

Development of Nitric Acid Benefication Technology of Phosphorite from in Presence of Ethanol

DehkanovZulfikaxarKirgizbayevich

Namangan Institute of Engineering and Technology, Republic of Uzbekistan, Doctor of Sciences
(DSc)zulfikaxor78@mail.ru

AripovXayrullaxanShukrullaevich

Namangan Institute of Engineering and Technology, Republic of Uzbekistan, Doctor of
Philosophy (PhD)aripov.khsh@gmail.com

UsmonovaZulfiyaToxitjonovna

Associate Professor, Namangan Institute of Engineering and Technology, Republic of
Uzbekistan

AliyevaMuhayyoShavkatqizi

Associate Professor, Namangan Institute of Engineering and Technology, Republic of
Uzbekistan

KamalovAkmalxonVoxido'g'li

Associate Professor, Namangan Institute of Engineering and Technology, Republic of
Uzbekistan

Abstract.The enrichment of phosphorites of Central Kyzilkum containing big amount of carbonates with nitric acid allows to obtain phosphorite's concentrates applicable for sulfuric acid extraction. The optimum parameters of that process applied to phosphorite flour, mineralised mass and washed and dried phosphorite's concentrate of CentalKyzilkum's phosphorites were offered.

Keywords:phosphoconcentrate, ethanol, nitric acid, mineralized mass,decarbonization,calcium nitrate, PK-and NPK fertilizer.

INTRODUCTION

Rational application of mineral fertilizer is the main factor for growing high and qualitative yield of agriculture plant. Therefore, optimal prevention of agriculture by mineral fertilizer is one of the topicality issues.

Uzbekistan is a country that has a large agricultural sector. In 2015, in the agriculture of the republic more than 7 million 500 thousand ton of grain and more than 3 million 350 thousand ton of cotton were collected. In addition, to cotton and grain a rich harvest of other crops was grown. In particular, 12 million 592 thousand of ton of vegetables and potatoes, 1 million 850 thousand of ton of melon macerator, 1 million 556 thousand ton of grapes and 2 million 731 thousand ton of fruit were harvested.

Currently, three joint stock companies: "Ammophos-Maxam", "Samarkandkimyo" and "Kokand superphosphate plant" produce phosphate fertilizers, which consists of a range of ammophos, Suprefos, the PS-Agro, nitrocalciumphosphate, simple and enriched superphosphate. In 2015, these companies produced 153.8 thousand ton of phosphate fertilizer (based on 100% P₂O₅). This year, startup of complex NPK-fertilizer production on the JSC "Samarkandkimyo" capacity of 240 thousand ton per year is being planned. All these plants are provided by raw

material phosphate of Kyzylkum phosphorite complex (KPC), developing deposits of the Central Kyzylkum (CK).

In order to increase production of phosphorus fertilizers on KPC increased production capacity of washed calcined phosphoconcentrate (WCPC) from 400 to 716 thousand ton per year with an average content of 26% P_2O_5 . However, the volume produced WCPC (186.16 thousand ton of P_2O_5) can not drastically change the situation, so that it does not cover the needs of agriculture in phosphate fertilizer (525.21 thousand ton of P_2O_5). In addition, now functioning on KPC enrichment scheme can not be considered rational. Increasing concentrations P_2O_5 in the WCPC (26%) as compared to its concentration in the original phosphate ore (17.4%) by only 8.6% and decrease in the series with a calcium module based on initial one by only 26.3% (2.85 to 2.1-2.3) occur on the background of the annual loss of P_2O_5 (100.9 thousand ton of P_2O_5 , or 35% of the initial P_2O_5 in phosphate ore, with the level of production in 1650 thousand ton of ore), with tails of enrichment with the status of "off-balance ore". It is necessary to find alternative methods of beneficiation of phosphate rock of the CK. In this regard, chemical enrichment approach is the most perspective one. Chemical enrichment method using nitric acid in comparison with thermal calcining, has a number of advantages: low expenditure of heat-and-power engineering; efficiency increasing of enrichment of phosphate ore more than 2 times due to the simultaneous removal from it of two ballast components (CaO and CO_2), reflecting the decrease in calcium module in the phosphoconcentrate to 1.5-1.7, thereby reducing the consumption of sulfuric acid in subsequent stages of processing; practically avoids the formation of both solid and liquid wastes, that is HNO_3 used two-sided: as a source of active hydrogen ion for the extraction of carbonates from raw material and as a nitrogen carrier - a useful part of the liquid and solid fertilizers[1].

The level of knowledge of the problem. In scientific literature, there are materials on flotation and chemical enrichment of the CK phosphorite (Nabiyev M.N., Boyko V.S., Karmyshev V.F., Amirova A.M., Madaliev S.H., Pyagay A.G.,

NamazovSh.S., Beglov B.M.). However, Kyzylkum phosphorite, along with a high degree of carbonation characterized by thin intergrowth of phosphate mineral with calcite, so some attempts to enrich them with the flotation have not led to positive results. Numerous attempts have been made to enrich Kyzylkum phosphate raw by chemical techniques using dilute solutions of nitric acid and hydrochloric acid, solutions of calcium nitrate and magnesium nitrate, allowing to increase the content of P_2O_5 in the phosphate concentrate, as well as simultaneous reducing calcium modulus to the desired value. Their main drawback is the strong foaming, a large amount of dilute solutions formation and P_2O_5 losses with them as a 100% extraction selectivity of carbonates can not be achieved.

It is presented that interest the use of dilute solutions of organic acids such as formic and acetic acid as a solvent of calcium oxide from thermo concentrate and carbonates of phosphate raw materials of the CK, which hardly decompose phosphate mineral of raw materials (NamazovSh.S., Beglov B.M., Seytnazarov A.R.). However, acetic and formic acid is produced in our in small capacity, and they are clearly not enough for large-scale production of phosphate concentrate. Second, there is the formation of large volumes of dilute solutions of acetate and calcium formate, which must somehow recycle. In addition, organic acids are very expensive.

In our conditions, the most realistic way of chemical processing of phosphate rock of the CK is the use of nitric acid followed by leaching calcium nitrate with an organic solvent - ethanol. The peculiarity of this method is simplicity of regeneration scheme of the consumable reagent - ethanol and returning it into the production cycle, thereby obtaining concentrated calcium nitrate solution is easily processed into the desired product. To prevent loss of P_2O_5 in the liquid phase prior to separation of the pulp is neutralized with ammonia; resulting soluble phosphorus transfers into dicalcium phosphate that remains in the phosphoconcentrate. The main selection criteria of HNO_3 as a reagent are: accessibility, availability of cheap raw materials base <http://annalsofrscb.ro>

and the direct demands for calcium nitrate in agriculture. In the literature there is no information on enrichment carbonate phosphate with nitric acid, followed by leaching of calcium nitrate with ethanol.

Connection of the thesis research with the thematic plans of research scientific work.

The dissertation research was carried out within the framework of the plan of scientific research innovation project of the Institute of General and Inorganic Chemistry, Uzbek Academy of Sciences: FA-2I-TO8 "Development and implementation of technology of phosphorus-potassium and nitrogen-phosphorus-potassium fertilizers on the basis of nitric acid processing phosphorite Central Kyzylkum and chloride potassium" (2011-2012), scientific and technical grant: FA-A12-T171 "Development of effective resource-saving technology of the chemical enrichment of the Central Kyzylkum phosphorite and obtaining highly concentrated phosphate fertilizers" (2012-2014).

The research objective is study Kyzylkum phosphorite enrichment by nitric acid in the presence of ethanol, followed by the processing of phosphorite concentrate in phosphorus compound fertilizers and calcium nitrate in the liquid and solid nitrogen-calcium nitrate.

