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TECHNOLOGICAL AND ECONOMIC ESTIMATION OF ACID DISSOLUTION OF LANGBEINITE CONCENTRATE WITH PROCESSING THE OBTAINED SOLUTIONS IN THE FERTILIZER

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Abstract. The technological and economic evaluation of two processes of langbeinite concentrate processing in a conditioned fertilizer was carried out with using mineral acids (nitric and phosphatic acid) for its dissolution. The first process allows to obtain non-chloride fertilizer (potassium-magnesium), and the second one allows to obtain not only potassium-magnesium, but such complex nitrogen-phosphorus fertilizer as diammophos. The optimal conditions for realization processes of acid dissolution, salting-out of schoenite from obtained acid-saline solutions using isopropyl alcohol, neutralization of solution phosphoric acid by ammonia were determined. It is shown that the obtained products entirely meet the requirements of standards. Technical and economic calculations confirmed the profitability and feasibility of the proposed technological processes.

Keywords: langbeinite concentrate, dissolution, salting-out, potassium-magnesium, neutralization, diammophos.

1. Introduction

As it is well known, Ukraine, which possesses powerful Carpathian deposit of polymineral potash ore with reserves of more than 7 billion tons, turns into the importer of potash fertilizers rather than remains their powerful producer. Primarily this is conditioned by low efficiency of existing technologies processing of these ores, namely low extract of useful components, the formation of numerous large-tonnage solid and liquid wastes and very low quality of the obtained fertilizers. Therefore, intensification of the dissolution process of not easily soluble potassium minerals, particularly langbeinite concentrate, increasing the degree of extraction of valuable components from it and obtaining fertilizer by using mineral acids cause considerable practical interest. An effective way of potassium-magnesium salts selective extraction from obtained acid-saline solutions is the use of organic solvents, which allow to get a clean final product with a high yield, significantly accelerate the fertilizers crystallization process and reduce energy consumption for its implementation.

The aim of this work was:

- defining of processes technological parameters of langbeinite concentrate dissolution in aqueous solutions of nitric and phosphoric acids;
- definition of the regularities and conditions of potassium-magnesium salts salting process from the obtained acid-saline solutions using isopropyl alcohol, with its next distillation from mother waters and cyclic usage;
- determination of the conditions of neutralizing the phosphatic saline solution with the help of ammonia and processing the obtained solution into a complex NP-fertilizer;
- performing of an economic analysis of new technological processes of langbeinite concentrate processing and estimation of their effectiveness.

2. Experimental

The langbeinite concentrate, used in the researches, was obtained from a representative sample of potash ore Stebnik deposits with a high content of sparingly soluble minerals of such composition (wt %): langbeinite $K_2SO_4 \cdot 2MgSO_4$ – 27.03; halite NaCl – 20.055; polyhalite $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$ – 2.89, kainite $KCl \cdot MgSO_4 \cdot 3H_2O$ – 44.75; kieserite $MgSO_4 \cdot H_2O$ – 3.875; insoluble residue – 1.395 and H_2O – 0.025. Preliminarily the ore was milled in a ball mill drum; fraction with particle size less than 1 mm was sifted out and treated with 50 % aqueous solution of isopropyl alcohol in the mass ratio between ore and extractant 1:3 during 30 min according to the method described in [1]. Chloride minerals of ore (halite and kainite) were extracted in the solution and the sulfate minerals (langbeinite, polyhalite, kieserite) remained in the solid phase. The content of individual ions in a filtered solid phase, which is called langbeinite concentrate, was analyzed according to such well-known methods as K^+ and Na^+ – flame photometry [2], Mg^{2+} and Ca^{2+} – complexometry, Cl^- – mercurrometry and SO_4^{2-} – gravimetric analysis [3]. The content of isopropyl alcohol was determined by the combined method, namely by its oxidation in the strong acid solution by potassium dichromate to acetone with the following iodometric definition of its content [4], which was calculated for isopropyl alcohol. The water content in the langbeinite concentrate was calculated as the difference between 100 % and the content of the corresponding ions and isopropyl alcohol in it. Composition of the langbeinite concentrate individual samples, derived from above cited ore composition under the same extraction conditions is slightly different (Table 1).

In the studies the selected fraction of the langbeinite concentrate with a particle size of less than 1 mm was used. Bulk density of the selected fraction of langbeinite concentrate was determined in accordance with the well-known method for bulk materials [5]. It was 1380 kg/m^3.

The influence of temperature, concentration of acid solution, mass ratio between the liquid and solid phases (L:S) and hydrodynamic conditions on the degree of potassium and magnesium sulfates extraction was studied in the temperature-controlled glass reactor, which was equipped with a bilobate stirrer made of faolite. Geometric simplexes of the reactor corresponded to industrial simplexes. Periodically the samples of liquid phase were collected using a special sampler, connected to a vacuum pump and equipped with a millipore Schott filter (porosity 40), that prevented the ingress of undissolved solids and clay particles in the sample. In collected samples the content of K^+ and Mg^{2+} was determined using above cited methods; as a result the corresponding degrees of extraction were calculated.

