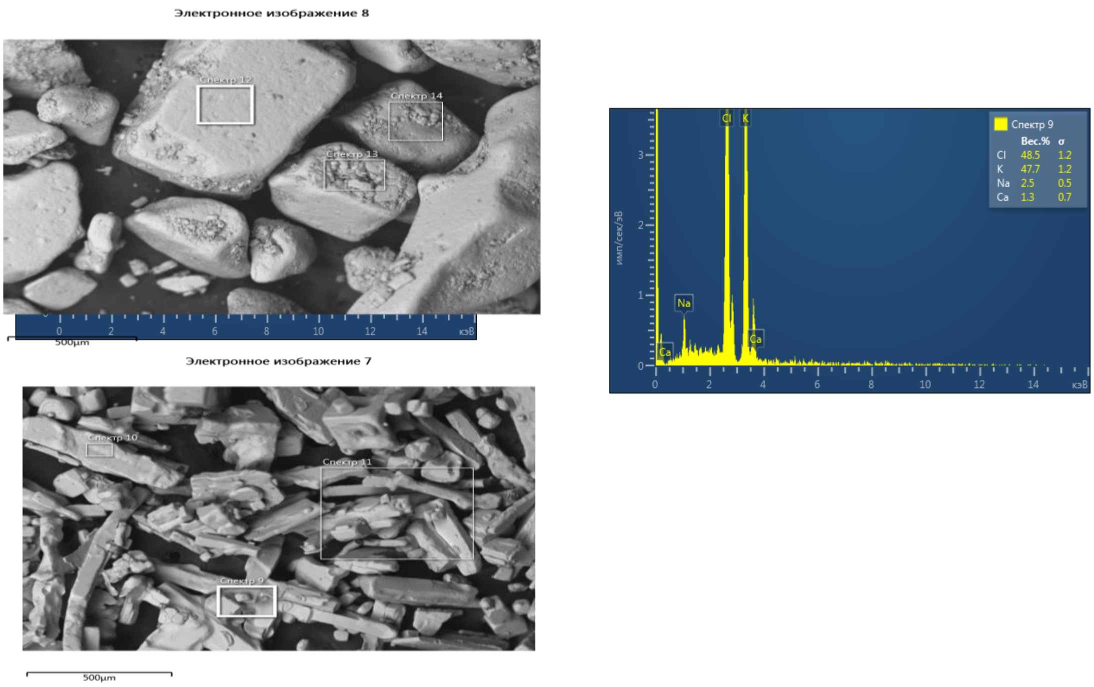


Figure 1. The energy-dispersive spectrum of initial potassium chloride samples.
a - White crystalline potassium chloride
b - Flotation potassium chloride

When comparing the data obtained from the energy dispersive analysis of the initial chlorides, it was revealed that (Güler *et al*., 2021) their elemental composition is very diverse. White crystalline potassium chloride has the chemical contents showed in Table 1 and in flotation potassium chloride, the content of elements is, showed in Table 2.

Table 1. Element content (wt. %) of white crystalline potassium chloride

Element	Spectrum number		
	12	**13**	**14**
K	51,56	51,19	51,48
Cl	47,69	47,67	47,59
Na	0,75	0,90	0,75
Ca	-	0,24	0,18
Total:	100,00	100,00	100,00

Table 2. Element content (wt. %) of flotation potassium chloride

Element	Spectrum number		
	9	**10**	**11**
K	47,67	48,08	47,805
Cl	48,53	50,43	50,485
Na	2,51	1,23	1,51
Ca	1,29	0,26	0,20
Total:	100,00	100	100

When obtaining potassium hydroxide by the electrochemical method, it is necessary to conduct research on the purification of the initial solution from impurities of oxides of bivalent and trivalent metals, in particular, calcium and magnesium, which adversely affect the electrolysis process. In this regard, we have studied the purification process of a saturated solution of potassium chloride, the data of which are presented in Table 3. 30% solution of potassium carbonate was used to precipitate calcium and 32% solution of potassium hydroxide was used to precipitate magnesium.

