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Production of Complex and Mixed Fertilizers by Acidic Processing of Phosphorites [†]

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Abstract: This article examines the process of digesting phosphorites in an acidic solution to create complicated and mixed fertilizers. This study focuses on improving the nutritional content of phosphorus fertilizers by utilizing mineral acids, such as phosphoric, nitric, and sulfuric acids. In particular, the research looks into how phosphate raw materials, such as poor-quality phosphorites from the Central Kyzylkum region, are treated to create fertilizers that are nitrogen-phosphorous (NPh), phosphorpotassium (PhP), and nitrogen-phosphorus-potassium (NPhP). Phosphorites are broken down by nitric acid in the process, yielding calcium nitrate salts and other byproducts that can be treated further. A scanning electron microscope was used in the investigation to examine the fertilizers' surface microstructure. The findings emphasize how crucial it is to clean and neutralize phosphorus fertilizers in order to enhance product quality and lessen the amount of undesirable salts. The results offer insightful information about enhancing fertilizer output and raising agricultural productivity.

Keywords: complex fertilizer; sulfuric acid; nitrogen-phosphorous (NPh); phosphorpotassium (PhP); nitrogen-phosphorus-potassium (NPhP); scanning electron microscope

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1. Introduction

One interesting way to improve the usage of phosphate raw materials is through the manufacture of double superphosphates using the liquid phase circulation method. This strategy offers a more efficient cycle than conventional approaches, which frequently result in excessive phosphoric acid usage and deterioration due to the use of phosphorites of different quality and chemical–mineral composition. Neutralizing monocalcium phosphate (MCP), sulfating the primary circulating solution, isolating phosphogypsum, and reintegrating into the acid generation cycle are the major phases in the process. Calcium dihydrophosphate, also known as monocalcium phosphate-double superphosphate, crystallizes and separates from the primary circulation solution during this cycle. With a P_2O_5 content of 50–59 wt.%, the resultant double superphosphate represents an impressive accomplishment in phosphate mineral breakdown (98–99 wt.%). Though conceptually similar to chamber or chamber-flow methods, this method is unique in that it uses large amounts of acidic reagents (between 30.0 wt.% and 80.0 wt.%). It also functions primarily in the liquid phase and uses a significant amount of phosphoric acid. One significant benefit of this method's cyclical structure is its capacity to produce high-quality double superphosphates from particular phosphate source materials by processing them with phosphate-sulfuric acid in a single cycle [1–4].

It is crucial to comprehend the fundamental principles of this cyclic technology in order to create salts that are produced in large quantities and used in various agricultural fields. It has been demonstrated that this method can produce salts such as ammonium, potassium, and barium chloride, as well as sodium and ammonium thiosulfates, with high energy efficiency [3].

After the Kingisepp flotation phosphoconcentrate (28.9 wt.% P_2O_5) was stoichiometrically digested with thermal phosphoric acid (TPA), which contains 55–65 wt.% of P_2O_5 and EPA at 40.0–60.0 wt.%, anhydrous MCP crystals were filtered. With a breakdown rate of 95–98 wt.%, the phosphoconcentrate broke down after 1.0–1.5 h at a temperature of 110–130 °C. Fresh phosphoric acid (58.3 wt.% P_2O_5) was cycled up to five times in the phosphoric acid cycling solutions, showing the production of spherical MCP with an average diameter of 70 um. Following five cycles, ammoniation and double superphosphates were added to the separated solid phase. The resulting composition (weight wt.%) was as follows: 50–52.5 wt.% of the absorbed P_2O_5 was found in the 51–54 wt.% P_2O_5 solution overall, and 39–50.7 wt.% was found in the aqueous portion. Free P_2O_5, CaO, and N contents in this solution are 13–14, 2.0–5.9, and 0–8 wt.%, respectively. The processes listed in the patent are utilized to create cyclic double superphosphates: apatite concentrate (TPA with 53 wt.% P_2O_5 or EPA with 53 wt.% P_2O_5 and circulating solution combination) is added after the precipitated product has been neutralized and the circulating solution and cycle have been restarted. The decomposition reaction is carried out at 60 °C for three hours. The suspension is then evaporated for one to four hours at a temperature of 90 to 110 °C, allowing the monomolecular MCP to change from the resultant $Ca(H_2PO_4)_2{\cdot}H_2O$ into the anhydrous form ($Ca(H_2PO_4)$), with a P_2O_5 content of 58 to 60 wt.% in the liquid phase. The final product, which contains 8.6–10.5 wt.% P_2O_5 in free form, is neutralized with chalk ($CaCO_3$) and produces double superphosphates with the following weight-per-weight percentages: 2.8–3.0 $P_2O_{5,free}$, absorbed by the fertilizer P_2O_5 59.0–59.8 wt.%, and 2.8–3.0 wt.% H_2O [1,3].

