



Recycling of Local Phosphate Waste - mineralized Mass into Activated Phosphorus Fertilizers

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CSJI/2023/v32i6875

Open Peer Review History:

This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: <https://www.sdiarticle5.com/review-history/110442>

Original Research Article

Received: 08/10/2023

Accepted: 12/12/2023

Published: 14/12/2023

ABSTRACT

The manuscript provides the results of the process of obtaining activated phosphorus fertilizer (APF) by nitric acid processing of mineralized mass (MM) of phosphate waste, which formed during the sorting stage of thermal beneficiation of Central Kyzylkum (CK) phosphorites. For experiments was used MM with content 14.60% $P_2O_{5total(t.)}$; 3.07% $P_2O_{5acceptable}$ by citric acid (ac.c.a.); 43.99% CaO_{t.}; 1.01% MgO; 14.11% CO₂; 1.04% Al₂O₃; 0.89% Fe₂O₃; 1.58% SO₃; 1.30% F; 1.02% H₂O; CaO:P₂O₅ – 3.01 and 10.82% insoluble residual. The optimal concentrations and norms of nitric acid have been determined. Phosphorus fertilizer suspensions were neutralized with Ca(OH)₂ suspension in order to prevent P₂O₅ from passing into the solution. APF obtained in optimal parameters has the following composition (weight, %): 20.42-20.58 $P_2O_{5total(t.)}$; 11.02-11.72 $P_2O_{5ac.c.a.}$; 38.87-39.01CaO_{t.}; 23,39-24,48 CaO_{ac.c.a.}. The degree of transition of P₂O₅ to liquid phase is 2.02-2.06%.

Keywords: Mineralized mass; nitric acid; acid concentration; acid norm; activated phosphorus fertilizer; degree of transition to liquid phase.

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1. INTRODUCTION

The main phosphate raw material in Uzbekistan is Central Kyzylkum (CK) phosphorites with low quality and high carbonate, and from them are produced simple and complex fertilizers with different content of phosphorus. These phosphorites are considered to be very poor in terms of the main component (P_2O_5). Despite the large reserves of this phosphate raw material (PRM), the average amount of P_2O_5 in it is 16.2%. Currently, there are various ways of using these phosphorites: thermal beneficiation, direct acidification and processing with various reagents, etc. One of the currently widely used methods is the processing of phosphorites with sulfuric acid [1-2].

In the world practice is known, that the phosphate raw materials, applicable for sulfur acid extraction should be with content of P_2O_5 not less than 24.5%, CO_2 should be not more than 8%, $(R_2O_3 : P_2O_5) \cdot 100$ can not be more than 12%, $(MgO : P_2O_5) \cdot 100$ can not be more than 7-8%. The recommend value of the calcium module ($CaO : P_2O_5$) is 1.6 and chlorine is not more than 0.04% in the raw materials. Therefore the poor raw material has to be enriched.

Currently, CK phosphorites are thermally enriched at Kyzylkum Phosphorite Combine, and at least 1.800.000 tons of phosphate raw materials are used for this enrichment.

This enrichment method includes the following steps: separation of mined phosphorites into rich fractions, washing of rich phosphorites from chlorine, and high-temperature incineration of the resulting phosphorite raw materials. The main drawbacks of existing technology of enrichment are the following:

- 1) Formation of phosphate waste called mineralized mass (MM) with a size greater than 5 mm and containing 12-14% P_2O_5 during separation of phosphorites into rich fractions. Its amount is one third of mined phosphate raw materials;
- 2) During chlorine washing of phosphate raw materials, 15-25% of total P_2O_5 transition to waste in the form of phosphorite powder (sludge). This phosphorite sludge (PS) was also not reused in any way. In total, 42% of the P_2O_5 in the phosphate raw material goes to the mineralized mass and phosphorite sludge waste;

- 3) The high value of the calcium module ($CaO:P_2O_5=2.0-2.1$) in washed and burned concentrate (WBPC), as removal of the CaO free formed at decomposing of lime carbonate is not provided.

For the first time in world practice Sh.S. Namazov and others [3-6] developed and put into practice the production technology of nitrocalcium phosphate fertilizer by processing CK phosphorites with nitric acid. Currently, Joint Stock Company (JSC) of "Samarkandkimyo" is producing a large amount of nitrocalcium phosphate fertilizer based on this technology. But even so, this technology is has some drawbacks: waste of nitrogen oxides as a result of exiting the gas phase; large volume foaming processes; its high hygroscopicity is due to the difficulty of separating calcium nitrate and the large amount of calcium nitrate left in the obtained fertilizer.

