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Chemical Activation of Khojakul Phosphorites by Ammonium Salts

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Authors' contributions

This work was carried out in collaboration between all authors. Author TB designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors AR and ST managed the analyses of the study. Author TB managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Aims: To investigate chemical activation of low-grade phosphorite from Karakalpakstan, Khojakul by ammonium salts in order to obtain slow-acting phosphate fertilizers.
Study Design: The content of the total form N (N_t) was determined by method Kjeldahl method. Determination of total and acceptable forms (on 0.2 M solution of Trilon B) of phosphorus ($P_2O_{5tot.}$, $P_2O_{5wat.}$) was performed widely in the analysis of phosphate ores by differential method on photo colour meter PCM-3 (made in Russia, λ = 440 nm) as phosphorus-vanadium-molybdenum complex. This method is based on measuring the light transmission of yellow phosphorus-vanadium-molybdenum complex relative to the reference solution containing a certain amount of phosphates. The method allows analyzing the products with a relative error of determining $\pm$1%. The activation rate (K_a) was defined by relation acceptable P_2O_5 form to total P_2O_5 form. Decarbonization degree (K_d) was determined by changing $C0_2$ in the phosphate rock and final

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product. pH of ammonium salts solution and final products were defined after their agitation in 10% distiller water suspension. Further suspension obtained was measured by potentiometric method on ionomer I-130M (made in Russia) with electrode system of electrodes ESL 63-07, EVL-1M3.1.

Place and Duration of Study: The laboratory of phosphate fertilizers of the Institute of General and Inorganic Chemistry under Academy Science of the Republic of Uzbekistan, from July to August in 2016.

Methodology: Model laboratory device that obtains fertilizers consists of five-liter screw mixer made from stainless steel 12X18H10T equipped with stirrer, moved by electric motor. The laboratorial experiment is done in the following way: in the beginning measured sample of phosphorite was charged in screw mixer and then it was fed to 2, 5, 10 and 20% of ammonia solutions at different ratios proportions of mineral fertilizers (MF) and phosphorite powder (PHP), for 30 min with vigorous stirring components. Products obtained from interaction of components were analyzed for nitrogen content and different forms of phosphorus. The weight ratio of MF:PHP was in the range from 1: 1 to 1: 10. After completing activation process for 30 minute, wet products were dried in muffle oven at 90°C until dry condition.

Results: The chemical compositions of final products were determined during the experiment. Based on chemical activation of low-grade phosphorite fertilizers containing high acceptable form of phosphorus (v) oxide (P_2O_5) can be obtained. It had been found that degree of activation (Ka) of phosphorite powder depends on the nature of the ammonium solution and the pH of the medium. Ammonium sulphate is more acidic than ammonium nitrate, ammonium phosphate, and ammonium chloride. The pH of ammonium sulphate (10% of its solution) is 3.80. The decarbonization degree (K_d) of the fertilizers obtained from ammonium sulphate is in a range from 6.33 to 35.39%, which is higher than for other types. Therefore, there had been obtained the fertilizers containing high acceptable form of phosphorus (v) oxide in a range 35.30 – 59.07%. It was revealed that the more phosphate raw is used for activation process, the less is acceptable P_2O_5 in fertilizers obtained. Moreover, the fertilizers have high content of nitrogen, depending on the type of ammonium salts used, in a range 1.06 – 17.33% in the composition.

Conclusion: Based on the results it is possible to obtain effective slow-acting complex phosphate fertilizers with different ratios of nutrients by the activation of low-grade phosphate rock from Karakalpakstan, which do not have an industrial value, mineral salts, used in agriculture as a standard mineral fertilizer.

Keywords: Ammonium sulphate; ammonium nitrate; ammonium phosphates; ammonium chloride; low-grade phosphorite; activation.

1. INTRODUCTION

At the present time, mainly three phosphorite deposits of Karakalpakstan attract attention, mainly: Sultan-Uizdog, Khojeyli and the Lower Amudarya. The most perspective is considered to be Khojakul, as it is unlike other deposits by geographical location is very advantageous for operations [1]. The low content of the main component of P_2O_5 and a large number of undesirable impurities, particularly quartz, make Khojeyli's ore unsuitable for obtaining concentrated phosphate fertilizers. Radical way of increasing the content of P_2O_5 is beneficiation of ore that is very difficult [2,3]. It is known that phosphorites of Karakalpakstan consist mainly of insoluble in water salts. Therefore, the plant assimilates the phosphorus from them with difficulty, except in acid conditions [4,5].