One way of processing low-quality phosphorites without beneficiation is the cyclic phosphate-hydrochloric acid breakdown that results in MCP. This work includes the following elements: 15.50 wt.% P_2O_5, 27.30 wt.% CaO, 0.96 wt.% MgO, 3.29 wt.% Fe_2O_3, 3.80 wt.% Al_2O_3, and 43.03 percent (including 36.4 wt.% SiO_2). Phosphoric acid is used to treat the phosphorite powder from the Polpinsk mine, creating an insoluble residue. The calcium chloride that is still present after MCP separation is coupled with phosphoric acid, which is introduced to the procedure as the principal solution, and then it is delivered to the cycle as a circulating solution. The unique feature of this technological approach is that the MCP crystallizes alongside the insoluble residue. After washing, the final product will have the following components: total P_2O_5 (38.6–39.0 wt.%), own P_2O_5 (38.1–38.5 wt.%), water P_2O_5 (33.2–23.7 wt.%), 0.3–0.5 wt.% P_2O_5, 14.4 wt.% CaO, 0.3 wt.% MgO, 0.8–1.1 wt.% Cl, 2.0 wt.% Fe_2O_3, and 2.3 wt.% Al_2O_3. The following parameters, where K (rate of decomposition) is not less than 97.3 wt.%, were discovered to be ideal for the decomposition process: a decomposition temperature of 40 °C, a decomposition period of 20 min, and a phosphoric acid ratio of 11.00 wt.% [1].

The Purpose of This Study

To make fertilizers that use the least amount of nitric acid and have the most economic impact, phosphate raw materials with low P_2O_5 concentration and mineralized mass—a waste product of thermal enrichment of phosphorites—have not been integrated. The main objectives of this study are to develop methods for making phosphorus fertilizers and mixed fertilizers (NPh-, PhP-, and NPhP-type fertilizers) based on nitric acids, mineralized mass, and phosphate raw materials from CK (Central Kyzylkum), and to apply the findings and results [5–7].

2. Experimental Section

2.1. Methods of Conducting Experiments

The surface microstructure of the materials was examined using a scanning electron microscope of the type SEM-EVO MA 10 (Zeiss, Oberkochen, Germany). The tests that followed were conducted using a scanning electron microscope. A circular clamp composed of an alloy of metals and aluminum foil with a double-sided adhesive was placed on the surface of the sample powder being examined during the sample preparation procedure, or a portion that had been cut away from the sample was glued. Tablets with a diameter of 7 mm and a thickness of 2 mm were made using the pressing technique for evenly dispersed powders. The upper circular clamp was then used to secure the microscope table. The table was then installed in the vacuum-created microscope's operating chamber. A 15.00 kV voltage (EHT—extra high tension) was applied during the measurement process, and the working distance (WD—working distance) was 8.5 mm. Images of different sizes were collected using the SmartSEM program. Furthermore, images of various microparticles were taken.