We studied the possibility and necessary conditions for the precipitation of schoenite from salt solutions obtained after dissolving in nitric and phosphoric acids. The solutions were treated with 86–88 % aqueous solution of isopropyl alcohol, which fits the composition of condensate isopropyl alcohol after its distillation from aqueous salt solutions. In the experiments the ratio of added alcohol solution to the mass of the initial solution was changed. After mixing to due salting-out action of alcohol during 30–40 min schoenite precipitated.

The filtered saline mother waters of nitric acid were served for distillation of isopropyl alcohol, that was carried out under atmospheric pressure on a standard laboratory plant. The obtained condensate which has density of 0.820–0.826 g/cm^3 corresponding to 86–88 wt % of isopropyl alcohol, was used cyclically for precipitation of schoenite from the solution. After distillation water-alcohol phase solution cooled and the content of K^+, Na^+, Mg^{2+}, Cl^- and SO_4^{2-} was analyzed using above cited methods. Free nitric acid was determined by alkali titration in the presence of the methyl-orange indicator. This solution was re-used for dissolving the initial langbeinite concentrate.

The saline solution of phosphoric acid after filtration of schoenite splits into two phases: alcohol (top) and water (bottom). In the filtered sediment, water and alcohol liquid phases content of K^+, Na^+, Mg^{2+}, Cl- and SO_4^{2-} was determined using above cited methods as well as free phosphoric acid by titration with alkali in the presence of dimethyl yellow indicator [6]. Alcohol phase served to distillation of low-boiling fraction that after condensation was returned for salting-out of schoenite from the solution. Obtained after alcohol distillation, 19–20 % aqueous ammonia was added into a solution, as a result the solid was precipitated. Filtered precipitate and the filtrate were analyzed for the content of K^+, Na^+, Mg^{2+}, Cl^- and SO_4^{2-} ions using above cited methods as well as NH_4^+ – formaldehyde method [6]. Content of PO_4^{3-}ions in the solution was determined as the difference between the total equivalent concentration of cations and anions. This content is recounted in $H_2PO_4^-$ and HPO_4^{2-} depending on pH of the solution [7]. Content of HPO_4^{2-} in the sediment was determined by titration with a solution of hydrochloric acid in the presence of the methyl-orange indicator and $H_2PO_4^-$ – by titration of the same sample by alkali in the presence of phenolphthalein according to the method [6]. These concentrations were calculated into $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ salts.

Table 1

The composition of the obtained langbeinite concentrate samples

The sample of langbeinite concentrate	Content of minerals, salts and humidity, wt %									
	langbeinite	NaCl	polyhalite	Na_2SO_4	K_2SO_4	kieserite	bloedite	insoluble residue	humidity	
									isopropyl alcohol	H_2O
1	63.40	6.62	3.84	6.17	-	3.16	-	2.69	0.69	13.43
2	55.48	3.39	3.69	-	-	3.56	14.49	2.83	0.81	15.75
3	65.13	2.87	3.61	5.96	-	7.33	-	3.40	0.57	11.13
4	60.375	3.71	4.72	5.88	1.38	-	-	2.61	1.045	20.28

3. Results and Discussion

In Fig. 1 the dependency of the degrees extraction of potassium and magnesium sulfates in the solution on temperature is shown, which indicates that the degree of potassium sulfate extraction in the nitric acid solution with increasing temperature gradually increases, reaching 97.81 % at 323 K. The same technological characteristic for magnesium sulfate increases more rapidly with increasing temperature. However, with increasing degrees of extraction the main components of the fertilizer, which must be removed from the obtained saline solution of nitric acid (potassium and magnesium sulfates), the degree of calcium sulfate extracting in the liquid phase increases too from 42.70 % at 293 K to 70.80 % at 323 K. Calcium sulfate will pass into the fertilizer, contaminating it. Taking into account this fact, and the fact that with increasing temperature from 313 to 323 K the degree of potassium sulfate extraction in the solution does not change, we can establish that increasing the temperature of dissolution langbeinite concentrate in the solution of nitric acid above 313 K is inappropriate.

As shown in Fig. 1 degrees of extraction of potassium and magnesium sulfates in the solution of phosphoric acid (Fig. 1, *curves* 2, 4) with increasing temperature are increased gradually. However, increasing the temperature of the process above 323 K is impractical because it is evident that a relatively small increasing of the degree of potassium sulphate extraction at the same time will not be compensated by significant energy costs for heating.