The study of the solubility of the phosphorite powder showed that it is practically insoluble in water. However, the solubility of the phosphorite powder in 0.1 N hydrochloric acid solution is 4.96%, and in 2% solution of citric acid is 4.18%, and 0.2 M solution of Trilon-B is 4.13%. This property allows using nodule phosphorites of Karakalpakstan for direct application in the soil in form of powder. It is known that the application of it in agriculture on acid soils on the effectiveness it is not inferior to ordinary superphosphate [6-8].

However, our soils are neutral (and limed) and therefore, direct application of this phosphate without preliminary activation is ineffective. To extend the range of application of phosphorite powder and on neutral soils, it is necessary to increase the content of assimilable forms of phosphorus [9].

The most effective and quickly realizable technological solution to the use of low-grade phosphorites of Karakalpakstan is the chemical activation in presence of ammonium salts with getting slow-acting complex phosphate fertilizers.

2. MATERIALS AND METHODS

The phosphorite of the upper layer Khojakul field contents (weight. %): P_2O_5 (14.40), CaO (24.30), CO_2 (11.90), MgO (0.32), F (1.22), Fe_2O_3 (3.78), SO_3 (0.98), H_2O (1.70), which was used for study. To obtain standard grinding samples of phosphorite ore is milled in the ball mill. The dispersed composition of the resulting phosphorite powder is summarized in Table 1.

Table 1. The dispersed composition of the resulting phosphorite powder

Size of particles, mm	Fraction yield, %
-0.5 ÷ +0.315	1.3
-0.315 ÷ + 0.16	31.4
-0.16 ÷ + 0.10	27.4
- 0.10 ÷ + 0.063	22.7
-0.063 ÷ + 0.05	7.7
-0.05	9.5
Total	100

With the aim of developing simplified technology of phosphorus-containing fertilizers studied the chemical activation process of phosphorite powder by physiologically acidic mineral fertilizers such as ammonium sulphate, ammonium nitrate, ammonium phosphates and ammonium chloride, which are the main standard mineral fertilizers in agricultural production. In addition, these kind of salts have acidic property and therefore they named physiologically acidic ones.

Model laboratory device that obtains fertilizers consisted of five-liter screw mixer made from stainless steel 12X18H10T equipped with stirrer, moved by electric motor. The laboratorial experiment is done the following way: in the beginning measured sample of phosphorite was charged in screw mixer and then it was fed to 2, 5, 10 and 20% of ammonium solutions at different ratios of proportions of mineral fertilizers (MF) and phosphorite powder (PHP), for 30 min with vigorous stirring components. Products obtained of interaction of components were analyzed for nitrogen content and different forms of phosphorus [10]. The weight ratio of MF:PHP was in the range from 1: 1 to 1: 10. After completing activation process for 30 minute, wet products were dried in muffle oven at 90°C until dry condition.

2.1 The Formulas of Calculations

The decarburization degree (K_d) is calculated in the following way:

$$K_{\text{d}} = \left[1 - \frac{\omega(CO_{2\,inproduct}) \cdot 100}{\omega(CO_{2\,inrawphasp\,hate})}\right] \cdot 100\ \% \qquad (1)$$

Where $\omega(CO_{2\,in\ зкщвгсе})$ the mass fraction of CO2 in product obtained; $\omega(CO_{2\,in\ кфцзрщызрфеу})$ is the mass fraction of CO_2 in raw phosphorite;

The activation rate (K_a) is calculated in the following way:

$$K_a = \left[\ \frac{\omega(P_2O_{5\,iacceptabl\,e})}{\omega(P_2O_{5total})}\ \right] \cdot 100\ \% \qquad (2)$$

Where $\omega(P_2O_{5\,acceptable})$ is the mass fraction of acceptable form of P_2O_5 in product; $\omega(P_2O_{5\,ещефд})$ is the mass fraction of total form of P_2O_5 in initial phosphorite.

3. RESULTS AND DISCUSSION

The results obtained based on laboratorial tests are summarized in Table 2.

As it is seen from table that various types of ammonium salts effect considerably on phosphorite powder.

It should be noted that among the complex fertilizer obtained, there is high content of the product based on ammonium phosphate, which content from 55.92 to 90.33% of activation rate. As ammonium phosphate is complete assimilate and water soluble salt. However, can be described as follow:

> According to total P_2O_5 in the product is 37.95, 27.85, 22.25 and 18.85% with the same ammonium phosphate and then portion of the phosphorite flour is 6.90, 10.54, 11.75, and 13.37% of total P_2O_5. Therefore, it can be estimated the necessary amount of the total P_2O_5 of ammonium phosphate, which is equal to 37.95-6.90=31.05, and then 34.28-31.05=3.23, that is 3.23:6.90·100=46.81%, which is required amount. The rest amount can be calculated the same method. Based on there are the following: 43.26, 45.45, and 39.49%, respectively.