2.2. Chemical Processing of Phosphates

UPF (unenriched phosphorite flour) from Central Kyzylkum was used for laboratory work for scientific research. The main elements of these samples are listed in Table 1.

Table 1. The primary chemical constituent of the sample of phosphorite (SEM-EVO MA 10).

Sample Name	Components, wt.%											
	P_2O_5 Total	P_2O_5	CaO	MgO	CO_2	Al_2O_3	Fe_2O_3	SO_3	F	H_2O	CaO: P_2O_5	Unsoluble Fraction
UPF	17.76	3.15	47.51	1.42	13.93	0.98	0.78	3.27	1.48	1.05	2.68	5.27

Laboratory studies on the nitric acid-induced breakdown of phosphate raw materials were carried out in a tubular glass reactor with an electric motor-driven paddle stirrer. This reactor was located within a thermostat to keep the temperature constant. A pre-weighed sample of phosphorite was put to the reactor, and then nitric acid was slowly added. The temperature fluctuated between 35 and 50 °C, depending on the acidity level, and lasted for 25 to 30 min during the dissolution of the phosphorite. The temperature of the reaction mass was maintained constant at 40 °C. The following chemical processes occur when nitric acid breaks down phosphorites (gas release in the reaction-↑; sedimentation-↓;) [8–10]:

$$2Ca_5(PO_4)_3F + 14HNO_3 = 3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + 2HF\uparrow \quad (1)$$

$$Ca_5(PO_4)_3F + 4HNO_3 = 3CaHPO_4 + 2Ca(NO_3)_2 + HF\uparrow \quad (2)$$

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

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + CO_2\uparrow + H_2O \quad (4)$$

$$MgCO_3 + 2HNO_3 = Mg(NO_3)_2 + CO_2\uparrow + H_2O \quad (5)$$

$$2SiO_2 + 10HF = SiF_4\uparrow + H_2SiF_6 + 4H_2O \quad (6)$$

$$R_2O_3 + 6HNO_3 = 2R(NO_3)_3 + 3H_2O, R{=}Al, Fe \quad (7)$$

The suspension medium was then neutralized with a calcium hydroxide suspension until the pH was between 4.5 and 5.0 after the calcium nitrate phosphate acid porridges had broken down. Water was added until the water content was between 70 and 75 wt.%. Water was additionally replaced with a 10 wt.% calcium nitrate solution in order to boost the concentration of the resulting calcium nitrate solution. Every time, neutralization took between 1.5 and 2 h. The solid and liquid components of a neutralized phosphorus fertilizer solution were separated using vacuum filtration. When acidic nitrocalcium phosphate solutions are neutralized, the following steps happen:

$$H_3PO_4 + Ca(OH)_2 = CaHPO_4 \cdot 2H_2O\downarrow \quad (8)$$

$$Ca(H_2PO_4)_2 + Ca(OH)_2 + 2H_2O = 2CaHPO_4 \cdot 2H_2O\downarrow \quad (9)$$

In addition, the following reaction occurs in the suspension:

$$2R(NO_3)_3 + 2H_3PO_4 + 3Ca(OH)_2 = 3Ca(NO_3)_2 + 2RPO_4\downarrow + 6H_2O \quad (10)$$

and these procedures cause a little decline in the quality of phosphorus fertilizer.

Using a 1:1:2 ratio of FXA to water, the resulting wet phosphorus fertilizers were washed once in water that had been heated to between 80 and 90 °C. Wet phosphorus fertilizers produced by washing were dried at 80–90 °C.

Table 2 illustrates how the amount of nitrogen in the fertilizer increased as the concentration of nitric acid reacted with the primary component during fertilizer production. It should be noted that the components were at their greatest concentration in the final product with a nitric acid concentration of 58.78 wt.%. This illustrates that when concentration increases, the solid residue dissolves more efficiently.

Table 2. Chemical make-up of the porridges that broke down UPF with nitric acid.

