Balanced NP- And NPK-Fertilizers Based On Purified Ammophos Suspension, Nitrogen Fertilizers And Potassium Chloride

Sh.Yu.Nomozov, Sh.S.Namazov, A.R.Seytnazarov, B.M.Beglov, U.K.Alimov

Abstract: The process of liquid NP-and NPK-fertilizers preparation based on ammophos pulp (pH = 4.5; 5.5 and 6.5), nitric and potassium fertilizers has been studied. In ammonization of a low-concentrated wet-processing phosphoric acid (WPA) (16.5% P_2O_5) with various impurities, water-insoluble compounds of calcium, magnesium, iron, aluminum, and fluorine are formed, producing precipitate. It was shown that separation of the solid phase from the ammonium phosphate pulp allows to obtain a transparent suspension of improved quality. It serves as a basic solution for the preparation of liquid NP and NPK fertilizers with grades 1 : 0.5, 1 : 0.7, 1 : 1 and 1 : 0.5 : 0.3, 1 : 0.7: 0.5 and 1 : 1: 1 by adding to them nitrogen (NH_4NO_3, $(NH_2)_2CO$, CAM-32) and potassium (KCl) salts. So, with the use of $(NH_2)_2CO$ the product brand 1:1:1 contains 10.28% of the nutrient, that is, in total more than 30.8%. It contains $P_2O_{5assimilable}$: $P_2O_{5tot.}$ = 100%, and $P_2O_{5aqueous}$:$P_2O_{5tot.}$ = 98%. The material balance of the process of obtaining liquid NPK-fertilizers for 1: 1: 1 grade has been calculated.

Index Terms: WPA, ammophos pulp, sediment, basic solution, ammonium nitrate, carbamide, CAM, potassium chloride, liquid NP- and NPK-fertilizers, composition.

1 INTRODUCTION

THE demand of Uzbekistan's agriculture for mineral fertilizers in 2018 was 963.7 thousand tons of 100% N, 688.4 thousand tons of P_2O_5 and 313.6 thousand tons of K_2O. This year, industry satisfied the demand of agriculture by 94% for nitrogen fertilizers, by 23% for phosphate fertilizers and by 55% for potassium fertilizers. All fertilizers, with the exception of ammonium sulfate and potassium chloride, are produced in granular form, and these two - in crystalline form. From liquid fertilizers only single nitric - CAM (carbamide-ammonia mixture), calcium nitrate solution and liquid ammonia, are produced. The government pays the great attention to the development of mineral fertilizers production. According to the Decree of the President of the Republic of Uzbekistan No. PD-3983 dated October 25, 2018 "On Measures to accelerate the Development of the Chemical Industry of the Republic of Uzbekistan", the production of mineral fertilizers will double by 2030 (from 1.2 million tons to 2.4 million tons). Unfortunately, this Decree does not say anything about the need to manufacture liquid complex fertilizers (LCF). This is explained by the fact that Uzbekistan does not have deposits of rich phosphate raw materials, such as the Khibiny and Kovdorsky apatites (Russia), Florida phosphates (USA), and Moroccan phosphates (Africa), which can be used for any brand of phosphorus-containing fertilizers. Despite this, the Institute of General and Inorganic Chemistry under the Academy of Sciences of the Republic of Uzbekistan has accumulated a great deal of experience on obtaining both liquid, suspended and solid mineral fertilizers [1-8]. LCF is an aqueous solution or suspension containing two or more basic nutrient elements. They have several advantages [9, 10] over solid fertilizers:

- they do not dust, do not cake together, are free fluidity, and unfavorable climatic conditions do not adversely affect their quality indicators;
- LCF do not incorporate free ammonia, therefore their transportation is not necessarily in a sealed container;
- high uniformity of application, LCF can be applied not only to a certain depth in the soil, but also sprayed over the surface of the field, followed by embedding;
- the possibility of obtaining a wide range of liquid mixtures with a different ratio of nutrients and the simultaneous use of trace elements, some pesticides and growth stimulants;
- on carbonate soils with alkaline reaction (carbonated black soils, chestnut soils, gray soils), the agrochemical value of liquid forms, as a rule, is higher than that of granulated ones;
- the use of LCF allows to mechanize time-consuming processes of loading, unloading and applying into the soil; completely excluding manual labor and significantly reducing costs;
- LCFs are easy to use, do not ignite, are not explosive, are not poisonous, do not corrode ferrous metals; besides do not require the creation of high-power aggregates.