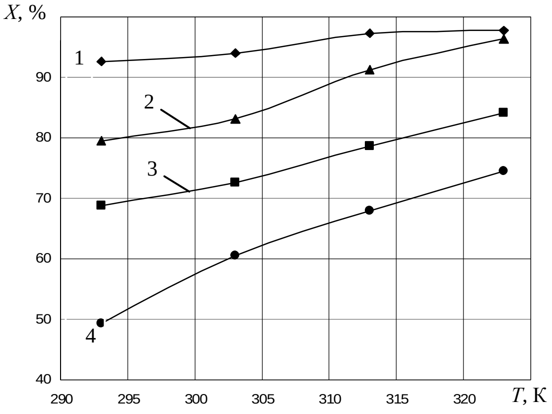

Fig. 1. Dependency of extraction degree of langbeinite concentrate components in the solution (*X*) on the temperature (*T*): potassium sulfate (1, 2) and magnesium sulfate (3, 4). Experimental conditions: solution of nitric acid (1, 3), sample of langbeinite concentrate number 1; solution of phosphoric acid (2, 4), the sample of langbeinite concentrate number 3; the temperature 293 K, the concentration of acid in the solvent 1.7 mol/l; the ratio between liquid and solid equalts to 3; time of dissolution 39 min

As it was expected, in the strong nitric acid solution, where components of langbeinite concentrate were dissolved much faster than in the weaker phosphoric acid solution, at the same temperature somewhat higher degrees of extraction were obtained. Thus, the obtained maximum degree of extraction of potassium sulfate under the experimental conditions at 313 K in the solution of nitric acid equals to 97.17 %, while in the solution of phosphoric acid it equals to 91.17 %. However, the dissolution of langbeinite concentrate in the phosphoric acid allows to introduce phosphate ions to the system and neutralizing of free phosphoric acid by ammonia $–NH_4^+$ ions, that will enable to process the obtained solutions into complex NP-fertilizer.

The research results of degree extraction of langbeinite concentrate basic components change in time (Fig. 2) show that the maximum values of these parameters in the nitric acid solution are reached during 15–20 min, while in the solution of phosphoric acid this time should be substantially increased to 25–35 min.

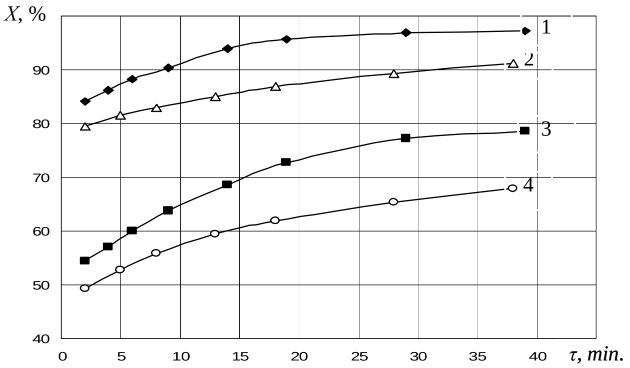

Fig. 2. Dependency of extraction degree of langbeinite concentrate components in the solution (*X*) on time (*τ*): potassium sulfate (1, 2) and magnesium sulfate (3, 4). Experimental conditions: solution of nitric acid (1, 3), sample of langbeinite concentrate number 1; solution of phosphoric acid (2, 4), the sample of langbeinite concentrate number 3; the temperature 313 K, the concentration of acid in the solvent 1.7 mol/l; the ratio between liquid and solid equals to 3

In addition to the temperature, the concentration of acid (hydrogen ions) in the solvent will greatly affect the degree of langbeinite concentrate dissolution components. The results of studying the influence of this factor on the potassium and magnesium sulphates extraction degrees in the solution of nitric and phosphoric acids are shown in Fig. 3, from which it follows that the degree of potassium sulphate extraction in the solution reaches 96.83 % at the concentration in the solvent 1.7 mol/l HNO_3 (Fig. 3, *curve* 1) and with its subsequent increase this degree does not change. The degree of magnesium sulfate extraction with increasing concentration of nitric acid in the solvent to 1.7 mol/l moderately increases (Fig. 3, *curve* 3). The degree of calcium sulfate extraction in the solution also increases with increasing concentration of nitric asid in the solvent and it amounts to 39.98 % at the concentration of 4.0 mol/l of HNO_3.