Table 2. Changing the chemical composition of complex fertilizer depending on the activation medium

pH of solution		MF:PHP	Content, %			K_a, %	K_d, %
Before activation	After activation		P_2O_5 total	P_2O_5 assimilable	N		
Activation with ammonium sulphate							
3.80	7.10	1:1	6.94	4.10	10.28	59.07	35.39
	7.10	1:2.5	10.01	4.46	6.38	44.56	21.47
	7.11	1:5	12.35	4.71	3.42	38.14	10.28
	7.16	1:10	13.40	4.73	1.94	35.30	6.33
Activation with ammonium nitrate							
4.80	7.24	1:1	6.88	3.60	17.33	52.33	23.03
	7.29	1:2.5	10.26	4.34	10.08	42.30	13.54
	7.36	1:5	11.56	4.29	5.96	37.11	9.22
	7.41	1:10	13.09	4.30	3.47	32.85	4.49
Activation with ammonium phosphate							
4.40	5.83	1:1	37.95	34.28	5.90	90.33	29.90
	6.79	1:2.5	27.85	21.87	3.41	78.53	23.80
	7.38	1:5	22.25	15.88	1.95	71.37	16.90
	7.49	1:10	18.65	10.43	1.06	55.92	5.01
Activation with ammonium chloride							
4.90	7.24	1:1	6.89	3.53	13.38	51.23	21.01
	7.31	1:2.5	9.75	4.00	7.78	41.03	12.47
	7.33	1:5	11.35	4.11	4.71	36.26	8.12
	7.39	1:10	13.62	4.28	2.65	31.43	3.24

It is found the degree of activation (K_a) of phosphorite powder (Table 2) depends on the nature of the ammonium solution and the pH of the medium.

The study showed that with increasing the concentration of the solution of MF increased the degree of activation (decomposition) of phosphorite powder.

For example, in a product in which the ratio MF:PHP=1:1, i.e. during processing phosphorite powder containing 0.288 g of P_2O_5 in 2% ammonium sulphate solution, the activation ratio of raw materials is 59.07%. Activated phosphorite powder by ammonium sulfate, i.e. complex fertilizer contains 10.28% of nitrogen, 6.94% of the total and 4.10% of assimilable P_2O_5 by plants.

The increase of the number of phosphorite powder activated in a solution of ammonium sulfate leads to decrease the degree of decomposition of raw materials. For example, when activation the phosphorite powder, containing 0.72 g of P_2O_5 in solution of ammonium sulfate (MF:PHP=1:2.5) were found that reduction of the activation rate to 44.56%. And in the processing of phosphorite powder, which contents 1.44 g and 2.88 g of P_2O_5, in the same solution (MF:PHP)=1:5-10) the activation ratio of the phosphate rock is reduced on average by 1.55 and 1.67 times, respectively.

It is observed that formation of a small amount of foam in the activation process of phosphorite powder by the ammonium sulfate solution. This confirms the decarbonization of phosphorite. The results of chemical analysis of activation products have showed a decrease of CO_2 content in their composition. It is established that with increasing concentration and norm of the activating solution, the phosphorite powder's decarbonization degree (K_d) is increased.

For example, when activation the phosphorite powder (0.288 g of P_2O_5) in 2% solution of ammonium sulfate, the degree of decarbonization was 35.39%. However, when activation such a number of phosphorite powder in 5, 10 and 20% solutions of ammonium sulfate under the same conditions its value is raised by 1.11, 1.27 and 1.64 times, respectively.

With the increase in solution the amount of activated phosphorite, the degree of decarbonization of raw material is decreased. For example, when activation of phosphorite powder (0.72 g of P_2O_5) in 2% solution of ammonium sulfate, the degree of decarbonization is reduced by 1.65 times. When the content of phosphorite powder in number

from 1.44 to 2.88g of P_2O_5 the degree of decarbonization of raw materials is of 10.28% and 6,33% , i.e. reduced by 3.44 and 5.59 times, respectively.

The dependence of the degree of decomposition of the phosphorite powder on the concentration of the ammonium sulphate solution can be explained as follows:

With the increase the concentration of the solution is changed its medium.

With increasing in the solution of ammonium sulphate from 2% to 20%, the pH value of the solution is reduced from 3.8 to 3.2, i.e., increased its acidity.

