PRODUCTION OF SLOW-RELEASE NPK FERTILIZERS FROM LOCAL RAW MATERIAL

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Abstract: This study investigates the decomposition of phosphate rock using nitric acid (HNO_3) for the production of new types of complex NPK fertilizers, utilizing secondary raw materials — washed and dried phosphate concentrate (WDP). The composition of WDP (wt.%): P_2O_5 – 22.74; CaO – 42.90; CO_2 – 9.04; MgO – 2.26; R_2O_3 – 2.76; SO_3 – 2.24; F – 1.71; H_2O – 1.04; Loss on ignition – 8.23. The following materials were used: potassium chloride (K_2O-60%) from the Dehqonobod Potash Fertilizer Plant, ammonium nitrate (34.5% N), urea from "Chirchiq Maksam" JSC, and 58.5% nitric acid. Stoichiometric calculations were carried out for converting phosphate and carbonate minerals into monocalcium phosphate and calcium nitrate. Different nitric acid dosages (25, 45, 65, and 85 units) were tested in the experiments. The highest decomposition and decarbonization rates were achieved at higher HNO_3 concentrations (65–85 units). The obtained NPK samples were analyzed using selected standard methods, and the formulations and compositional properties of the new fertilizers were discussed.

Keywords: NPK fertilizers, phosphate rock, washed and dried concentrate (WDP),

Аннотация: В данном исследовании изучено разложение фосфорита с использованием азотной кислоты (HNO_3) для получения новых видов сложных удобрений NPK на основе вторичного сырья — вымытого и высушенного фосфорного концентрата (WDP). Состав WDP (в масс. %): P_2O_5 – 22,74; CaO – 42,90; CO_2 – 9,04; MgO – 2,26; R_2O_3 – 2,76; SO_3 – 2,24; F – 1,71; H_2O-1,04; потери при прокаливании - 8,23. В качестве исходных компонентов использовались: хлорид калия (K_2O – 60%) из Дехканабадского завода калийных удобрений, аммиачная селитра (34,5% N), карбамид от АО «Чирчик Максам» и азотная кислота концентрацией 58,5%. Была рассчитана стехиометрия для превращения фосфатных и карбонатных минералов в монокальцийфосфат и нитрат кальция. Дозы HNO_3 варьировались в экспериментах по нормам: 25, 45, 65 и 85 единиц. Наибольшие показатели разложения и декарбонизации были достигнуты при высоких дозах HNO_3 (65–85 единиц). Полученные образцы NPK-удобрений были проанализированы с использованием стандартных методов, и обсуждены их формулы и составные характеристики.

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Ключевые слова: удобрения NPK, фосфорит, вымытый и высушенный концентрат (WDP), азотная кислота (HNO_3), степень разложения, декарбонизация, Кызылкумский фосфорит.

Annotatsiya: Ushbu tadqiqot ishida ikkilamchi qog‘oz xom-ashyosi va yuvilgan, quritilgan fosfor konsentratidan (WDP) yangi turdagi murakkab NPK o‘g‘itlarini ishlab chiqarish uchun fosforitni azot kislota (HNO_3) bilan parchalanishi o‘rganildi. WDP tarkibi (o’g’.%): P_2O_5 - 22,74; CaO - 42,90; CO_2 - 9,04; MgO - 2,26; R_2O_3 - 2,76; SO_3 - 2,24; F - 1,71; H_2O - 1,04; N.O. - 8,23. Dehqonobod kaliyli o‘g‘itlar zavodidan kaliy xlorid (K_2O - 60%), ammiakli selitra (34,5% N), “Chirchiq-Maksam” AJ karbamidi va 58,50% azot kislota (Nitrat kislota) ishlatildi. Fosfat va karbonat minerallarini monokalsiy fosfat va kaltsiy nitrat hosil qilish uchun zarur stokeometriya hisoblandi; HNO_3 dozalarining bir qismi (eksperimentlarda) turli normalar bilan (25, 45, 65 va 85 birlik) sinovdan o‘tkazildi. Eng yuqori parchalanish va dekarbonizatsiya ko‘rsatkichlari HNO_3 normalarining yuqori qiymatlarida (65-85 birlik) erishildi. Olingan NPK namunalar tanlangan standart metodlar bilan tahlil qilindi va yangi o‘g‘itlarning formulalari va tarkibiy xossalari muhokama qilindi.

