Section 4. Chemistry

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PROCESSING OF PHOSPHORITES CENTRAL KYZYLKUM

Abstract. It was carried out on the basis of the nitric acid method of decomposition of phosphorites of the Central Kyzylkum. Nitrocalcium slurry is divided into liquid and solid phases, the stages of neutralization of the liquid phase by organic substances are studied. The optimal conditions for the technological process were found: chemical processing of high-carbon phosphate raw materials, neutralization of liquid fertilizers and processing into nitrogen-phosphorus-potassium fertilizers.

Keywords: phosphate rock, nitric acid, liquid phase, nitrogen-phosphorus-potassium fertilizers, organic solvent.

Introduction

In the world, the most important factors determining the role of agriculture in the country's economy include the quantity and quality of food consumed by the population. The main prospect for the development of agricultural production is associated with an increase in crop yields through the introduction of the latest technologies for tillage, and, of course, the integrated use of mineral fertilizers and plant protection products. In conditions of acute shortage of water resources, liquid and suspended complex fertilizers with stimulating activity can effectively prove themselves, which can dramatically increase the yield of crops, when dripped as a foliar or root top dressing, where they are easily absorbed by plants.

For the production of phosphate fertilizers, an important problem is the provision of high-quality phosphate raw materials. Currently, for the production of phosphorus-containing fertilizers, the main raw material is granular phosphorites of the Central Kyzylkum. The average sample of phosphorites of the Jerooy-Sardara deposit contains

(wt.%): 16.2 P_2O_5; 46.2 CaO; CaO: P_2O_5 = = 2.85; 17.7 CO_2; 0.6 MgO; 2.9 (Fe_2O_3+Al_2O_3), 1.5 (K_2O+Na_2O); 2.65 SO_3; 1.94F; 0.1Cl; 7.8 insoluble residue. These phosphorites "suffer" from a low content of phosphorus (16.2% P_2O_5, and should be at least 24.5%), the presence of carbonates (17.7% CO_2, and should be no more than 8%), chlorine (0.1%, and the allowable standard is 0.04%) and an increased content of the calcium module (CaO: P_2O_5 – 2.85, and the recommended one is 1.6), which are unacceptable for sulfuric acid extraction. A high calcium index causes a large overrun of the acid reagent during the decomposition of raw materials.

To obtain high-quality phosphorus-containing fertilizers from the Kyzylkum phosphate raw material, it must be enriched. Therefore, the Kyzylkum Phosphorite Plant carried out the enrichment of this raw material, consisting of the following stages: crushing, screening, separation of the mineralized mass, washing from chlorine, drying to a moisture content of 6–7% and instant roasting to remove CO_2 [1–3]. Since 2020, KFK has been annually producing three types of phosphate raw materials: 400 thousand tons of washed calcined phosphorus concentrate, 200 thousand tons of washed dried concentrate and 200 thousand tons of phosphate rock.

Of these, only washed calcined phosphorus concentrate is the only feedstock suitable for the production of ammophos (10% N, 46% P_2O_5). WDC is sent to Kokand for the production of simple ammoniated superphosphate (1.5% N, 12.5% P_2O_5), and nitrocalcium phosphate fertilizer (10% N, 16% P_2O_5) is obtained from phosphate rock in Samarkand.

Objects and Methods of Research

For the development of a technology for obtaining a liquid complex fertilizer, information on the chemical and physico-mechanical properties of phosphorites of the Central Kyzylkum is important. Since the raw materials used, subjected to nitric acid decomposition, are powdery, their physical and mechanical properties change significantly with increasing moisture content and density. This circumstance causes a number of difficulties in the design and operation of delivery systems inside the factory transport, silos, dosing units. These indicators include bulk density, angle of repose, fluidity, disperse composition, hygroscopicity and moisture capacity. These indicators were determined by the methods described in the methods [4–11].

Three types of phosphate raw materials were chosen as the object of study: ordinary unenriched phosphate rock (UPR), washed dried concentrate (WDC) and washed calcined phosphate concentrate (WCPC) from phosphorites of the Central Committee. Their chemical and dispersed composition are given in (Table 1 and 2).

