

Research Article

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Enrichment of low-grade phosphorites by the selective leaching method

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Abstract: The selective leaching method presents a new and innovative approach for the enrichment of low-grade phosphate raw materials. The use of acetic acid as a reagent in the leaching process allows for the selective dissolution of carbonates, potassium-, and aluminum-containing compounds, offering a promising solution for the improvement of the recovery rates of valuable phosphorus compounds. This study presents the results of research on the selective leaching of carbonates from low-grade phosphate raw materials and evaluation of its efficiency using a combination of SEM, energy-dispersion and chemical analysis, X-ray diffraction, differential thermal, IR-Fourier spectroscopic, and mineralogical analysis techniques. The results showed an increase in the content of phosphorus(v) oxide from 14% to 22% through the selective leaching process. The enriched phosphate raw materials were also found to be suitable for the production of phosphorus-containing products. This research highlights the potential of the selective leaching method to overcome the challenges faced in the enrichment of low-grade phosphorites and provide a more efficient and sustainable solution for the industry.

Keywords: enrichment, low-grade phosphorite, selective leaching, acetic acid, carbonates

1 Introduction

Phosphorus is one of the most abundant elements on the Earth and plays an important role in geological and biological processes. In terms of mineralogy, phosphorites

are complex and varied in structure. The element phosphorus is an integral part of all biological/physiological processes in plants and animals. In addition, phosphate minerals are a valuable natural resource widely used as agricultural fertilizers [1].

Phosphorites occur in various geological environments and in many complex mineralogical structures. Representatives of the apatite group predominate in igneous and metamorphic rocks, in particular, phosphorites of the fluorapatite type [2]. Depending on the form of formation, phosphorites are divided into two different genetic groups: marine and terrestrial. Marine phosphorites, in turn, consist of a lithologic classification as follows: fine-grained, granular, nodular, and shell. The assignment of such names is not accidental, since each of them depends on the characteristics of the geological formation, location at stratigraphic levels, and geographical location [3].

One of the large deposits of microgranular phosphorites is the Karatau phosphorite basin in Kazakhstan, which serves as the main source of raw materials for the production of phosphorus compounds in the country. The Karatau phosphorite basin is located in the northeastern massif of the Malyy Karatau Range in South Kazakhstan and extends in a northwestern direction for about 120 km, 25 km wide.

The reserves of phosphorite rocks in the Karatau basin, in terms of P_2O_5 , are about 700 million tons [4]. The Karatau Phosphorite Basin, with a significant share of the world's phosphate reserves, is the leading exporter of phosphates and their derivatives. Most of the phosphorite reserves are sedimentary rocks with a significant amount of carbonate minerals.

In the studies of Bushinskiy [5], the bulk of the Karatau phosphorites is limited by a group of terrigenous-siliceous-carbonate formations. Within this group, two types of phosphorite formations can be named: shale-silica-dolomite and quartzite-shale-limestone (here quartzites are understood as quartz sandstone). Most of the phosphorite deposits of Karatau are representatives of shale-siliceous-dolomite formations. Also here, the phosphorite lining is laid with clay and siliceous-argillaceous

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shales and covered with the thickness of the Tamdinsky dolomites. From this it can be seen that the silicic-dolomite formation contains rich deposits of phosphorites. They arose under the conditions of medium and small deposits and phosphate occurrences.

Currently, Kazphosphate LLP is operating the main ordinary deposits of the Karatau phosphorite basin. At the mining and processing complex “Karatau,” the extraction of the necessary raw materials for the production of yellow phosphorus and wet-process phosphoric acid (WPA) by an open land method from the Kokzhon, Koksus, and Zhanatas deposits is carried out, followed by mechanical enrichment [6]. The reserves of deposits of this raw material are depleted, and the exploration and exploitation of new deposits require significant financial sources. Also, in the process of extraction and subsequent processing, the amount of waste containing a phosphate useful part increases. The disposal of these wastes is not well established. The use of low-grade phosphorite deposits in terms of P_2O_5 , is also not possible, since it requires scientific research and technological solutions for their enrichment.

2 Literature review

Low-grade phosphorites, which contain low concentrations of valuable phosphorus compounds, are a major challenge for the phosphate processing industry. The conventional methods for the enrichment of low-grade phosphorites, such as flotation and roasting, often result in low recovery rates and significant environmental impacts. To address this challenge, the development of new and innovative methods for the enrichment of low-grade phosphorites is needed.