The largest producers of LCF are the United States and Canada. Significant volumes of LCF are used in Western European countries such as Russia, the Great Britain, France, Denmark, Italy, Spain, Belgium, Holland, Poland, Czech Republic, Hungary, etc. In Russia, the producers of LCFs are Open Joint Stock Company (OJSC) "Kuybyshevfosfor", Cherkassky and Rovensky OJSC "Azot", Sumsky OJSC "Khimprom", Krasnodarsky, Balakovsky and Meleuzovsky chemical plants. The schematic diagram of the production of LCF is to neutralize phosphoric acid (thermal or superphosphoric) to a pH of about 6.5. Depending on the preparation scheme, aqueous or anhydrous ammonia is used as a neutralizing agent. The most widespread LCF

- *Sh.Yu.Nomozov, PhD student, Phosphate fertilizer laboratory, Institute of general and inorganic chemistry of Uzbek Academy of Sciences , Uzbekistan. Email: temirov-2012@mail.ru*
- *Sh.S.Namazov, Doctor of technical sciences, professor, academician, head of laboratory of Phosphate fertilizer, Institute of general and inorganic chemistry of Uzbek Academy of Sciences, Uzbekistan.*
- *A.R.Seytnazarov, Doctor of technical sciences (DSc), Chief Researcher of Phosphate fertilizer laboratory, Institute of general and inorganic chemistry of Uzbek Academy of Sciences, Uzbekistan.*
- *B.M.Beglov, Doctor of technical sciences, professor, academician, Chief Researcher of Phosphate fertilizer, Institute of general and inorganic chemistry of Uzbek Academy of Sciences, Uzbekistan.*
- *U.K.Alimov,* Tianjin University of Science and Technology, Tianjin, 300457, P.R. China

brands are 10:34:0, 11:37:0 and 8:24:0. So, in the LCF brands of 10:34:0 and 11:37:0, phosphorus is present in the form of ortho and polyforms, and in the brand of 8:24:0 in the ortho form [11]. LCF solutions of the 10:34:0 and 11:37:0 brands are obtained by neutralizing polyphosphoric acid (72 or 76% P_2O_5) with gaseous ammonia. LCF solution of the 8:24:0 brand is obtained by neutralizing with ammonia of concentrated phosphoric acid with a 54% P_2O_5 content. They are considered as basic solutions, used as a fertilizer or as a basis for the production of double and triple liquid fertilizers. This is achieved by adding to them nitrogen (urea, ammonium nitrate or their mixture) and potassium (potassium chloride, sulfate and nitrate) fertilizers. Here, potassium chloride is almost the only source of potassium for the triplex LCFs. However, due to its insufficient solubility it is impossible to obtain a concentrated LCF. Potassium nitrate is even less soluble, which is formed if ammonium nitrate is used as the nitrogen component for the LCF. In this case, stabilizers are offered: both natural and synthetic to obtain sufficiently stable dispersed systems that are in suspension. Usually, 28% suspension of attapulgite or a pure bentonite clay is used, which are added into a solution of 10:34:0, then urea – ammonium nitrate and, last of all, potassium chloride. With the use of superphosphoric acid, due to the relatively high solubility of ammonium polyphosphates, it is possible to obtain basic solutions and balanced LCFs with much higher concentrations than with phosphoric acid. In the USA, suspended LCFs are used for all major agricultural crops [12]. So, before sowing of corn, suspensions of 6:12:24 and 6:12:28, wheat - 20:10:10 and 14:14:14 are applied. When sowing corn and cotton, a suspension of 11:22:11 is used. At that, a basis for the preparation of NPK-suspension serves 10:34:0 brand, made from superphosphoric acid. That is, the most popular phosphoric components in the preparation of the suspension is a solution of ammonium polyphosphate. This also determines the high cost of LCF. In Uzbekistan, due to the lack of concentrated phosphoric acid or complex acting liquid fertilizer products in cultivation of crops during the vegetation, plants are treated with a suspension obtained by dissolving and mixing solid standard fertilizers - urea, ammonium nitrate, CAM, ammonium phosphate, superphosphate or potassium chloride. Therefore, economic pressure is pushing manufacturers to use cheaper materials. One of the ways to reduce the cost of LCF production is the replacement of expensive thermal or superphosphoric acid with ammophos, diammophos and standard WPA or its ammoniated solution. The typical composition of the 9:9:9 brand is as follows: $(NH_4)_2HPO_4$ - 12-15%, $NH_4(PO_4)_2$ - 2-4%, $(NH_2)_2CO$ - 12-13%, KCl - 13-14%, where the share of amide nitrogen to be 61-66%. It is accepted that in the LCF the amount of nutrients should contain, on the basis of ortho- and polyphosphoric acids, at least 27 and 33%, respectively. Such fertilizers can also be obtained on the basis of WPA. Therefore, the development of processing technology for low-concentrated WPA with a concentration of 16–18% P_2O_5 in the LCF is of the great challenge. The production of LCF should be organized in the complex with the production of solid fertilizers. The combination of these products in one cycle significantly reduces capital costs. The aim of this work is to prepare various brands of NP and NPK fertilizers based on the ammonization of a weakly concentrated WPA, followed by the addition of nitrogen and potassium fertilizers into the ammophos pulp.

