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Complex NPS-Fertilizers Based on Phosphorite Waste of KyzylKum and Ammonium Sulfate

Takhirova Nargisa, Mamataliyev Abdurasul

Assistant, Department of Chemical Technology, Navoi State Mining Institute, Navoi, Uzbekistan
Doctor of Philosophy (PhD), doctoral student, Institute of General and inorganic chemistry of the Academy of Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan

ABSTRACT: The paper studied the composition and physical and mechanical properties of phosphorite waste: mineralized mass and slurry phosphorite. Samples of NPS-fertilizers based on ammonium sulfate solution (AS) and Kyzylkum phosphorite waste (PhW) were obtained. In this case, the AS : PhW mass ratio varied from 100 : 5 to 100 : 50. The pelletizing method was used to granulate the NPS melt. It has been shown that the AS solution not only decarbonizes the phosphate raw material, but also activates its phosphate mineral, converting the indigestible form of P_2O_5 in it into a form that is assimilable for plants. At the same time, the processes of decarbonization and activation are most intensive in the case of the use of slurry phosphorite.

KEYWORDS: ammonium sulfate, mineralized mass (MM), slurry phosphorite (SPh), NPS fertilizer, composition and properties.

I. INTRODUCTION

The factories of Uzbekistan producing phosphorus-containing fertilizers are supplied with phosphate raw materials by the Kyzylkum phosphorite complex, annually producing 716 thousand tons of washed calcined phosphorus concentrate with an average content of 26% P_2O_5. At the same time, the volume of mined phosphorite ore with an average content of 17.58% P_2O_5 is 1874.6 thousand tons or 320.93 thousand tons of P_2O_5. This suggests that in the process of thermal enrichment, large losses of the phosphorus component occur. Thus, according to the existing enrichment scheme, the loss of useful substance (P_2O_5) in the form of off-balance ore is 42%. To date, it has accumulated about 13 million tons. These are mineralized mass (MM – 12-14% P_2O_5) and sludge phosphorite (SPh – 8-12% P_2O_5), which are not yet used in the production of mineral fertilizers. The first is formed during the dry sorting of phosphorite ore, and the second is the washing of raw materials from chlorine. We see in them a reserve for the production of phosphorus-containing fertilizers. It is necessary to find ways to process them into phosphorus-containing fertilizers. Previously [1, 2], the possibility of obtaining stabilized nitrogen-phosphorus fertilizers (AFU technology) was shown by introducing a mineralized mass (MM) into the melt of ammonium nitrate (AN) at 175°C and mass ratios of AN : MM from 100 : 3 to 100 : 48, followed by prilling of nitrophosphate melt on the grantower. It has been established that the saltpeter melt activates phosphate raw materials, that is, it converts the P_2O_5 form, which is indigestible in it, into a form assimilable for plants. Thus, a granulated product with a 1% P_2O_5 additive (AN : MM = 100 : 8) contains 31.71% N and $P_2O_{5res.}$ in relation to the total 77.45%. In this case, the strength of the granules is 5.5 MPa. And the product with a 5% addition of P_2O_5 (AN : MM = 100 : 48) contains 23.94% N and $P_2O_{5res.}$: P_2O_5 = 55.75% with a granule strength of 8.8 MPa. The closest to the proposed method for obtaining complex NPS fertilizers is the NArFU technology operating at Ferganaazot JSC - phosphorus- and sulfur-containing AS [3]. The essence of the technology lies in dusting the surface of AS granules with Central Kyzylkum phosphate flour (17-18% P_2O_5) in the presence of a saturated solution of ammonium sulfate. The mechanism of this process is to fill the surface of the saltpeter granules with a saturated sulfate solution and the adhesion of the powdering phosphate flour, as a result of which a protective layer is formed on the surface of the granules, consisting of salts with a lower solubility than that of ammonium nitrate; they act as a frame, isolating the hygroscopic substance - NH_4NO_3 from the external environment.

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II. SIGNIFICANCE OF THE SYSTEM

The paper studied the composition and physical and mechanical properties of phosphorite waste: mineralized mass and slurry phosphorite. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

III. METHODOLOGY

A significant disadvantage of these additives is that they are used in amounts (up to 5%) do not prevent the destruction of nitrate granules as a result of modification transformations that occur with varying temperature changes. In the method under consideration, granules are formed that have a defect-free surface only in the form of a thin surface layer, while the main inner part of the granule remains highly porous and loose, which causes thermal instability. The disadvantage is also a decrease in the effectiveness of the product due to shedding of the powder - phosphate flour from the surface of the granules and thus the dustiness of the production premises. SAFU contains only 1.5-3% P_2O_5 and up to 3% sulfate sulfur.

