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Low-Grade Phosphorite, Nitric and Sulfuric Acid Fertilizers Containing NPSCa

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ABSTRACT: In this study, research was conducted to obtain a NPSCa-containing fertilizer based on the Central Kyzylkum low-grade phosphorite mineralized mass, nitric and sulfuric acid. The stoichiometric norms of nitric and sulfuric acid for the decomposition of phosphorite samples from the implementation of experimental work are 100% (nitric and sulfuric acid = 100: 0; 90: 10; 80: 20; 70: 30; 60: 40; 50: 50; 40: 40:60; 30: 70) was calculated relative to the calcium oxide in the raw material. All forms of P₂O₅ and CaO (total, plant assimilation), total nitrogen, SO₃, carbon dioxide and carbonation levels, which are the main constituents of the samples, were analyzed

KEYWORDS: low grade phosphorite, mineralized mass, nitric acid, sulfuric acid, phosphorus five oxides, calcium oxide, carbon four oxides, nitrogen.

I. INTRODUCTION

Given the lack of water resources in Uzbekistan and the declining share of irrigated arable land per capita, it is important to address the issue of food security [1, 2]. This can only be done by intensifying the production of agricultural products and chemicalizing it. Each ton of mineral fertilizers meets the food needs of 5-6 people per year. The cost of production and application of fertilizers increases the cost of agricultural products by 2-3 times. The use of mineral fertilizers provides an average increase in crop yields of 40-50%. The effectiveness of the use of mineral fertilizers and chemical plant protection products serves not only to increase productivity, but also to significantly increase labor productivity in agriculture. This can be seen in the following. For example, between 1900 and 1940, labor productivity in agriculture increased by 60 percent, and by 1980, with the widespread use of chemicals, it had increased 11-fold over the next 40 years. Therefore, there is an increase in the production of mineral fertilizers around the world. In 1980, world production of mineral fertilizers amounted to 124.6 million tons of nutrients, while in 2014 it amounted to 186.8 million tons. The second half of the 20th century was called the "era of chemicalization" because of the widespread use of mineral fertilizers and pesticides. Worldwide use of mineral fertilizers has increased tenfold in 40 years (1951-1990) - from 14 million to 140 million tons [4, 5].

In addition, Uzbekistan has created a strong technological base for the production of mineral fertilizers, which is able to meet the current demand for these products. Three joint-stock companies (OJSC): Maksam-Chirchik, Navoiyazot and Ferganaazot produce nitrogen fertilizers, the range of which consists of ammonium nitrate, urea and ammonium sulfate. Three AJs: Ammophos-Maxam and Kokand Superphosphate Plant produces phosphorus fertilizers, the range of which includes ammophos (10% N and 46% P₂O₅), suprefos-NS (8-15% N and 20-24% P₂O₅), nitrocalcium phosphate (6% N and 16% P₂O₅) and simple ammonium superphosphate (1.5% N and 13.5% P₂O₅). Among them, Ammophos-Maxam is a leader in the production of phosphorus fertilizers, which account for about 70% of the domestic market for these products. Dehkanabad Potash Fertilizer Plant is the only producer of potassium fertilizer in the form of potassium chloride in the country. The technology of decomposition of phosphorite on the basis of nitric acid allows the use of primary technological raw materials and their complete processing into commercial products, including complex fertilizers. In some countries, the method of processing phosphorite raw materials in nitric acid plays a leading role. In the XXI century, new capacities for the processing of raw materials by the method of nitric acid are being launched. In addition, the presence of excess calcium in the form of Ca(NO₃)₂ in the compound formed during the decomposition of phosphorites in nitric acid adversely affects the physicochemical properties of the fertilizer. Due to the fact that the decomposition of phosphorite in nitric acid has several disadvantages, the use of combined methods in the decomposition of phosphorite in the combination of nitric and sulfuric acids, the resulting fertilizer is additionally enriched with sulfur and improves the properties of the product. Scientific work on the decomposition of



phosphorites on the basis of nitric acid is being carried out by our scientists, who have studied the production of various mineral and organomineral fertilizers [6-10].