2 MATERIALS AND METHODS.

In the experiments, WPA was used based on the dihydrate method from a thermal concentrate (26% P_2O_5) at JSC "Ammofos-Maxam" (Uzbekistan) and having a composition (wt.%): 16.46 P_2O_5, 0.06 CaO, 1.11 MgO, 0.27 Fe_2O_3, 0.41 Al_2O_3, 2.98 SO_3 and 0.99 F, with a density of 1.18 g/cm^3 was used. In technical conditions for WPA [13] the lower limit of the concentration of P_2O_5, the content of sulfur in sulfate and solid sediment are regulated. Exception, sulfur in sulfate, the acid contains dissolved ions of Fe, Al, Ca, Mg, and F. The solid residue may contain calcium sulphates, precipitated upon cooling, acids, phosphates of iron and aluminum - $(Fe,Al)_3(H_3O)H_8(PO_4)_6 \cdot 6H_2O$, silicofluorides Na_2SiF_6, K_2SiF_6, $NaKSiF_6$, chuchrovit $CaSO_4AlSiF_{13} \cdot 10H_2O$, ralstonite $(Ca,Mg)NaAlF_6 \cdot 2H_2O$ [14]. The process of neutralization of WPA was carried out with gaseous ammonia (100% NH_3) in a special reactor with vigorous stirring to a pH value of 4.5; 5.5 and 6.5. The pH value of ammoniated pulps was measured using an I-130M brand ionomer with an electrode system of electrodes ESL 63-07, EBL-1M3.1 and TKA-7 with an accuracy of 0.02 pH units. In neutralization of WPA with ammonia, its temperature rises to 65-70°C. At pH=4.51 a solution of monoammonium phosphate is formed, and at higher pH (from 5.53 to 6.56) an additional diammonium phosphate is formed. The water-insoluble part of the ammophos pulp includes calcium and magnesium phosphates, ammonium salts of iron, aluminum, magnesium and fluorine, which are precipitated in the solid phase during the ammonization of WPA. Here, it is appropriate to present the results of the determination of solid phases formed upon ammonization from pH 2.0 to 8.0 WPA from Karatau phosphorite (Kazakhstan) [15-19]. WPA from Karatau phosphorite contains (wt.%): 20.3 P_2O_5; 0.24 CaO; 2.72 MgO; 1.04 Al_2O_3; 1.02 Fe_2O_3; 2.1 SO_3; 1.72 F. As can be seen, the composition of this acid is close to the composition of WPA from thermal concentrate (Uzbekistan). Therefore, ammonization of these acids to high pH values can give comparable results. Below we provide a list of chemical compounds, the formation of which is possible in neutralization of WPA by ammonia from Karatau phosphorites with different composition and impurity content [18]. So, in ammonization of WPA from Karatau phosphorites to pH approximately 2.5, water soluble compounds $NH_4H_2PO_4$, $NH_4HSO_4 \cdot NH_4H_2PO_4$, $(NH_4)_2SiF_6$, and citrate soluble complexes of iron and aluminum phosphates $(Fe, Al)_3NH_4H_8(PO_4)_6 \cdot 6H_2O$, $(Fe, Al)NH_4HPO_4F_2$ and $Mg(Fe, Al)NH_4(HPO_4)_2F_2$ are formed. The first complex salt is well crystallized, easily filtrated and separated. The second is amorphous, forms colloidal non-settling and poorly filtered sediments. Less soluble compound $Mg(Fe, Al)NH_4(HPO_4)_2F_2$ forms in magnesium contained acids and is well crystallized. In ammonization to pH about 2.5 almost all ions of iron, part of aluminum, magnesium, and fluorine are precipitated. With an increase in pH to 5.5, the formation of $NH_4H_2PO_4$ continues, the complex phosphates of iron and aluminum are converted to $Mg(Fe,Al)(NH_4)_2(HPO_4)_2F_3$, $(Fe,Al)NH_4(PO_4)_2 \cdot 0.5H_2O$, $(Fe,Al)NH_4HPO_4F_2$, precipitate disubstituted calcium and magnesium phosphates, magnesium fluoride phosphate, precipitated hydroxylapatite, forms unstable in aqueous solution intermediate magnesium phosphate $Mg_3(NH_4)_2(HPO_4)_4 \cdot 8H_2O$, which decomposes with the formation of $MgNH_4PO_4 \cdot H_2O$. All phosphates, except hydroxylapatite, are citrate soluble. Neutralization to pH=8

leads to the formation of $(NH_4)_2HPO_4$. Complex compounds of iron and aluminum are converted into indigestible phosphates $(Fe,Al)_2NH_4(PO_4)_2OH•2H_2O$, $(Fe,Al)(NH_4)_2(HPO_4)_2F$, compounds $MgHPO_4$ and $Mg_3(NH_4)_2(HPO_4)_4•8H_2O$ transfer to $Mg(NH_4)_2(HPO_4)_2•4H_2O$ mertelet, which decomposes with the formation of $MgNH_4PO_4•H_2O$. The interaction of magnesium ammonium phosphate with diammonium phosphate leads to the formation of $Mg(NH_4)_2(HPO_4)_2•4H_2O$ and the loss of ammonia due to the decomposition of $(NH_4)_3PO_4$. Neutralization of WPA in the presence of fluoride or ammonium silicon fluoride can lead to the formation of a number of fluorides of iron, aluminum, calcium and magnesium. In the absence of fluorides and ammonium silicon fluorides, hydroxides are formed.