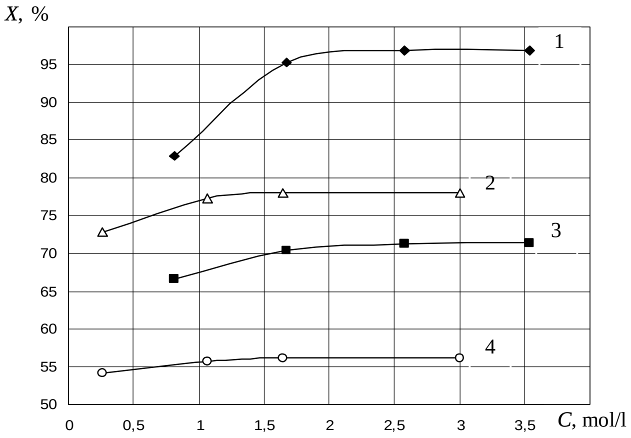

Fig. 3. Dependency of extraction degree of langbeinite concentrate components in the solution (*X*) on acid concentration (*C*): potassium sulfate (1, 2) and magnesium sulphate (3, 4). Experimental conditions: solution of nitric acid (1, 3), sample of langbeinite concentrate number 2; solution of phosphoric acid (2, 4), sample of langbeinite concentrate number 3; the temperature 293 K; the ratio between liquid and solid equals to 3

So, on the basis of the research results we can assume that the concentration of HNO_3 in the initial solvent should not exceed 1.7 mol/l. Extraction degrees of potassium and magnesium sulfates in solutions of phosphoric acid are much lower compared with solutions of nitric acid and they gradually increase in the investigated range of concentration to1.7 mol/l H_3PO_4 (Fig. 3, *curves* 2 and 4).

As it is known [8, 9], the mass ratio between the liquid and solid phases (L:S) during dissolution has a great influence on its characteristics. If in the process of potassium ore minerals dissolution the solvent is fed insufficiently, it is possible to obtain a saturated solution with a high concentration of salt, but under these conditions it is impossible to achieve necessary complete dissolution of minerals. Excess amount of liquid phase over optimal one determines that the solution does not reach the required degree of salts saturation. In both cases, the yield of final product (potassium-magnesium fertilizer) will dramatically decrease. Therefore our further researches focused on the selection of the L:S optimal value, which would ensure a high degree of extraction of K^+ and Mg^{2+} ions in the solution.

Degrees of potassium and magnesium sulfates extraction in nitric acid solution increase with increasing the amount of the liquid phase (Fig. 4, *curves* 1 and 3). Ratio L:S = 3:1 allows to achieve the highest degrees of potassium sulphate (95.68 %) and magnesium sulfate (71.14 %) extraction. The extraction degree of calcium sulfate in the solution increases from 9.97 to 31.45 % with an increase the ratio of L:S from 2:1 to 3:1. Therefore, increasing the value of L:S by more than 3:1 is obviously impractical, as at the same time volumes of solutions, needed to process, will increase without a significant increase in the extraction degree of basic components fertilizer – potassium and magnesium sulfates. Also, the extraction degree of calcium sulfate, which in the form of ballast gypsum polluted the obtained fertilizer, will increase.

Degrees of potassium and magnesium sulfate extraction in the solution of phosphoric acid, similarly as in nitrate acid, with an increase of the liquid phase in the system are increased (Fig. 4, *curves* 2 and 4). Realization of dissolution at the ratio of L:S = 3:1 under experimental conditions enables to achieve the degree of potassium sulphate extraction of 90.60 %, and for magnesium sulfate this value is 67.21 %. Further increase of L:S, as in the solution of nitric acid, is obviously impractical in view of the above cited reasons. Thus, we conclude that to achieve the required technological parameters of the dissolution expedient the ratio L:S which equals to 3:1 is necessary.

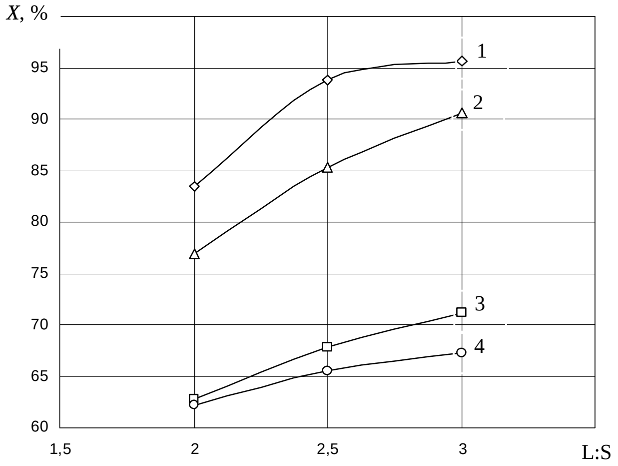

Fig. 4. Dependency of extraction degree of langbeinite concentrate components in the solution (*X*) on the mass ratio between the liquid and solid phases (L:S): potassium sulfate (1, 2) and magnesium sulphate (3, 4). Experimental conditions: solution of nitric acid (1, 3), sample of langbeinite concentrate number 2; solution of phosphoric acid (2, 4), sample of langbeinite concentrate number 4; the temperature 293 K; the concentration of acid in the solvent 1.7 mol/l