The flotation enrichment method, commonly used in phosphate processing plants, has limitations that hinder its efficiency and effectiveness. One major limitation is the high cost of flotation reagents, which increases the operational expenses of processing plants. The method also generates significant waste, adding to the environmental impact of phosphate processing [7].

Additionally, the high dispersibility of phosphate grains during the flotation process reduces the recovery rates of valuable phosphorus compounds. The flotation properties of calcium and magnesium carbonates, commonly found in the composition of low-grade phosphorites, are similar to those of the phosphate, making it difficult to separate the two components. Contamination of the concentrate with aluminum and iron oxides also limits the efficiency of the flotation process.

Finally, the low volume of products produced and the low content of useful substances in the concentrate, coupled with the complex hardware and technological design required, further highlight the disadvantages of the flotation enrichment method.

Abbes *et al.* [8] and Rizk [9] identified several disadvantages of the calcination method: at high temperatures, the solubility and reactivity of phosphorite decrease. That is, the burnt phosphorite concentrate requires a longer retention period so that it again acquires the solubility of simple phosphorite. This condition may be associated with physical and chemical changes in phosphate rocks at high temperatures during the heat treatment. Thus, it was found that the solubility of chlorine in phosphorous raw materials decreases after calcination [10]. When calcining carbonates/dolomites contained in phosphorites, their complete decomposition should occur. This is because the products formed during their decomposition prevent the use of phosphorite concentrate in the process of subsequent sulfuric acid decomposition. Therefore, it is necessary to extend the calcination time at 900–950°C or increase the temperature. This, in turn, leads to subsidence and melting of the phosphate part [11]. Also, magnesium oxide formed during the decomposition of dolomite during high-temperature treatment can turn into an insoluble compound of magnesium hydroxide [12]. It is known that an excessive amount of magnesium compounds prevents the production of WPA and fertilizers.

The selective leaching method presents a promising solution for the enrichment of low-grade phosphorites. This method uses an acid reagent to selectively dissolve carbonates from low-grade phosphorites, resulting in an enriched concentrate with improved recovery rates of valuable phosphorus compounds. Despite the potential of the selective leaching method, there is limited research on its application for the enrichment of low-grade phosphorites.

The efficiency of dissolving carbonates is high, low cost, technologically simple design, and the possibility of reuse of the used acid demonstrate the advantages of this method. According to the literature review, organic acids such as formic, acetic, lactic, succinic, citric and maleic acids have been used in many studies. The main effectiveness of all acids lies in the fact that they have the property of selective leaching of carbonate compounds in the composition of phosphorite. Among other carboxylic acids used in the enrichment process, there are studies of the effect of lactic and succinic acids on low-grade phosphorites [13,14]. At certain optimal parameters, such as 45°C, the ratio of solid/liquid is equal to 1:7, the

acid concentration is 8%, and the content of phosphoric anhydride increased to 33–34%.

The use of acetic acid in the selective leaching of carbonates from low-grade phosphorites has received growing attention in recent years. As an organic monocarboxylic acid, acetic acid offers several advantages for the enrichment process, including its widespread availability and relatively low cost in the market. The property of acetic acid to selectively dissolve carbonates from low-grade phosphorites makes it a promising reagent for the improvement of the recovery rates of valuable phosphorus compounds.

The purpose of this study is to evaluate the efficiency of the selective leaching method for the enrichment of low-grade phosphorites and to explore new areas for improvement. The results of this study will provide a comprehensive evaluation of the selective leaching method and highlight new areas for exploration in the enrichment of low-grade phosphorites.

3 Materials and methods

Studies on the enrichment of low-grade phosphorites consisted of the following stages: preparation of raw materials, acid leaching, analysis of the composition, and the structure of the products obtained.

3.1 Description of laboratory equipment and acetic acid

A laboratory ball mill MSHL-1 was used to prepare the raw materials. The drum in the mill is filled with balls made of durable steel material and current raw materials. When the drum rotates, the material is crushed as a result of the impact action of the balls. A vibro-sieve of the brand “Analysette” was used to sift the crushed raw materials.

For acid leaching of crushed low-grade phosphorites, a laboratory installation has been designed with an attached magnetic stirrer of the IKA C-MAG HS 7 brand with a fully controlled temperature regime and mixing frequency, and a laboratory ionomer I-160MI was used to control the pH value of the pulp formed when mixing acid and raw materials.