The following research tasks have been formulated in order to achieve this objective:

study of the chemical enrichment of the carbonate phosphorite of CK with nitric acid, subsequent by leaching of the resulting calcium nitrate using of ethanol depending on the norm of acid and the weight ratio of phosphorite to ethanol;

investigation of ammoniation process of nitrogen-calcium-phosphate alcoholic slurry in order to prevent loss of P_2O_5 in the calcium nitrate solution;

study of the solubility diagrams of 4 fourfold component system of $Ca(NO_3)_2 - NH_4NO_3 - C_2H_5OH - H_2O$, consisting of 3 triple: $Ca(NO_3)_2 - C_2H_5OH - H_2O$; $NH_4NO_3 - C_2H_5OH - H_2O$; $Ca(NO_3)_2 - NH_4NO_3 - H_2O$ and 3 triple binary systems of $Ca(NO_3)_2 - H_2O$; $NH_4NO_3 - H_2O$ and $C_2H_5OH - H_2O$, justifying the process of extraction of calcium and ammonium nitrate off nitrogen-calcium-phosphate slurry produced during nitric acid enrichment of high carbonate phosphorite of CK with ethanol in a wide temperature and concentration range;

study of nitrogen-calcium-phosphate alcoholic slurry separation process into liquid and solid phases;

regeneration of the organic solvent - ethanol in order to return it into the cycle and study of physicochemical properties of the concentrated solution of calcium nitrate that is a by-product of the nitric acid concentration;

study of processing of calcium nitrate solution into a liquid and a solid calcium nitrate;

finding optimal conditions for the conversion of calcium nitrate into NH_4NO_3 and $CaCO_3$ using CO_2 and NH_3 ;

study of processing of chemically enriched phosphoconcentrate in wet-processing phosphoric acid (WPA);

study processes of PK- and NPK-fertilizer by mixing chemically enriched phosphoconcentrate with ammonium nitrate and potassium chloride;

working out regimes of nitric acid beneficiation of CK phosphorite on pilot plant of JSC "Samarkandkimyo" with the subsequent processing phosphoconcentrate in PK- and NPK-fertilizer and agrochemical tests of novel types of fertilizer;

technical and economic estimate of the reasonability of the production organization of chemically enriched phosphoconcentrate.

The scientific novelty of the thesis research is as follows:

for the first time there have been obtained the new data on the chemical enrichment of the CK phosphorite with nitric acid followed by leaching of the resulting calcium nitrate by ethanol solution, depending on the norm of acid and the ratio of phosphorite to ethanol;

It has been established that ammoniation of nitrogen-calcium-phosphate slurry to pH = 3 that allows to completely prevent the loss of P_2O_5 in the liquid phase;

solubility diagram studied 4 fourfold component system of $Ca(NO_3)_2$ - NH_4NO_3 - C_2H_5OH - H_2O , consisting of 3 triple: $Ca(NO_3)_2$ - C_2H_5OH - H_2O ; NH_4NO_3 - C_2H_5OH - H_2O ; $Ca(NO_3)_2$ - NH_4NO_3 - H_2O and 3 triple binary systems of $Ca(NO_3)_2$ - H_2O ; NH_4NO_3 - H_2O and C_2H_5OH - H_2O , result in which minimum amount of ethanol were defined, depending on the technological parameters of the nitric acid beneficiation of carbonate containing phosphorite;

there have been defined the physicochemical properties nitrogen-ammonium-calcium solution and in case the addition of bentonite to the solution can be obtained a granulated calcium nitrate with improved properties;

there been found the optimum conditions of the conversion of calcium nitrate that is a by-product of the nitric acid beneficiation of CK phosphorite in NH_4NO_3 and $CaCO_3$ using CO_2 and NH_3 ;

there been developed the technology for processing of chemically enriched phosphoconcentrate in WPA, PK- and NPK-fertilizer.

The practical results of the study are as follows:

there has been developed the technology for nitric acid beneficiation of calcareous phosphate raw of CK in presence of ethanol allowing to remove off raw CaO and CO_2 ballast and thereby can be reduced considerably amount of sulfuric acid, using for processing the phosphorite in WPA;

there has been regenerated the ethanol in according to scheme, and the resulting concentrated solution of $Ca(NO_3)_2$ is easily processed into liquid and solid nitrate. This HNO_3 used double-sided: as a source of active hydrogen ion for the extraction of carbonates from raw material and as a nitrogen carrier that is a useful part of the liquid and solid fertilizer;

there has been developed the flowsheet and material balance of production of chemically enriched phosphoconcentrate and on the its basis of WPA, PK-, NPK-fertilizers. Enrichment technology has been tested on a pilot plant of the JSC "Samarkandkimyo" with the yield of an experimental batch of phosphorite concentrate and agrochemical tests of PK- and NPK-fertilizer have been conducted.

Theoretical and practical signification of the research findings.

Theoretical significance of the research is to establish a scientific basis for the technology of selective extraction of carbonates from phosphorite of CK by nitric acid in the presence of ethanol using solubility diagrams of 4 fourfold component system of $Ca(NO_3)_2$ - NH_4NO_3 - C_2H_5OH - H_2O . Ethanol regeneration from the alcoholic suspension of $Ca(NO_3)_2$. Study of physical and chemical properties of the concentrated solution of $Ca(NO_3)_2$ and obtaining from it liquid and solid fertilizer. Finding the optimal conditions for the conversion of $Ca(NO_3)_2$ in NH_4NO_3 and $CaCO_3$. Obtaining WPA, PK- and NPK-fertilizer based on chemically enriched phosphoconcentrate.

The practical significance of the work lies in the selective extraction of carbonates off phosphorite with nitric acid in the presence of ethanol that can sharply reduce the consumption of sulfuric acid going to processing of phosphorite in phosphoric acid. As a by-product of the nitric acid beneficiation is obtained of calcium nitrate solution that is physiologically alkaline fertilizers, so necessary for cotton, especially in saline soils. Chemically enriched phosphoconcentrate can be served not only as a raw material for sulfuric acid extraction, but also a good ingredient for the preparation of various types of compound-mixed granular fertilizer, because of the increased content of relative acceptable form of phosphorus[2-8].

Implementation of the research findings. On the way to the enrichment of CK phosphorite by nitric acid in the presence of ethanol Uzbekistan was received a patent (№IAP 04973 "Method of enrichment high calcareous phosphorite"). The developed technology of enrichment of the CK phosphorite was tested in a pilot plant of the JSC "Samarkandkimyo" and

produced 400 kg of chemically enriched phosphoconcentrate (The act of “Samarkandkimyo” of 15th April 2016 and a certificate of “Uzkimyo sanoat” from July 14, 2016 №03-2342/14).

“Studies of the process of extraction of calcium nitrate and ammonium nitrate from nitrogen-calcium-phosphate slurry produced during nitric acid enrichment of high calcareous phosphorite in the presence of ethanol” of the thesis refers to the study of chemical beneficiation of phosphorite of CK. To leach carbonates from phosphorite CK 57.87% of HNO₃ and technical ethyl alcohol (EA) containing 96% concentration were used. To enrich the CK phosphorite were taken different brands (phosphorite flour - OPF three grades and mineralized mass - MM, waste production of WCPC on KPC). Their characteristics are summarized in Table. 1.

The norm of HNO₃ was taken based on decomposition of CaO in the phosphate raw (PR). The main raw materials in phosphate raw are fluorine-carbonate-apatite and calcium carbonate. When treatment with nitric acid the following reactions:

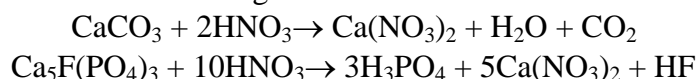
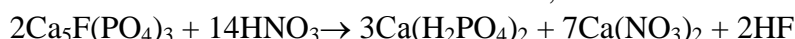


Table 1
Initial phosphate raw characteristic

Samples number	Type of phosphorite	Содержание компонентов, вес. %			P ₂ O _{5acc.} : P ₂ O _{5tot.} by citric acid, %	CaO : P ₂ O ₅
		P ₂ O _{5tot.}	CaO _{tot.}	CO ₂		
1	OPF	16.60	47.13	17.23	10.20	2.84
2	OPF	17.52	47.53	15.23	17.68	2.71
3	OPF	18.70	47.80	15.30	18.49	2.56
4	MM	15.06	44.27	14.11	9.10	2.94

If the amount of nitric acid is less than Stoichiometric one, the reaction takes place as follow:



In order to prevent loss of P₂O₅ in the liquid phase, before the divide nitrogen-calcium-phosphate alcoholic suspension (NCPA) into liquid and solid phases, it is proposed the suspension ammoniated with ammonia to pH = 3. The ammoniation process interaction between the calcium nitrate and calcium monophosphate with NH₃ is occurred, thereby it is formed that dicalcium phosphate and ammonium nitrate by the reaction:



Thus, generated CaHPO₄ precipitates and the result all phosphorus remains in the phosphoconcentrate. It is appeared that possibility to use for enriching much higher norm of HNO₃ and thereby significantly reduce the value of the unit of calcium modulus in the phosphate materials. The lower CaO: P₂O₅ in the enriched phosphorite, the smaller required sulfuric acid reagent during its extraction and the smaller the amount of phosphogypsum is threw out into the spoil.