Investigation of langbeinite concentrate dissolution under different hydrodynamic conditions in the reactor showed, that the degree of extraction of potassium sulfate in the nitric acid solution reaches 97.17 % (Fig. 5, *curve* 1) at medium turbulence corresponding to Reynolds criterion (Re) 11800. This index in the solution of phosphoric acid is somewhat lower and amounts to 93.25 % (Fig. 5, *curve* 2). Degrees of magnesium sulfate (Fig. 5, *curves* 3 and 4) extraction are gradually increased as the reaction medium becomes more turbulent. The research results show that for medium considerable turbulence (Re > 16000) when the concentration of magnesium ions in the solution continues to increase, and the concentration of potassium ions is close to saturation, salting-out action of the same name SO_4^{2-}-ions in the composition of dissolved $MgSO_4$ suppresses further dissolution of potassium sulphate, so the degree of its extraction in the solution does not change. These data allow us to select the optimal mixing intensity, which corresponds to Re 11800 in the medium of nitric acid and Re 10400 in the medium of phosphoric acid.

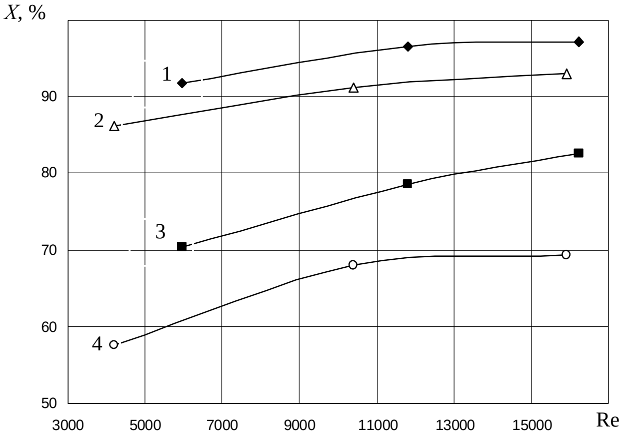

Fig. 5. Dependency of extraction degree of langbeinite concentrate components in the solution (*X*) on value of Reynolds criterion (Re): potassium sulfate (1, 2) and magnesium sulfate (3, 4). Experimental conditions: solution of nitric acid (1, 3), sample of langbeinite concentrate number 1; solution of phosphoric acid (2, 4), the sample of langbeinite concentrate number 4; the temperature 313 K; the concentration of acid in the solvent 1.7 mol/l; the ratio between liquid and solid equals to 3

As a result of langbeinite concentrate dissolution of composition number 2 in the aqueous solution of nitric acid under optimum conditions the solution of the following composition (wt %) is obtained: K^+ – 2.89, Mg^{2+} –1.64, Ca^{2+} – 0.05, Na^+ – 0.86, Cl^- – 0.53, SO_4^{2-} – 11.29, HNO_3 – 11.68, isopropyl alcohol – 0.21 and H_2O – 70.85. The aqueous solution of isopropyl alcohol containing 86–88 wt % of C_3H_7OH is added to this solution. The mass ratio between the aqueous solution of alcohol and saline solution of nitric acid (m_2: m_1) is changed within the limits of 1.5–3.0. As a result of salting-out action of isopropyl alcohol the sediments are allocated in the solid phase. Yield and composition of these sediments are shown in Table 2.

As it can be seen, with increasing amount of added alcohol the content of schoenite $K_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$ in obtained sediments decreases and the content of epsomite $MgSO_4{\cdot}7H_2O$, on the contrary, increases sharply due to the increase of alcohol salting-out action on the latter salt. Yield of sediments by weight, potassium and magnesium sulfates increases with the increase of ratio to the value of m_2:m_1 = 2.5. With the further increase of this ratio the product yield by weight and magnesium sulfate continues to increase, whereas it is virtually unchanged by potassium sulfate. The obtained data allow to consider that the ratio m_2:m_1 = 2.5 is the optimal one for the salting process realization.

The precipitate, obtained at mass ratio m_2:m_1 = 2.5, was dried to a constant weight at the temperature of (393 ± 0.2) K and analyzed for the content of K^+, Mg^{+2}, Ca^{2+}, Cl^- and SO_4^{2-} using above cited methods. The obtained product contains in dry weight (wt %): K_2O – 28.7; MgO – 14.7; Cl^- – traces. The water content in the product does not exceed 12 wt %. Consequently, the obtained fertilizer entirely meets the standard specifications for potassium-magnesium of grade A [10].

Mother solution after separation of the precipitate was fed for low-boiling fraction distillation. Distillation was finished at the temperature of vapors 353.3 K. The obtained condensate, which had density of 0.820–0.826 g/cm^3, that corresponds to the composition (wt %): 86–88 of C_3H_7OH and 12–14 of H_2O, was re-used for salting-out of sulfate potassium-magnesium salts. The solution, obtained after distillation of isopropyl alcohol containing (wt %): K_2SO_4 – 0.74, $MgSO_4$ – 3.94, NaCl – 1.04, Na_2SO_4 – 1.89, HNO_3 –13.76, isopropyl alcohol – 0.13, H_2O – 78.50, was used cyclically for dissolution of langbeinite concentrate.