Thus, it has been shown that the more acidic the environment of the ammonium sulphate solution, the larger the degree of activation of the phosphate rock. After completion of the activation process, the environment is become as neutral (pH=7.10-7.16).

The mechanism of the activation process of phosphorite powder by solutions of mineral salts can be explained that under the action of ammonium salt solutions, the decomposition of the basic minerals (fluorapatite and calcite) of phosphate rock is occurred. Moreover, an exchange reaction among the components of the raw material and the activating reagent is took place. As a result of dissociation of ammonium sulfate in solution is formed acid environment according to below.

$$(NH_4)_2SO_{4(s)} + H_2O = 2NH_{4\,(aq)}^{+} + SO_{4(aq)}^{-2}$$

The formed acid ions enter firstly the reaction with the minerals calcite. In the next stage with the inflow of ions in fluorine-carbonate-apatite minerals the diffusion process is accelerated and their specific acting surface is increased. It is formed that water soluble and assimilable by plants P_2O_5 forms of phosphate minerals in the solution.

Conducted studies have shown that the mechanism of the activation process of phosphorite powder with ammonium nitrate, ammonium phosphate and ammonium chloride practically is not differed from the solution of ammonium sulfate, but it is slower in comparison with ammonium sulphate. It is established that the activation coefficient of phosphorite powder samples depends on the concentration, norm, and medium of the ammonium nitrate solution. So, in a 30 minute activation of phosphorite powder that contents 0.288 g of P_2O_5, in 2% solution of ammonium nitrate (MF:PHP=1:1), the content of $P_2O_{5assem.}$ in the product is 3.60% or 52.33% of P_2O_5 is assimilated by plants form. The degree of decarbonization of phosphorite powder is 23.03%. After processing, the phosphorite powder with solution of ammonium nitrate reaction medium is become as neutral (pH = 7.24).

There has been reduced the activation degree of activated phosphorite with increasing its content during the activation process. For example, when activation the phosphorite powder (MF:PHP=1:0.1-4, i.e., from 0.72 g of P_2O_5 to 2.88 g of P_2O_5) in 2% solution of ammonium nitrate, acceptable form of P_2O_5 is reduced from 42.30% to 32.85%, respectively.

Ammonium nitrate (ammonium nitrate) is considered to be physiologically acidic nitrogen fertilizer, but the acidity of its solution is weaker than ammonium sulfate. Therefore, the degree of activation of the samples of phosphorite powder with ammonium sulphate is higher compared to ammonium nitrate.

When activation the phosphorite powder that contents 0.288 g of P_2O_5 in 2% solution of ammonium phosphate (MF:PHP=1:1), the amount of P_2O_5 assim. in the product is 37.95% or 90.33% of P_2O_5 is assimilated by the plant form, and a water-soluble form of P_2O_5 is 72.99%. With the increase the content of activated phosphorite powder, reduced degree of decomposition. For example, when activation the phosphorite powder, containing 0.72, 1.44, and 2.88 g of P_2O_5 in 2% solution of ammonium phosphate (MF:PHP=1:2.5-10), assimilable plant form of P_2O_5 is 78.53, 71.37, and 55.92%, respectively.

In the process of activation also observed the decomposition of carbonate minerals of phosphate rock. With the increase the concentration and norm of ammonium phosphate, the degree of decarbonization of the phosphate rock is increased.

The degree of decarbonization of the phosphorite powder, depending on the ratio of the components is of 5.01-29.90%. After processing, the phosphorite powder with solution of ammonium phosphates, the pH of the reaction medium, depending on the number of phosphate rock is 5.83-7.49.

The difference of the activation mechanism of phosphorite powder by solutions of ammonium chloride is that the activation of raw materials takes place in hydrochloric acid medium. When the processing phosphorite powder in 2% ammonium chloride solution (MF:PHP=1:1) the degree of activation is 51.23%. With the increase the content of phosphorite powder (MF:PHP=1:2.5-10) it is reduced on average from 1.25 to 1.63 times.

The result of the research was compiled following row on efficiency mineral salts for the activation of phosphorite: ammonium sulphate ammonium> ammonium phosphate> nitrate ammonium> ammonium chloride.

A simplified flowsheet producing complex slow-acting fertilizers with minimal moisture by treatment with binding solution of a mixture of phosphate rock and fertilizer used in a screw mixer.

4. CONCLUSION

Thus, based on the results was shown that principle possibility of obtaining effective slow-acting complex phosphate fertilizers with different ratios of nutrients by the activation of low-grade phosphate rock from Karakalpakstan, which does not have an industrial value, mineral salts, used in agriculture as a standard mineral fertilizer.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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