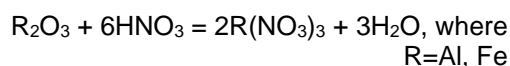
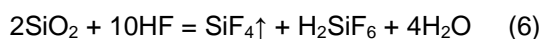
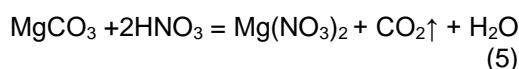
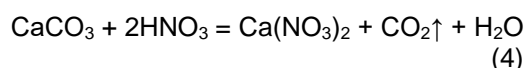
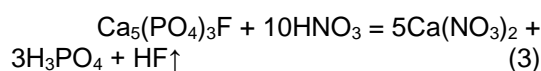
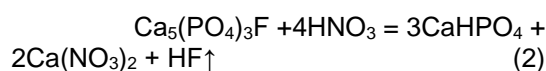
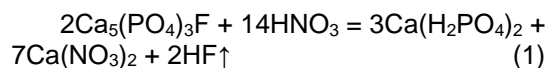
CK phosphorites were reacted with 20, 40 and 60% concentrated solutions of nitric acid, and it was shown that effective nitrogen-phosphorus fertilizers can be obtained with low consumption of acid reagent [7]. However, MM and PS were not used in this work. Scientific studies on obtaining organomineral fertilizers (OMF) from MM and FS have been extensively studied in [8-12]. But even so, there are no scientific research works on processing of MM and PS with nitric acid.

2. METHODS

That's why we started scientific research on obtaining ordinary activated and complex fertilizers containing phosphorus by processing FSs with nitric acid [13-15]. The following MM sample was taken for laboratory research: 14.60% P_2O_{5st} ; 3.07% $P_2O_{5ac.c.a.}$; 43.99% CaO; 1.01% MgO; 14.11% CO_2 ; 1.04% Al_2O_3 ; 0.89% Fe_2O_3 ; 1.58% SO_3 ; 1.30% F; 1.02% H_2O ; $CaO:P_2O_5 - 3.01$ and 10.82% insoluble residue. MM this chemical composition was decomposed with nitric acid at concentrations 30.0; 35.0; 40.0; 45.0; 50.0; 55.0 and 58.78% and it at a norm of 100% relative to the formation of dicalcium phosphate.

The interaction of the MM with nitric acid was performed at 35 - 40°C in a glass reactor equipped with stirrer. This reactor is placed in a thermostat to keep the temperature constant. A pre-weighed sample of phosphorite is placed in the reactor, and then a fixed amount of nitric acid is slowly added. The temperature during the

decomposition of phosphorite varies between 35-50°C depending on the acid level and lasts 25-30 minutes. The temperature of the reaction mass is kept at 40°C. When phosphorites are decomposed with nitric acid, the following chemical reactions occur:



Sufficient water is added to the resulting calcium nitrate phosphate slurry after decomposition and the suspension is filtered under vacuum. The resulting wet phosphorus fertilizer is washed once with hot water (80-90°C) in the ratio of

MM:H₂O=1.0:1.0 and wet fertilizer samples was dried at 90°C. The obtained activated phosphorus fertilizer samples were analyzed accordingly to the methods presented in [16-18].

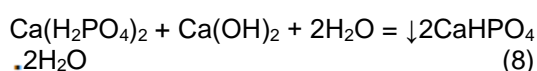
3. RESULTS AND DISCUSSION

The laboratory tests results are shown in Table 1. It is seen that the concentration of nitric acid does not significantly affect the quantitative indicator of P₂O_{5t}, which is the main nutrient component in the activated phosphorus fertilizer samples. For example, nitric acid was taken at a concentration of 30% the amount of total P₂O_{5t} in the fertilizer sample is equal to 17.23%, and when 58.78% nitric acid is used, it is equal to 17.59%, that is, it increases by only 0.36%. The acceptable forms of P₂O₅ and CaO increase from 7.41 to 8.17% (by 0.76%) and from 19.15 to 20.94% (by 1.79%), respectively. It can be seen that it slightly effects the concentration of nitric acid. All the obtained samples of activated phosphorus-activated fertilizers have relative acceptable values of P₂O₅ and CaO from 43.00 to 46.44% and from 48.96 to 52.98%, respectively, and fertilizers with such quantitative indicators do not answer the requirements by agriculture: the fertilizers have to relative content of P₂O_{5ac.c.a.} no less 50% the . Another drawback of these obtained results is that 24.06 to 25.76% of the total P₂O₅ in the phosphate feedstock passes into the liquid phase, i.e. as waste.