To determine the possibility of processing the saline solution of phosphoric acid into NP-fertilizer the studies were fulfiled, where the solution was obtained by dissolution of langbeinite concentrate number 3 in phosphoric acid under process optimum conditions. It contains (wt %): K^+ – 3.14, Na^+ – 0.80, Ca^{2+} –0.02, Mg^{2+} – 1.82, SO_4^{2-} – 12.26, Cl^- – 0.45, C_3H_7OH – 11.77 and H_2O – 69.74.

In the first stage of studies the sulfates were crystallized by addition of aqueous solution of isopropyl alcohol containing 86–88 wt % of C_3H_7OH. The ratio mass of added solution of alcohol (m_2) to the mass of the initial solution (m_1) was changed within the limits of 1.0–3.0. Yields of the obtained sediments by weight, potassium and magnesium sulfates and their compositions at different ratios m_2:m_1 are given in Table 3. As it can be seen, the yield of sediment as the main technological parameter of the process increases with the increase of mass of added nonsolvent. With increasing value m_2:m_1 the content of schoenite in sediments increases and the content of ballast gypsum decreases. However, increasing the ratio m_2:m_1 over 3.0 is obviously impractical, since large amounts of formed solutions will need great energy costs for distillation of isopropyl alcohol. It enables to affirm that exactly the above-mentioned value of this ratio (m_2:m_1 = 3:1) is optimal.

The precipitate obtained at mass ratio m_2:m_1 = 2.5 and dried to a constant weight at the temperature of (393 ± 0.2) K contains in dry weight (wt %): K_2O –31.2, MgO – 14.0, Cl^- – traces. The water content in the product does not exceed 12 wt %. Thus, the fertilizer obtained from saline solution of phosphoric acid, similar as from saline solution of nitric acid, entirely meets the standard specifications for potassium-magnesium of grade A [10].

After filtration of precipitate sulphates, the liquid phase separates into two: alcoholic (top) and aqueous (bottom). The research results show that with the increase of the added for salting-out mass isopropyl alcohol the ratio between the masses of alcoholic and aqueous phases is increased, the degree of phosphoric acid extraction in alcoholic phase is increased too. For the ratio m_2:m_1 = 3:1 this degree reaches 90.18 %. Therefore, we conclude that exactly the alcoholic phase after alcohol distillation should be used to neutralize the phosphoric acid by ammonia to produce nitrogen-phosphorus fertilizer. The aqueous phase containing great quantity of potassium and magnesium sulfates, should be returned to the stage of salting-out sulfates from solution of phosphoric acid.

The solution obtained after isopropyl alcohol distillation containing (wt %): K_2SO_4 – 0.44, $MgSO_4$ – 0.81, NaCl – 1.28, H_3PO_4 – 18.09, isopropyl alcohol – 0.22, H_2O – 79.16, was neutralized at different pH by means of 19–20 % aqueous NH_4OH. Due to neutralization the precipitates were isolated into the solid phase, the yield and composition of which are given in Table 4.

According to the results of studies at low molar ratio NH_3: H_3PO_4 = 1.3–2.0 (pH 7.0–8.0) the precipitations of ammonium-magnesium phosphate hexahydrate in mix with a small amount of monoammonium and diammonium phosphate, are formed in the solid phase. Humidity of obtained precipitations through their fine-dyspersated dimensions is significant and equals to 33–39 %. Precipitations yield is low (2.8–4.4 g from 100 g of solution), extraction degrees of NH_4^+ and PO_4^{3-} ions are also very low and do not exceed 3.0–5.5 %. Thus, at relatively small amount of added ammonia the ammophos (a mixture of monoammonium and diammonium phosphate) in the solid phase is not formed. With the increasing amount of added ammonia the output of precipitate is increased, extraction degrees of NH_4^+ and PO_4^{3-} ions are also significantly increased. At pH = 10.0 (molar ratio NH_3:H_3PO_4 = 2.5) $H_2PO_4^-$ and HPO_4^{2-} ions in the solution are absent, *i.e.* the complete extraction of phosphates in the sediment is achieved. Thus, the added ammonia is a reagent for forming the diammonium phosphate (NH_3:H_3PO_4 = 2.2), and the excess of ammonia serves as a salting-out agent of salt in the solid phase (NH_3:H_3PO_4 > 2.2).