No.	**The Main Chemical Composition of Porridges, wt.%**						
	$P_2O_{5,tot.}$	**$P_2O_{5,insolu.}$ 2-wt.%**	**P_2O_5**	**$CaO_{tot.}$**	**$CaO_{insolu.}$ 2-wt.%**	**CaO**	**N**
HNO_3—30 wt.%							
1	6.84	5.12	2.81	20.43	16.07	11.36	2.70
HNO_3—35 wt.%							
2	7.18	5.40	2.89	20.85	16.89	11.94	2.89
HNO_3—40 wt.%							
3	7.52	5.67	3.01	21.28	17.45	12.78	2.99
HNO3—45 wt.%							
4	7.85	5.95	3.29	22.09	18.33	13.96	3.37
HNO_3—50 wt.%							
5	8.24	6.26	3.52	23.17	19.69	14.92	3.43
HNO_3—55 wt.%							
6	8.89	6.77	3.89	24.18	21.08	15.90	3.59
HNO_3—58.78 wt.%							
7	9.51	7.27	4.24	25.36	22.35	16.63	3.85

According to these findings, the amounts of total P_2O_5 and total CaO in the porridges made with increasing nitric acid concentrations also increased, from 6.84 to 9.51 wt.% and from 20.43 to 25.36 wt.%, respectively. The levels of absorbed and water-soluble P_2O_5 in the subsequent porridges ranged from 5.12 to 7.27 wt.% and from 2.81 to 4.24 wt.%, respectively. Additionally, the nitric acid porridge formed a significant amount of calcium nitrate salt throughout the process, making it difficult to treat this semi-product. The proportional quantities of absorbed and water-soluble forms of P_2O_5 were found to be between 74.85 and 76.45 wt.% and 41.08 and 44.58 wt.%, respectively, in these porridges.

3. Reaction Results and Discussion of Results

The application to the industrial scale production of various mixed and complex fertilizers based on CK phosphate raw materials and nitric acid, simple phosphorous and this fertilizer, and ammonium nitrate and potassium chloride requires information describing their physico-chemical and mechanical properties. These qualities allow for the efficient use of raw materials and the selection of appropriate sizes for the necessary facilities and equipment.

When it comes to obtaining mixed fertilizers from phosphorus-containing fertilizers, combining phosphorus fertilizers (NPh-, PhP-, and NPhP-fertilizers) yields the following fertilizers. The phosphorous fertilizer, ammonium nitrate, and potassium chloride, together with the other combining components, are all first crushed and passed through a 0.25 mm screen. Pre-calculated samples of ammonium nitrate and phosphorus fertilizer are mixed, blended, and crushed into granules with the right quantity of humidity to create NPh-fertilizer. The NPh-fertilizer is subsequently dried at a temperature between 80 and 90 °C. The same techniques are used to obtain additional types of blended fertilizers.

Different types of phosphorus, calcium, magnesium, sulfur, aluminum, iron, fluorine, carbonates, nitrogen, and potassium are assessed in the raw materials to create phosphorus fertilizers. We look at the main nutrients and how they manifest themselves in blended fertilizers.

Utilizing the complexonometric approach, the titrometer was used to determine the CaO and MgO content of the raw materials and fertilizers produced. Fluorexone and chrome blue were utilized as indicators in the analysis of the solutions, and a 0.05 N solution of trilon-B was used for the titration. The complexonometric approach was also used to study absorbed forms of oxides like Al_2O_3 and Fe_2O_3. The concentration of CO_2 in the samples was assessed quantitatively. Hydrochloric acid was used in this approach to break down the carbonate minerals in the sample.

Nitric acid was used to break down the samples, and then an ionometric method was used to determine how much fluorine was present in the raw materials and final items. This method depends on utilizing a fluorine-selective electrode to directly measure the concentration of fluorine in the solution.

The water content of the samples was determined by drying them to a constant weight in a drying chamber at 100–105 °C.

