Technology of obtaining liquid complex fertilizers in the presence of monoethanolamine based on phosphorites of the Central Kyzylkum

Doniyor Sherkuziev*, and *Solijon* Zokirov

Namangan Engineering-Technological Institute, Namangan, Uzbekistan

Abstract. The possibility of producing liquid fertilizers based on nitric acid processing of washed dried concentrate in the presence of monoethanolamine is shown. On the basis of nitric acid extract and monoethanolamine, liquid complex fertilizers with stimulating activity were obtained, composition: P2O5tot. - 10-11%, CaOtot. - 6-7%, Ntot. 12-13% and K2O- 5-6%. They contribute to the acceleration of plant growth by 10-12 days and an increase in yield by an average of 8-10% compared to the control variant. It can be concluded that they can be recommended as liquid complex fertilizers for drip application.

1 Introduction

The range of granulated mineral fertilizers, although it allows solving the problem of providing plants with nutrients, does not fully satisfy the growing needs of agriculture for the organization of highly efficient cultivation of crops. According to leading foreign experts, the main requirements for mineral fertilizers, especially for foliar top dressing, can only be met when using liquid forms of fertilizers. Agricultural science and practice in recent decades convincingly show that the place of traditional mineral fertilizers is increasingly occupied by liquid, i.e., the future belongs to liquid concentrated mineral fertilizers. The only way to increase the concentration of nutrients in liquid fertilizers is to use suspensions instead of solutions [1].

An assessment of the technical and economic factors that characterize the production and use of solid and liquid fertilizers indicates the high efficiency of the use of liquid fertilizers. The cost of production of 1 ton of P2O5 in the form of a fertilizer mixture produced based on ammophos is 138% in relation to liquid complex fertilizers [2-4].

The largest volume of production of liquid fertilizers among developed countries was achieved in the USA, England, and France. According to experts, in developed countries, in the next 5-10 years, the volume of production of the liquid complex fertilizers (LCF) and their consumption in agriculture will increase by 2-4 times. The world market for liquid fertilizers in 2016 was estimated at 11. 108 million dollars and is expected to reach 13. 530 million dollars by 2023. USA, with an average annual growth rate of 2.8%. The following companies are key producers in the global housing market: Agrium Incorporated (Canada),

* Corresponding author: doniyorsherquziev@gmail.com

Yara International ASA (Norway), K+S Aktiengesellschaft (Germany), Triangle Chemical Company (USA), Fox farm Fertilizer (USA), Compo Expert GmbH (Germany), Basf, Bayer, Dupont (Germany),Tessenderio Group (Belguim), Kugler Company (USA), Agro Liquid (USA), Plant Food Company (USA), as well as the countries of the Middle and Far East - Israel Chemical Ltd. (Israel), Haifa Chemicals Ltd. (Israel), Agrotiger (Turkey), Nutri-Tech Solutions (Australia).

The Russian agrochemical industry has about 30 major manufacturers such as CJSC «PhosAgro AG», «Uralkaliy» JSC «Acron» JSC-MHK «EuroChem», JSC UCC «Uralchem», etc [5].

The process of the production of suspended NP- and NPK-fertilizers with insecticidal activity [6-11]. The experiments used free CK phosphate (17.55% P2O5), ground sulfur, potassium chloride (K2O-60%), carbamide and 58.5% HNO3. The optimum decomposition of phosphate flour is the addition of 10% sulphur hammer, the rate of nitric acid is 20-70%, the temperature is 35-40oC. The resulting NPS- and NPKS-suspensions contain, weight. % - 7.02-12.63 and 5.69-11.42 N, 5.70-7.83 and 5.20-6.92 P2O5, 7.55-13.83 and 6.16-11.53 CaOwes., 3.74-5.13 and 3.41-4.53 S and have protective properties against plant diseases [12].