Table 2

Yield and composition of sediments from saline solution of nitric acid at different mass ratios between salting-out agent and solution (*m_2*: *m_1*)

m_2:m_1	Yield of sediments, %			Composition of sediments, wt %						
	by weight	by potassium sulfate	by magnesium sulfate	Schoenite $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$	K_2SO_4	Epsomite $MgSO_4 \cdot 7H_2O$	Gypsum $CaSO_4 \cdot 2H_2O$	Free HNO_3	Humidity	
									isopropyl alcohol	H_2O
1.5:1	12.21	77.16	41.81	90.12	2.25	–	1.42	0.43	3.23	2.55
2:1	12.96	78.16	46.41	91.12	–	2.46	1.20	0.38	3.04	1.79
2.5:1	16.76	89.09	61.36	81.22	–	10.47	1.31	0.60	3.96	2.44
3:1	20.16	90.00	81.58	65.41	–	26.75	0.73	0.62	4.66	1.83

Table 3

Yield and composition of sediments from saline solution of phosphoric acid at different mass ratios between salting-out agent and solution (m_2: m_1)

m_2:m_1	Yield of sediments, %			Composition of sediments, wt %				
	by weight	by potassium sulfate	by magnesium sulfate	Schoenite $K_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$	Epsomite $MgSO_4{\cdot}7H_2O$	Gypsum $CaSO_4{\cdot}2H_2O$	Free H_3PO_4	Humidity
1:1	9.51	53.30	27.43	92.82	4.40	0.80	0.38	1.60
1.5:1	11.81	72.83	36.21	93.80	3.54	0.60	0.18	2.00
2:1	13.00	79.17	39.00	94.47	2.46	0.52	0.08	2.47
2.5:1	14.26	81.72	41.15	94.88	2.02	0.39	0.22	2.49
3:1	14.74	84.45	43.33	94.88	3.18	0.36	0.17	1.41

Table 4

The results of neutralization solution by means of ammonia at different molar ratios of NH_3:H_3PO_4

Solution pH	NH_3:H_3PO_4 molar ratio	Yield of damp prepicitation, g from 100 g of solution	Degree of extraction from solution, %		Composition of obtained sediments, wt %								
			NH_4^+	PO_4^{3-}	$NH_4MgPO_4{\cdot}6H_2O$	K_2SO_4	Na_2SO_4	$NH_4H_2PO_4$	$(NH_4)_2HPO_4$	Na_3PO_4	NaCl	$(NH_4)_2SO_4$	hygroscopic H_2O
7.0	1.3:1	2.83	3.20	3.69	56.96	0.11	0.43	4.91	3.89	-	-	0.46	33.24
8.0	2.0:1	4.37	3.05	5.50	56.45	0.13	0.49	0.39	3.08	-	-	0.21	39.25
9.0	2.2:1	6.67	39.79	47.38	10.21	0.04	0.21	-	74.99	0.02	-	-	14.53
9.5	2.3:1	12.64	67.25	79.06	3.98	0.07	0.28	-	74.53	0.50	-	-	20.64
10.0	2.5:1	21.67	76.10	100.00	2.86	0.04	0.13	-	74.70	0.78	0.15	-	21.34

Table 5

Cost of raw materials and energy for producing 1 ton of potassium-magnesium

Items of expences	Unit	Price, UAH	Using nitric acid		Using phosphatic acid	
			quantity	sum	quantity	sum
1. Raw materials:						
1.1. Langbeinite concentrate	ton	135.08	2.13	287.72	2.19	295.83
1.2. Isopropyl alcohol (negative profit)	kg	12	69.20	830.40	11.67	140.04
1.3. 57 % nitric acid (negative profit)	kg	3.20	46.61	149.15	-	-
1.4. Technical phosphatic acid (85 % H_3PO_4)	ton	4829.98	-	-	1.051	5076.31
1.5. 100% technical liquid ammonia	ton	1600	-	-	0.508	812.80
Total according to item 1	-	-	-	1267.27	-	6324.98
2. Energy costs:						
2.1. Electricity	kilowatt-hour	1.30	40.42	52.55	81.00	105.30
2.2. Water steam	Gcal	533.32	5.78	3082.59	9.43	5029.21
2.3. Fuel (natural gas)	1000 м^3	3702.09	0.0555	205.47	0.0463	171.41
2.4. Recycled cooled water	м^3	0.42	169.38	71.14	144.87	60.85
Total according to item 2	-	-	-	3411.75	-	5366.77
3. Accompanying commodity products:						
3.1. Diammophos	ton	7000	-	-	1.271	8897.00
Total (items 1 + 2 – 3)	-	-	-	4679.02	-	2794.75

Filtered damp sediment, containing 74.7 % of $(NH_4)_2HPO_4$ and 21.33 % of hygroscopic H_2O, was dried at the temperature of (333 ± 0.2) K to the constant weight and analyzed for the content of NH_4^+, K^+, Na^+, Mg^{+2}, Cl^-, SO_4^{2-}, HPO_4^{2-} and $H_2PO_4^-$ using cited above methods. The obtained product contains (wt %): N – 20.15; digestible phosphates in accounting on P_2O_5 – 52.01, H_2O – 1.0 and entirely meets the standard specifications for diammonium phosphate (diammophos) [11].