As can be seen from the radiographic and salt compositions of the fertilizer that are displayed, the PhK-type mixed fertilizers generated in combination with KCl and its UPF-based phosphorus fertilizer are quite different from one another. KCl, $CaHPO_4 \cdot 2H_2O$, francolite ($Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH$), KNO_3, $CaSO_4 \cdot 2H_2O$, $MgHPO_4$, K_2HPO_4, CaF_2, $CaCl_2$, $Ca(NO_3)_2$, iron and aluminum phosphates, Ca_2SiO_4, and the insoluble residue make up the majority of the salt content of the PhK-type mixed fertilizer sample (Table 3).

Table 3. The salt content of PK-type mixed fertilizer is given.

Potassium Mixed Fertilizer	wt.%	PhP-Mixed Fertilizer	wt.%
Francolite ($Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH$)	10.02	$CaCl_2$	3.54
KCl	18.98	Ca_2SiO_4	12.22
$CaHPO_4 \cdot 2H_2O$	10.26	CaF_2	4.43
$CaCO_3$	9.29	$AlPO_4$	4.30
$CaSO_4 \cdot 2H_2O$	7.42	$FePO_4$	2.12
$MgHPO_4$	0.89	An insoluble residue	6.12
K_2HPO_4	4.34	$Ca(NO_3)_2$	6.07

The elemental analysis of the PhK-fertilizer, which was made using KCl and UPF-based phosphorus fertilizer, is shown in Figures 1 and 2. The results of element analysis are shown in Table 4. The table shows the composition of the initial potash fertilizer and the PhP-fertilizer obtained in the process, and their difference is clearly described.

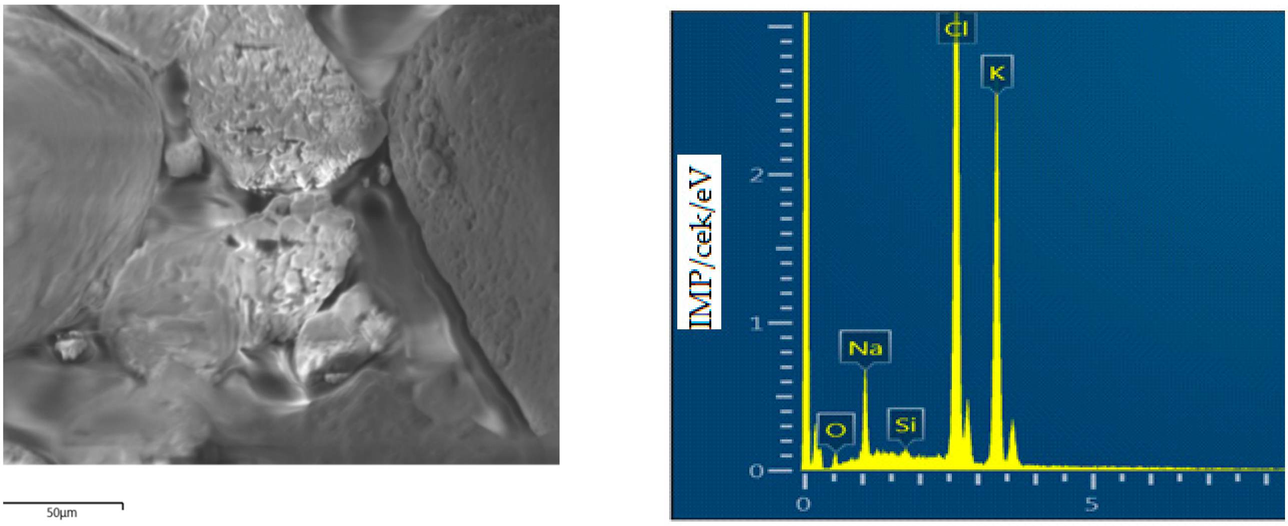

Figure 1. Electron microscopic appearance and elemental analysis of KCl.