IV. EXPERIMENTAL RESULTS

In this paper, the proposed method for producing complex NPS fertilizers based on ammonium sulfate (AS) solution and Kyzylkum phosphorite waste, followed by granulation of the sulfate-phosphate mass in a drum granulator. In this case, it is not necessary to transport the phosphate rock to the top of the tower, which is the case in the AFU technology. This solution allows diversifying production and mastering new types of products. The new technology also allows you to quickly change the composition of the product, introduce other nutrients into it and, in general, is a waste-free production technology. The advantage of using $(NH_4)_2SO_4$ as part of complex fertilizers is the presence of sulfur in it, which is part of proteins and amino acids during crop formation. Sulfur provides prevention of the occurrence of late blight and the appearance of root rot. According to the physiological role in plant nutrition, sulfur should be ranked fourth after nitrogen, phosphorus, and potassium [4]. The main advantage of the method developed by us is that during its implementation all the nutrients will be in one granule. In experimental work, mineralized mass and slurry phosphorite were used as phosphate raw materials, the composition and properties of which are given in tables 1-3. The chemical composition shows that they consist mainly of fluorocarbonate apatite and calcite. The mineralized mass contains 33.4%, and slurry phosphorite 47.5% $CaCO_3$. Both the mineralized mass and slurry phosphorite contain a significant amount of insoluble residue - quartz. In table. Table 1 also gives the value of the assimilable form of P_2O_5 in phosphorites, determined from the solubility in 2% citric acid. Table 3 shows the dispersed composition of phosphorite waste used for research.

Table 1
Chemical composition of phosphorite waste

Content of components, wt. %	Types of phosphate raw materials	
	mineralized mass	Slurry phosphorite
P_2O_5	14.32	11.56
CaO	43.02	41.08
MgO	1.19	0.61
CO_2	14.70	20.91
Al_2O_3	1.18	1.84
Fe_2O_3	1.38	1.42
F	1.85	1.52
SO_3	2.22	0.46
H.O.	13.23	14.9
$P_2O_{5res.} : P_2O_{5total.} * 100$	9.01	11.50

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TABLE 2
Physical and mechanical characteristics of phosphorite waste

Properties phosphate raw materials	Indicators	
	mineralized mass	slurry phosphorite
Initial humidity, %	2.15	1.73
Free bulk density, g/см^3	1.06	0.81
Density with seal, g/см^3	1.36	1.04
Slope angle, hail.	24°46´	39°29´
Dissipation, sec.	Evenly, without any difficulty	
hygroscopic point, %	47.5	46.7
moisture capacity, %	5.6	7.4
pH 10 % suspension	7.14	9.40

Table 3
Disperse composition of phosphorite waste

Size, mm	Fraction yield, wt. %	
	mineralized mass (MM)	Slurry phosphorite (SPh)
- 2 + 1	-	-
-1+0.63	0.2	-
-0.63+0.4	0.6	-
- 0.4 + 0.315	1.4	-
- 0.315 + 0.2	23.9	0.4
- 0.2+0.16	9.9	43.8
- 0.16 + 0.1	36.5	41.6
- 0.1 + 0.05	19.0	9.4
- 0.05	8.5	4.8
Initial mass	100	100

To develop an innovative method for obtaining new types of complex fertilizers based on ammonium sulfate solution and waste phosphorites, information is needed on the physicochemical and physico-mechanical properties, especially of phosphate raw materials. These properties include : dispersed composition, humidity, bulk density, angle of repose, fluidity, pH, hygroscopicity, moisture capacity. These properties are determined by the methods described in [5, 6]. The results of the table. 2 show that at the initial moisture content (2.15%), the free bulk density of the mineralized mass is 0.81 g/cm^3, and with compaction it is 1.36 g/cm^3. For slurry phosphorite, these indicators are 0.81 and 1.04 g/cm^3, respectively. Among the parameters that make it possible to evaluate the mobility of phosphate raw materials is the angle of repose of its free surface. The smaller the slope angle, the greater the mobility of the particles of the granular medium. The angle of repose is 24 degrees for the mineralized mass and 39 degrees for the slurry phosphorite. The relatively high slope angle of slurry phosphorite is explained primarily by the presence of clay minerals in its composition. But in any case, their flowability is uniform, dissipates without any difficulty. The hygroscopic point turned out to be 47.5% for the mineralized mass, and 46.7% for the slurry phosphorite. The limiting moisture capacity of samples of phosphate raw materials is 5.6-7.4%, and at higher humidity they lose their friability. These phosphorites, having a pH of 7.14 to 9.40, naturally neutralize the acidity of NH_4NO_3, primarily sludge phosphorite. All this shows that, according to their physical and mechanical characteristics, they are quite suitable for processing into complex fertilizers. For the preparation of samples of NPS fertilizers, industrial crystalline ammonium sulfate (AS – 21.2% N and 24.2% S) served as the main component. The studies used a 35% SA solution. 35 g of AS were placed in a metal beaker, 65 g of distilled water were poured and then dissolved. Then, a weighed portion of phosphorite waste (PW) was introduced into the resulting 35% AS solution at weight ratios AS : PW from 100 : 5 to 100 : 50. The sulfate-phosphorite mixture was kept for 20 minutes,