On the basis of the solubility diagrams 4 fourfold component system of Ca(NO₃)₂ - NH₄NO₃ - C₂H₅OH - H₂O, consisting of 3 triple: Ca(NO₃)₂ - C₂H₅OH - H₂O; NH₄NO₃ - C₂H₅OH - H₂O; Ca(NO₃)₂ - NH₄NO₃ - H₂O and 3 triple binary systems of Ca(NO₃)₂ - H₂O; NH₄NO₃ - H₂O and C₂H₅OH - H₂O, was explained by the process of extraction of calcium

nitrate and ammonium nitrate from nitrogen-calcium phosphate slurry produced during nitric acid beneficiation of high calcareous phosphorite of CK by ethanol in a wide temperature and concentration range (Figure 1.).

In polytermic charts of solubility can be concluded that the components of these systems have a salting-out effect on each other. In the studied temperature and concentration intervals of novel chemical compounds systems are not formed, the system includes a simple eutonic type. On the basis of the results identified the main technological parameters of the process of enrichment of carbonate containing phosphorite of CK by nitric acid followed by leaching calcium nitrate from nitrogen-calcium phosphate slurry by ethyl alcohol.

Based on the found technological parameters investigated the process nitric acid beneficiation of phosphorite from CK in the presence of EA. Norm of the acid was ranged from 30-60% stoichiometry on decomposition of CaO in the rawmaterial. However, because different phosphate raw CO₂ content differs from each other and the norm of nitric acid on decomposition of CaCO₃ in the raw material (at the same norm for acid decomposition of CaO in the raw material) for each raw material differ from each other. Treatment of PR by nitric acid was carried out for 20-30 min. The temperature of the reaction mass is 40°C. After the decomposition of phosphate rock with nitric acid obtained nitrogen-calcium-phosphate slurry is of viscous consistency. The pulp was repulped by EA at various weight ratios of PR: EA = 1: (3 ÷ 10) and stirred for 3-4 minutes after which the contents were separated into liquid and solid phases by filtration under vacuum. Then moist phosphoconcentrate was washed clean EA at a ratio of PR: EA = 1: 2. Wet cake dried at 100°C. The dried cake and the filtrate was subjected to chemical analysis by well known techniques. The results are summarized in Fig. 2-4. The overall picture of the results of enrichment of different types of phosphate rock with nitric acid is similar. They differ among themselves only in the absolute value of the content of components in the phosphoconcentrate.

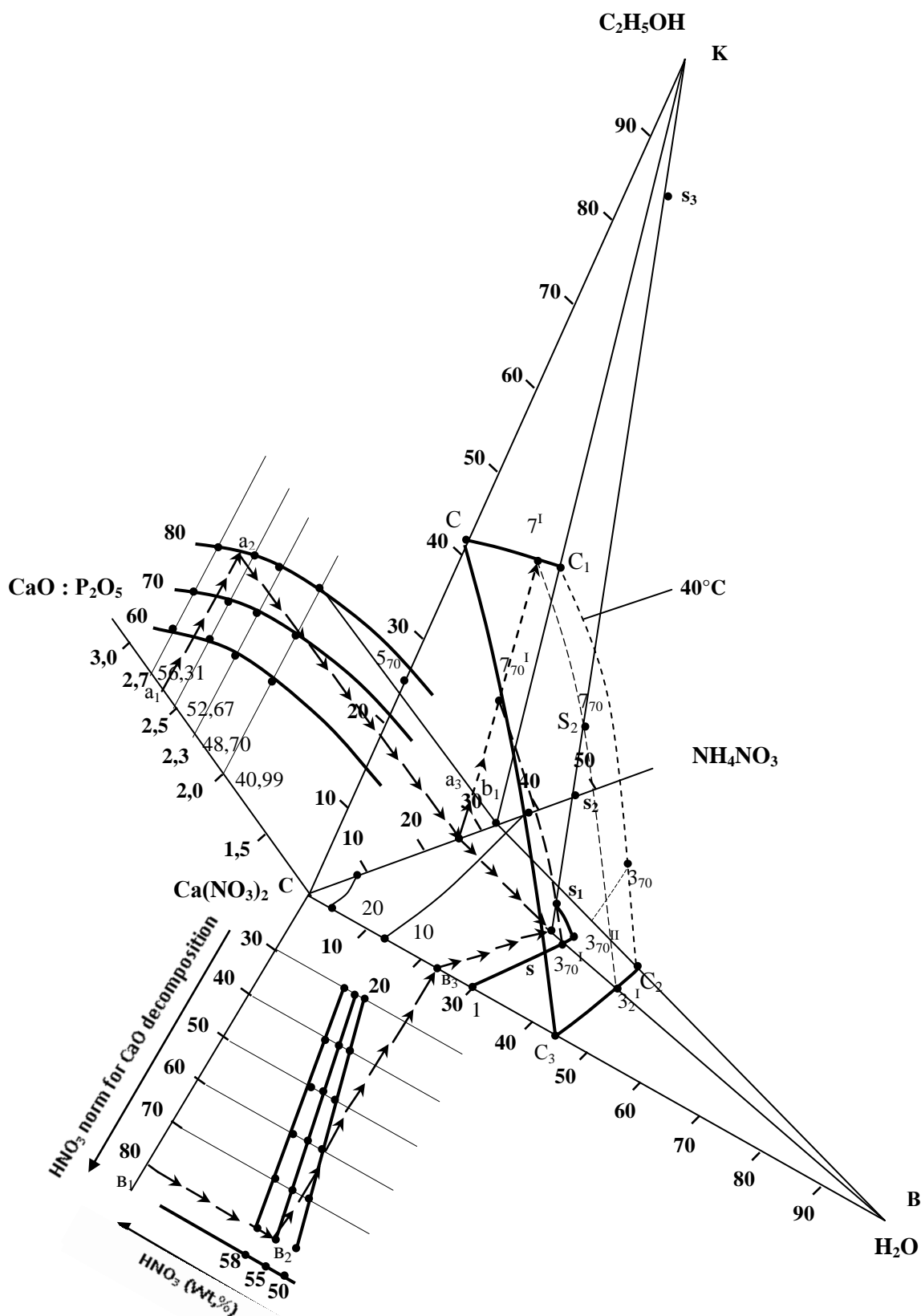


Fig. 1. Diagram solubility of $\text{Ca}(\text{NO}_3)_2$ - NH_4NO_3 - $\text{C}_2\text{H}_5\text{OH}$ - H_2O in the process of extraction of calcium and ammonium nitrates and evaporation of extract.

The higher the norm of acid, the lower is the CO_2 content and the higher is the content of P_2O_5 in the phosphoconcentrate. For the three brands OPF at enrichment by nitric acid phosphorite concentrate generated, which in composition differ themselves. So, if OPF with composition of 16.60% P_2O_5 ; 47.13% CaO ; 17.23% of CO_2 ; $\text{CaO} : \text{P}_2\text{O}_5 = 2.84$ is enriched by nitric acid compliance with its norms of 30-45% of the stoichiometry on the decomposition of CaO in the raw materials and the ratio of PR: EA from 1: 3 to 1: 10 $\text{P}_2\text{O}_{5\text{tot}}$ content in the phosphoconcentrate increases from 16.60% starting from 21.62 to 23.74% (Fig. 3-a), CO_2 content is reduced to 17.23% from the initial 7.62 to 4.26%. The degree of phosphate raw material decarbonation increases from 60 to 82% (Fig. 2-a). The calcium module is reduced from the original 2.84 from 1.95 to 1.60. The weight ratio of PR: EA very little effect on the content of P_2O_5 in the phosphoconcentrate. For example, with increasing number EA i.e. with the change of the ratio of PR: EA from 1: 3 to 1: 10 P_2O_5 content in the phosphoconcentrate increases just from 21.62 to 21.85; from 21.89 to 22.13; from 22.19 to 22.69 and 23.25 from 23.74% respectively to standards for HNO_3 - 30, 35, 40 and 45%. Calcium module respectively varies from 1.95 to 1.89; from 1.88 to 1.82; from 1.79 to 1.71 and from 1.67 to 1.60. In processing this phosphorite flour by 30% norm of nitric acid phosphate mineral is not decomposed, but 35-45% of nitric acid of stoichiometry P_2O_5 transition is occurred into the liquid phase and depending on the ratio of PR: EA is 0.55-8.69% (Fig. 4-a). In case 50% norm of HNO_3 and the ratio of PR: EA = 1 : 5, this transition is already 21.05%. That is, the yield of P_2O_5 in the phosphoconcentrate decreased from 99.45 to 78.95%. This circumstance is explained that decarbonization of phosphate raw material in nitric acid along with calcium carbonate, as well as phosphate mineral is decomposed to form water-soluble calcium monophosphate which, together with calcium nitrate passes into the liquid phase. Studies on enrichment OPF containing 17.52% P_2O_5 by its decarbonization in nitric acid show that normal acid is 40% (100% norm for CaCO_3 decomposition), and the ratio of PR: EA = 1: 5 in the obtained phosphoconcentrate (wt. %). $\text{P}_2\text{O}_{5\text{tot}}$ 24.20; $\text{P}_2\text{O}_{5\text{acc}}$ by citric acid 17.71; $\text{P}_2\text{O}_{5\text{acc}}$ by Trilon B 12.20; CaO_{tot} 39.67; CaO_{acc} 28.66; $\text{CaO}_{\text{wat-sol}}$ 3.84; N 0.65; $\text{CaO} : \text{P}_2\text{O}_5 = 1.64$, with a degree of decarbonization of raw materials is 82.5%. P_2O_5 output in the phosphoconcentrate is 94.75%.