II. SIGNIFICANCE OF THE SYSTEM

In this study, research was conducted to obtain aNPSCa-containing fertilizer based on the Central Kyzylkum low-grade phosphorite mineralized mass, nitric and sulfuric acid. The study of literature survey is presented in section III, methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and conclusion.

III. METHODOLOGY

Modern scientific and technical development in the field of phosphorus fertilizers includes the introduction of non-traditional methods of processing low-grade phosphorites, ie the development of technology for the production of primary phosphorus and complex fertilizers by activating phosphorites by processing them with less acid than required for complete decomposition. It is necessary to determine the optimal conditions for the activation of nitric and nitric sulfate acids. Based on the above, we set ourselves the goal of studying the process of obtaining NPSCa-fertilizers to accelerate the process of nitric acid activation of phosphorite by nitric acid activation of low-grade phosphorite and the addition of sulfuric acid. In order to study this process, experimental work was carried out to obtain a fertilizer containing NPSCa based on low-grade phosphorite, nitric and sulfuric acids. The composition of all the raw materials was studied before the experiments were carried out. Then the stoichiometric norms of nitric and sulfuric acid for decomposition of phosphorite samples are 100% (nitric and sulfuric acid = 100: 0; 90: 10; 80: 20; 70: 30; 60: 40; 50: 50; 40: 60 ; 30: 70) was calculated relative to the calcium oxide in the raw material. The chemical composition of the resulting porridge is organized. The chemical composition of phosphorites of the Central Kyzylkum (Table 1.) was organized.

Table 1.
Chemical composition of low-grade Central Kyzylkum phosphorite samples.

| Components | Powdered phosphorite | Mineralized mass | Sludge phosphorite |
|-------------------------------------|----------------------|------------------|--------------------|
| P ₂ O ₅ | 18,67 | 14,78 | 10,68 |
| CaO | 44,72 | 41,93 | 41,84 |
| MgO | 0,92 | 1,79 | 0,58 |
| CO ₂ | 15,97 | 18,15 | 19,88 |
| SO ₃ | 2,18 | 2,54 | 2,56 |
| F | 2,22 | 2,00 | 2,27 |
| H ₂ O | 1,05 | 1,17 | 1,24 |
| Fe ₂ O ₃ | 0,84 | 1,08 | 0,58 |
| Al ₂ O ₃ | 0,98 | 1,27 | 1,17 |
| CaO : P ₂ O ₅ | 2,56 | 3,20 | 3,92 |
| E.q. | 4,38 | 5,27 | 4,97 |

Physico-mechanical and commodity properties of phosphorite samples used in scientific research were studied (Table 2).

Table 2.
Physico-mechanical and commodity properties of Kyzylkum phosphorite sample

| Phosphorite samples | Humidity, % | Density, g/sm ³ | Volumetric weight g/sm ³ | Natural slope angle, grad. | Readability, seconds |
|---------------------|-------------|----------------------------|-------------------------------------|----------------------------|----------------------|
| Mineralized mass | 1,15 | 2,730 | 1,415 | 41 | 20 |
| | 2,45 | 2,895 | 1,586 | 42 | 23 |
| | 2,95 | 2,920 | 1,725 | 42 | Not readable |

Moisture, density, bulk density, natural slope, ductility, and other physical and mechanical properties of raw materials are important in the design of on-site transportation, warehousing, and packaging of many powdered materials.

Table 3.
Grain level of raw materials, %

| Granular size, mm | Mineralized mass | Powdered phosphorite |
|-------------------|------------------|----------------------|
| -3—+5 | 13,00 | 9,00 |
| -1—+3 | 10,00 | 10,50 |
| -1—+0,5 | 7,40 | 10,20 |
| -0,5—+0,315 | 1,50 | 4,60 |
| -0,315—+0,16 | 15,00 | 22,90 |
| -0,16—+0,1 | 21,50 | 21,10 |
| -0,1—+0,063 | 21,40 | 10,40 |
| -0,063≥ | 10,20 | 14,30 |
| Jami | 100 | 100 |

