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Production of Complex Fertilizers from Phosphorite Waste of the Central Kyzylkum

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Abstract:

The article presents research findings on the production of complex fertilizers by neutralizing phosphorite waste from the Central Kyzylkum Desert with an ammonia solution after partial decomposition using nitric acid. The study examines complex mineral fertilizers containing nitrogen and phosphorus (PN), produced by decomposing phosphorite samples at varying rates (40-90%) and neutralizing the resulting sludge with an ammonia solution at pH levels between 5.5 and 8.5. The research analyzes all forms of P2O5 and CaO (total, plant-soluble, and water-soluble), along with the total nitrogen content, which were the key components in the produced samples.

Keywords: phosphorite, nitric acid, ammonia, fertilizers, phosphorus, nitrogen, calcium.

Introduction: The key prospects for global agricultural development focus on the adoption of advanced soil cultivation technologies, the development of high-yielding crop varieties, and boosting productivity through the use of high-quality mineral fertilizers. In this context, enhancing the physicochemical and consumer characteristics of mineral fertilizers, a critical element in producing abundant and high-quality crops, has gained attention [1-2].

There has been a global rise in the demand for phosphorus fertilizers, driven by their role in improving the phosphorus nutrition of both soils and plants. Phosphorus fertilizers not only enhance the size and quality of crop yields but also promote plant growth and resilience to challenging climatic conditions. Consequently, increasing the production of phosphorus and complex phosphorus fertilizers, as well as expanding their variety, is crucial [3-6].

In our country, comprehensive scientific efforts are being made to develop technologies for producing complex fertilizers from local raw materials, as well as applying cost-effective

techniques for their use in agriculture. Special attention is given to fertilizers like ammophos, nitrophos, superphosphate, and ammonium nitrate, which enhance crop yields. However, the fact that many of these fertilizers lack sufficient content to maximize crop yields, and require significant energy for their production, has been overlooked [7-9].

The third pillar of the Strategy of Actions on the Further Development of the Republic of Uzbekistan outlines essential goals related to "the progressive development of agricultural production, strengthening food security, expanding the production of eco-friendly products, and significantly increasing agricultural export potential." In line with this, creating efficient production technologies for new, high-quality complex fertilizers based on high-carbonate Central Kyzylkum phosphorites becomes a priority task.

Currently, significant attention is being given to the development of innovative technologies and research within the chemical industry, particularly in the production of mineral fertilizers. These efforts focus on maximizing the use of each nation's raw material resources. Scientists and experts in this field are working to address scientific and technical challenges, which are increasingly important today. Methods that incorporate inexpensive, widely available materials, and make use of chemical and mining waste are being extensively utilized. In the research on phosphorite ore extraction and processing, as well as in the development of new technologies, the focus is on producing efficient and high-quality mineral fertilizers from lower-grade phosphorites [10-14].

The Kyzylkum Phosphorite Complex supplies phosphate fertilizer plants in Uzbekistan with phosphate raw materials, producing a washed-burnt concentrate containing an average of 26% P_2O_5 annually. This yields 186,000 tons of P_2O_5 in the form of mineral fertilizers from the phosphate raw materials. However, 1,874.6 thousand tons of phosphorite ore are mined, equating to 320.93 thousand tons of P_2O_5. This highlights significant P_2O_5 losses (42% of the total ore volume) in the thermal enrichment process, primarily in the form of phosphorite waste, including mineralized masses, sludge, and powder phosphorites. The country’s agricultural phosphorus fertilizer demand currently meets only 23% of the need, making the inclusion of phosphorite waste in agriculture a critical issue.

Methodology:

To address this, experiments were conducted to produce PN-containing fertilizer using powdered phosphorite waste and nitric acid. The composition of the raw materials was analyzed, and the stoichiometric amounts of nitric acid required for phosphorite decomposition were calculated, ranging from 40–90%, relative to the calcium oxide content. The resulting slurry’s pH was neutralized to a range of 4.5–8.5.