Table 1.– Chemical composition of samples of Kyzylkum phosphorites

Types of phosphate raw materials	Content of components. wt.%									CaO: P_2O_5
	P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	CO_2	SO_3	н.о.	
UPR	18.70	47.52	0.95	0.73	1.79	2.0	17.23	3.27	5.27	2.54
WDC	25.62	52.17	1.15	0.63	1.20	2.27	2.10	1.34	6.78	2.04
WCPC	26.08	51.47	1.02	0.31	0.89	3.41	9.95	1.59	2.49	1.92

Table 2.– Disperse composition of the feedstock

UPR		WDC		WCPC	
Particle size, mm	**Exit,%**	**Particle size, mm**	**Exit,%**	**Particle size, mm**	**Exit,%**
+ 1	1.4	+ 2.0	0.6	+1	1.4
+ 0.5	2.9	+ 1.0	0.6	+0.63	1.9
+ 0.315	10.1	+ 0.5	2.5	+0.4	2.4
+ 0.25	5.1	+ 0.315	3.4	+0.315	7.0
+ 0.16	16.1	+ 0.20	12.2	+0.2	8.3
+ 0.10	12.2	+ 0.16	13.2	+0.16	41.1
+ 0.065	13.9	+ 0.10	25.7	+0.1	26.6
+ 0.05	21.6	+ 0.05	36.0	+0.05	8.5
– 0.05	16.7	– 0.05	5.8	– 0.05	2.8
Initial mass	100	Initial mass	100	Initial mass	100

Table 3.– Physical and mechanical properties of Kyzylkum phosphorites

Properties of phosphate raw materials	**Indicators**		
	UPR	**WDC**	**WCPC**
Initial humidity, %	1.23	0.27	0.92
Free bulk density, g/cm^3	0.89	1.21	1.23
Density with seal, g/cm^3	1.37	1.52	1.56
Slope angle, deg.	°37 18′	°39 28′	°28 32′
Dissipation, sec.	Evenly. without any difficulty		
Hygroscopic point, %	55	51.5	59.2
Moisture capacity, %	7.6	4.9	6.2
pH 10% suspension	8.67	11.92	7.07