In this regard, acetic acid produced at the JSC Nevinnomysky Azot plant in accordance with the regulatory requirements of TC 9182-086-00203766-2005 was

used as the selected reagent for the enrichment of low-grade phosphorites.

3.2 Instrumental methods of analysis

The following installations were used to carry out instrumental physicochemical analysis methods:

1. The JEOL JSM-6490 LV Electronic Scanning Microscope (Japan) makes it possible to determine the element-weight composition of the sample under study by obtaining micrographs of various materials of inorganic nature and energy dispersion analysis.
2. The IR-Prestige 21 Infrared Fourier Spectrometer (Japan) is a modern device with a single-beam optical system equipped with a quick-release Michelson interferometer. The spectral range includes wavelengths of $7,800\text{--}350\text{ cm}^{-1}$. It is provided with the IRsolution software package for processing the received analytical materials.
3. The NEOPHOT-21 metallographic microscope (Germany) was used to determine the mineralogical structure of low-grade phosphorites. It is equipped with computer software for processing the received micrographs. For the preliminary preparation of raw materials in determining the mineralogical structure, installations of the STRUERS brand (Denmark) were used.
4. The Q-1500 D derivatograph (Hungary) was used for differential thermal analysis of materials. It allows one to study the heat resistance of various materials and the processes of hydration and dehydration.
5. The phase structure of the materials was determined using a Bruker D8 diffractometer (Germany). In addition, DiffracPlusSearch was used to process the data obtained for phase detection and a database of PDF2 radiographs consisting of more than 450,000 known compounds.
6. Thermodynamic analysis of the processes of enrichment of low-grade phosphorites with acetic acid was carried out on a modern, multifunctional software package HSC 9.3, based on the principle of maximum entropy and minimization of Gibbs energy. For heterogeneous reactions, the specified module “Reaction Equations” is used to calculate the change in the values of enthalpy ΔH , entropy ΔS , and Gibbs free energy ΔG in accordance with the following equations [15]:

$$\Delta H_T = \sum S_i H_{i(\text{product})} - \sum S_i H_{i(\text{reagent})} \quad (1)$$

$$\Delta S_T = \sum S_i S_{i(\text{product})} - \sum S_i S_{i(\text{reagent})} \quad (2)$$

$$\Delta G_T = \sum s_i G_{i(\text{product})} - \sum s_i G_{i(\text{reagent})} \quad (3)$$

where s_i is the stoichiometric coefficients.

The possibilities of the online application “Statistics” were used for the statistical processing of the experimental data obtained. Differences were analyzed via a two-tailed paired Student’s t -test; $p < 0.05$ was considered as statistically significant.

3.3 Description of the experimental part and calculation of the main parameters of the process

Crushed raw materials were used for experimental studies. The temperature range of the process was 20–40°C and the enrichment time was 15–45 min. The liquid/solid ratio = 3:1 was determined by calculating the amount of acetic acid required for the complete decomposition of CaCO_3 , MgCO_3 , K_2O , and Al_2O_3 compounds in phosphate raw materials and the volume of water required for dilution, based on its solubility in water ($40 \text{ g}\cdot\text{L}^{-1}$). Also, the density $d = 1.030$ for dilute acetic acid, the pH value was 2.33, and $\text{p}K_a = 6.2 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$. Based on the pH values of the dilute acid and the resulting pulp, the concentration (C , $\text{mol}\cdot\text{L}^{-1}$) was calculated using the expression $[\text{H}^+] = 10^{-\text{pH}}$. Then, using these values, the level of consumption of acetic acid for the enrichment process (α) was calculated by the following equation:

$$\alpha = \frac{(C_1 - C_2)}{C_1} \cdot 100 \quad (4)$$

where C_1 is the concentration of dilute acetic acid ($\text{mol}\cdot\text{L}^{-1}$) and C_2 is the pulp concentration ($\text{mol}\cdot\text{L}^{-1}$).

Based on this value, the reaction rate is calculated using the following equation:

$$v = \frac{\Delta n}{V \Delta \tau} \quad (5)$$

where Δn is the change in the number of moles of starting substances (mol), V is the volume of the mixture (L), and $\Delta \tau$ is the time (min).