3 RESULTS AND DISCUSSIONS

. In order to improve the marketability of LCF, i.e., to obtain more transparent suspensions and increase in them water-soluble phosphorus, it is necessary to clean the ammonium phosphate pulp from solid suspended matter. To do that, the pulp (at 65°C) was separated into solid and liquid phases by centrifuging. In order to avoid ammonia loss, the wet solid phase was dried at 60°C to a constant weight, determining the moisture content of the solid mass. It was established that the humidity of the precipitation formed is 60% H_2O. Then, the filtrate and the dried precipitates were analyzed for the content of various components. Their composition is given in Table 1. It can be seen that at the studied pH values, the maximum deposition of ions of calcium, magnesium and one-and-a-half oxides (iron and aluminum), as well as complex salts of fluoride compounds from ammonium phosphate solutions occurs. The increase in their content with increasing pH occurs as a result of crystallization, first of mono-ammonium phosphate, and then of diammonium phosphate. In the water-insoluble part of the product 99.42-99.85 and 72.82-79.21% of phosphorus is in assimilable and water-soluble forms for plants in relation to its total content. They can be used as an independent solid nitrogen-phosphate fertilizer - ammophos. The degree of precipitation of the components from the WPA into the solid phase was calculated from the compositions of the solid and liquid phases. The results are shown in Table 2. As shown in Table 2, in all cases the maximum degree of transition of water-insoluble components (MgO – 88-89%, 86-88% Fe_2O_3, 83-89% Al_2O_3, 59-75% F) to the solid phase was achieved. Depending on the pH, the composition of the liquid, also the transparent part of the pulps is as follows: 4.77-6.18% N, 14.05-14.66% P_2O_5, 0.17-0.18% MgO, 3.64-4.07% SO_3, 0.034-0.051% Fe_2O_3, 0.064-0.097% Al_2O_3, 0.37-0.55% F, herewith the composition of the ammophos suspension is significantly improved (in the initial ammophos pulp, the ratio of $P_2O_{5aq.}$:P_2O_{5total} was 92.15-94.13%, and in the purified one it became 95.30-97.51%). Only there was a decrease in the total phosphorus content (from 16.46 to 14.05-14.66% P_2O_5). It should be noted that due to the free sulfuric acid in WPA (2.98% SO_3 or 4.92% H_2SO_4), a water-soluble sulfate ion is present in the purified ammophos pulp due to the formation of $(NH_4)_2SO_4$. This gives liquid products a new quality. Sulfur is considered a part of proteins and amino acids in the formation of the crop. According to the physiological role in plant nutrition, S should be ranked fourth after N, P and K [19]. In addition, due to the long-dominant tendency to switch to the production of concentrated fertilizers, the sulfur deficiency in soils has significantly increased.

TABLE 1

Composition of precipitation and filtrates obtained from ammophos pulp at different pH values

pH of pulp	Component content, weight %								$\frac{P_2O_{5assim.}}{P_2O_{5total.}}$ %	$\frac{P_2O_{5aq.}}{P_2O_{5total.}}$ %
	N	$P_2O_{5total.}$	CaO	MgO	SO_3	Fe_2O_3	Al_2O_3	F		
Filtrate										
4.5	4.77	14.66	отс.	0.17	3.64	0.051	0.097	0.55	99.42	95.30
5.5	5.12	14.50	отс.	0.17	4.07	0.035	0.091	0.42	99.67	96.93
6.5	6.18	14.05	отс.	0.18	3.72	0.034	0.064	0.37	99.85	97.51
Dried solid precipitate										
4.5	7.68	46.75	1.30	7.90	2.76	1.91	2.76	4.73	92.20	79.21
5.5	11.76	47.20	1.29	7.17	2.32	1.82	2.68	5.01	89.57	73.58
6.5	14.28	46.05	1.29	6.35	3.36	1.55	2.24	4.78	92.40	72.82

TABLE 2

Degree of deposition (%) of the various components in the ammonization of extraction of phosphoric acid

pH of pulp	N	P_2O_{5total}	MgO	SO_3	Fe_2O_3	Al_2O_3	F
4.5	21.50	35.10	88.0	11.45	86.14	82.58	59.04
5.5	31.34	39.32	88.56	13.06	87.68	84.02	70.38
6.5	35.25	43.54	89.01	17.57	87.82	89.02	75.17

