УДК 661.632.14

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RATIONAL SOLUTION OF THE ISSUE OF PROCESSING OFF-BALANCE ORE INTO CONCENTRATED NITROGEN-PHOSPHATE FERTILIZERS USING CYCLIC METHOD

Abstract: *The technology of highly concentrated nitrogen-phosphorus fertilizers such as monoammonium and diammonium phosphate (MAP and DAP) is produced from concentrated phosphoric acid of standard phosphates such as Khibiny apatite (39.4% P_2O_5), Florida pebble phosphorite (33% P_2O_5) and phosphate concentrates of the Far and Middle East (35% P_2O_5). However, the reserves of these types of raw materials will be depleted, and therefore it is more necessary to deal with low grades of phosphorites. Phosphorites of the Central Kyzylkum are the poorest raw materials in terms of phosphorus, from which it is not possible to obtain standard phosphate fertilizers. Cyclic technology is a method of processing low-grade phosphorites is a promising way.*

A study was carried out on the processing of mineralized mass, a waste of the Kyzylkum phosphorite complex, into a concentrated nitrogen-phosphorus fertilizer. Products contain N from 9.31 to 11.41; P_2O_{5tot}. from 54.15 to 57.40; $P_2O_{5assimilabe}$ for citric acid from 52.61 to 57.04; $P_2O_{5assimilable}$ for trilon B from 52.00 to 56.08; P_2O_{5aq}. from 43.34 to 47.21. The static life of fertilizers is in the range of 3.12-4.78 MPa. A product with this content is completely superior to grade A ammophosphate produced at the Balakovo Production Association of the Mineral Fertilizers in Russia, which contains (wt.%): N 9.78; P_2O_{5tot}. 50.25; $P_2O_{5assimilable}$ for trilon B 47.60; P_2O_5assimilable for citric acid 43.2; P_2O_{5aq}. 40.

Keywords: phosphorites Central Kyzylkum, phosphoric acid, cyclic technology, minerasllized mass, NP-fertilizer.

It is known that a number of agronomic measures (land cultivation, melioration, selection and collection of seeds) and the use of pepticides significantly affect the development of crops. However, we should not forget the fact that there is not a single crop of agriculture, which would not use mineral fertilizers in one way or another doses of the nutrient element (N, P, K, S, Ca, Mg) for cultivation.

If nitrogen plays a key role on the gain of green mass, the phosphorus and potassium as a fruit element enhances the development of reproductive organs of plants. Sulfur, calcium and magnesium are also important. Sulfur is a component of essential amino acids molecules (cystine, cysteine, methionine), calcium is a building material for stem cells and magnesium is a catalyst of photosynthesis process. In general, crop yields are provided by an average of 50% due to the use of mineral fertilizers [1].

Among these nutrients, phosphorus is a non-renewable nutrient element and the need for it is not covered at the proper level. The fact is that the reserves of the raw material source of phosphorus, both natural phosphorites and apatites are depleted year after year. In addition, their quality is decreasing, their extraction is becoming more difficult and more expensive [2].

Highly concentrated types of fertilizers include those products in which the content of nutrients exceeds 60%. First of all, highly concentrated phosphate fertilizers usually include ammophos, diammophos or MAP and DAP (in foreign literature IDA and DAP). These two-component nitrogen-phosphorus (NP) fertilizers contain nitrogen in ammonium form (NH_4^+ cation) and phosphorus in the form of the PO_4^{-3} anion. They are one- or two-substituted ammonium phosphates in amounts of 2-20% and 10-30% for MAF and DAP, respectively.

According to GOST 18918-85 the granulated MAF must contain 12% N and 52% P_2O_5, and according to the requirements of TU 113-08-537-83 - DAP 18% N and 48% P_2O_5 [3]. Whereas, according to the specifications of the Fertilizer Control System (FCO) MAF must meet the mark 11-52, and DAP 18-46 [4]. Production of both types of fertilizers accounts for 64.1% of the total

amount of phosphate-based fertilizers produced in the world. According to the traditional technology MAF and DAP are produced on the basis of concentrated ESP from conditioned phosphates, in particular Khibiny apatite (39.4% P_2O_5), Florida pebble phosphate (33% P_2O_5) and phoconcentrates of the Far and Middle East (35% P_2O_5). Due to low content of impurities (magnesium, iron and aluminophosphates) EPC on their basis can be easily evaporated to 40-55% P_2O_5. However, the reserves of these raw materials will be exhausted without compensation, and sooner or later the industrialists and researchers in this field will face the problem of improving the quality of export-oriented ammonium phosphate from low-grade phosphate rock, the reserves of which are quite large [2, 5]. More and more producers of phosphate industry have to deal with low-grade phosphate (14-16% P_2O_5 and high carbonate content up to 20% CO_2, which accounts for 65% of all phosphate reserves in the world [2].