Kalit so‘zlar: NPK o’g’itlar, fosforit, yuvilgan quritilgan konsentrat (WDP), nitrat kislota (HNO_3), parchalanish darajasi, dekarbonizatsiya, Qizilqum fosforiti.

Introduction

The efficient decomposition of phosphate raw materials under industrial conditions is a critical issue for agronomy and the fertilizer industry. Through the formation of monocalcium phosphate and calcium nitrate, phosphate ores can be converted into more readily available and plant-absorbable forms, enabling the production of complex NPK fertilizers. Phosphorites from the Central Kyzylkum Desert are characterized by high calcium and carbonate content. Their decomposition and decarbonization via reaction with nitric acid must be optimized in terms of energy consumption, reagent use, and product quality. The aim of this study is to decompose washed and dried phosphate concentrate (WDP) using nitric acid at various dosages (experimental concentrations), evaluate the degree of decomposition and decarbonization, and develop formulations for new complex NPK fertilizers based on the resulting materials.

LITERATURE REVIEW

The development of efficient and economically viable technologies for the production of complex NPK fertilizers is one of the priority directions in modern agrochemistry. In particular, there has been extensive research into processing local phosphate raw materials and obtaining high-performance fertilizers from them. Many studies have shown that local phosphorites contain significant amounts of carbonate and silicate impurities, which hinder their complete decomposition in

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sulfuric acid [1–2]. As a result, decomposition of phosphate using nitric acid is being considered as an alternative method with economic and technological advantages. For instance, research conducted by A.B. Jumayev et al. [3] investigated the decomposition kinetics of Uzbek phosphorites under the influence of HNO_3. It was revealed that the carbonates in the phosphate rock decompose with CO_2 release during the reaction, thereby increasing the reaction rate. Moreover, the treatment of phosphate with HNO_3 was found to be exothermic in nature, which offers potential energy savings during processing [4]. Other sources, such as the work of G.V. Karapetyan [5], emphasize that monocalcium phosphate and calcium nitrate compounds are key components in the synthesis of complex fertilizers. In nitric acid-based technologies, the natural formation of these compounds improves the biological activity of the fertilizers and enhances their effectiveness for crops.

Furthermore, international literature also provides comprehensive information on technologies for phosphate decomposition using nitric acid. For example, researchers from China and India [6–7] studied the effects of nitric acid at different concentrations on phosphate rock, finding that the optimal reaction time is 10–20 minutes and that the stoichiometric amount of acid significantly influences product quality. The decarbonization process is also of major importance. Removing carbonates improves the solubility and availability of phosphorus, thus enhancing the agronomic effectiveness of NPK fertilizers [8]. At the same time, several studies suggest that incorporating secondary local raw materials — such as wastepaper or other industrial by-products — can reduce the cost and environmental impact of complex fertilizers. These methods align well with the approach taken in this study.

Overall, the available literature confirms the relevance of the research direction pursued in this work. However, your study stands out by specifically focusing on Central Kyzylkum phosphorites, utilizing WDP (washed and dried concentrate), and aiming to produce NPK fertilizers using real industrial by-products (urea, potassium chloride, and recycled paper).

RESEARCH METHODOLOGY

Stoichiometric calculations were carried out to determine the required amount of nitric acid (HNO_3) for the decomposition of phosphate and carbonate minerals into monocalcium phosphate and calcium nitrate. In practical trials, various concentrations of HNO_3 were applied — 25, 45, 65, and 85 units, as specified in the experimental report. The exact units of HNO_3 concentration should be defined according to the referenced source; in this study, values were adopted as indicated in the experiment tables. The phosphate concentrate was treated with HNO_3 under vigorous stirring for 10–20 minutes. It was observed that the reaction was completed within 10–15 minutes and had an exothermic nature, with

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temperatures rising up to 40–45°C. After cooling, the resulting product was analyzed using standard chemical methods. The parameters determined included: Total and plant-available P_2O_5 (in 2% citric acid), CaO, CO_2, H_2O, and other relevant components. To synthesize new types of complex NPK fertilizers, we used both secondary paper-based raw material and washed dried phosphate concentrate (WDP) with the following composition (wt.%): P_2O_5 – 22.74; CaO – 42.90; CO_2 – 9.04; MgO – 2.26; R_2O_3 – 2.76; SO_3 – 2.24; F – 1.71; H_2O – 1.04; Loss on ignition – 8.23. The additional raw materials used were: Potassium chloride (K_2O – 60%) from the Dehqonobod Potash Fertilizer Plant, Ammonium nitrate (34.5% N), Urea produced by "Chirchiq-Maksam" JSC, Nitric acid at a concentration of 58.50%. The stoichiometric rate of nitric acid required for the decomposition of phosphate and carbonate minerals into monocalcium phosphate and calcium nitrate was calculated. For the experiments, HNO_3 was applied at 40% and 60% of the stoichiometric requirement. The resulting NPK fertilizer samples were analyzed using recognized standard methods.