Table 3. Study of the influence of the ratio of potassium hydroxide and carbonate on the degree of purification of the solution from Ca^{2+} and Mg^{2+} ions at a temperature of 50 °C

№	Rate, %	pH	S:L	Viscosity, cP	Density, g/sm^3
White crystalline potassium chloride					
1.	90	7,01	1: 18,2	2,793	1,177
2.	100	11,38	1: 16,3	2,876	1,179
3.	110	11,50	1: 15,7	2,907	1,180
4.	122	11,53	1: 15,4	2,972	1,183
Flotation Potassium Chloride					
5.	90	11,96	1: 4,43	3,140	1,187
6.	100	12,03	1: 4,89	3,154	1,189
7.	110	12,12	1: 5,13	3,209	1,192
8.	122	12,17	1: 5,42	3,269	1,194

Duration of mixing time is 30 min

It can be seen from Table 3 that while cleaning a solution of white crystalline potassium chloride with an increase in the ratio of potassium hydroxide and potassium carbonate from 90 to 122%, the pH of the solutions increases from 7,01 to 11,53 and while using flotation potassium chloride, this indicator changes slightly, i.e. from 11,96 to 12,17.

The analysis results show the pH of the system while using flotation potassium chloride is higher than using halurgic potassium chloride, which is associated with a relatively high content of Ca^{2+} and Mg^{2+} ions in the solution, requiring a significant amount of precipitating alkaline reagents hydroxide and potassium carbonate.

When white crystalline potassium chloride solutions are used for purification, with an increase in the S:L ratio, the density values increase slightly from 1,177 to 1,179 g/cm^3 and the viscosity increases slightly - from 28,76 to 29,07 cPs. When using flotation potassium chloride, with an increase in the ratio of S:L, the density of the solution does not change and the viscosity shows a slight increase from 11,54 to 12,69 cPs (Fernández *et al*., 2012). Table 4 shows the data on the chemical composition of the liquid phase after the purification of the solutions.

The degree of purification of the solution from Mg is more than 99%.

Table 4 shows that with an increase in the rate of precipitation solutions from 100 to 122% during the purification of white crystalline potassium chloride, the degree of purification from calcium ions increases.

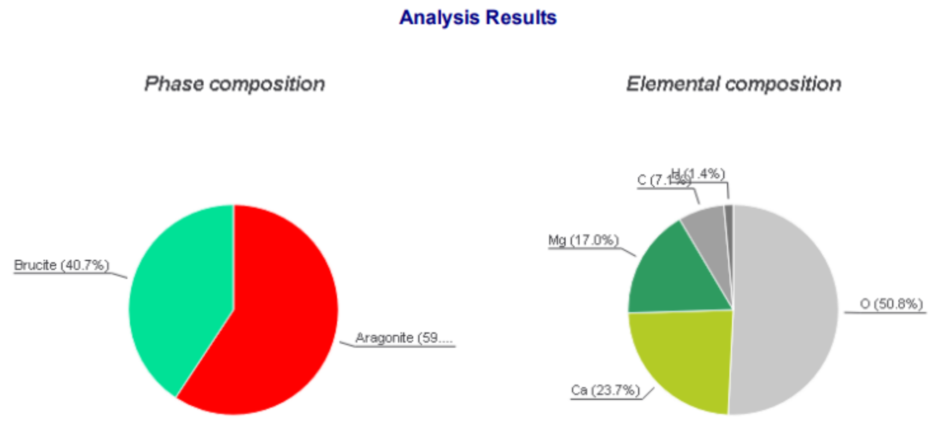
Table 4. Chemical contents of the liquid phase after the purification process

Sample numbers correspond to sample numbers in Table 3		K	Na	Ca	Mg	Degree of purification from Ca, %
White crystalline potassium chloride	2	14,76	0,54	0,04	-	69,05
	4	15,37	0,51	0,03	-	81,63
Flotation Potassium Chloride	6	14,61	3,64	0,09	-	71,43
	8	15,84	3,17	0,05	-	79,12