Although increasing the norm of nitric acid to 44% of stoichiometry improves the quality indicators of phosphoconcentrate (low calcium modulus), but leads to decrease of P_2O_5 output in the phosphoconcentrate to 89.91% due to the increase of its transition into a liquid phase (10.09%). It is found that during the decomposition of the OPF at the norm of 48% for CaO , or 120% norm for CaCO_3 of nitric acid and the ratio of PR: EA -1: 5 in the liquid phase passes to 12.51% P_2O_5 in the form of calcium monophosphate, which reduces the yield and content of P_2O_5 in the phosphoconcentrate.

When the OPF enrichment composition (wt.%): 18.70 P_2O_5 ; 47.8 CaO ; 15.3 CO_2 and $\text{CaO} : \text{P}_2\text{O}_5 = 2.56$ by nitric acid at a ratio of PR: EA = 1: 5, phosphorite concentrate obtained with the following composition (wt.%) at a norm of 36% HNO_3 - $\text{P}_2\text{O}_{5\text{tot}}$ 24.22; $\text{P}_2\text{O}_{5\text{acc}}$ by citric acid 16.83; $\text{P}_2\text{O}_{5\text{acc}}$ by Trilon B 12.29; CaO_{tot} 40.77; CaO_{acc} 29.64; $\text{CaO}_{\text{wat-sol}}$ 1.50; $\text{CaO} : \text{P}_2\text{O}_5 = 1.68$ with a degree of decarbonization - 77.5%; and at a norm of 40% HNO_3 - $\text{P}_2\text{O}_{5\text{tot}}$ 26.19; $\text{P}_2\text{O}_{5\text{acc}}$ by citric acid 18.88; $\text{P}_2\text{O}_{5\text{acc}}$ by Trilon B 13.84; CaO_{tot} 39.92; CaO_{acc} 29.47; $\text{CaO}_{\text{wat-sol}}$ 1.67; $\text{CaO} : \text{P}_2\text{O}_5 = 1.52$ with a degree of decarbonization - 79.7% (Figure 2-c.). Enrichment of MM, which is CK waste by nitric acid, converts it to a conditioned phosphate raw material. So, HNO_3 compliance standards is 30-45%, and the ratio of PR: EA from 1 : 3 to 1 : 10 are obtained phosphorite concentrates containing from 18.61 to 21.20% P_2O_5 , from 38.50 to 41.54% CaO , from 3.01 to 6.80% CO_2 and calcium module from 1.82 to 2.23. When processing of the raw material with 35-45% norm of HNO_3 on stoichiometry phosphate mineral is decomposed and P_2O_5 transition into the liquid phase and depending on the ratio of PR: EA is 0.77-8.81% (Figure 4 d.). At a norm of HNO_3 - 60% and the ratio of PR: EA = 1 : 5, this value is increased to 24.80%. Increasing the ratio of PR: EA from 1 : 3 to 1 : 10 does not significantly affect on the composition of the resulting phosphoconcentrate, i.e. the content of P_2O_5 in the

phosphoconcentrate increases from 18.61 to 18.81% and from 20.50 to 21.20% for HNO_3 norms is 30 and 45%, respectively.

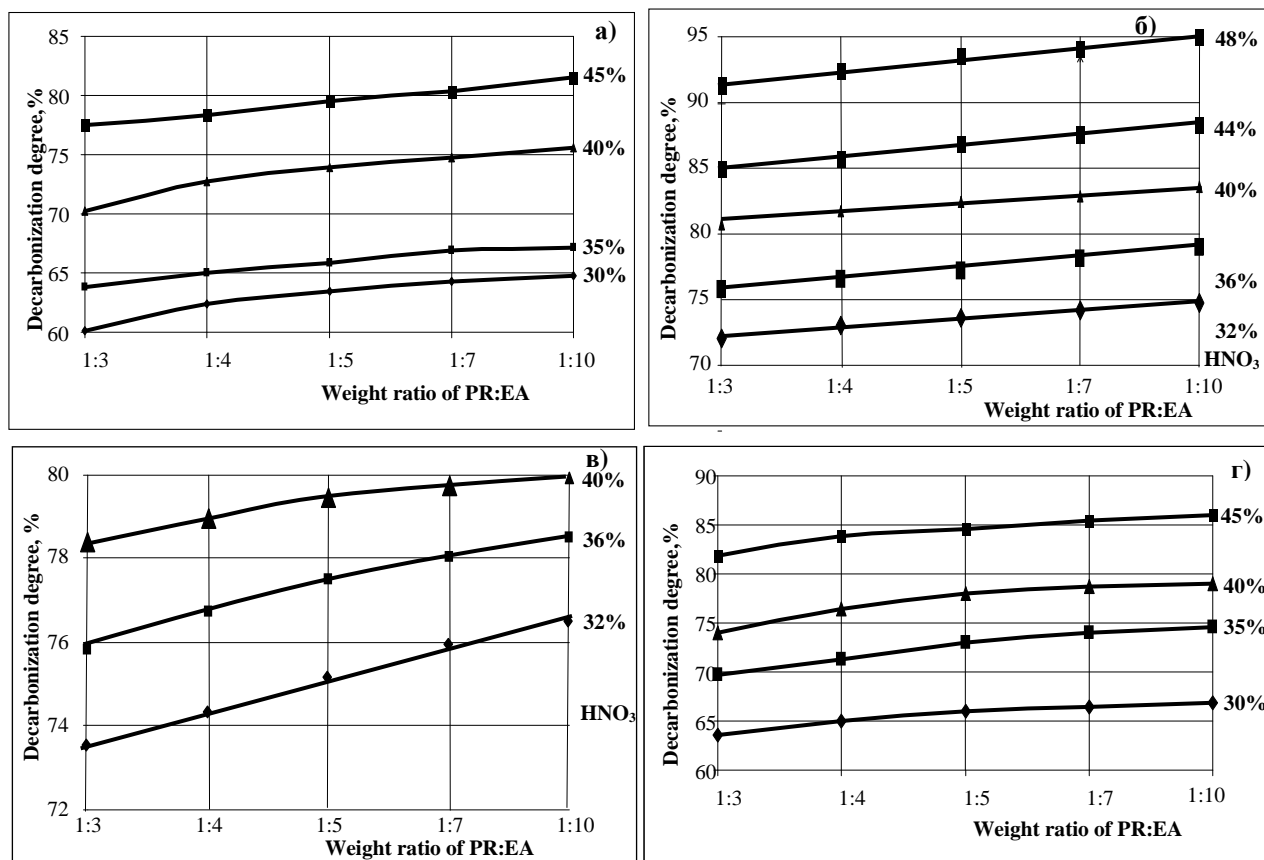


Fig. 2. Degree of decarbonization of phosphate raw materials, depending on the ratio of PR: EA and norm of HNO_3 : a) the OPF - (16.60% P_2O_5); b) The OPF - (17.52% P_2O_5); c) The OPF - (18.7% P_2O_5) D) MM - (15.06% P_2O_5).