Table 1. Chemical composition of activated phosphorus fertilizers (norm of HNO₃ -100%)

No of experiments	Chemical composition, %							Degree of transition of P ₂ O ₅ to liquid phase, %
	P ₂ O _{5t}	P ₂ O _{5ac.c.a.}	P ₂ O _{5w.s}	CaO _t	CaO _{ac.c.a.}	CaO _{w.s}	N	
Concentration of HNO₃ – 30.0%								
1	17.23	7.41	2.41	39.11	19.15	2.80	1.02	24.06
Concentration of HNO₃ – 35.0%								
2	17.27	7.51	2.45	39.12	19.35	2.89	1.04	24.44
Concentration of HNO₃ – 40.0%								
3	17.32	7.62	2.48	39.14	19.56	2.92	1.08	24.86
Concentration of HNO₃ – 45.0%								
4	17.38	7.73	2.50	39.22	19.99	2.99	1.11	25.20
Concentration of HNO₃ – 50.0%								
5	17.44	7.84	2.55	39.27	20.15	3.09	1.13	25.35
Concentration of HNO₃ – 55.0%								
6	17.48	7.96	2.58	39.33	20.40	3.18	1.18	25.57
Concentration of HNO₃ – 58.78%								
7	17.59	8.17	2.61	39.52	20.94	3.22	1.20	25.76

In order to eliminate the above drawbacks, in further laboratory experiments the norm of nitric acid was increased to 110% and obtained suspension was neutralized with a $\text{Ca}(\text{OH})_2$ suspension till pH 4.5. This achieves two goals: firstly, the transfer of total P_2O_5 to waste is almost eliminated, and due to this, activated phosphorus fertilizers contain the amount of increases significantly total P_2O_5 ; secondly, increased the content of $\text{P}_2\text{O}_{5\text{ac.c.a.}}$ and $\text{CaO}_{\text{ac.c.a.}}$ in obtained fertilizer samples. When the precipitated suspension is neutralized with calcium hydroxide, the following reactions occur:



Dicalcium phosphate is formed from phosphoric acid and monocalcium phosphate and it precipitates. The order of performing the experiments is the same as the previous ones. The obtained results are presented in Table 2. From the results presented in Table 2, it can be seen that the total P_2O_5 will be equal to 20.22% in the fertilizer sample obtained when 30% nitric acid was used. Degree of transition of P_2O_5 to liquid phase, i.e. its wastage, is only 2.16%. In this case, the amounts of acceptable forms of P_2O_5 and CaO are equal to 10.30 and 22.19%, respectively. $\text{P}_2\text{O}_{5\text{t}}$ in the sample of activated

phosphorus fertilizer formed when of acid concentration is 58.78% at this norm, slightly increases the value of and it is equal to 20.58%. It can be seen that the amounts of acceptable forms of P_2O_5 and CaO are equal to 11.72 and 24.15%, respectively. At this concentration, the amount of P_2O_5 wastage is 2.02%. In general, $\text{P}_2\text{O}_{5\text{water solubility(w.s.)}}$, $\text{CaO}_{\text{w.s.}}$ and N in samples of activated phosphorous fertilizers formed when the concentration of nitric acid increased from 30.0 to 58.78% are observed to increase slightly, and this situation can be explained by the increase of its activity when the acid concentration increases.

In addition to what was discussed above, it can be noted that during the decomposition of MM in nitric acid concentrations of 30-45%, the formation of large foams was observed, while in its concentrations of 50.0-58.78%, the formation of such level of foams was not observed. Therefore, it is desirable to use higher concentrations of acid in the processes of interacting of MM with nitric acid. As can be seen from the data presented in Tables 1 and 2, the increase of amount of $\text{P}_2\text{O}_{5\text{ac.c.a.}}$ and $\text{CaO}_{\text{ac.c.a.}}$ forms in the obtained phosphorus fertilizers depends on the norms and concentrations of nitric acid. The change of acceptable values of $\text{P}_2\text{O}_{5\text{ac.c.a.}}$ in activated phosphorus fertilizers obtained at two different norms nitric acid for increasing its concentration is given in Fig. 1a and 1b. In Fig. 1a and 1b is seen, the form of