As a result of increasing moisture and density of raw materials, their physical and mechanical properties change dramatically, which leads to many inconveniences in the design of equipment for transportation, storage and packaging of raw materials. Therefore, the moisture and density of the mineralized mass were studied. It is necessary to determine the volume weight for the design of warehouses, the selection of bunkers and transport equipment. For example, samples of mineralized mass have an average bulk density of 1.110 g / cm³ and a specific gravity of 2.096 g / cm³ at an average humidity of 1.20%. When the moisture content increases to 3.30%, its value increases by an average of 2.75 times. In phosphorites, the natural slope angle is 41-44 °. The experiments were performed in a laboratory in thermostatic glass reactors equipped with a mixer. A pre-weighed phosphorite sample is added to the reactor, followed by the gradual addition of a specified amount of nitric and sulfuric acids. The temperature during the decomposition of phosphorite varies from 40 to 55 ° C, depending on the acidity, and lasts for 25 minutes. At the end of the decomposition time, all forms of P₂O₅ and CaO (total, plant-soluble and water-soluble), total nitrogen, SO₃, carbon dioxide, and carbonation were analyzed. General and plant-absorbing forms of R₂O₅ are determined in accordance with GOST 20851.2-75, and general and plant-absorbing forms of SO₃ are determined in accordance with GOST 26715-85. The chemical composition and salt content of the phosphorite samples were chemically analyzed using standard methods. The results obtained are presented in tables and figures.

IV. EXPERIMENTAL RESULTS

The results of chemical analysis of the resulting sample (Table 4) show that the decomposition rates of phosphorite vary depending on the acid content, and with the increase of the sulfuric acid ratio relative to nitric acid, the total P₂O₅ and CaO, P₂O₅ it was found that plant absorption increased relative to total but the plant absorption form of CaO decreased relative to total. For example, when the stoichiometric norms of nitric and sulfuric acid in the decomposition of phosphorite are 100:10, P₂O₅, the total and plant-absorbing form of CaO, the plant-absorbing form of CaO is 6.0%, 17.01% and 5.35%, 15.53%, acidity was 100.40, 6.80%, 19.30% and 6.33%, 17.05%, respectively. when the norms were 100:70, they were 7.83%, 22.20%, and 7.43%, respectively, 18.96%. The plant susceptibility of

P₂O₅ and CaO was 89.12% and 91.25%, respectively, when the stoichiometric norms of nitric and sulfuric acids were 100:10 and the acid norms were 100:40, respectively. 93.07% and 88.34%, respectively, while the acid norms were 100.90 and 94.96% and 85.39%, respectively.

Table 4.
Dependence of the total and assimilated form of P₂O₅ and CaO on the acidity of samples based on mineralized mass, nitric and sulfuric acids,%

| HNO ₃ and H ₂ SO ₄ norm, % | P ₂ O ₅ | | | CaO | | |
|--|-------------------------------|-------------|---------------------|----------|------------|--------------------------------|
| | general. | resilience. | o'zl./um. * 100% | general. | resilience | resilience./general. * 100% |
| 100 : 0 | 5,77 | 5,04 | 87,38 | 16,37 | 15,17 | 92,65 |
| 100 : 10 | 6,00 | 5,35 | 89,12 | 17,01 | 15,53 | 91,25 |
| 100 : 20 | 6,25 | 5,70 | 91,33 | 17,72 | 16,10 | 90,87 |
| 100 : 30 | 6,52 | 6,01 | 92,18 | 18,48 | 16,52 | 89,35 |
| 100 : 40 | 6,80 | 6,33 | 93,07 | 19,30 | 17,05 | 88,34 |
| 100 : 50 | 7,12 | 6,68 | 93,93 | 20,19 | 17,72 | 87,78 |
| 100 : 60 | 7,45 | 7,04 | 94,48 | 21,15 | 18,25 | 86,29 |
| 100 : 70 | 7,83 | 7,43 | 94,96 | 22,20 | 18,96 | 85,39 |

In the decomposition of phosphorite samples, it was found that the total amount of nitrogen decreased and the total amount of SO₃ increased with increasing levels of sulfuric acid relative to nitric acid. The results are shown in Figure 1, when the stoichiometric norms of nitric and sulfuric acids in the decomposition of phosphorite were 100:10, the total content of nitrogen and SO₃ was 7.93% and 3.46%, when the acid norms were 100:40.5.99% and 12.20%, respectively, while the acid norms were 3.45% and 23.55% at 100:70.