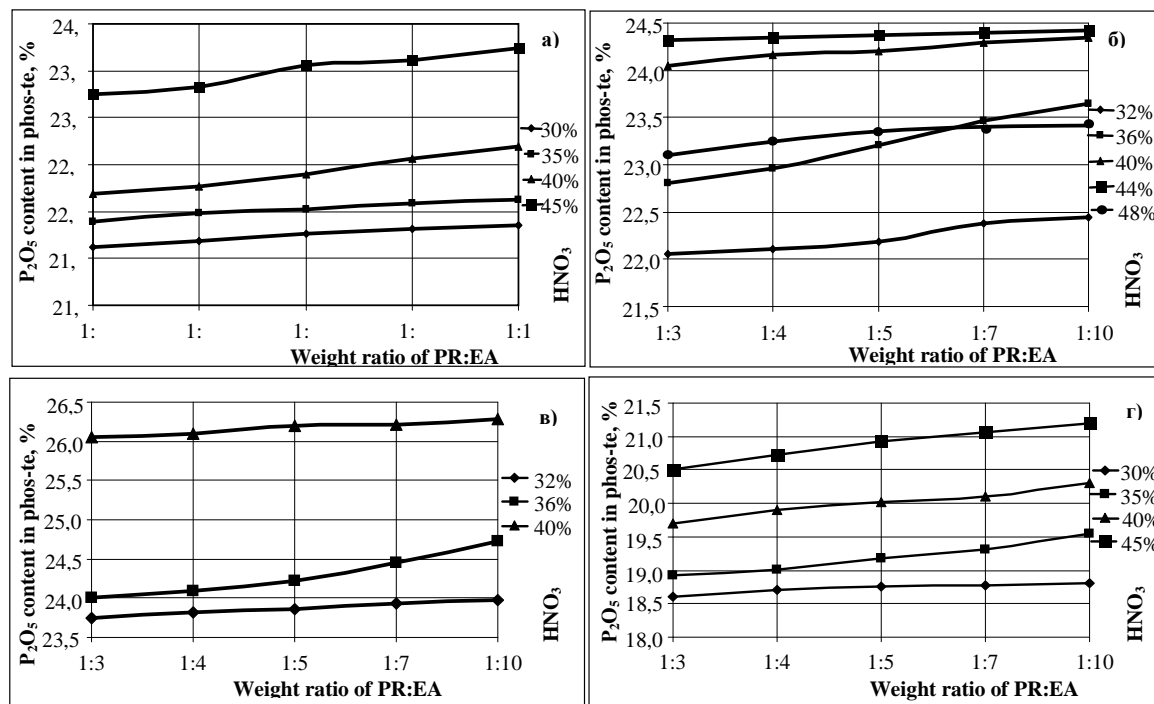


Fig. 3. The content of P_2O_5 in the phosphoconcentrate, depending on the ratio of PR: EA and norm of HNO_3 : a) the RPF - (16.60% P_2O_5); b) The OPF - (17.52% P_2O_5); c) The OPF - (18.7% P_2O_5) d) MM - (15.06% P_2O_5).

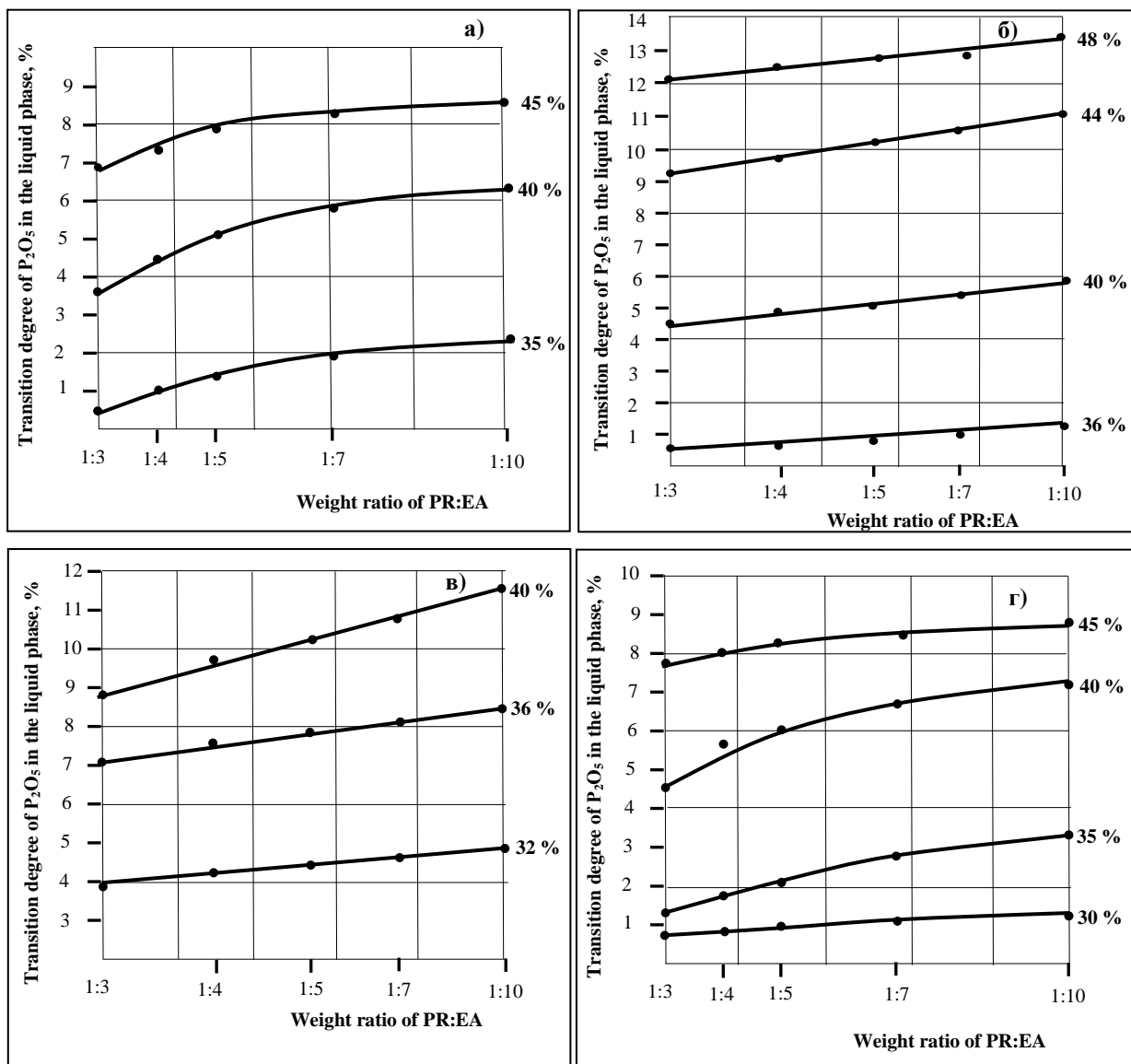


Fig. 4. The degree of transition P_2O_5 in the liquid phase, depending on the ratio of PR: EA and norm of HNO_3 : a) the OPF - (16.60% P_2O_5); b) The OPF - (17.52% P_2O_5); c) The OPF - (18.7% P_2O_5) d) MM - (15.06% P_2O_5).

By developing ways of enrichment in order to achieve the fullest leaching of calcium nitrate from phosphoconcentrate and considerable reduction of EA consumption for washing, as well as more concentrated alcoholic solution of calcium nitrate, washing wet phosphoconcentrate proposed to carry out scheme by counter-simulating industrial washing conditions of phosphogypsum. There has been estimated that material flow process the preparation of chemically enriched phosphoconcentrate from OPF containing 17.52% P_2O_5 .

As it noted that the enrichment of carbonate CK phosphorite by nitric acid has one major drawback: when extracting calcium carbonate from the phosphate raw material, though in a lesser degree, partial decomposition its phosphate mineral occurs to form $Ca(H_2PO_4)_2$, passing into the liquid phase. This significantly reduces the yield and content of P_2O_5 in the concentrate. It is desirable to return it to the solid phase in order to increase P_2O_5 content in the phosphoconcentrate. To do this, before divide nitrogen-calcium-phosphate alcoholic slurry into liquid and solid phases we subjected it for neutralization with gaseous ammonia to pH = 3. This soluble phosphorus is recycled in the phosphoconcentrate as dicalcium phosphate.

Phosphate raw materials, suitable to obtain from it WPA by sulfuric acid extraction, should be met the following requirements: P_2O_5 content not less than 24.5%, CO_2 no higher than 8%, and the value of the of calcium module ($CaO : P_2O_5$) not more 1.6. In view of economy acid consumption, its optimum norm for enrichment process can be considered OPF 50% and the weight ratio of PR: EA = 1: 5. For example, when enrichment OPF containing 17.52% P_2O_5 ; 47.53% CaO ; 15.23% CO_2 and $CaO : P_2O_5 = 2.70$ (sample 3) with a 50% norm of HNO_3 , pH 3 of nitrogen-calcium-phosphate slurry and weight ratio of PR: EA equal to 1: 5 obtained concentrate composition (wt.%): P_2O_{5tot} . 26.20; CaO_{tot} . 38.25; CO_2 2.80 and $CaO : P_2O_5 = 1.46$ (Table 2.). The yield of P_2O_5 in the concentrate is 100%. As the value of calcium module it is close to the best phosphate raw materials as Khibiny apatite concentrate (1.32). The liquid phase of slurry is a solution of calcium nitrate and EA with a small amount of ammonium nitrate. The alcohol is easily distilled and returned to the process cycle. After distilling off the alcohol obtained concentrated nitrogen-ammonium-calcium solution (NACS) containing 50% $Ca(NO_3)_2$ and 3% NH_4NO_3 .

