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DEVELOPMENT OF TECHNOLOGIES FOR THE PRODUCTION OF SODIUM BICARBONATE, BURKEITE AND AMMONIUM SULFATE FROM SULFATE SALTS OF KARAKALPAKSTAN

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The aim of the study is to create a resource-saving waste-free technology for the production of sodium bicarbonate, burkeite and ammonium sulfate by conversion of sulfate salts of Karakalpakstan with ammonium bicarbonates.

RESEARCH OBJECTIVES:

investigation of the conversion process of sodium sulfate by carbon ammonium salts using thermodynamic analysis and isotherms of solubility of a three- and four-component mutual system $2NH_4^+$, $2Na^+//2HCO_3^-$, SO_4^{2-}-H_2O at temperatures of 30^0 and 70 ° C; study of the process of purification of solutions of natural mirabilite by the lime method in the presence of recycled carbonate-sulfate solutions;

determination of the nature of the influence of input technological parameters on the analytical indicators of the process of obtaining sodium bicarbonate and burkeite by conversion methods;

investigation of the process of evaporation of masterbatch solutions with the production of ammonium sulfate in the intervals of variation of technological parameters determined from the system Na^+, NH_4^+ // $1/2SO_4^{2-}$-H_2O;

study of the influence of technological parameters on the optimal

technological parameters of obtaining burkeite by salting soda ash from purified solutions of natural mirabilite;

determination of rheological properties of solutions and suspensions formed in intermediate stages, and mineralogical compositions of solid sediments and products using modern physico-chemical analysis methods;

The object of the study is mirabilite of the Tumryuk deposit; soda ash OOO "Kungrad Soda Plant", ammonium carbonate salts, sodium bicarbonate conversion products, ammonium sulfate and burkeite.

The subject of the study is the development of a technology for complex processing of natural mirabilite by conversion and salting method to obtain burkeite, sodium bicarbonate and ammonium sulfate.

INTRODUCTION.

It is impossible to imagine the development of the economy in the world without the chemical industry, the branches of which should be based on high technologies, and the products manufactured according to the nomenclature should meet international standards. Therefore, the modernization of the chemical industry and the localization of the raw material base of manufacturing enterprises are relevant.

Today in the world it is important for the localization and use of raw materials for the production of non-phosphate, environmentally friendly and high-quality detergents with high functional value based on natural organic and inorganic substances, the following scientific solutions can be justified: to determine the optimal conditions of the mirabilite purification process; to determine the main technological factors affecting the process of obtaining soda ash, burkeite and ammonium sulfate; theoretical justification of the complex processing of chlorine-free fertilizers into ammonium sulfate; creation of a technology for the synthesis of burkeite based on sulfate and sodium carbonate.

In our republic, as a result of extensive scientific research and technological developments, certain results have been achieved for the production of detergents based on local resources and waste. In this regard, productively using local raw materials, the development of technologies for the production of sodium bicarbonate, burkeite and ammonium sulfate from sulfate salts of Karakalpakstan is important.

Scientific research works on the production of sodium bicarbonate and other soda products are widely covered in the literature.

In Uzbekistan, research on the development of technology for the production of soda ash and soda products used in the metallurgical, chemical, glass, food industry and other sectors of the economy; compositions of various soda products have been created and introduced into production; technological processes for obtaining construction and other materials from their waste have been developed.

The results of thermodynamic evaluation [1] of the probability of the reaction of mirabilite and thenardite with carbon ammonium salts (NH_4HCO_3, NH_2COONH_4 and $(NH_4)_2CO_3$), physico-chemical studies of three- and four-component complex water systems, including sulfates, carbonates and bicarbonates of sodium and ammonium:

At application Na_2SO_4:

1. $(NH_4)_2CO_3+Na_2SO_4 \rightarrow Na_2CO_3+ (NH_4)_2SO_4$

2. $2(NH_4)_2CO_3+Na_2SO_4 \rightarrow 2NaHCO_3+ (NH_4)_2SO_4+ 2NH_3$

3. $2NH_4HCO_3+Na_2SO_4 \rightarrow 2NaHCO_3+(NH_4)_2SO_4$

4. $2NH_2COONH_4+Na_2SO_4 \rightarrow 2NH_2COONa+(NH_4)_2SO_4$

5. $2NH_2COONH_4+Na_2SO_4+4H_2O \rightarrow 2NaHCO_3+2NH_4OH+(NH_4)_2SO_4$

6. $2NH_2COONH_4+ Na_2SO_4 \rightarrow Na_2CO_3+(NH_4)_2SO_4+(NH_2)_2CO$

At application $Na_2SO_4 \cdot 10H_2O$:

1. $(NH_4)_2CO_3 + Na_2SO_4 \cdot 10H_2O \rightarrow Na_2CO_3+ (NH_4)_2SO_4 + 10H_2O$

2. $2(NH_4)_2CO_3+Na_2SO_4\cdot10H_2O\rightarrow2NaHCO_3+(NH_4)_2SO_4+2NH_3+10H_2O$

3. $2NH_4HCO_3+Na_2SO_4\cdot10H_2O\rightarrow2NaHCO_3+(NH_4)_2SO_4+10H_2O$

4. $2NH_2COONH_4+Na_2SO_4\cdot10H_2O\rightarrow2NH_2COONa+(NH_4)_2SO_4+10H_2O$

5.

$NH_2COONH_4+Na_2SO_4\cdot10H_2O+4H_2O\rightarrow2NaHCO_3+NH_4OH+(NH_4)_2SO_4+10H_2O$

6.

$2NH_2COONH_4+Na_2SO_4\cdot10H_2O\rightarrow Na_2CO_3+(NH_4)_2SO_4+(NH_2)_2CO+11H_2O$

From the results of thermodynamic evaluation of sulfate systems, it is established that the solid-phase reaction in the system Na_2SO_4-NH_4X-H_2O (where X – CO_3^-, HCO_3^-, NH_2COO^-) with education Na_2CO_3, $NaHCO_3$, $(NH_4)_2SO_4$, $(NH_2)_2CO$ and NH_4OH in temperature ranges 273-383 K is unlikely when using sodium sulfate. When using mirabilite (in the presence of water) at a temperature above 343 K, the probability of its occurrence appears [2].

However , in the system under study , the component NH_4X it is desirable to use in the form of NH_4HCO_3.

It is established that the degree of conversion of carbonates in a number of stability systems $(NH_4)_2CO_3$-Na_2SO_4-H_2O < NH_2COONH_4-Na_2SO_4-H_2O < NH_4HCO_3-Na_2SO_4-H_2O noticeably increases. The present phenomenon is associated with the reduced temperature resistance of ammonium carbonate, i.e. decomposition $(NH_4)_2CO_3$ with education NH_4HCO_3 and NH_3.

Based on the above, it can be assumed that the interaction of ammonium carbonates with sodium sulfates in an aqueous medium can form Na_2CO_3, $NaHCO_3$, $(NH_4)_2SO_4$, $2Na_2SO_4\cdot Na_2CO_3$ and $Na_2SO_4\cdot (NH_4)_2SO_4\cdot 4H_2O$.

The mutual system has been studied by graphical and analytical methods of analysis [3] $2Na^+$, $2NH_4^+$ // $2HCO_3^-$, SO_4^{2-} - H_2O at a temperature of 15, 35°C and in the intervals the ratio $1 > Na_2SO_4 / 2NH_4HCO_3 > 1$, which was the theoretical basis for the conversion of ammonium carbonate sulfate salts to

produce sodium bicarbonate and ammonium sulfate. It is established that the more content in the system Na_2SO_4, the higher the proportion of ammonia use and the smaller the amount Na_2SO_4, the greater its degree of transformation into $NaHCO_3$.

As the thermodynamic analysis of the chemical reactions of sodium sulfates with ammonium carbonate salts and the mutual solubility of the four-component system shows Na^+, NH_4^+ // ½ SO_4^{2-}, HCO_3^- - H_2O, the system may form $NaHCO_3$, Na_2CO_3, $(NH_4)_2SO_4$ and their double salts $2Na_2SO_4 \cdot Na_2CO_3$, $Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$.

When soda and ammonium sulfate are obtained from mirabilite , the following reaction occurs.

$$Na_2SO_4+2NH_4HCO_3 \quad 2NaHCO_3 \pm (NH_4)_2SO_4$$

For laboratory studies, a 28% purified solution of mirabilite from the Temryuk deposit and a solution of ammonium bicarbonate obtained in laboratory conditions were used.

The influence of the ratio was determined J : T, the norms of ammonium bicarbonate, the concentration of the circulating solution of ammonium sulfate and the temperature of the process (Table 1).