Experiments were performed in thermostatic glass reactors with mixers, where pre-measured phosphorite samples were added, followed by gradual nitric acid addition. The temperature during decomposition ranged from 40–55 °C, depending on the acid ratio, lasting for 25 minutes. The slurry was neutralized with ammonia at the end of the process. Key components such as P_2O_5 and CaO (in total, plant-soluble, and water-soluble forms) and total nitrogen content were analyzed in the final product.

Results:

The results obtained are summarized in Table 1.

The chemical processing of phosphorite with nitric acid follows the reactions outlined below [3].

$$Ca_5(PO_4)_3F + 10HNO_3 = 3H_3PO_4 + 5Ca(NO_3)_2 + HF$$

$$Ca_5(PO_4)_3F + 14HNO_3 = 3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + HF + 1252\ kJ/\ mol$$

$$Ca_5(PO_4)_3F + 4HNO_3 = 3CaHPO_4 + 2Ca(NO_3)_2 + HF + 89,7\ kJ/\ mol$$

$$CaCO_3 + 2\ HNO_3 = Ca(NO_3)_2 + CO_2 + H_2O + 63,5\ kJ/\ mol$$

$$MgCO_3 + 2\ HNO_3 = Mg(NO_3)_2 + CO_2 + 3H_2O + 1850\ kJ/\ mol$$

$$CaCO_3 + 2HNO_3 + 3H_2O = Ca(NO_3)_2 \cdot 4H_2O + CO_2$$

Table 1. Chemical composition of fertilizers based on powdered phosphorite,%

HNO_3 norm, %	N	P_2O_5			CaO		
		P_2O_5 total	$P_2O_{5ass.}$	P_2O_5 soluble in water.	CaO total	$CaO_{ass.}$	CaO soluble in water.
40	6,78	13,45	4,88	0,17	33,30	14,53	6,44
50	7,99	12,66	5,78	0,41	31,36	15,78	7,98
60	9,06	11,97	6,26	0,65	29,65	17,01	9,42
70	10,03	11,35	6,84	0,84	28,11	18,48	10,54
80	10,90	10,79	7,39	0,91	26,72	19,70	11,91
90	11,68	10,28	7,74	0,94	25,46	20,74	13,05

The chemical analysis of the produced fertilizers reveals that the decomposition rates of powdered phosphorites vary depending on the applied nitric acid ratio. For instance, the total P_2O_5 content in the nitrogen-phosphorus complex fertilizer from decomposed phosphorite ranges between 13.45% - 10.28%, while the plant-available form is between 4.88% - 7.74%. Additionally, the fertilizer contains 6.78% to 11.68% nitrogen and 33.30% to 25.46% calcium oxide.

The quality of the product is diminished by the presence of hygroscopic calcium nitrate, which results from the decomposition of phosphorite at higher acid ratios. The calcium nitrate increases the fertilizer's hygroscopicity, reducing its commercial properties.

To address this issue, the slurry formed from phosphorite decomposed in nitric acid was neutralized with ammonia at a pH of 5.5–8.5 to produce improved samples.

Ca(NO3)2 + H3PO4 + 2NH3 = CaHPO4 + 2NH4NO3

The results demonstrated that as the pH increased, the nitrogen content of the samples rose, enhancing the product's commercial properties, while the total, plant-soluble, and water-soluble forms of P_2O_5 decreased only slightly. In conclusion, the study explored the development of complex mineral fertilizers containing nitrogen and phosphorus, where Central Kyzylkum waste phosphorite was decomposed in varying proportions of nitric acid, and the resulting slurry was neutralized with an ammonia solution. The findings revealed that the decomposition rates of powdered phosphorite are influenced by the acid ratio and pH levels, with higher acid norms leading to increased absorption of phosphorus pentoxide. Additionally, the overall nitrogen content increases as the pH rises, further improving the fertilizer's effectiveness.