On a basis of found optimal parameters of the enrichment process, we tried to apply for the enrichment of the OPF and two other types of MM, the compositions of which are given in the Table. 1. HNO_3 norm for MM is 60% from stoichiometry on the leach CaO .

Table 2
Chemical composition of concentrates from phosphorite of CK

Type of phosphorite raw material	P_2O_{5tot} .content In the initial raw, %	Norm of HNO_3 for CaO in raw of stoichiometry, %	Components content, wt. %			$P_2O_{5acc.}$: P_2O_{5tot} by citric acid, %	$CaO : P_2O_5$
			P_2O_{5tot} .	CaO_{tot} .	CO_2		
OPF	16.60	50	24.66	38.47	3.52	57.95	1.54
OPF	17.52	50	26.20	38.25	2.80	59.88	1.46
OPF	18.70	50	26.83	39.73	2.91	64.85	1.48
MM	15.06	60	24.21	35.97	2.07	58.44	1.48

Enrichment results are summarized in Table. 2. From this it can be seen that the enrichment of different types of phosphate rock by nitric acid concentrates obtained on the composition, which is different. For example, of the OPF with the content of 16.60% P_2O_5 , 17.23% CO_2 and $CaO : P_2O_5 = 2.84$ (sample 1) obtained concentrate, which has 24.66% of P_2O_5 and $CaO : P_2O_5 = 1.54$. From the third OPF sample containing 18.7% of P_2O_5 and $CaO : P_2O_5 = 2.60$ obtained concentrate that has 26.85% of P_2O_5 and $CaO : P_2O_5 = 1.59$. MM (sample 4) with the content of 15.06% P_2O_5 , 14.11% CO_2 and $CaO : P_2O_5 = 2.94$ converted into an enriched raw material with $CaO : P_2O_5 = 1.48$ and is quite suitable for sulfuric acid extraction.

However, P_2O_5 content increased in it from 15.06% to 24.21%. The rheological properties of ammoniated nitrogen-calcium-phosphate alcoholic slurry and the process of its separation into liquid and solid phases were studied. The positive effect on the separation of pulp can be achieved by filtering belt vacuum filter that effectively applied on KPC when washing microgranular phosphorite flour. It was estimated that material balance for process.

“Investigation of the regeneration process of ethanol from the extract with generation concentrated solution of calcium nitrate and ammonium nitrate” of the regeneration of ethyl alcohol from the nitrogen-ammonium-calcium solution (NACS) that is a by-product of phosphorite enrichment of CK and its processing into liquid and solid nitrogen-calcium fertilizer. As above noted, that the enrichment OPF having 17.52% of P_2O_5 at a norm of HNO_3 - 50%, pH of the slurry and the ratio of OPF : EA = 1 : 5, phosphoconcentrate was obtained containing 26.2% of P_2O_5 . The liquid phase of slurry is a solution of calcium nitrate with small amounts of ammonium nitrate and EA. The latter is easily distilled off and returned to the production cycle. Theoretical analysis of alcohol recovery from NACS with using solubility <http://annalsofrscb.ro>

diagrams of 4-fourfold component system of $\text{Ca}(\text{NO}_3)_2$ - NH_4NO_3 - $\text{C}_2\text{H}_5\text{OH}$ - H_2O , which presents results of calculating the alcohol recovery process and determines the interval of variation of process parameters, taking into account the composition of the starting water-alcohol solutions and final products.

It was conducted that regeneration of the EA from NACS, in which EA return degree in a cycle reaches 98-99%. After distillation, NACS was obtained, containing 50% of $\text{Ca}(\text{NO}_3)_2$, 3% of NH_4NO_3 . In this case, when generation of a ton of the phosphoconcentrate from the OPF with the content of 17.52% P_2O_5 , observing the process parameters described above, produced 1.87 ton of NACS, in which contains 1.35 ton of calcium nitrate tetrahydrate.

The physicochemical properties (rheological properties, vapor pressure, boiling point and crystallization temperature) of NACS was studied depending on the concentration of $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 . In order to carry out the experiments NACS were prepared in different concentrations (53.02-84.77% of $\text{Ca}(\text{NO}_3)_2$ and 3.02-4.77% of NH_4NO_3) by evaporation of initial solution (50% of $\text{Ca}(\text{NO}_3)_2$ and 3% of NH_4NO_3).

Saturation vapor pressure of NACS in the range of 20-40°C makes 0.44-6.38 kPa, which gives on low volatility in a hot climate of Central Asia. The concentration range of 53.02-65.71% the crystallization temperature is in the range of $(-75) \div 12.0^\circ\text{C}$ that allows being used them in the spring and summer, as the liquid-NCa fertilizer. In the temperature range 30-90°C NACS has a density 1.3873-1.6377 g/cm^3 and viscosity 2.43-18.85 cps with the indicated concentrations. In case NACS has good rheological properties. However, more concentrated NACS (67.83-84.77% of $\text{Ca}(\text{NO}_3)_2$, 3.83-4.77% of NH_4NO_3) before use should be diluted with water, because crystallization temperature is 29-60°C. As determination of the density and viscosity of the NACS with a concentration in the range of 69.94-78.43 and 80.54- 84.77%, respectively, at 30-50°C and 30-60°C not be possible due to the crystallization of $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 from evaporated solution.

As results show that concentration increase of NACS, as well as boiling point is raised. Thus, when the concentration NACS is of 53.02% (50% of $\text{Ca}(\text{NO}_3)_2$, 3.02% of NH_4NO_3) at 760 mm of mercury column (NTP) its boiling point is 108°C, and at NACS is of 84.77% (80% of $\text{Ca}(\text{NO}_3)_2$, 4.77% of NH_4NO_3), this value rises to 152 °C. Lowering the pressure lowers the boiling point of solutions. Thus, if the pressure of 760 mm. mercury column, boiling point of 63.6% NACS (60% of $\text{Ca}(\text{NO}_3)_2$, 3.6% of NH_4NO_3) is 130°C, while the pressure is 460 mm. mercury column it is equal to 112°C.

NACS was treated in granular calcium nitrate. To improve the properties of the latter is used various bentonite clay as additive. There were have been determined the commodity properties of the obtained products. It is shown that any addition of bentonite increases the hygroscopic point and strength of calcium nitrate granules. So, with the addition of bentonite from Kattakurgan its hygroscopic point increases from 38.7 to 44.99%, Lagonsk bentonite up to 55.55%, Navbakhor bentonite grades: PBG - up to 54.99% and PPD - up to 57.07%, while this increases the strength of granules from 1.98 to 3.45 MPa; up to 4.48 MPa; up to 3.55 MPa and 5.31 MPa, respectively. The nitrogen content of the products is within 14.49-14.69% (Table. 3).

Table 3
Composition and property of calcium nitrate

Samples number	Weight ratio of $\text{Ca}(\text{NO}_3)_2$: bentonite	content, wt. %		Moisture, %	Strength, MPa	Hydroscopic point, %
		CaO	N			
1	$\text{Ca}(\text{NO}_3)_2$	27.76	15.58	1.29	1.98	38.7
When addition Kattakurgan bentonite						
2	100 : 6	26.51	14.49	1.19	3.45	44.99
When addition Lagonsk bentonite						