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at which both decarbonization and PW activation. After a 20-minute interaction of the components, the sulfate-phosphorite suspension was poured into a porcelain cup and vigorously stirred with a glass rod. As it cooled, round solid particles formed. The mass was cooled and then dispersed according to particle size. Particles with a size of 2-3 mm were tested for strength according to GOST [7]. After that, the products were crushed and analyzed according to known methods [8]. Digestible forms of P_2O_5 were determined by solubility in 2% citric acid. The degree of decarbonization of phosphate raw materials was calculated from the change in the CO_2 content. The pH value of 10% aqueous suspensions of finished fertilizers was measured in an I-130M laboratory ionometer with an accuracy of 0.05 pH units.

The results are shown in Table 4. The results show that the AS solution decomposes the carbonates of both types of phosphate raw materials within 20 minutes and simultaneously activates their phosphate mineral, converting the indigestible form of P_2O_5 into a plant-assimilable form. At the studied AS : PW ratios, the products with the highest content of total P_2O_5 were obtained in the case of the use of mineralized mass (MM). So, in the range of ratios AS : MM = 100 : 5 - 0.69%; at 100 : 25 - 2.86% and at 100 : 50 - 4.76% P_2O_{5tot}. In the case of using slurry phosphorite (SPh), this indicator is 0.56; 2.31 and 3.95% respectively. But at the same time, the process of both decarbonization and activation of phosphate rock is going on most intensively. For example, if at AS : SPh = 100 : 20 the degree of decarbonization of slurry phosphorite and the relative content of the assimilable form P_2O_5 of the product are 50.45 and 54.92%, then in the case of using mineralized mass, these indicators are 48.13 and 53.78%. For other AS : PW ratios, a similar picture is observed. An increase in the mass fraction of phosphate raw materials from 5 to 50 g relative to 100 g of AS solution, although it allows to increase the content of total P_2O_5, but leads to a decrease in the content of nitrogen, sulfur and assimilable forms of P_2O_5 in products. At a mass ratio of AS : MM from 100 : 5 to 100 : 50, it leads to a decrease in the nitrogen content from 20.17 to 14.06% and at AS : SPh from 100 : 5 to 100 : 50 from 20.23% to 14.12 %. At the same time, the sulfur content decreases from 23.05 to 16.08%, and from 23.11 to 16.18%, respectively.

Table 4
The chemical composition of NPS fertilizers obtained by activating the Kyzylkum phosphorite waste with AS

№	Mass ratio SA : FO	pH suspensions		N	$P_2O_{5total.}$	$P_2O_{5res.}$	S	The degree of decarbonization, %
		Before activation	After activation					
mineralized mass + 35 %- solution $(NH_4)_2SO_4$								
1	100 : 5	3.94	6.87	20.17	0.69	0.42	23.05	57.64
2	100 : 10	3.86	6.92	19.30	1.35	0.81	22.0	54.40
3	100 : 15	3.80	6.85	18.41	1.91	1.09	21.17	51.28
4	100 : 20	3.71	6.90	17.62	2.38	1.28	20.24	48.13
5	100 : 25	3.63	7.01	16.89	2.86	1.45	19.36	44.72
6	100 : 30	3.55	7.06	16.27	3.32	1.57	18.61	41.56
7	100 : 35	3.42	7.15	15.76	3.74	1.64	17.93	38.39
8	100 : 40	3.39	7.24	15.13	4.10	1.68	17.29	35.41
9	100 : 45	3.27	7.38	14.65	4.53	1.70	16.72	31.08
10	100 : 50	3.08	7.53	14.06	4.76	1.71	16.08	25.81
Slurry phosphorite + 35% solution $(NH_4)_2SO_4$								
11	100 : 5	4.26	7.10	20.23	0.56	0.37	23.11	60.36
12	100 : 10	4.33	7.16	19.34	1.07	0.68	22.04	56.61
13	100 : 15	4.42	7.24	18.47	1.52	0.89	21.23	53.84
14	100 : 20	4.57	7.33	17.72	1.93	1.06	20.27	50.45
15	100 : 25	4.61	7.42	16.95	2.31	1.20	19.42	46.28
16	100 : 30	4.70	7.51	16.31	2.68	1.31	18.68	43.07
17	100 : 35	4.78	7.59	15.79	3.04	1.38	17.96	39.32
18	100 : 40	4.94	7.65	15.26	3.35	1.40	17.35	37.53
19	100 : 45	4.95	7.72	14.68	3.60	1.41	16.76	32.90
20	100 : 50	5.13	7.88	14.12	3.95	1.43	16.18	27.42

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V. CONCLUSION AND FUTURE WORK

Thus, the scientific study of a complex of scientific research provides a good basis for the practical application of the results in the development of a flexible technological scheme for obtaining a wide range of complex fertilizers and, in general, is a waste-free production technology.

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