The phosphorites of Karatau and Kyzylkum can be referred to these types of phosphorites. However, ammophos from phosphorites of Karatau and Kyzylkum contains 44 and 46% assimilable P_2O_5 and nitrogen 10 and 11% respectively. High consumption rates of sulfuric acid per 1 ton of 100% P_2O_5 in them, often amounts to 3.5 and 4.3 tons, whereas for apatite concentrate 2.5 tons.

Phosphate rock of Central Kyzylkum on the origin belong to granular high-carbonate types of raw materials with the content of 16-18% P_2O_5, 46-48% CaO and 16-18% CO_2. All traditional methods of beneficiation such as dry screening, flotation, etc. are not acceptable. In this regard, the Kyzylkum phosphate complex established production of thermal method with a low yield of P_2O_5 58% in the concentrate and with a high release of phosphate waste in the dump with the status of "off-balance ore" in the amount of about 14 million tons.

However, the method of phosphate decomposition by high rate of concentrated phosphoric acid with subsequent separation of calcium-phosphate suspension by filtration, filtrate cooling under isohydric conditions, crystallization of monocalcium phosphate, its neutralization by ground limestone, phosphoric

acid, ammonia, etc. is known, and the mother liquor with addition of fresh portion of phosphoric acid is returned to the cycle [6, 7].

Based on the foregoing, this report considers the issue of obtaining highly concentrated nitrogen-phosphorus fertilizers by neutralizing the acidic MCF, from the cycle processing, with ammonia, which in addition to nitrogen and phosphorus will contain calcium - the fifth element in nutritional value.

As an object of research used mineralized mass composition (weight %): 14.33 P_2O_5; 43.02 CaO; 1.19 MgO; 1.38 Fe_2O_3; 1.18 Al_2O_3; 2.22 SO_3; 14.70 CO_2 and clarified evaporated ESP of composition (wt. %): 35.69; 40.76 and 44.98 P_2O_5; 0.1 - 0.035CaO; 0.85-0.74MgO; 0.98-0.81 Fe_2O_3; 0.97-0.84 Al_2O_3; 2.79-3.84 SO3 total. To obtain the latter, the composition (wt.%) was used as the initial EFC: 18.44 P_2O_5; 0.21 CaO; 0.44 MgO; 0.33 Fe_2O_3; 0.79 Al_2O_3; 1.50 SO_3. It was concentrated by evaporation. The rate of EFC depending on the concentration was taken in the range of 200-300%, 400-500 and 400-600% of stoichiometry. Experiments were carried out under laboratory conditions as follows: in a thermostatic reactor with a known amount of evaporated ESP and equipped with a paddle stirrer a load of crushed mineralized mass was loaded in portions. The process of raw material decomposition was carried out at 450% EFC for one hour at 90□C. After cooling of the filtrate and crystallization of $Ca(H_2PO_4)2$ at 40□C for 2 hours the crystals of the latter were separated, neutralized with ammonia gas to pH = 4.5. Granulation of ammoniated mass was carried out by pelletizing. The granules were dried at 90□C. After drying, the fertilizer granules had a rounded shape. The dried products were analyzed for the content of nitrogen and various forms of phosphorus and calcium according to the methods [8-10]. The static strength of granules of products with a particle size of 2-3 mm was determined according to [11] (Table 5.11). Analysis was conducted in accordance with GOST 21560.2-82 on device MIP-10-1 [12].

The results are given in Tables 1 and 2:

Chemical composition of highly concentrated nitrogen-phosphorus fertilizers obtained by decomposition of RFM phosphorites of Central Kyzylkum by evaporated ESP using cyclic method

Table 1.