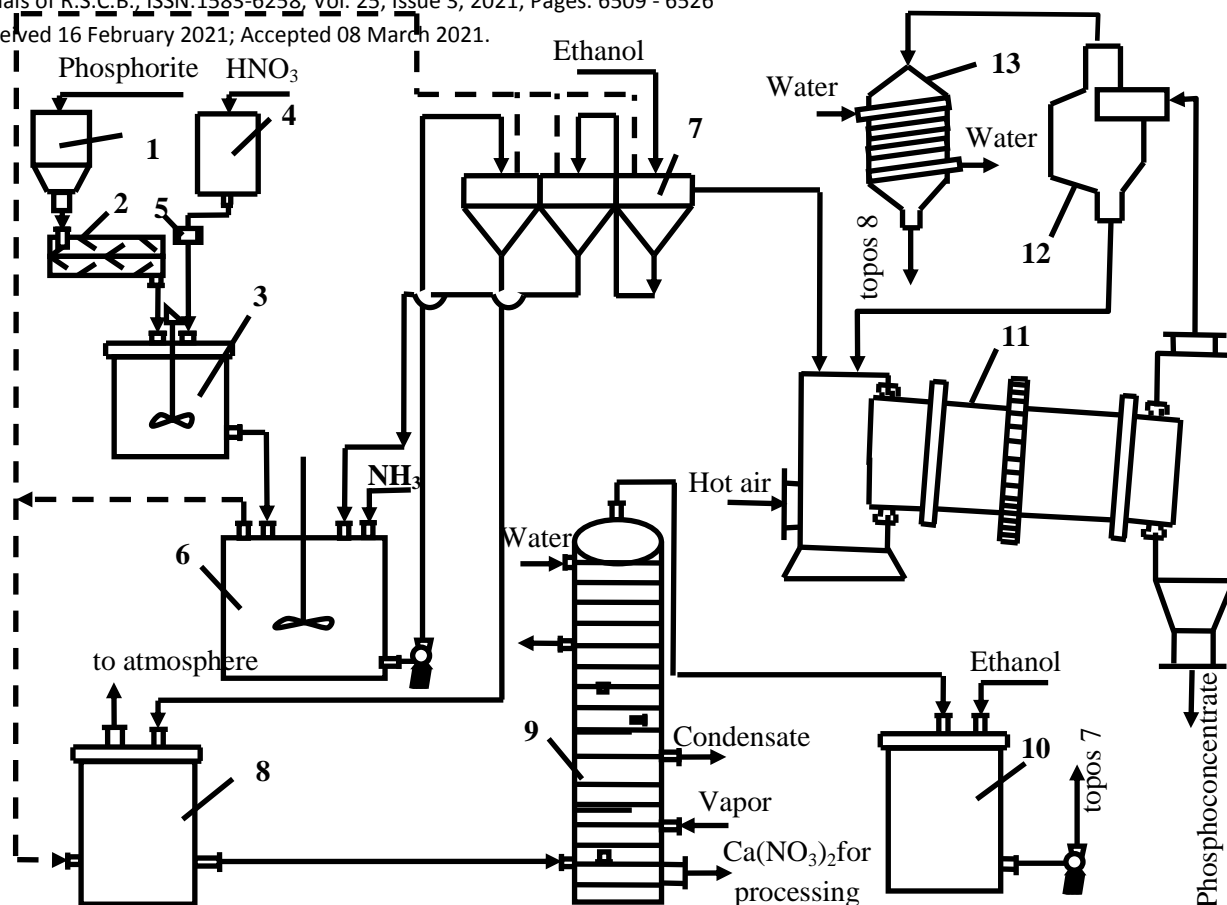
3	100 : 6	26.97	14.69	1.16	4.48	55.55
When addition Navbakhor bentonite (PBG)						
4	100 : 6	26.59	14.57	1.11	3.55	54.99
When addition Navbakhor bentonite (PPD)						
5	100 : 6	27.32	14.60	1.03	5.31	57.07

The addition of bentonite considerable improves the sorption moisture capacity of calcium nitrate. This is due to the ability of swelling bentonite in water and retention in interplanar spaces of a large number of solutions containing nutrients as nitrogen and calcium[9-11].

The process of conversion of NACS calcium nitrate in NH_4NO_3 and CaCO_3 using ammonium carbonate was studied. The results obtained as the optimal conditions of the conversion process suggest the following: solution concentration of $\text{Ca}(\text{NO}_3)_2$ is 37%; the norm of ammonium carbonate is 120% of the stoichiometry conversion, boiling point is 70°C ; stirring time is 120 min. The degree of conversion of $\text{Ca}(\text{NO}_3)_2$ is max 99.94%, and the concentration of the solution NH_4NO_3 is 45%.

“Technology development of nitric acid benefication phosphorite from Central Kyzylkum in the presence of ethanol and processing phosphoconcentrate in WPA and complex fertilizer” presents results of testing the chemical enrichment technology of CK phosphorite in the pilot plant, as well as obtaining of phosphorite concentrate WPA, PK- and NPK-fertilizer.

On the aggregated laboratory model install the technology of chemical processing of phosphorite of CK by nitric acid was worked off in the presence of ethanol at norm HNO_3 40; 45 and 50% of the stoichiometry for CaO in the raw material and a weight ratio of PR: EA = 1 : 3 and 1 : 5. It has been shown that the composition of the obtained samples of phosphoconcentrate in a model setup were identical to the product obtained in the laboratory conditions. In the pilot plant of JSC “Samarkandkimyo” tests on enrichment technology of OPF were carried out with the content (wt.%): P_2O_5 17.52; CaO 47.53; CO_2 15.23, CaO: P_2O_5 = 2.7 HNO_3 at norms of 40 and 50%, ratio of PR: EA = 1: 5.



1 - tank for phosphorite; 2 - tape measuring; 3 - decomposition reactor; 4 - pressure tank for nitric acid; 5 - flow meter; 6 - repulpator; 7 - vacuum filter; 8 - receiver of alcoholic solution of calcium nitrate; 9 - rectification column; 10 – capacity for storage of ethanol; 11 - drum-dryer; 12 - cyclone; 13 - trap for ethanol.

In this case, depending on the norm of HNO₃phosphoconcentrate's composition changed (wt.%): P₂O₅_{tot}. from 24.20 to 26.05; P₂O₅_{acc.} by citric acid from 13.68 to 15.89; P₂O₅_{acc.} by Trilon B from 9.75 to 11.71; CaO_{tot} from 38.55 to 40.31; CO₂ from 2.79 to 3.89; CaO: P₂O₅ from 1.48 to 1.66. During the tests, experimental batches of chemically enriched phosphoconcentrate were gained in the amount of 100 kg for each norm of HNO₃.

Based on the results of laboratory experiments, laboratory experiments in the enlarged model installation and pilot plant of JSC “Samarkandkimyo” established the basic indicators of the technological mode of phosphorite enrichment CK by nitric acid in the presence of ethanol. The material balance has complied and the technological scheme of production of chemically enriched phosphoconcentrate has proposed (Fig. 5). Studies on the production of WPA from chemically enriched phosphoconcentrate with composition (wt.%): P_2O_{5tot} . 26.20; P_2O_{5acc} . by citric acid, 15.69; P_2O_{5acc} . by Trilon B 11.77; CaO_{tot} . 38.25; CaO_{acc} . 19.04; $CaO_{wat-sol}$. 2.28; CO_2 2.80; N 1.46; $CaO : P_2O_5 = 1.46$ were conducted in dihydrate mode depending on the norms of H_2SO_4 (from 100 to 103% of stoichiometry for CaO), the weight ratio of L: S (from 2.5: 1 to 3.5: 1) and concentration of circulating WPA (from 12.0 to 16.9% P_2O_5). Results of laboratory experiments show that at the same norm of H_2SO_4 and the concentration of WPA an increase of mass ratio of L: S from 2.5: 1 to 3.5: 1 leads to an increase of expansion coefficient ($K_{exp.}$) phosphate rock, washing coefficient ($K_{was.}$) of phosphogypsum, yield coefficient of P_2O_5 (K_{yei}) and slurry filtration rate. However, the concentration of productional WPA reduced. Increase of

circulating WPA concentrations independently of H_2SO_4 norm and ratios of L: S leads to a reduction of these indicators, while allowing to obtain a more concentrated WPA for P_2O_5 .

Based on the data, there were found the optimal conditions for sulfuric acid extraction of the above composition: the norm of H_2SO_4 is 103%; the concentration of circulating WPA is 15% of P_2O_5 , and the ratio of L: S = 3: 1. In this case $K_{exp.} = 98.73\%$; $K_{was.} = 98.57\%$, $K_{yei.} = 92.87\%$, a filtration rate is $1312 \text{ kg} / \text{m}^2 \cdot \text{hour}$, and the concentration of phosphoric acid is 20.19% of P_2O_5 . Content of $CaO_{tot.}$; $SO_{3tot.}$; $P_2O_{5tot.}$ and $P_2O_{5wat.}$ is 31.21; 43.23; 1.43 and 0.27%, respectively in the dried phosphogypsum. Moreover, phosphogypsum is composed of 92% calcium sulfate dihydrate, and 6.63% of insoluble residue. Material balance process of producing one tonne of P_2O_5 in the form of WPA was estimated. Laboratory studies have shown the fundamental possibility of generation of WPA and ammophos of chemically enriched phosphorite concentrate from CK phosphorite with good processing performance. Chemically enriched phosphoconcentrate is suitable not only for sulfuric acid extraction, but also for direct application to the soil as phosphate fertilizer. This is evidenced by the high relative content of acceptable form of P_2O_5 (60%). In the initial OPF, the value was 18.5%. This means that at the same time during the enrichment and activation of phosphate raw materials is taken place. Therefore, the concentrate can be a good component for the production of compound-mixed granular fertilizer. Hence the process of obtaining PK- and NPK-fertilizers was studied with different ratios of nutrient by wet mixing phosphoconcentrate, potassium chloride and ammonium nitrate. The amount of initial components taken from this calculation that the final product ratio of N : P_2O_5 : K_2O is from 1 : 0.7 : 0.3 to 1 : 0.7 : 0.6 and 1 : 1 : 0.3 to 1 : 1 : 2. All grades of PK- and NPK-fertilizers contain a high concentration of nutrients. Thus, PK-fertilizer obtained in the range of weight ratios P_2O_5 : K_2O from 1 : 0.3 to 1 : 2 contain from 14.21 to 23.74% P_2O_{5tot} from 6.96 to 28.01% of K_2O , $P_2O_{5acc.}$ towards P_2O_{5tot} from 66.34 to 69.66%. For the ratio of N : P_2O_5 : K_2O = 1: 0.7: 0.3 is obtained NPK-fertilizer with 16.52% of N, 11.68% of P_2O_5 , 4.83% of K_2O and the amount of nutrients makes 33.03%. The relative content of acceptable P_2O_5 form in it is 77.99%. When the ratio of N : P_2O_5 : K_2O = 1 : 1 : 0.3 the product contains 13.79% of N, 13.95% of P_2O_5 , 4.12% of K_2O in the amount of P_2O_5 31.85% and acceptable form of P_2O_5 is 76.63%. When the ratio of N : P_2O_5 : K_2O = 1 : 1 : 1 in the product contained 11.98% of N, 12.01% of P_2O_5 , 11.92% of K_2O are in amount 35.91% and acceptable for plant form of P_2O_5 is 74.19% of total P_2O_5 . Granules obtained all grades of NPK-fertilizer have high strength (from 3.67 to 6.58 MPa).