We calculated the material and energy costs to produce 1 ton of potassium-magnesium from the solutions after langbeinite concentrate acid dissolution (Table 5). To calculate the langbeinite concentrate price, data of Ref. [1] were used accounting 2012 prices. The prices of another substances were taken from Ref. [12] for isopropyl alcohol, [13] – for 1 ton of 57 % nitric acid, [14] – for 85 % technical phosphatic acid, [15] – for technical 100 % liquid ammonia and [16] – for diammophos. The prices of kilowatt-hour of electricity, 1000 m^3 of natural gas, 1 Gcal of heat and 1 m^3 of recycled cooled water were taken according to JSC "Rivneazot", December 1, 2012.

Taking into account the cost of raw materials and energy listed in Table 5, the expected prime cost of 1 ton of potassium-magnesium obtained from saline solution of nitric acid, is 7798.37 UAH; from saline solution of phosphatic acid – 4657.91 UAH. Compared with the existing cost of 12225 UAH [17] one can see that the proposed processes of langbeinite concentrate proccesing into fertilizer are profitable and feasible for the industrial realization.

4. Conclusions

On the basis of the research results, the technological and economic estimation was carried out for langbeinite concentrate proccesing in conditioned fertilizers using mineral acids (nitric and phosphatic acids) for its dissolution. The first of this processes allows to obtain non-chloride fertilizer (potassium-magnesium), and the second one – not only potassium-magnesium, but such complex nitrogen-phosphorus fertilizer as diammophos.

Optimum conditions for realization a langbeinite concentrate dissolution in an aqueous solution of nitric acid are the following: the temperature of 313 K, time of 15–20 min, the contents of nitric acid in the initial solvent 1.7 mol/l, the mass ratio between the liquid and solid phases (L:S) 3:1, the mixing intensity, that corresponds to Reynolds criterion (Re) 11800. Realization of the dissolution process under these conditions allows to achieve extraction degrees of K_2SO_4 97–98 % and $MgSO_4$ 83–84 %. To realize the process of langbeinite concentrate dissolution in an aqueous solution of phosphoric acid are necessary such conditions – the temperature of 323 K, time 25–35 min, acid content in the solvent 1.7 mol/l, L:S = 3:1, the mixing intensity, which corresponds to Re 10400. Following these conditions allows to reach extraction degrees of K_2SO_4 93–95 % and $MgSO_4$ 73–75 %. Adding into saline solutions, obtained after dissolution, 86–88 % aqueous solution of isopropyl alcohol in the mass ratio of 1:(2.5–3.0) allows to isolate schoenite into the solid phase. After schoenite dehydration the conditioned fertilizer – potassium-magnesium – was obtained, that meets the standard specifications for potassium-magnesium of grade A.

Precipitate of diammonium phosphate with 100 % yield of PO_4^{3-}-ions is generated in the solid phase after neutralizing of phosphatic acid by ammonia aqueous solutions (molar ratio of $NH_3:H_3PO_4$ = 2.5). After precipitation drying the conditioned NP-fertilizer was obtained which meets the standard specifications for diammonium phosphate (diammophos). Cyclic using of aqueous isopropyl alcohol solution and nitric acid is envisaged. The expected prime cost of 1 ton of potassium-magnesium obtained from saline solution of nitric acid equals to 7798.37 UAH, and from saline solution of phosphatic acid – 4657.91 UAH, that with the price of potassium-magnesium 12225 UAH confirms the profitability and feasibility of the industrial realization of proposed processes of langbeinite concentrate proccesing into fertilizer.

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ТЕХНОЛОГІЧНА ТА ЕКОНОМІЧНА ОЦІНКА КИСЛОТНОГО РОЗЧИНЕННЯ ЛАНГБЕЙНІТОВОГО КОНЦЕНТРАТУ З ПЕРЕРОБЛЕННЯМ ОДЕРЖАНИХ РОЗЧИНІВ У ДОБРИВА

Анотація. *Виконана технологічна та економічна оцінка процесів перероблення лангбейнітового концентрату в кондиційні добрива з використанням для його розчинення мінеральних кислот (нітратної і фосфатної), перший з яких дає змогу одержати безхлоридне калійно-магнієве добриво (калімагнезію), а другий – калімагнезію і складне азотно-фосфорне добриво – діамофос. Визначено оптимальні умови здійснення процесів кислотного розчинення, висолювання шеніту з одержаних кислотно-сольових розчинів за допомогою ізопропілового спирту, нейтралізації фосфатнокислотного розчину аміаком. Показано, що одержані продукти повістю відповідають вимогам чинних технічних умов. Техніко-економічні розрахунки підтвердили прибутковість та доцільність промислової реалізації розроблених технологічних процесів.*

Ключові слова: *лангбейнітовий концентрат, розчинення, висолювання, калімагнезія, нейтралізація, діамофос.*