The norm of EFC from stoichio-metry, %	pH of 10% soluti on	Chemical composition, mass %								$\frac{P_2O_{5усв}}{P_2O_{5общ}}$, In the 2% lim. sour, %	$\frac{P_2O_{5усв}}{P_2O_{5общ}}$, 0.2M tril,B, %	$\frac{P_2O_{5вод}}{P_2O_{5общ}}$, %	$\frac{CaO_{усв}}{CaO_{общ}}$, In the 2% lim. sour, %	$\frac{CaO_{вод}}{CaO_{общ}}$, %
		$R_2O_{5общ.}$	$R_2O_{5усв}$ in 2% lim, kt	$P_2O_{5усв}$ by 0.2M tril,B	$R_2O_{5вод.}$	$SaO_{общ.}$	$SaO_{усв.}$	$SaO_{вод.}$	N					
EFC-based (P_2O_5 35.69%)														
200	5,12	54,15	52,61	52,00	43,34	7,97	7,84	1,66	9,56	97,16	96,03	80,04	98,37	20,83
250	4,89	54,36	53,40	52,64	44,29	6,48	6,39	1,38	10,03	98,23	96,84	81,47	98,61	21,30
300	4,97	56,53	56,24	55,47	46,47	4,75	4,69	1,07	11,41	99,49	98,12	82,20	98,74	22,53
EFC-based (P_2O_5 40.76%)														
400	4,61	54,49	54,23	53,81	46,69	6,75	6,72	1,43	9,71	99,52	98,75	85,75	99,56	21,19
450	4,96	54,28	53,93	53,66	45,71	6,24	6,19	1,40	9,59	99,36	98,86	84,21	99,20	22,43
500	5,12	55,24	55,16	54,51	47,41	5,43	5,39	1,26	9,86	99,84	98,68	85,83	99,26	23,20
EFC-based (P_2O_5 44.98%)														
400	5,07	54,57	54,31	53,32	44,61	6,22	6,15	1,02	9,91	99,52	97,71	81,75	98,87	16,40
450	5,11	56,81	56,67	55,29	46,23	7,37	7,29	1,26	9,68	99,75	97,32	81,38	98,91	17,09
500	5,30	56,10	55,89	54,58	46,47	6,67	6,58	1,18	9,93	99,63	97,29	80,05	98,65	17,69
550	5,02	57,40	57,04	56,08	47,21	6,91	6,78	1,25	9,31	99,37	97,70	82,25	98,12	18,09
600	5,23	57,27	56,78	55,59	46,20	6,60	6,48	1,24	9,43	99,14	97,07	80,67	98,18	18,79

Static strength of highly concentrated nitrogen-phosphate fertilizers

Table 2.

The norm of EFC from stoichio-metry, %	Initial humidity, %	$P_2O_{5общ.}$, %	N, %	Granule strength		
				kg/granule	kgf/cm^2	MPa
1	2	3	4	5	6	7
EFC-based (P_2O_5 35.69%)						
200	1,06	53,16	9,89	1,70	34,27	3,36
250	1,03	54,13	9,96	1,97	39,71	3,89
300	0,93	55,60	10,85	2,21	44,55	4,37
EFC-based (P_2O_5 40.76%)						
300	1,52	53,01	9,51	1,58	31,85	3,12
350	1,48	54,43	9,78	2,02	40,72	3,99
400	1,84	55,36	9,89	2,38	47,98	4,71
EFC-based (P_2O_5 44.98%)						
300	1,31	54,17	9,64	1,70	34,27	3,36
400	1,29	55,69	9,81	1,98	39,92	3,92
500	1,43	57,12	9,97	2,42	48,79	4,78

The table shows that the products obtained by neutralization of acidic MCF with ammonia water are highly concentrated nitrogen-phosphorus fertilizers with

significant nitrogen content. Depending on experimental conditions and the type of phosphorite used the composition of nutrients in fertilizers varies (wt%): N from 9.31 to 11.41; P_2O_5 total from 54.15 to 57.40; P_2O_5usv. by citric acid from 52.61 to 57.04; P_2O_5usv. by trilon B from 52.00 to 56.08; P_2O_5water from 43.34 to 47.21.

The relative content of digestible by citric acid, trilon B and aqueous forms of P_2O_5 ranged from 97.16-99.84%; 96.03-97.71% and 80.04-84.21%, respectively. As the experimental data show, the type of phosphorite has almost no effect on the fertilizer composition.

Static strength of nitrogen-phosphorus fertilizers is 3.12-4.78 MPa, This suggests that this type of fertilizer is acceptable and available for transportation and use in agriculture.

According to the content of nutrient components they surpass the traditional highly concentrated MAF and DAP (more than 60%). In addition, the obtained products contain assimilable and water-soluble CaO. As a bio-element, calcium is among the six most essential plant nutrients.

Such kinds of fertilizers, containing in their composition besides nitrogen and phosphorus also calcium, are called ammophosphates.

Ammophosphate of grade "A" is produced at Balakovsky PO Minudobrenia in Russia and contains (wt%): N 9.78; P_2O_5 total. 50,25; P_2O_{5usv}. by trilon B 47,60; P_2O_5usv. by citric acid 43,2; P_2O_5water. 40 [13]. In our case, depending on the type of CK phosphorites, using EFC concentration of 35.69% P_2O_5 and its rate of 250% yields high-quality ammophosphates of the composition (wt.%): N 9.96-10.03; P_2O_5 total. 54,13-54,36; P_2O_{5cv}. by trilon B 52,64-52,75; P_2O_{5cv}. by citric acid 53,40-53,42; P_2O_{5water}. 44,01-44,29.

Thus, based on the research and analysis of the data obtained it can be concluded that the phosphate rock can be rationally and efficiently processed into a highly concentrated nitrogen-phosphorus fertilizer, and the composition and properties of the resulting products are not inferior to ammophosphate production of Balakovsky PO "Minudobreniya".

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