Studies on the development of technology for the creation of complex new types of liquid nitrogen fertilizers, which have physiological activity on the basis of CAS through the introduction of physiological andactive substances obtained from the industrial waste - the light-volatile acetic acid fraction of AS "Navoiazot" by neutralization with monoethanolamine [13-16]. Three new compounds have been synthesized:

$$CO(NH_2)_2 \cdot CH_3COOH \cdot NH_2C_2H_4OH,\ CO(NH_2)_2 \cdot HCOOH \cdot NH_2C_2H_4OH,$$
$$CO(NH_2)_2 \cdot 2HCOOH \cdot NH_2C_2H_4OH.$$

The method of isomolar series studied the solubility and interaction of components in 3 systems, including the physico-chemical substantiation of the process of obtaining PAS (physiological active substance), and also made a material balance of production [17].

The conducted analysis of literary sources shows that, although previously carried out studies on nitrogen acid processing of phosphate of Central Kyzylkum in LCF and LNCF of various brands, However, to date, the processes for producing LCF and SNCF with stimulating activity by the nitrogen acid decomposition of the carbonate phosphate of CK in monoethanolamine binder to increase the agrochemical efficiency of LCF have not been studied at all.

It follows from the above that it is necessary to develop a technology for the production of complex slurry fertilizers with stimulating activity on the basis of nitric acid processing of Kyzylkum phosphate is the subject of this study.

Table 1. Phosphate raw material composition.

Phosphate raw materials	**Component content, weight. %**									**CaO:P_2O_5**
	P_2O_5	**CaO**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**F**	**CO_2**	**SO_3**	**i.p.**	
WDC	25.62	52.17	1.15	0.63	1.20	2.27	2.10	1.34	6.78	2.04

To study the complete decomposition of Kyzylkum phosphate raw materials with nitric acid, the essence of which is to obtain suspended liquid complex fertilizers (SLCF). In the experiments, washed dried concentrate (WDC) was taken as a phosphate raw material, the composition of which is given in Table 1.

2 Materials and methods

At the beginning of the experiments the influence of the norm of nitric acid on the decomposition rate ($K_{dec.}$) of phosphate raw materials was studied. Acid standards ranged from 80 to 120% of stoichiometry at CaO in the raw material.

It is known that $K_{dec.}$ phosphate raw materials is the determining indicator for the disclosure of phosphate raw materials. For this purpose, 57% concentration of nitric acid was placed in a thermostatic reactor equipped with a screw mixer. The speed of the mixer was 250-300 rev/min. The decomposition process was carried out at a temperature of 40 ºC, the mixing time was 30 min. The temperature was controlled by a thermostat. After reaching the temperature of 40ºC, the reactor was added the calculated amount of phosphate raw material. After decomposition, the resulting product in the reactor was filtered on a heated Büchner funnel at a pressure of 150 mm.Hg. (0.2 atm.). At the beginning, the solid sediment was washed with water with a temperature of 85-90ºC and acetone. After washing the sludge samples dried at 100-105ºC, then determined the quantitative content of $P_2O_{5total.}$ and $P_2O_{5water.}$ in precipitation.

It is known that when the carbonates contained in the phosphate raw material are decomposed, the phosphate mineral is decomposed to form water-soluble calcium dihydrophosphate and orthophosphoric acid by the following reactions:

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2\uparrow + H_2O$$

$$2Ca_5F(PO_4)_3 + 14HNO_3 \rightarrow 3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + 2HF\uparrow$$

$$Ca_5F(PO_4)_3 + 10HNO_3 \rightarrow 3H_3PO_4 + 5Ca(NO_3)_2 + HF\uparrow$$

As shown by the results of the studies, with an increase in the norm of nitric acid from 80 to 120% (stoichiometry on CaO in raw materials) in various types of Kraz phosphate raw materials. will increase from 82 to 96 respectively for WDC.

Kraz. phosphate raw materials with further increase in the norm of nitric acid hardly change. This is due to the fact that the structure of the phosphate raw material contains acidic tungsten oxide and the formation of silicophosphate. On this basis, 80-95% of stoichiometry, regardless of the phosphate raw material, can be considered the optimal norm of nitric acid.

The main chemical composition of the nitrogen acid extractors (NAE) derived from the phosphate raw material of the WDC is given in Table 2.

3 Results and discussions

The data show that nitric acid levels have a significant impact on the recovery of many components in phosphate raw materials. However, the recovery of these components from phosphate raw materials varies. As the nitric acid ratio increases from 80 to 95 per cent, the nutrient content increases significantly.