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Table 1

The effect of technological parameters on the conversion process of sodium sulfate with ammonium bicarbonate at J:T = 2:1

No.Experience	(NH4)2SO4 in reverse	The norm	Температура,	Content of components, mass.%							Na^+ output in the solid phase
				Liquid phase				Solid phase			
				Na^+	CO_2	SO_4^{2-}	NH_3	Na^+	CO_2	SO_4^{2-}	
	0	100	30	3,72	5,22	29,07	10,31	20,21	30,81	-	72,92
			40	3,70	5,54	28,12	9,97	21,04	27,49	-	72,12
			50	3,30	6,21	25,80	9,14	21,12	21,02	-	71,90
		110	40	3,44	3,49	23,82	8,44	21,71	39,14	-	74,41
			50	3,80	4,11	25,43	9,01	20,81	29,65	-	74,32
			60	4,00	4,60	34,82	12,35	23,03	30,10	-	73,34
	10	100	40	3,56	4,85	33,75	11,97	27,42	39,91	13,19	73.80
			50	4,12	4,61	30,67	10,87	26,51	33,64	15,38	72.60
			60	4,08	4,55	36,25	12,85	28,45	51,32	13,64	72,02
		110		4,31	2,18	36,89	13,08	27,83	40,74	12,2	75,85

0		10	0							2	
1			0	4,47	4,85	33,61	11,92	28,02	39,21	12,73	74,59
2			0	4,91	4,96	30,29	10,74	29,41	31,94	13,84	73,86
3	20	100	0	4,25	2,84	38,04	13,49	29,24	40,41	16,46	74,04
4			0	4,56	2,91	38,69	13,72	26,61	39,62	18,61	73,33
5			0	4,94	4,94	43,19	15,31	23,52	24,94	17,64	72,89
6		110	0	4,34	2,88	39,81	14,11	30,04	39,35	18,24	80,22
7			0	4,62	4,05	43,12	15,29	27,81	34,15	17,88	80,07
8			0	5,11	5,55	43,30	15,35	25,61	34,87	18,11	79,84

The density of the suspension and filtrate fluctuate in the intervals 1,29-1,33 and 1,17-1,29 g/sм^3 accordingly , at J:T= 2:1 and 3:1. The humidity of the product is 22,18 - 48,40%, which increases with an increase in the norm of ammonium bicarbonate, the content of ammonium sulfate in the circulating solution and the temperature of the process.

The filtration rate for all samples is at least 977,12 kg/m^2· hour and fluctuates in intervals 535,33-3094,71 kg/m^2·hour.

With an increase in the content of ammonium sulfate in the circulating solution, the content of the product simultaneously increases SO_4^{2-} by more than 18%, the output Na^+ in the solid phase by 3-5% and the filtration rate by 109-

380 kg/m^2 hour. With an increase in J:T in the suspension, the density of the suspension, filtrate and filtration rates decrease by almost 1.5-2 times, and the moisture content of the product increases.

Analysis of the experimental data obtained allows us to conclude that the optimal conditions for the conversion of mirabilite to sodium bicarbonate and ammonium sulfate are the following: the norm of the ammonium bicarbonate solution is 100-105%, the concentration of the circulating ammonium sulfate solution is 0-10%, the temperature is 30-40 ° C, the ratio is J: T – (2.5-3):1. Under these conditions, the conversion rate is more than 85% and the concentration of the resulting ammonium sulfate solution (31-36%) is quite sufficient for its processing into a dry product.

Based on the literature data, binary systems and nodal points of the triple system are analyzed Na_2CO_3-Na_2SO_4-H_2O, which made it possible to determine the optimal conditions for obtaining burkeite by salting out sodium sulfate with the addition of sodium carbonate. For this purpose, the mutual solubility of salts in the system has been studied Na_2CO_3-Na_2SO_4-H_2O isothermal method at temperatures 25, 30 and 70°C.

The solubility diagram of the system at 25 ° C consists of the crystallization branches of ten-water sulfate and sodium carbonate.

Isothermal solubility diagram at a temperature of 30°C consists of branches of crystallization of mirabilite ($Na_2SO_4 \cdot 10H_2O$), thenardite (Na_2SO_4), ten- and seven-way sodium carbonate and double compound composition $2Na_2SO_4 \cdot Na_2CO_3$ (burkeite).