The decomposition coefficient (K_p) was calculated using the following formula:

$$\mathbf{Kp=(P_2O_{5usv}/P_2O_{5obsh}) \cdot 100},$$

Here, P_2O_{5usv}. is the digestible form of P_2O_5 in 2% citric acid, for total P_2O_5. Analytical methods: the samples were analyzed using recognized standard methods.

ANALYSES AND RESULTS

Experimental results showed a significant increase in the decomposition and decarbonization degrees of phosphorite with increasing HNO_3 concentration. The key data are presented in the table below (Table 1). To determine the decomposition and decarbonization degree of phosphorites from the Central Kyzylkum Desert depending on the concentration of nitric acid, a calculated amount of phosphorite was treated with acid under vigorous and thorough stirring for 10–20 minutes. The reaction of Kyzylkum phosphorites with nitric acid proceeds very easily, with almost no foaming, and completes within 10–15 minutes. The process is exothermic, and depending on the concentration and rate of nitric acid addition, the temperature rises to 40–45 °C. After cooling, the resulting mass was subjected to chemical analysis.

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Table 1

Chemical composition of the products obtained from the decomposition of the washed concentrate with nitric acid, %

HNO_3 Concentration (norm)	N	Waste paper, g	P_2O_5			CaO			CO_2	H_2O	Kr, %	Kd, %
			Total	Digestible	Water-soluble	Total	Digestible	Water-soluble				
25	2.63	0.5	10.9	10.7	10.1	33.38	9.3	5.27	5.8	8.84	27.64	34.88
45	4.47	1	10.8	10.6	10	29.6	15.79	8.95	3.74	14.8	53.35	58.8
65	5.79	1.5	11.5	11.2	11.1	25.17	20.44	11.58	1.8	19.42	77.01	80.07
85	6.79	2	12.9	12.5	12.2	21.72	13.95	0.94	0.94	95.38	96.01	21.72

The total P_2O_5 and the amount of P_2O_5 digestible in 2% citric acid slightly increased with increasing HNO_3 dosage — this indicates that higher HNO_3 concentrations effectively dissolve phosphate minerals and produce readily digestible phosphates. The decreases in CaO and CO_2 contents confirm that decarbonization occurred: HNO_3 decomposes carbonates, releasing CO_2 and converting calcium carbonate into calcium nitrate. As a result, calcium nitrate forms in the solution and the content of soluble phosphates increases. The coefficients of decomposition and decarbonization rose sharply across the HNO_3 norm range from 25 to 85; notably, very high values (77–96%) were recorded at 65 and 85 units, indicating that the reaction is nearly complete at high HNO_3 dosages. The reaction rate (10–15 minutes) and its exothermic character are important from an energy-saving perspective in practical production; however, at high HNO_3 dosages reagent consumption and corrosion risk increase, so an economically and technically optimal dosage must be determined. The obtained decomposition products were formulated into complex NPK fertilizers by adjusting with sources of N, P and K in accordance with the reagents specified in the experiment. Based on the analysis results (Table 1), it was clearly established that the degree of phosphorite decomposition increases with the rate (dosage) of nitric acid.

CONCLUSION

When decomposing the washed, dried phosphate concentrate from the Central Kyzylkum Desert with nitric acid, increasing the HNO_3 dosage

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significantly increases the degrees of phosphorite decomposition (digestible fraction of P_2O_5) and decarbonization. Under the experimental conditions the reaction is rapid (10–15 minutes), exothermic, and the temperature rises to 40–45 °C. At higher HNO_3 norms (65–85 units), decomposition and decarbonization reached high values (77–96%). The resulting decomposition products were evaluated as suitable raw materials for producing complex NPK fertilizers; however, for industrial implementation the consumption of HNO_3, safety issues and corrosive effects must be considered, and the optimal dosage and technological regime determined. Future studies are recommended to evaluate the optimal HNO_3 dosage from an economic-energy standpoint, to develop waste neutralization procedures, and to protect production equipment from corrosion.

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