Thus, purified ammonium phosphate solutions with a high economic effect can be used in greenhouses (in gardens, berries, vineyards and under other crops), especially in foliar feeding by drip application. In the subsequent stage, this suspension served as the basic solution for the preparation of complex mixtures with a given ratio of nutrients. Based on the ammonium phosphate suspension, samples of balanced NP-fertilizers were prepared at mass ratios N : P_2O_5 = 1 : 0.5; 1 : 0.7 and 1 : 1. Powdered ammonium nitrate (34.6 N) and urea (46.2% N), powdered to a particle size of 0.25 mm, as well as a CAM solution – a urea-ammonia mixture with a content of 32% served as additional nitrogen sources. CAM is a liquid nitrogen fertilizer, the method of production of which is based on mixing in a certain ratio of aqueous solutions of urea (68-71%) and ammonium nitrate (89-91%), neutralization of free NH_3 and inhibition of the resulting product. CAM contains a corrosion inhibitor (usually 0.2-0.5% P_2O_5 in the form of ammonium phosphates). The formation of crystals and the short-term freezing of CAM solutions in storage tanks do not induce a danger, since with an increase in temperature, the crystals dissolve and the fertilizers completely restore their original qualities. CAM is transported in conventional rail and

tank trucks. CAM practically does not contain free ammonia, which excludes nitrogen losses during loading, transportation, storage and introducing into the soil.

TABLE 3

Composition of liquid NP-fertilizers based on purified ammophos pulp and ammonium nitrate

Mass ratio N : P_2O_5	Content of components, %		$\frac{P_2O_{5assim.}}{P_2O_{5total.}}$ %	$\frac{P_2O_{5aq.}}{P_2O_{5total.}}$ %
	N	$P_2O_{5total.}$		
Purified ammophos suspension with pH = 4.5				
1 : 0.5	18.48	9.25	99.59	95.32
1 : 0.7	14.85	10.40	99.70	95.42
1 : 1	11.94	11.94	99.79	95.51
Purified ammophos suspension with pH = 5.5				
1 : 0.5	17.74	8.87	99.69	96.95
1 : 0.7	14.59	10.21	99.78	97.12
1 : 1	11.78	11.78	99.84	97.51
Purified ammophos suspension with pH = 6.5				
1 : 0.5	17.90	8.95	99.91	97.55
1 : 0.7	15.16	10.61	99.94	97.62
1 : 1	11.97	11.97	99.96	97.89

To obtain LCF solutions, the calculated amount of NH_4NO_3, $(NH_2)_2CO$ or CAM-32 was added to the basic solution of ammophos, obtained at different pH values with constant stirring. The temperature of the ammonium phosphate solution was maintained at 70°C. The compositions of liquid products are given in Tables 3-5.

TABLE 4

Composition of liquid NP-fertilizers based on purified ammophos pulp and urea

Mass ratio N : P_2O_5	Content of components, %		$\frac{P_2O_{5assim.}}{P_2O_{5total.}}$ %	$\frac{P_2O_{5aq.}}{P_2O_{5total.}}$ %
	N	$P_2O_{5total.}$		
Purified ammophos suspension with pH = 4.5				
1 : 0.5	20.12	10.06	99.65	95.42
1 : 0.7	16.08	11.26	99.78	95.53
1 : 1	12.61	12.61	99.87	95.60
Purified ammophos suspension with pH = 5.5				
1 : 0.5	19.64	9.82	99.79	97.05
1 : 0.7	15.75	11.02	99.87	97.21
1 : 1	12.40	12.40	99.92	97.29
Purified ammophos suspension with pH = 6.5				
1 : 0.5	18.06	9.03	99.94	97.43
1 : 0.7	14.74	10.32	99.97	97.57
1 : 1	11.23	11.23	99.98	97.96

TABLE 5

Composition of liquid NP-fertilizers based on purified ammophos pulp and urea-ammonia mixture (CAM)

Mass ratio N : P_2O_5	Content of components, %		$\frac{P_2O_{5assim.}}{P_2O_{5tot.}}$ %	$\frac{P_2O_{5aq.}}{P_2O_{5tot.}}$ %
	N	$P_2O_{5total.}$		
Purified ammophos suspension with pH = 4.5				
1 : 0.5	17.79	8.90	99.62	95.36
1 : 0.7	14.43	10.10	99.74	95.49
1 : 1	11.70	11.70	99.83	95.57
Purified ammophos suspension with pH = 5.5				
1 : 0.5	17.09	8.54	99.74	96.98
1 : 0.7	14.18	9.92	99.85	97.16
1 : 1	11.54	11.54	99.89	97.25
Purified ammophos suspension with pH = 6.5				
1 : 0.5	17.27	8.64	99.93	97.41
1 : 0.7	14.77	10.34	99.95	97.55
1 : 1	11.78	11.78	99.97	97.94