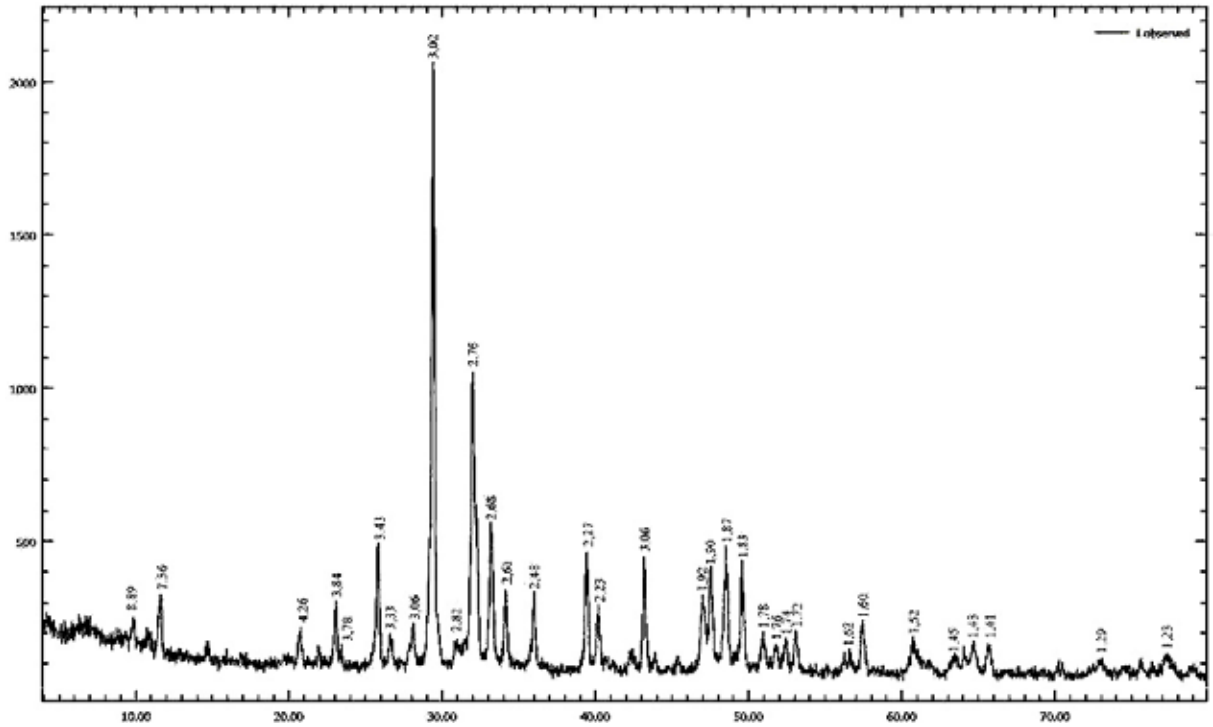

Figure 1. X-ray of unenriched phosphate rock

In (table 3) shows the physical and mechanical properties of raw materials. As can be seen from the table, all indicators of the initial phosphorites are quite consistent for their processing into qualified phosphorus-containing fertilizers.

The hygroscopic point of WDC turned out to be equal to 51.5% and this value is explained by the presence of a hygroscopic substance, CaO, in its composition. X-ray patterns of phosphate raw materials are shown in (Fig. 1–2).