When used, the acid content ranges from 105 to 120%, ranging from 17.04 to 11.88; 0.501 to 0.971; 0.153 to 0.264 and 0.13 to 0.18%, respectively, for CaO, Al2O3, Fe2O3 and MgO.

In all nitric acid standards, the nitrogen content increases from 6.03 to 7.52% due to the introduction of the nitric component in the acid reagent. Thus, it can be concluded that the optimal standards of nitric acid for the decomposition of Kyzylkum phosphate are 80-95%. In further experiments, the process of obtaining a suspended solution of liquid complex fertilizers (LCF) based on nitrogen acid extractors (NAE) obtained at different nitric acid standards (80-120%) was studied from stoichiometry with further separation of insoluble residue by centrifugation. According to the technological scheme, it is thrown into a pile or can be recommended as a building material. The color of the liquid phase depends on the type of raw material: WDC vary from light orange to transparent.

Table 2. Main chemical composition of nitric acid extract according to nitric acid standard for different phosphate feedstock.

Quantity HNO_3, g.	Types of phosphate flour	Norm of HNO_3, %	Component content, %					
			P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	N
42.00	WDC	80	8.60	10.92	0.381	0.116	0.09	6.03
44.60		85	8.87	12.15	0.405	0.123	0.10	6.40
47.25		90	9.08	12.50	0.429	0.131	0.11	6.78
49.87		95	10.15	14.37	0.453	0.138	0.12	7.16
52.50		105	6.20	17.04	0.501	0.153	0.13	6.55
55.12		110	6.11	15.75	0.612	0.186	0.15	6.79
57.75		115	6.05	14.45	0.694	0.211	0.16	7.05
60.37		120	6.00	11.88	0.971	0.264	0.18	7.52

In order to obtain the main suspension of liquid complex fertilizers, the resulting transparent liquid phase was neutralized with a 50% solution of monoethanolamine (MEA) in the reactor at intensive mixing to pH values of 3.0-3.2. In the process of neutralization of the nitric acid phosphate extract by monoethanolamine, the phosphoric acid, monocalcium phosphate, calcium nitrate and monoethanolamine interact to form a liquid nitrogen phosphorus-calcium suspension by reaction:

$$Ca(H_2PO_4)_2 + Ca(NO_3)_2 + HO(CH_2)_2NH_2 \rightarrow HO(CH_2)_2NH_3H_2PO_4 + CaHPO_4 + Ca(NO_3)_2$$

$$H_3PO_4 + HO(CH_2)_2NH_2 = HO(CH_2)_2NH_3H_2PO_4$$

The result is a suspension of dicalcide phosphate, calcium nitrate and phosphate monoethanolamine. It should be noted that the neutralization of this transparent monoethanolamine liquid part produces a stable white suspension consisting of a light white suspension which is practically not precipitated during storage for several months.

The main chemical composition of NAE liquid phase neutralization products from WDC is shown in Table 4.

The data show that the main solution from the WDC is the LCF, where with an increase in the nitric acid content between 80 and 120% the nutrient content of P_2O_5, CaO and N from 4.87 to 9.21, 9.89 to 16.11 and 7.15 to 8.67%, respectively.

Table 3. Basic chemical composition of LCF solution obtained by neutralization of the liquid phase of the nitric acid extractor with monoethanolamine.

Norm of HNO_3, %	Types of phosphate flour	pH	P_2O_5, %	CaO, %	Al_2O_3, %	Fe_2O_3, %	MgO, %	N, %
80	WDC	3.2	7.48	9.89	0.381	0.116	0.09	7.15
85			7.78	11.12	0.405	0.123	0.10	7.48
90			8.18	11.48	0.429	0.131	0.11	7.86
95			9.21	12.43	0.453	0.138	0.12	8.14
105			5.22	16.11	0.501	0.153	0.13	7.47
110			5.18	14.68	0.612	0.186	0.15	7.84
115			5.03	13.47	0.694	0.211	0.16	8.11
120			4.87	10.85	0.971	0.264	0.18	8.67

Here the P_2O_5 and CaO content are lower on average at 1.10-1.23 and 1.06-1.19 times, respectively, while the nitrogen content is higher at 1.15-1.19 times, due to the injection of a nitrogen-containing agent monoethanolamine. This is also true for Al_2O_3, Fe_2O_3 and MgO.