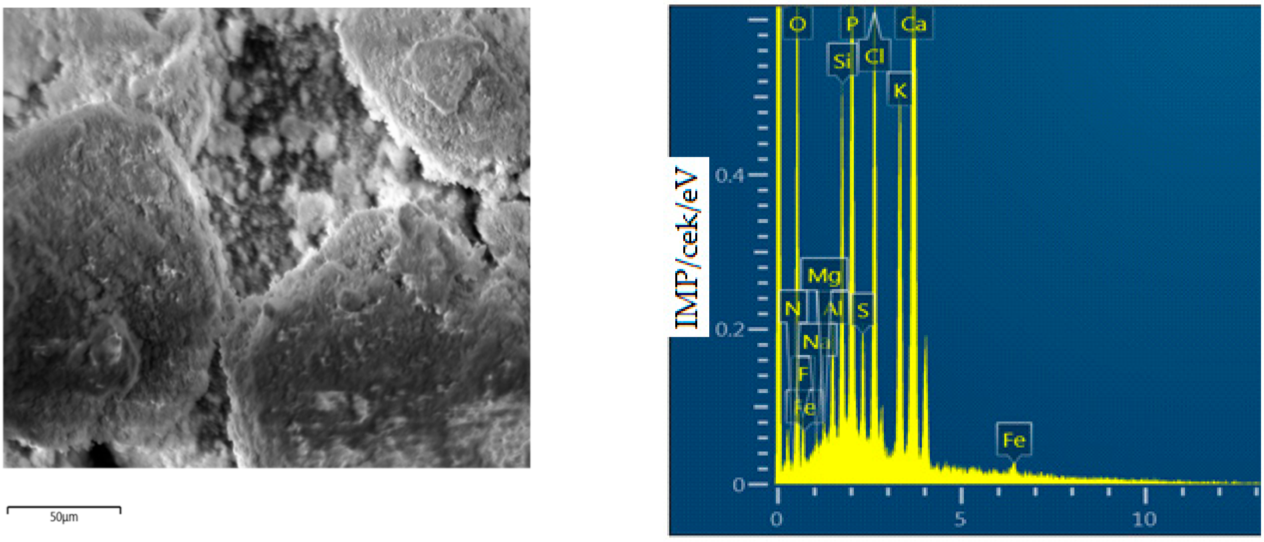

Figure 2. Electron microscope view and elemental analysis composition of PhK-fertilizer obtained together with phosphorus fertilizer based on KCl and UPF.

Table 4. Elemental composition of PhP-fertilizer obtained from phosphoric fertilizer based on KCl.

KCl													
Element	**O**		**Na**		**Si**		**Cl**		**K**		**Others**		
Mass., wt.%	1.42		2.18		0.29		46.33		49.56		0.22		
PhK fertilizer derived from phosphoric fertilizer based on KCl													
Element	N	O	F	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Others
Mass., wt.%	1.29	33.98	2.29	0.17	0.21	1.09	3.50	7.23	1.53	7.34	13.74	25.65	0.93	1.05

4. Conclusions

When CK UPF is processed with nitric acid, the consumption of acid is much higher because of the high calcium modulus in it. At the same time, as a result of processing phosphorite with nitric acid, mainly calcium nitrate salt is formed. It is necessary to remove this salt from phosphorus fertilizer samples, because the more this salt remains in the phosphorus fertilizer sample, the more it causes a negative impact on the product properties of ready and mixed fertilizers obtained on its basis. In order to reduce these negative effects, it is necessary to wash the wet phosphorus fertilizer with water at different amounts and temperatures. Fertilizer sampling uses a UPF raw material sample and different fertilizer samples should be taken according to agricultural requirement.

Different phosphorite samples should also be taken directly from phosphorous fertilizer samples that are regenerated with a small amount of nitric acid (calculated from the raw material to dicalcium phosphate). In addition, it is necessary to receive various mixed fertilizers (NPh-, PhP- and NPhP-type fertilizers) based on phosphorus fertilizers.

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