Table 2. Chemical composition of activated phosphorus fertilizers obtained after neutralization with $\text{Ca}(\text{OH})_2$ (norm of HNO_3 -110%)

No of experiments	Chemical composition, %							Degree of transition of P_2O_5 to liquid phase, %
	$\text{P}_2\text{O}_{5\text{t}}$	$\text{P}_2\text{O}_{5\text{ac.c.a.}}$	$\text{P}_2\text{O}_{5\text{w.s}}$	CaO_{t}	$\text{CaO}_{\text{ac.c.a.}}$	$\text{CaO}_{\text{w.s}}$	N	
Concentration of HNO_3 – 30.0%								
1	20.22	10.30	2.20	39.63	22.19	2.99	1.09	2.16
Concentration of HNO_3 – 35.0%								
2	20.28	10.43	2.26	39.34	22.41	3.07	1.17	2.12
Concentration of HNO_3 – 40.0%								
3	20.32	10.56	2.31	39.21	22.73	3.13	1.23	2.10
Concentration of HNO_3 – 45.0%								
4	20.37	10.74	2.35	39.11	23.07	3.18	1.26	2.09
Concentration of HNO_3 – 50.0%								
5	20.42	11.02	2.38	39.01	23.39	3.22	1.30	2.06
Concentration of HNO_3 – 55.0%								
6	20.47	11.35	2.42	38.89	23.73	3.27	1.33	2.05
Concentration of HNO_3 – 58.78%								
7	20.58	11.72	2.45	38.87	24.15	3.31	1.35	2.02

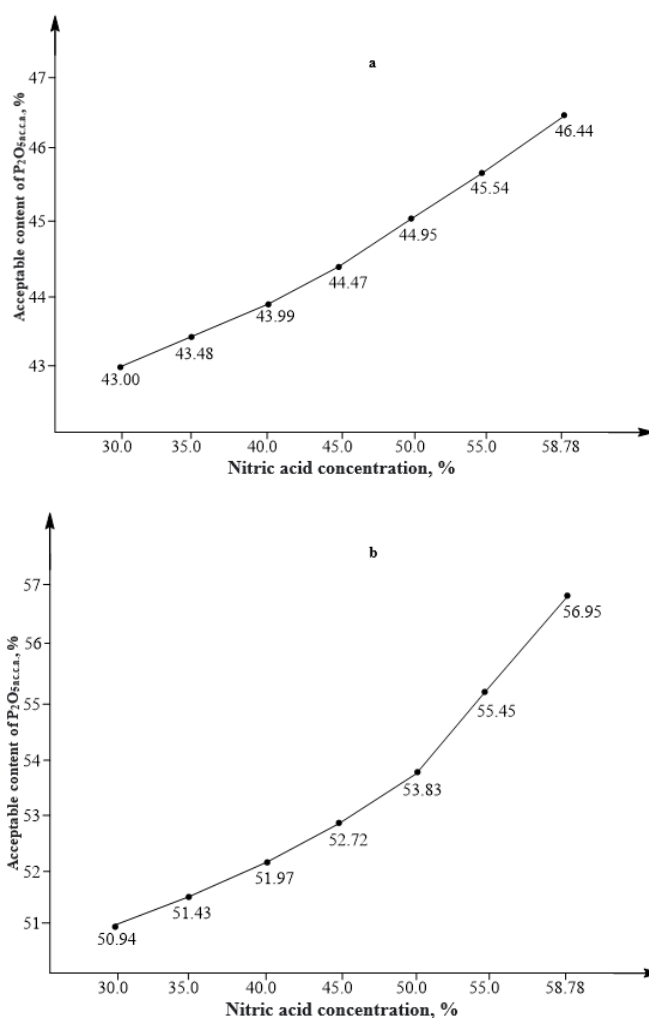
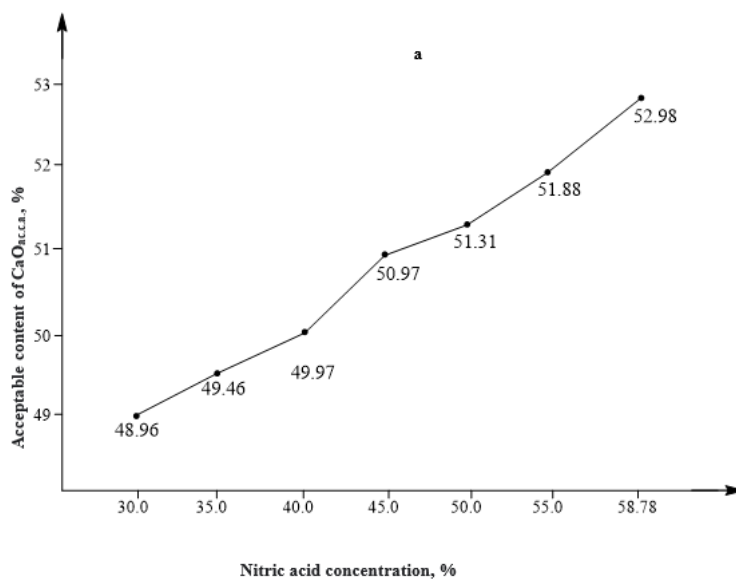