The viscosity and density of the main LCD solution, obtained on the basis of neutralization of the liquid phase by monoethanolamine, have been studied at 80-120% nitric acid and 20-60oC. The data are summarized in Figure 1.

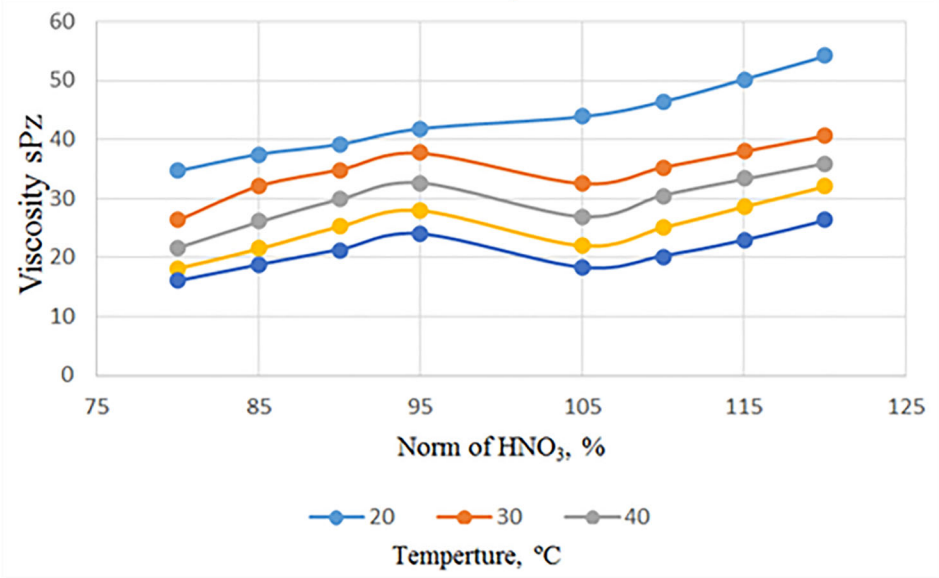

Fig. 1. Viscosity of the main LCD solution obtained by neutralization of the liquid phase of the nitric acid extract by monoethanolamine (for WDC).

A similar picture is observed for the slurry density for WDC, that is, the density decreases from 1.336 to 1.289 g/sm^3 and from 1.415 to 1.379 g/sm^3. At the above temperatures and standards, the rheological properties (viscosity and density) of the main housing unit from the WDC are as follows: viscosity decreases from 41.85 to 16.08 and from 54.11 to 18.38 sPz (Figure 1.) and density from 1.544 to 1.476 g/sm^3 and from 1.481 to 408 g/sm^3.

Thus, an increase in temperature contributes to a decrease in the density and viscosity of neutralized nitrogen acid extracts due to internal ion interactions. The rheological properties of these suspensions fully satisfy the technical requirements of the suspensions during the automation and control of the process, as well as their transfer from one apparatus to another without any difficulties.

In further studies the basic composition of insoluble residue and white light suspension was studied by infrared spectroscopic methods. For this purpose, the NAE and the main suspension of the housing, obtained at 90% of the norm of nitric acid, were filtered under a vacuum 550-600 mm Hg. On the Büchner funnel with a diameter of 5.5 cm, using one layer of filter paper. The residue produced on the filter was dried together with the filter paper in the drying cabinet at 60ºC. The results of the white suspension and insoluble residue samples are presented in Figure 2.

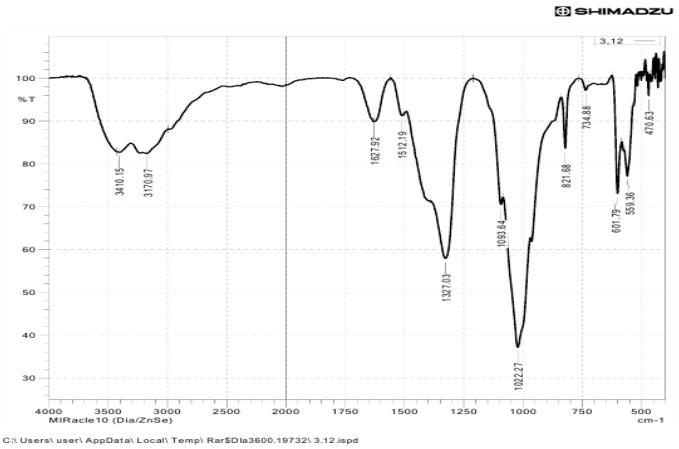

Fig. 2. IR spectra of white suspension from solution obtained after separation of WDC from insoluble sediment.