As shown, that with an increase in the number of nitrogen components in the finished suspensions, although the phosphorus content decreases, without affecting the relative content of its assimilable form, the nitrogen content increases. Increasing the pH of the ammophos suspension practically does not affect the relative content of the assimilable form of phosphorus, only slightly increases the content of its water-soluble form. Suspensions prepared on the basis of ammonium phosphate solution with pH = 4.5; 5.5; 6.5 and dry NH_4NO_3 contain 17.90-18.48% N, 9.25-11.94% $P_2O_{5tot.}$, $P_2O_{5aq.}$: $P_2O_{5tot.}$ = 95.32-97.55%, 14.85-15.16% N, 10.40-10.61% $P_2O_{5tot.}$, $P_2O_{5aq.}$: $P_2O_{5tot.}$ = 95.42-97.62% and 11.78-11.97% N, 11.78-11.97% $P_2O_{5tot.}$, $P_2O_{5aq.}$: $P_2O_{5tot.}$ = 95.51-97.89%, respectively, for the weight ratios N : P_2O_5 = 1: 0.5; 1: 0.7 and 1: 1 (Table 3). Suspensions prepared on the basis of dry urea had the highest nutrient concentrations, rather than NH_4NO_3 or CAM-32. That is, urea in this respect somewhat improves the composition of the products. So, depending on N : P_2O_5 at pulp pH 5.5, the resulting liquid NP-fertilizers have from 12.61 to 20.12% N, from 10.06 to 12.61% $P_2O_{5tot.}$, $P_2O_{5aq.}$: $P_2O_{5tot.}$ from 95.42 to 95.60% and at pH = 6.5 from 11.23 to 18.06% N, from 9.03 to 11.23% $P_2O_{5tot.}$, $P_2O_{5aq.}$: $P_2O_{5tot.}$ from 97.43 to 97.96% (Table 4). A similar picture is observed with the use of CAM-32 solution (Table 5). Only products have a relatively low nutrient content than in using nitrate and urea. The final task was to obtain a balanced liquid NPK-fertilizers based on a purified solution of ammophos, nitrogen fertilizers and potassium chloride. In this case, the mass ratio of N : P_2O_5 : K_2O varied from 1: 0.5: 0.3 to 1: 1: 1. For this, to the basic ammonium phosphate solution, firstly ammonium nitrate, carbamide or CAM-32 were added, and lastly potassium chloride. The compositions of LCFs are presented in Tables 6-8.

TABLE 6

Composition of liquid NPK-fertilizers based on purified ammophos pulp, ammonium nitrate and potassium chloride

Mass ratio N : P_2O_5 : K_2O	Nutrient content, %			$\frac{P_2O_{5assim.}}{P_2O_{5total.}}$ %	$\frac{P_2O_{5aq.}}{P_2O_{5tot.}}$ %
	N	P_2O_{5total}	$K_{total.}$		
Purified ammophos suspension with pH = 4.5					
1 : 0.5 : 0.3	16.90	8.45	5.07	99.58	95.31
1 : 0.7 : 0.5	13.12	9.18	6.56	99.58	95.39
1 : 1 : 1	9.82	9.82	9.82	99.76	95.45
Purified ammophos suspension with pH = 5.5					
1 : 0.5 : 0.3	16.12	8.06	4.83	99.68	96.94
1 : 0.7 : 0.5	12.90	9.03	6.45	99.76	97.10
1 : 1 : 1	9.75	9.75	9.75	99.81	97.39
Purified ammophos suspension with pH = 6.5					
1 : 0.5 : 0.3	16.42	8.21	4.93	99.90	97.52
1 : 0.7 : 0.5	13.60	9.52	6.81	99.92	97.58
1 : 1 : 1	9.84	9.84	9.84	99.94	97.67

TABLE 7

Composition of liquid NPK-fertilizers based on purified ammophos pulp, urea and potassium chloride

Mass ratio N : P_2O_5 : K_2O	Nutrient content, %			$\frac{P_2O_{5assim.}}{P_2O_{5total.}}$ %	$\frac{P_2O_{5aq.}}{P_2O_{5tot.}}$ %
	N	P_2O_{5total}	$K_{total.}$		
Purified ammophos suspension with pH = 4.5					
1 : 0.5 : 0.3	14.87	9.29	5.57	99.64	95.36
1 : 0.7 : 0.5	11.47	9.85	7.03	99.75	95.52
1 : 1 : 1	10.28	10.28	10.28	99.83	95.64