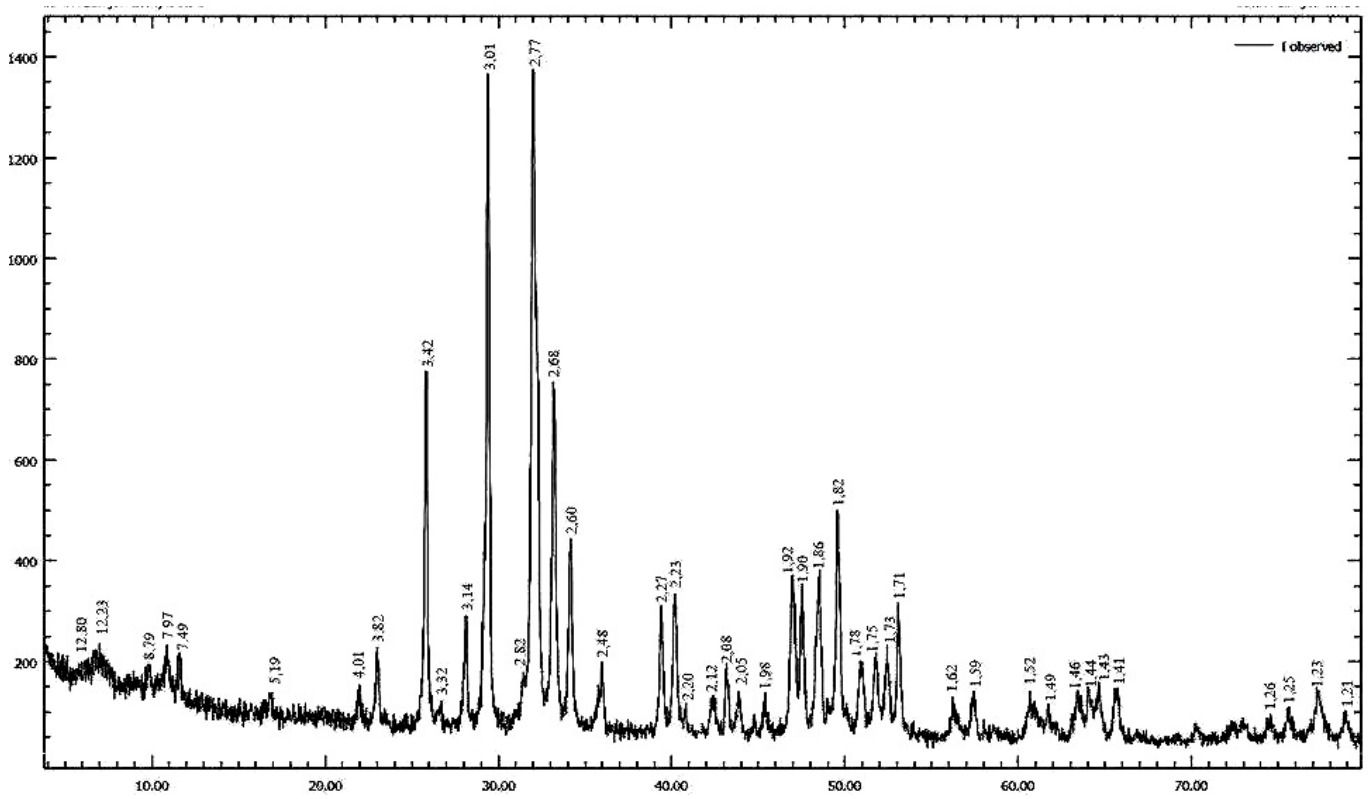

Figure 2. X-ray of the washed dried concentrate

Interplanar distances 3.43; 3.16; 2.79; 2.71; 1.936; 1.877; 1.837 and 1.780Å belong to fluorocarbonate apatite, and 3.03; 2.29; 1.908Å calcite, 3.32Å belongs to quartz.

Results and its discussion

During the decarbonization of phosphate raw materials, along with carbonates, the phosphate mineral also dissolves with the formation of water-soluble monocalcium phosphate and phosphoric acid according to the reactions:

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

$$Ca_5F(PO_4)_3 + 8HNO_3 \rightarrow Ca(H_2PO_4)_2 + H_3PO_4 + 4Ca(NO_3)_2 + HF\uparrow$$

Before neutralizing the forming nitric acid phosphate extract by centrifugation, the insoluble residue was removed. Then the clarified acid mixture was neutralized with monoethanolamine, diethanolamine and triethanolamine to pH = 3.2. In the process of ammonization, the interaction between monocalcium phosphate, calcium nitrate and monoethanolamine occurs with the formation of a liquid nitrogen-phosphorus-calcium suspension according to the reaction:

$$Ca(H_2PO_4)_2 + Ca(NO_3)_2 + HO(CH_2)_2NH_2 \rightarrow HO(CH_2)_2NH_3H_2PO_4 + CaHPO_4 + Ca(NO_3)_2 \quad (1)$$

$$H_3PO_4 + HO(CH_2)_2NH_2 = \\ =HO(CH_2)_2NH_3H_2PO_4 \quad (2)$$

$$Ca(H_2PO_4)_2 + Ca(NO_3)_2 + \\ + (HOCH_2CH_2)_2NH \rightarrow \\ \rightarrow (HOCH_2CH_2)_2NH_2H_2PO_4 + \\ + CaHPO_4 + Ca(NO_3)_2 \quad (3)$$

$$Ca(H_2PO_4)_2 + Ca(NO_3)_2 + \\ + (HO\text{-}CH_2CH_2)_3N \rightarrow \\ \rightarrow (HOCH_2CH_2)_3NHPO_4 + CaHPO_4 + \\ + Ca(NO_3)_2 \quad (4)$$

The result is a suspension of dicalcium phosphate, calcium nitrate and monoethanolamine phosphate. Further, the neutralization products were mixed with ammonium nitrate, ammophos, urea and potassium chloride at various mass ratios in order to obtain liquid calcium-containing NP- and NPK-fertilizers of grades 1:1:0.5; 2:1:0.5; 3:1:0.5 and 1:1:1; 2:1:1; 3:1:1 respectively.

After that, the suspension was mixed with ammophos pulp at a ratio of FCF: Ammophos = 4: 1, which served as a basic solution, then ammonium nitrate and potassium chloride were added here in order to obtain balanced liquid NPCa- and NPKCa-fertilizers with a given ratio of N: P_2O_5 and N: P_2O_5: K_2O. Then into balanced liquid NPCa- and NPKCa-fertilizers in the amount of 1–1.5% of the total mass. The results of the chemical analysis of finished products are summarized in (Table 4).

It can be seen from it that with the same content of ammophos and potassium chloride, an increase in the proportion of ammonium nitrate leads to an increase in the amount of nitrogen from 8.77 to 15.11% and from 6.74 to 13.15%, respectively, for NP and NPK grade HUS. At the same time, the content of phosphorus and potassium is reduced to 6.82–4.77%; 9.09–5.11% and 6.12–4.41, respectively, for the indicated types of housing and communal services.