Figure 2. shows the IR spectrum of the white suspension from the solution obtained after separation of the MNT from the insoluble sediment. From this spectrum, detect that OH absorption lines have valence oscillations at 3410 cm^{-1}, deformation oscillations at 1450 cm^{-1}, 601 cm^{-1} and 599 cm^{-1}; absorption lines of group -C = C- have valence oscillations at 1627 cm^{-1}; deformation oscillations at 1821 cm^{-1}, 1734 cm^{-1}; C-O-group absorption lines have valence oscillations at 1022cm^{-1}; absorption lines =CH have valence oscillations at 3040cm^{-1}, deformation oscillations at 1327 cm^{-1}; CH_2 represents valence oscillations at 1425 cm^{-1}. These results confirm that the valence oscillations of 1000-1100 cm^{-1} refer to -PO43-, and the organic matter produced by the reaction is monoethanolamine phosphate.

The elasticity of water vapours over the main LCF solution, obtained from the neutralized liquid phase of the NAE by the method, has been studied further.

Vapour elasticity is known to characterize vapour volatilization over liquids or solutions. The firmness of vapours depends significantly on the temperature and the mass fraction of the salts in the solutions. Using the Clausius-Klaiperon equation, the heat of evaporation and boiling at different temperatures was calculated. This is necessary to calculate the thermal balance, taking into account the volatilization of water from the main solution of housing. The results of the experimental measurement of the saturated vapour pressure as well as the LCF crystallization temperature obtained from the neutralized liquid phase of the NAE from the WDC are given in Table 5.

From these Table 5 It can be seen that A and B values vary between 8.3762-8.8094 and 2125.0-3151.8, respectively, depending on the type of phosphate feedstock and the nitric acid standard. The pressure of saturated vapours of the studied LCF in the range of 293-343^{o}C is 20.22-0.91 kPa. At the same time, there is a significant increase in steam pressure over the main LCF solution, starting from 323^{o}C and above. This suggests that housing and communal services have low volatility in Central Asia.

Table 4. Pressure of saturated vapours (kPa) on LCF solutions and their crystallization temperature.

Norm of HNO_3, %	Types of phosphate flour	Kind of equation lgP=A-(B/K),	Vapour pressure (kPa) at temperature, K = (273+°C, °C=20-70)						Temperature Christalliz. °C
			293	303	313	323	333	343	
80	WDC	lgP= 8.3762-2125,0/T	1.77	3.08	5.15	8.36	13.17	20.22	-20
85		lgP= 8.6074-2233,8/T	1.26	2.56	4.07	6.08	11.54	18.63	-22
90		lgP= 8.7254-2290.0/T	1.08	1.96	3.42	5.76	9.41	15.68	-25
95		lgP= 8.8094-3151.8/T	0.91	1.67	2.37	4.28	8.84	13.64	-27
105		lgP= 8.5066-2194.5/T	1.39	2.45	4.17	6.88	11.00	17.12	-20
110		lgP= 8.6074-2233.8/T	1.26	2.14	4.07	6.08	10.54	15.63	-28
115		lgP= 8.7254-2290.0/T	1.08	1.96	3.42	5.76	9.41	14.93	-36
120		lgP=8.8094-23151.8/T	0.91	1.54	2.37	4.28	8.84	12.63	-42

The temperature of crystallization of the LCF varies from -20 to -42ºC and this ensures the complete preservation of the LCF with less volatility and low crystallization for a long time without changing its physico-chemical properties.

4 Conclusion

Thus, the above results show the possibility of storing the main fertilizers suspension in housing and communal services in the hot climate of Uzbekistan. Nitrogen, phosphorus and potassium containing components were used to produce LCF with different formulations.

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