Fig. 1. The effect of HNO₃ concentrations to the acceptable content of P₂O_{5ac.c.a.} in the obtained activated phosphorus fertilizers. a- at the norm of HNO₃-100% and b- at the norm of HNO₃-110%



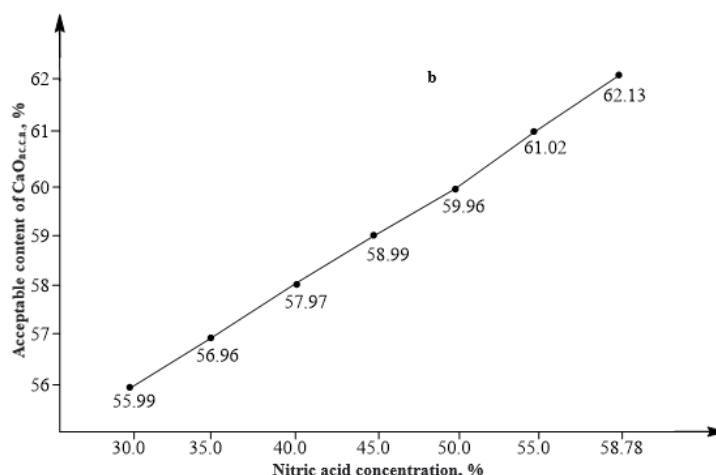


Fig. 2. The effect of HNO₃ concentrations to the acceptable content of CaO_{ac.c.a.} in the obtained activated phosphorus fertilizers. a- at the norm of HNO₃-100% and b- at the norm of HNO₃-110%

P₂O_{5ac.c.a.} in samples of activated phosphorus fertilizers obtained with nitric acid at 100%, it can be seen that the acceptable values of increase from 43.00 to 46.44% depending on the acid concentrations and from 50.94 to 56.95% at 110% norm of acid. The change of acceptable values of CaO_{ac.c.a.} in activated phosphorus fertilizers obtained at two different norms nitric acid for increasing its concentration is given in Fig. 2a and 2b. In Fig. 2a and 2b is seen, the form of CaO_{ac.c.a.} in samples of activated phosphorus-activated fertilizers obtained with nitric acid at 100%, it can be seen that the acceptable values of increase from 48.96 to 55.99% depending on the acid concentrations and from 52.98 to 62.13% at 110% norm of acid.

So, the content of P₂O_{5ac.c.a.} and CaO_{ac.c.a.} in activated phosphorus fertilizers obtained when 110% norm of nitric acid are not less than 50.0%. Samples of activated phosphorus fertilizers quite meet the requirements of agriculture about P₂O_{5t.}, P₂O_{5ac.c.a.} and CaO_{ac.c.a.} forms and this type of phosphorus fertilizers can be successfully used in this field.

4. CONCLUSION

Activated phosphorus fertilizer (APF) was obtained from phosphate waste, called MM, formed during separation of phosphorites into rich fractions, interacting with nitric acid. The optimal concentrations and norm of nitric acid when obtaining activated phosphorus fertilizer were determined. The optimal norm and concentrations of nitric acid are 110% and 50.0-

58.78%, respectively. APF obtained in optimal parameters has the following composition (wt., %): 20.42-20.58-P₂O_{5t.}; 11.02-11.72-P₂O_{5ac.c.a.}; 23.39-24.15-CaO_{ac.c.a.}. Relative content of P₂O_{5ac.c.a.} and CaO_{ac.c.a.} in the obtained APFs are 53.83-56.95% and 59.96-62.13%, respectively.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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