The efficiency of the process under study was determined with P_2O_5 (%). The degree of increase in P_2O_5 (%) is calculated by the following equation:

$$\text{P}_2\text{O}_5 \text{ DI} = \left[\frac{B \cdot b}{P \cdot p} \right] \cdot 100 \quad (6)$$

where B is the weight of the enriched raw materials (g), b the amount of P_2O_5 in the enriched raw materials (%), P is

the weight of the initial raw material (g), and p is the amount of P_2O_5 in the initial raw material (%).

The concept of “mineral efficiency” was used as the degree of completeness of the increase in the useful component in the concentrate, the criterion for improving the enrichment process [16]. The determination of this indicator is based on the calculation of efficiency criteria using analytical methods for the yield of enrichment products and the amount of the corresponding component contained in them according to the following equation:

$$E = \frac{\text{P}_2\text{O}_5 \text{ DI} \cdot (100 - B)}{100 - A} \quad (7)$$

where $\text{P}_2\text{O}_5 \text{ DI}$ is the degree of increase in P_2O_5 (%), A is the amount of P_2O_5 in the initial raw material (%), and B is the amount of P_2O_5 in the enriched raw materials (%).

The degree of concentration (K) indicator was also calculated, which determines how much the content of the useful component in the concentrate increased compared to its content in the initial material [16]. The useful component in the concentrate is defined as the ratio of the amount (B) of P_2O_5 in the enriched raw material to the amount (A) of P_2O_5 in the initial raw material according to the following equation:

$$K = \frac{B}{A} \quad (8)$$

where A is the amount of P_2O_5 in the initial raw material (%) and B is the amount of P_2O_5 in the enriched raw materials (%).

4 Results and discussion

4.1 Material composition of low-grade phosphate raw materials

The chemical analysis of low-grade phosphorites is presented in Table 1.

Based on chemical analysis, it was found that the content of phosphoric pentoxide in phosphate raw materials was 14.51%, and those of calcium and magnesium oxides were 31.43% and 2.08%, respectively. The content of aluminum oxide was 1.16% and that of iron oxide was 0.51%.

Micrographs of phosphorites were magnified 40 and 800 times (acceleration voltage: 20 kV), and the element-weight compositions obtained from four different spectra

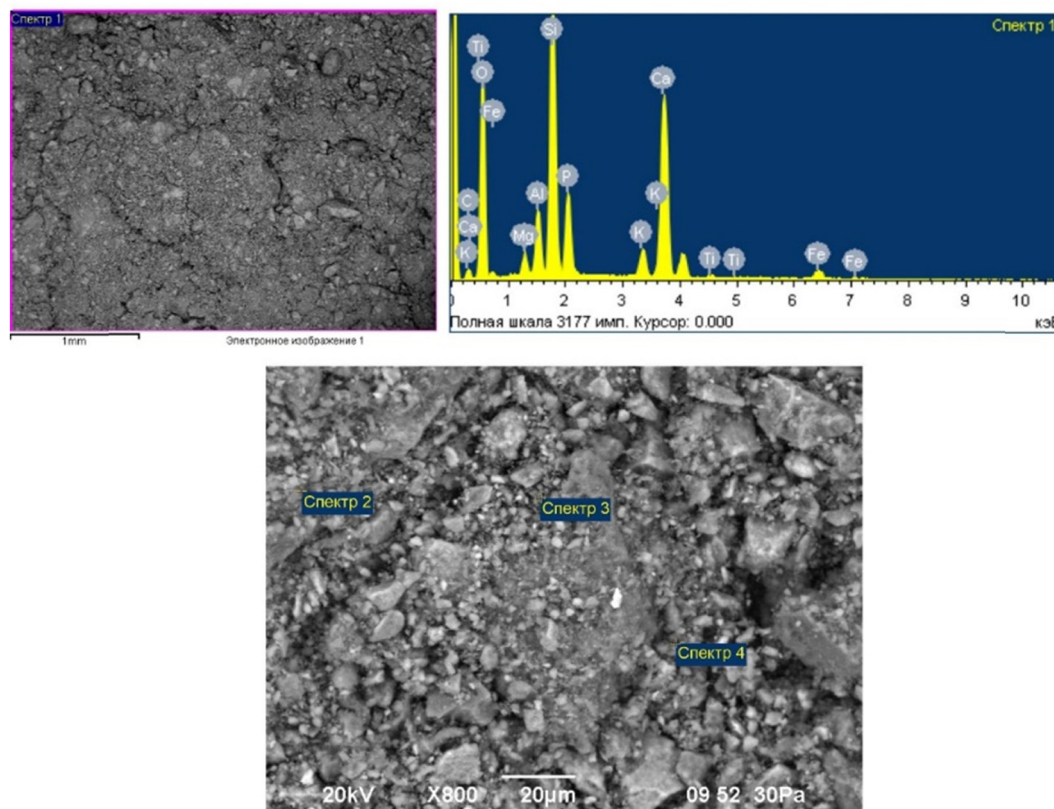


Figure 1: Micrographs of low-grade phosphorites, and the results of energy dispersion analysis.