On the aggregated laboratory setup mode for produce of PK- and NPK-fertilizer was worked out. PK-fertilizer was obtained with a ratio of P_2O_5 : K_2O = 1 : 0.5 and NPK-fertilizer with the ratio of N : P_2O_5 : K_2O = 1 : 0.7 : 0.5 to 30 kg, the compositions of which are summarized in the Table. 4. Results agrochemical tests indicate that PK-and NPK-fertilizer with their properties do not rebate ammophos and have the same effect on the flow of nutrients into the cotton plant and their accumulation in the soil[12-18].

Table 4

Composition of PK-and NPK fertilizer based on chemically enriched phosphoconcentrate, potassium chloride and ammonium nitrate

Weight ratioe	Chemical composition, wt. %							Strength, MPa
	N	P_2O_{5tot}	K_2O	$CaO_{tot.}$	$P_2O_{5acc.}$: $P_2O_{5tot.}$ %	$P_2O_{5acc.}$: $P_2O_{5tot.}$ %	$CaO_{acc.}$: $CaO_{tot.}$ %	
P_2O_5 : K_2O	PKfertilizer							
1 : 0.5	-	21.77	10.77	33.81	67.25	47.77	45.25	1.50
N: P_2O_5 : K_2O	NPKfertilizer							
1 : 0.7 : 0.5	15.5	11.02	7.74	15.71	76.86	49.64	75.75	5.46

The results allowed to develop the basic technological scheme on producing PK-and NPK-fertilizer. Material balance of production of one ton of both PK- and NPK- fertilizer has complied. Fig. 6 is given a block diagram of complex and non-waste processing of CK phosphorite by nitric acid.

CONCLUSION

Solubility diagram 4 fourfold component system of $\text{Ca}(\text{NO}_3)_2$ - NH_4NO_3 - $\text{C}_2\text{H}_5\text{OH}$ - H_2O has been studied, consisting of 3-triple: $\text{Ca}(\text{NO}_3)_2$ - $\text{C}_2\text{H}_5\text{OH}$ - H_2O ; NH_4NO_3 - $\text{C}_2\text{H}_5\text{OH}$ - H_2O ; $\text{Ca}(\text{NO}_3)_2$ - NH_4NO_3 - H_2O and 3 triple binary systems of $\text{Ca}(\text{NO}_3)_2$ - H_2O ; NH_4NO_3 - H_2O and $\text{C}_2\text{H}_5\text{OH}$ - H_2O , justifying the process of extraction of calcium nitrate and ammonium nitrate from nitrogen-calcium- phosphate slurry produced during nitric acid enrichment of phosphorite CK by ethanol in a wide temperature and concentration range. Diagram allows to define the range of variation of technological parameters of the extraction process based on CaO : P_2O_5 phosphate raw materials and the conditions of its nitric acid decomposition.

The process of enrichment of various kinds of carbonate phosphorite from CK in HNO_3 at a norm of 30 to 60% of the stoichiometry on the decomposition of CaO in the raw material and a weight ratio of PR: EA = 1: (3-10). The overall picture of the results of enrichment of different types of phosphate rock in HNO_3 is similar. Thus, the enrichment of relatively high concentrated OPF with the content (wt.%) P_2O_5 18.70; CaO 47.8; CO_2 15.3; SO_3 2.05 and CaO : P_2O_5 = 2.56 at a norm of HNO_3 is 40% on the decomposition of CaO (100% for CaCO_3) and the ratio of PR: EA = 1: 5 is obtained phosphorite concentrate containing 26.19% of P_2O_5 , and calcium module 1.52. This concentrate is quite suitable for the production of concentrated phosphate fertilizers. To prevent the transition of P_2O_5 into a liquid phase before divide nitrogen-calcium-phosphate alcoholic suspension (NCPAS) into liquid and solid phases, it was ammoniated to pH = 3. This made possibility to use for enrichment much higher norm of HNO_3 and thus reduce the value of CaO : P_2O_5 in the raw material. Norm acid is ranged from 40-80% stoichiometry for CaO in the raw material. Taking into account the cost savings of HNO_3 its optimal norm for the enrichment of various types of Kyzylkum phosphorite can be considered 50% and the weight ratio of PR: EA = 1: 5. And for MM acceptable norm is of 60%. So, when RPF enrichment, containing 17.52% of P_2O_5 ; 47.53% of CaO ; 15.23% of CO_2 and CaO : P_2O_5 = 2.71 with a 50% norm of HNO_3 , pH of the slurry and the ratio of PR 3: EA = 1: 5 obtained concentrate composition (wt.%): $\text{P}_2\text{O}_{5\text{tot.}}$ - 26.20; $\text{CaO}_{\text{tot.}}$ - 38.25; CO_2 - 2.80; CaO : P_2O_5 = 1.46. The yield of P_2O_5 in the concentrate is 100%.

The theoretical analysis of the regeneration of the NACS with the use of solubility diagrams of 4 fourfold component system of $\text{Ca}(\text{NO}_3)_2$ - NH_4NO_3 - $\text{C}_2\text{H}_5\text{OH}$ - H_2O , the result it was calculated alcohol recovery process and determined the interval of variation of process parameters, taking into account the composition of the starting water-alcohol solutions and final products. The kinetics of the distillation EA from NACS depending on the temperature and pressure has been studied. Applying a vacuum pressure of 0.3 atm. provides EA distillation for a short time (60 minutes at 80°C). When the regeneration EA from calcium nitrate solution, which is a by-product of the nitric acid concentration of CK phosphorite, degree EA return to the cycle reaches 98-99%. After distilling off the NACS has been obtained containing 50% $\text{Ca}(\text{NO}_3)_2$ and 3% NH_4NO_3 .

Physicochemical properties of the initial and productional NACS depending on the concentration of $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 . It is shown that in the concentration range of 53.02-65.71% of NACS the crystallization temperature is in the range of $(-75) \div 12.0^\circ\text{C}$ that allows to be used them in the spring and summer, as a liquid nitrogen-calcium fertilizer. NACS has good rheological properties. However, more concentrated NACS (67.83-84.77% of $\text{Ca}(\text{NO}_3)_2$, 3.83-4.77% of NH_4NO_3) before use should be diluted with water, as the crystallization temperature is 29-60°C. It was found that with increasing concentration NACS increases its the boiling point.

NACS was processed in granular calcium nitrate. To improve the properties of the latter various bentonite clay deposits are used as additives. The products obtained with a ratio of $\text{Ca}(\text{NO}_3)_2$: Bentonies = 100 : 6 nitrogen content is in a range of 14.49-14.69%. Physical and chemical properties of the resulting products have been defined. Optimal conditions for the conversion of calcium nitrate of NACS in NH_4NO_3 and CaCO_3 using ammonium carbonate. Based on the results of studies recommended the following conditions conducting the conversion process: concentration of calcium nitrate solution is 37%, the norm of ammonium carbonate is 120% of the stoichiometry, conversion of temperature is 70°C, mixing time is 120 minutes. The degree of conversion of calcium nitrate is maximum 99.94%, and the concentration of ammonium nitrate solution is 45%.

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