The composition of these fertilizers contains an element digestible by plants – calcium in the range of 3.12–5.12 and 6.52–10.63%.

Table 4. – Composition of experimental batches of suspended NPCa- and NPKCa-fertilizers on a model laboratory unit

Brand type	**N**	**P_2O_5**	**CaO**	**K_2O**	**MgO**	**H_2O**
N: P_2O_5	**With the ratio of IKF: Ammophos=4:1**					
1:1	8.77	9.09	5.12	–	0.08	43
2:1	11.71	6.27	4.63	–	0.03	43
3:1	15.11	5.11	3.12	–	0.03	43
1:0.7	12.84	9.21	5.07	–	0.07	43
N: P_2O_5: K_2O	**With the ratio of IKF: Ammophos=4:1**					
1:1:1	6.74	6.82	10.63	6.12	0.20	40.20
2:1:1	10.17	5.90	8.35	5.14	0.10	41.37
3:1:1	13.15	4.77	6.91	4.41	0.05	42.14
1:0.7:0.5	13.03	10.69	6.52	5.62	0.18	40.26

Conclusion

Thus, the possibility of producing NPCa and NPCa fertilizers based on nitric acid processing of MSFC in the presence of monoethanolamine with the addition of ammonium nitrate, ammophos, and potassium chloride has been shown. It can be concluded that they can be recommended as HCS for use during foliar processing of cotton and grain crops.

References:

1. Kuchersky N. I., Tolstov E. A., Mikhin O. A., Mazurkevich A. P., Inozemtsev S. B., Sokolov V. D., Smirnov Yu. M. Combined technology of enrichment of granular phosphorites // Mining industry.– No. 4. 2001.– P. 48–51.
2. Ismagilov M. M. Kyzylkum phosphorite complex of Navoi Mining and Metallurgical Complex // "Actual problems of chemical processing of phosphorites of the Central Kyzylkum": Materials of the republic. scientific – tech. conf.– Tashkent, November 23, 2006.– P. 19–22.
3. Caesar Norbert V. Industrial removal of chlorides from phosphate ore during wet enrichment in extreme conditions of the Kyzylkum desert // Mining Bulletin of Uzbekistan.– No. 4. 2008.– P. 54–58.
4. Methods for the analysis of phosphate raw materials, phosphate and complex fertilizers, feed phosphates / M. M. Vinnik L. N.
5. Khoshimkhanova M. A., Ismoilova G. I., Dekhkanov Z. K., Aripov Kh. Sh. Study of the physicochemical properties of ammoniated calcium nitrocalcium phosphate alcohol pulp // Universum: Chemistry and Biology.– No. 4(70). 2020.– P. 25–28.
6. Dekhkanov Z. K., Ibragimov G. I., Namazov Sh. S., Sadykov B. B., Zakirov B. S. Obtaining extraction phosphoric acid from chemically enriched phosphorus concentrate of phosphorites of the Central Kyzylkum // Uzbek chemical journal.– No. 32011.– P. 51–55.
7. Dekhkanov Z. K., Seitnazarov A. R., Namazov Sh. S., Sultanov B. E., Beglov B. M. Complex granular fertilizers based on chemically enriched phosphorite phosphorite concentrate from the Central Kyzylkum // Reports of the Academy of Sciences of the Republic of Uzbekistan – No. 22012.– P. 46–49.
8. A.s. 340644 USSR. Cl. SO5B11/06. The method of enrichment of natural phosphates / A. M. Polyak, I. B. Yanovich, L. P. Ryzhevich, I. S. Sviridova.– B. I. 1972.– No. 18.
9. Azimov R. A. The physiological role of calcium in the salt tolerance of cotton.– Tashkent: FAN, 1973.
10. Pozin M. E. Technology of mineral salts. Vol. 2.– L.: Chemistry, 1970.– 1558 p.
11. Dekhkanov Z. K., Seitnazarov A. R., Namazov Sh. S., Beglov B. M. Processing of calcium nitrate – a product of chemical enrichment of Kyzylkum phosphorites – granular calcium nitrate // Chemical Technology. Control and management.– No. 5. 2013.– P. 14–23.