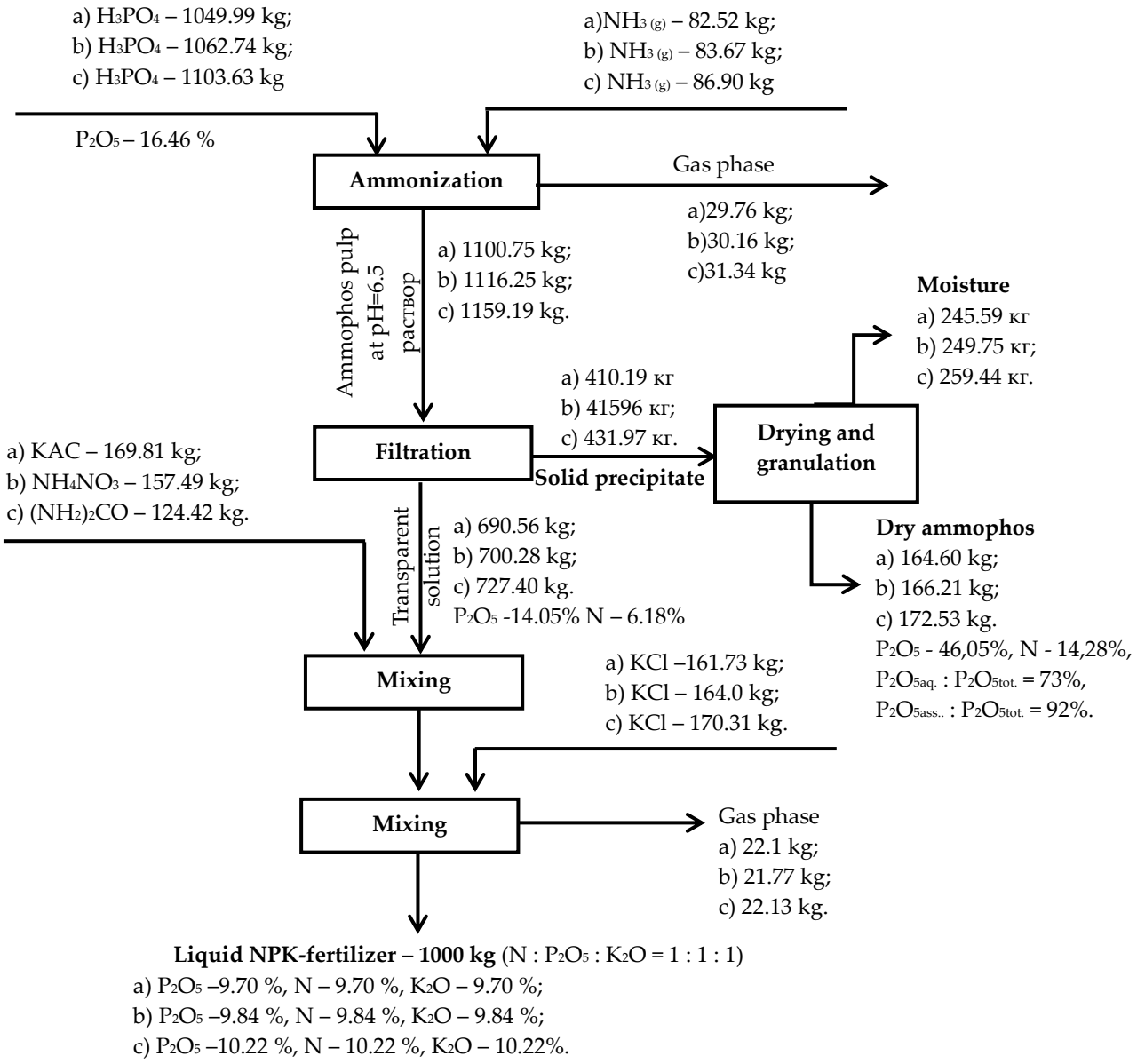
Purified ammophos suspension with pH = 5.5					
1 : 0.5 : 0.3	14.22	8.85	5.31	99.76	97.05
1 : 0.7 : 0.5	11.33	9.67	6.91	99.87	97.19
1 : 1 : 1	10.19	10.19	10.19	99.93	97.53
Purified ammophos suspension with pH = 6.5					
1 : 0.5 : 0.3	14.61	8.98	5.38	99.94	97.58
1 : 0.7 : 0.5	12.08	10.13	7.24	99.97	97.66
1 : 1 : 1	10.22	10.22	10.22	99.99	97.79

TABLE 8

Composition of liquid NPK-fertilizers based on purified ammophos pulp, CAM and potassium chloride

Mass ratio $N : P_2O_5 : K_2O$	Nutrient content, %			$\frac{P_2O_{5assim.}}{P_2O_{5total.}}$ %	$\frac{P_2O_{5aq.}}{P_2O_{5tot.}}$ %
	N	P_2O_{5total}	$K_{total.}$		
Purified ammophos suspension with pH = 4.5					
1 : 0.5 : 0.3	17.60	8.16	4.90	99.60	95.33
1 : 0.7 : 0.5	13.70	8.95	6.38	99.71	95.45
1 : 1 : 1	9.66	9.66	9.66	99.79	95.52
Purified ammophos suspension with pH = 5.5					
1 : 0.5 : 0.3	16.78	7.79	6.74	99.71	96.96
1 : 0.7 : 0.5	13.47	8.81	7.99	99.82	97.14
1 : 1 : 1	9.60	9.60	9.60	99.91	97.41
Purified ammophos suspension with pH = 6.5					
1 : 0.5 : 0.3	17.06	7.95	4.77	99.92	97.54
1 : 0.7 : 0.5	14.15	9.30	6.65	99.95	97.60
1 : 1: 1	9.70	9.70	9.70	99.98	97.72