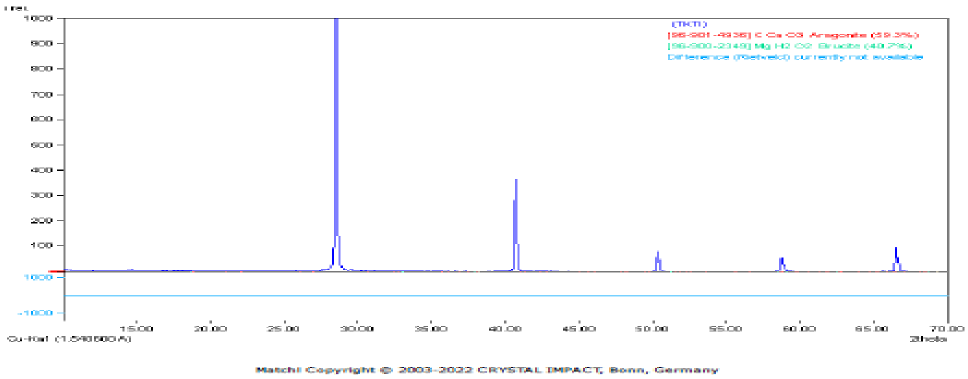
In the case of using white crystalline potassium chloride, the degree of purification from calcium increases from 69.05 to 81.63 and in the case of flotation potassium chloride, from 71.043 to 79.12 %. In accordance with this, the content of sodium, potassium and calcium ions also changes (Barbara *et al*., 2018; Lokshin, 2009). The degree of purification of the solution from magnesium ions in all samples was high and reached almost 100%.

Thus, the maximum degree of purification from calcium ions (81,63 %) was achieved using flotation potassium chloride at a rate of 122%.

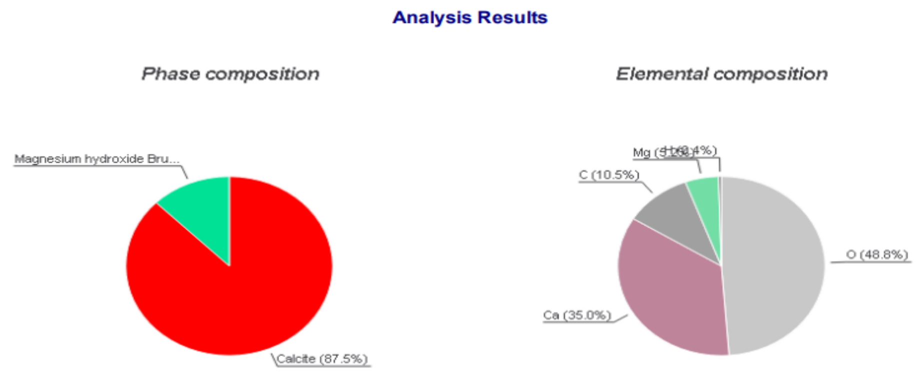
According to the data in X-ray phase analysis (Figure 2), obtained precipitates consist mainly of calcium carbonate and magnesium hydroxide.



Sample 3



Sample 7



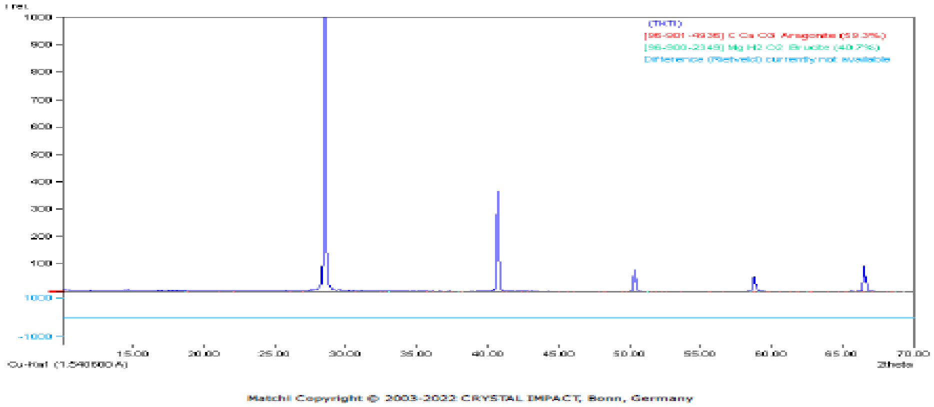


Figure 2. X-ray patterns of the obtained precipitation

Previously obtained experimental data (Teir *et al*., 2007) and physicochemical analyzes (Mah *et al*., 1999) showed that an increase in the duration and temperature of electrolysis has a positive effect on the electrolysis process.