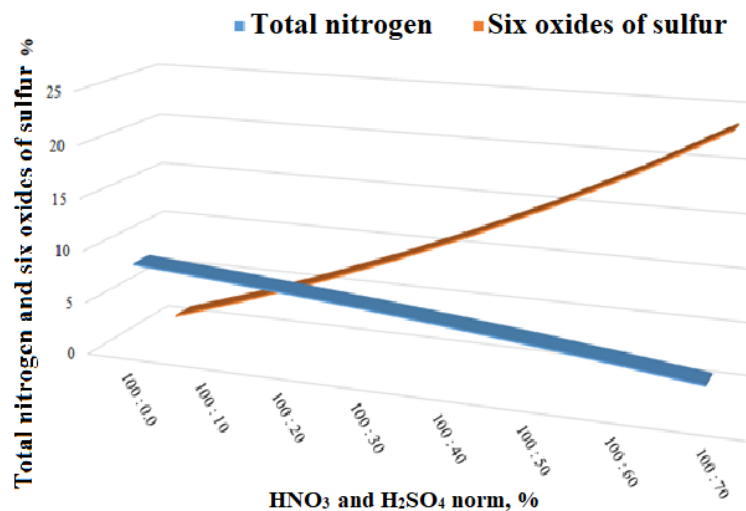


Figure 1. The dependence of the change of total nitrogen and sulfur dioxide in the samples obtained on the basis of mineralized mass, nitric and sulfuric acids on the acid norm,%

It is known that since the oxidizing property of sulfuric acid is higher than that of nitric acid, it was found that the decarbonization rate of total carbon dioxide increased with increasing sulfuric acid relative to nitric acid during decomposition. The results are shown in Figure 2, where the stoichiometric rate of nitric and sulfuric acids was 100:10, the decarbonization rate of total carbon dioxide was 82.36%, and the acidity rate was 90.89 at 100:40.%, while the acid norm was 94.87% when it was 100:70.

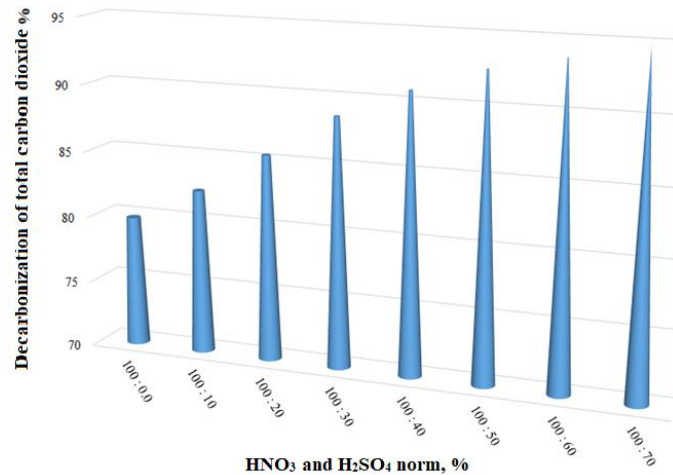


Figure 2. Dependence of the degree of decarbonization of total carbon dioxide on samples based on mineralized mass, nitric and sulfuric acids on the acid norm, %

V. CONCLUSION AND FUTURE WORK

It can be concluded from the study that the general form of P₂O₅, CaO and SO₃, the ratio of P₂O₅ to the total plant absorption, the total carbon an increase in the decarbonization rate of the four oxides was found, as well as a decrease in the ratio of total nitrogen and CaO to total plant uptake. The samples contained 5.77–7.83% of the total P₂O₅, 5.04–7.43% in the form of plant-assimilated P₂O₅, 3.43–8.47% nitrogen, 16.37–22.20% calcium oxide, 0.99–23.55% of the total SO₃.

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