It can be obviously seen, that for all brands of liquid NPK-fertilizers, the amount of nutrient compounds is 30 percent or more. For example, using ammonium nitrate, depending on the pH values, the composition of the liquid and purified NPK composition for the ratio $N : P_2O_5 : K_2O = 1 : 0.5 : 0.3$ looks like 16.1-16.9% N, 4.83-5.07% K_2O, 8.06-8.45% P_2O_5, of which 95.31-97.52% is in water-soluble form. For the ratio of $N: P_2O_5 : K_2O = 1: 0.7: 0.5$, these indicators are within 12.9-13.6%, 9.03-9.52%, 95.39-97.58%, respectively (Table 6). For the most demanded brand 1: 1: 1, the product contains 9.82% of the nutrient compounds, that is, a total of 29.46%. It contains $P_2O_{5aq.} : P_2O_{5tot.}$ = 95.45-97.67%. If dried urea is used as a source of additional nitrogen, then the composition of liquid NPK-fertilizers is as follows: for the ratio $N : P_2O_5 : K_2O = 1: 0.5: 0.3$ - 14.22-14.87, 5.31-5.57% K_2O, 8.85-9.29% P_2O_5, of which 95.36-97.58% of phosphorus is in water-soluble form and for $N: P_2O_5: K_2O = 1: 0.7: 0.5$ - 11.33-12.08% N, 6.91-7.24% K_2O, 9.67-10.13% of P_2O_5, of which 95.52-97.66% of phosphorus is in water soluble form. And for $N: P_2O_5: K_2O = 1: 1: 1$, the solution contains 10.28% of the nutrient compound, in the amount of 30.84% and the ratio $P_2O_{5aq.} : P_2O_{5tot.}$ = 95.64-97.53% (Table 7). The use of CAM-32 results in the production of NPK-fertilizers, which are less concentrated in components than urea and ammonium nitrate (Table 8). Depending on pH and brands, NPK-suspensions containing from 9.60 to 17.6% N, from 4.77 to 9.70 K_2O and from 7.79 to 9.70% P_2O_5 were obtained, of which from 95.33 to 97.72% are in water-soluble form for plants. It should be noted that in all the studied NP- and NPK-fertilizer variants, all the phosphorus remains in a form that is assimilable for plants. The material balance for the production of 1 ton of liquid NPK-fertilizers was calculated for the mass ratio $N : P_2O_5 : K_2O = 1: 1: 1$ using CAM-32, NH_4NO_3 or $(NH_2)_2CO$ and KCl (figure).



Thus, the low concentrated WPA is quite suitable for the preparation of liquid complex fertilizers after its purification by the precipitation method. In order to increase the concentration of nutrient elements, it is recommended to use ammonium nitrate, urea, CAM, and as a potassium component – potassium chloride. In the case of the use of sulphate, phosphate or potassium nitrate can be obtained more concentrated towards to nutritional components chlorine-free LCFs.

4 CONCLUSION

In the process of obtaining NP- and NPK-fertilizers by ammonization (to pH = 4.5, 5.5 and 6.5) slightly concentrated WPA, followed by the addition of nitrogen and potassium fertilizers into the ammophos pulp: - in order to increase the marketability of LCFs, that is, to obtain transparent suspensions, and to increase water-soluble phosphorus in them, the process of separating solid suspensions from ammophos pulp was carried out by centrifuging;

- a precipitate containing a high content of total, assimilable and aqueous forms of phosphorus (46-47% $P_2O_{5tot.}$, $P_2O_{5ass.}$: $P_2O_{5tot.}$ = 90-92% и $P_2O_{5aq.}$: $P_2O_{5tot.}$ = 73-79%) is proposed as an independent solid nitrogen-phosphorus fertilizer – ammophos;

- based on the purified ammonium phosphate suspension – a basic solution (containing 14.05-14.66% P_2O_5 and 4.77-6.18% N) of urea, ammonium nitrate, CAM-32, and potassium chloride, samples of balanced in nutrients of NP- and NPK-fertilizers were obtained. So, with the use of urea, the 1: 1: 1 product brand contains 10.28% of the nutrient compound, that is, in total more than 30%;

- the material balance for the process of obtaining liquid NPK-fertilizers was calculated for the mass ratio of N: P_2O_5: K_2O = 1: 1: 1 using CAM-32, NH_4NO_3 or $(NH_2)_2CO$ and KC1.

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