Table 5. The mineralogical composition of the obtained precipitation

Sample numbers correspond to the numbers in table 3	Name of minerals	Entry number	Formula sum	Crystal system	Unit cell	Content, wt%	
						When using the original potassium chloride	
						Flotation at the rate	Halurgic at the rate
3.	Calcite	96-901-4936	$CaCO_3$	orthorhombic	a = 4,9713 Åb=8,0311 Åc=5,8141 Å	-	110
	Magnesium hydroxide	96-900-2349	$Mg(OH)_2$	trigonal (hexagonal axes)	a = 3,1264 Åc=4,7315Å		
7.	Calcite	96-901-6707	$CaCO_3$	trigonal (hexagonal axes)	a = 4,9844 Åc=17,0376Å	110	-
	Magnesium hydroxide	96-100-0055	$Mg(OH)_2$	trigonal (hexagonal axes)	a = 3,1420 Åc=4,7660Å		

In accordance with this, the duration and temperature of the process were 30 min and 55°C, respectively. Further, to obtain potassium hydroxide by electrolysis, studies were carried out, the results of which are presented in Table 6. It can be seen from this that under given conditions, with an increase in the duration of the passage of the initial solutions (with an increase in the time of supply to the electrolyzer), the concentration of potassium hydroxide increases from 29,098 to 129,828 %.

The effect of current density on the output parameters of the process of obtaining potassium hydroxide by the electrolysis method has been studied. In this case, the direct current density was varied in the range of 1-5,5 A/dm^2. Electrolysis was carried out: at a temperature of 30 °C and a concentration of potassium chloride of 30% (Table 6). The output parameter is the concentration of hydrogen ions in anolyte and catholyte solutions.

Table 6. The dependence of the product yield on the duration of the process at a temperature of 30 °C

№	The density of the KOH solution inflowing the cathode at 15 C, g/sm^3		KOH concentration in catholyte after electrolysis, %	Current density, A/dm^2	Increase of KOH concentration in catholyte, %	pH of solutions after electrolysis	
	before electrolysis	after electrolysis				Catholyte, KOH.	Anolyte, KCl
1.	1,267	1,273	29,098	1	0,61	13,58	2,35
2.		1,275	29,258	2	0,77	13,68	2,35
3.		1,277	29,468	3	0,98	13,67	2,35
4.		1,278	29,588	4	1,10	13,71	2,75
5.		1,279	29,748	5	1,26	13,76	2,91
6.		1,280	29,828	5,5	1,34	13,78	3,75

* Duration of electrolysis – 30 min
** The initial concentration of the KOH solution inflowing the electrolyzer is 28,49 %

It was found that within 20 minutes it is possible to increase the concentration of the potassium hydroxide solution by 1% (Table 7).

Table 7. The dependence of the product yield on the duration of the process at a temperature of 55 °C and a current density of 5 A/dm^2

№	Process duration, min	KOH density at 15 ºC, g/cm^3		KOH concentration before electrolysis, %	KOH concentration after electrolysis, %	The ratio of solutions entering the electrolysis		Increase in KOH concentration, %	pH of KOH solution after electrolysis
		before electrolysis	after electrolysis			KOH	KCl		
1.	20	1,267	1,271	28,488	29,508	1,036	1	1,02	13,62
2.	26		1,265		29,798	1,048	1	1,31	13,68
3.	33		1,275		29,878	1,066	1	1,39	13,73
4.	40		1,278		30,038	1,077	1	1,55	13,82
5.	50		1,285		30,228	1,098	1	1,74	13,88

4. Conclusion

Thus, as a result of the research, the elemental composition of white crystalline and flotation potassium chloride used to obtain potassium hydroxide was determined, which showed the need for their purification from calcium and magnesium ions. The highest degree of purification of solutions from calcium (81,63 %) was achieved at a ratio of 122% and from magnesium - at almost all rates from 100 to 122%.

With electrolysis for 20 minutes, it is possible to increase the concentration of the potassium hydroxide solution by 1,0 %, which is considered the optimal indicator by many enterprises.

It has been established that with an increase in the anodic current density, the concentration of potassium hydroxide in the solution increases.

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