At the solubility isotherm at 30 ° C, the crystallization of mirabilite in solution is observed at a concentration of solutions Na_2SO_4 26,18-29,15% and 0,0-8,07% Na_2CO_3. Crystallization of thenardite is observed in the concentration range 15,18-24,00% and 10,23-20,45% for Na_2SO_4 and Na_2CO_3 accordingly. Concentration interval of solutions 9,67-14,39% for Na_2SO_4 и

20,75-25,40% for Na_2CO_3 corresponds to the crystallization of a double compound of the composition $2Na_2SO_4 \cdot Na_2CO_3$. In the concentration ranges of 7.9-9.36% and 25.70-26.43%, respectively, for sodium sulfate and carbonate, crystallizes in the system $Na_2CO_3 \cdot 7H_2O$. Ten-aqueous sodium carbonate crystallizes in the concentration range of 0.0-7.3% for sodium sulfate and 26.50-27.80% for sodium carbonate [4].

The liquidus curve of the solubility diagram at 70 ° C is characterized by the presence of three branches of crystallization of the initial components and a double compound $2Na_2SO_4 \cdot Na_2CO_3$. Rectilinear rays emanating from the liquidus line of this junction intersect at a point located on the anhydrous side of the concentration triangle. This indicates that this compound does not contain crystallization water.

From the locations of the crystallization area of sodium sulfates and carbonates, their crystallohydrates and double salts, it follows that it is technologically possible to isolate a double salt of burkeite, which can be used in the preparation of synthetic detergents and in the glass industry with the replacement of imported sodium sulfate.

Based on the study of isothermal diagrams, experiments were carried out under different conditions. Studies have shown that at a temperature not lower than 70 ° C, the duration of the process is 30-60 minutes, the yield of burkeite increases to 98.75% (Table 2).

Table 2

The results of the analysis of the bouquet obtained at the model installation

	t °C	The chemical composition of the bouquet of masses.: %			SO_4^{2-}/CO_3	Na_2CO_3/Na_2SO_4	The content of burkeite, mass. %	Output for the first cycle, mass. %
		Na^-	SO_4^{2-}	CO_3^{2-}				
	70	33,97	45,73	20,33	2,25	0,90	69,23	30,24
	90	35,19	41,45	23,36	1,77	0,90	55,31	58,09
	90	34,57	48,39	17,04	2,84	0,89	98,75	51,73

The rheological properties and filterability of the suspension formed during the conversion of a purified solution of sodium sulfate with ammonium carbonate salts, the evaporation of the mother liquor and the salting of sodium sulfate with soda ash in wide ranges of variation of technological parameters depending on temperature were studied,

J : T, liquid phase concentrations. It is established that in the studied ranges of parameter variation, the rheological properties and filterability of the resulting suspensions fully meet the technological requirements.

CONCLUSION

The research results allow us to formulate the following general conclusions:

For the purpose of physicochemical substantiation of the conversion process of sodium sulfate by ammonium carbonate salts, a thermodynamic analysis of all possible reactions was carried out and heterogeneous phase equilibrium in the systems was investigated $2NH_4^+$, $2Na^+$ // SO_4^{2-}; HCO_3^{2-} - H_2O; Na_2CO_3 - Na_2SO_4 – NaCl - H_2O; Na_2SO_4 - $(NH_4)_2SO_4$ - H_2O which are the scientific basis for the development of a waste-free technology for processing natural mirabilite into sodium bicarbonate, burkeite and ammonium sulfate.

It was found that the conversion of ammonium bicarbonate with mirabilite solution is carried out at a rate of 105-115% of stoichiometry, a temperature of 30-40 ° C and the concentration of a circulating solution of ammonium sulfate is 0-10%, the ratio of liquid and solid phase is (2.5-3): 1, under these conditions the conversion rate is more than 85%.

USED LITERATURE

1. Karapetyants M.H. Methods of comparative calculation of physico-chemical properties. M., "Science", 1965.

2. Koshanova B.T., Erkaev A.U., Sharipova H.T., Terekhin E.L. Thermodynamic study in sulfate systems Na_2SO_4-NH_4HCO_3(CO_3^{2-}, NH_2COO^-)-H_2O. UzMU Khabarlari, Tashkent 2013.

3.Koshanova B.T., Erkaev A.U., Tairov Z.K., etc. Mutual system $2Na^+$, $2NH_4^+$ // $2HCO_3^-$, SO_4^{2-} -H_2O and its application to the substantiation of the technology of obtaining soda from mirabilite. // Chemistry and Chemical Technology. No. 3 - Tashkent, 2012, - From 15-20.

4.№ IAP 05034. Koshanova B.T., Erkaev A.U., Begdullaev A.K., Burashev N.B., Tairov Z.K. The method of obtaining burkeite. Patent of the Republic of Uzbekistan. -Tashkent, 2018.