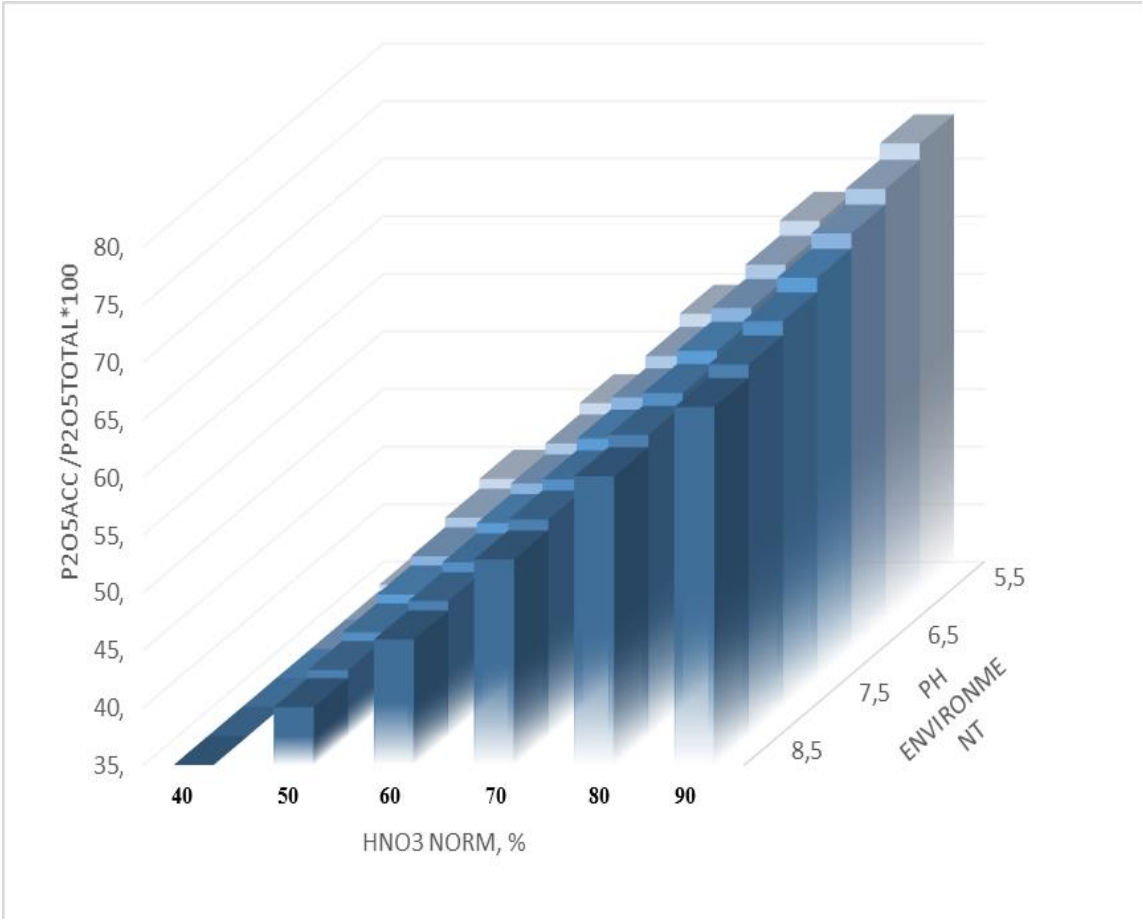

Figure 1. Plant-assimilated form of P_2O_5 in fertilizers based on powdered phosphorite

Conclusion:

The study shows that phosphorite waste from the Central Kyzylkum Desert can be effectively utilized to produce high-quality complex fertilizers. By adjusting the decomposition rate and pH levels, fertilizers with improved nitrogen content and enhanced phosphorus availability can be produced, contributing to sustainable agricultural practices.

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