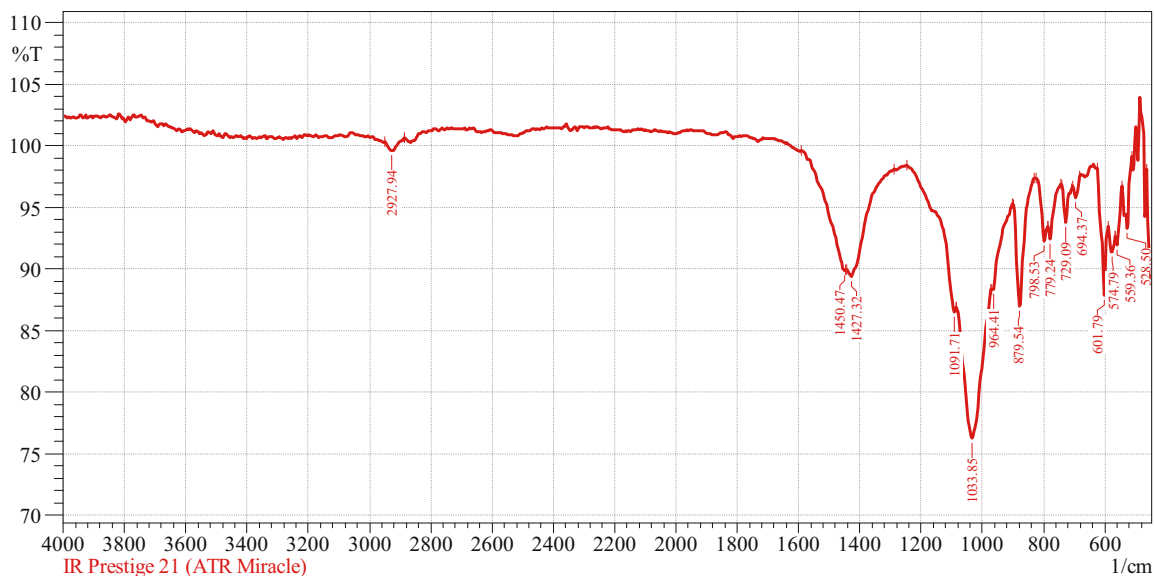


Figure 2: IR spectra of low-grade phosphorites.

These findings demonstrate the complexity of the mineral composition of low-grade phosphorites, highlighting the need for efficient methods to selectively extract valuable phosphorus compounds.

The differential thermal analysis was performed on a Q-1,500 D derivatograph with a maximum heating temperature of 1,000°C, and the results are presented in Figure 4.

Table 3: Peaks of IR spectra

Phase bonding	Peak	Intensity	Corr. intensity	Base (H)	Base (L)	Area	Corr. area
Si–O–Si	455.20	90.145	4.472	462.92	447.49	0.595	0.159
Si–O–Si	528.50	93.260	4.651	543.93	513.07	0.601	0.338
P–F	559.36	91.907	2.136	567.07	547.78	0.559	0.106
P–F	574.79	91.353	1.345	586.36	567.07	0.711	0.076
Al	601.79	87.874	7.127	624.94	590.22	1.235	0.540
Al	694.37	95.813	1.320	705.95	682.80	0.359	0.073
Al	729.09	93.787	2.912	740.67	709.80	0.616	0.158
Al	779.21	92.390	1.672	786.96	744.52	0.949	0.087
Si–O–Si	798.53	92.226	2.389	825.53	786.96	0.905	0.112
Si–O–Si	879.54	86.966	8.850	898.83	829.39	2.152	1.029
Si–O–Si	964.41	88.310	0.410	968.27	902.69	2.205	0.007
Si–O–Si	1,033.85	76.294	11.224	1,083.99	972.12	9.942	3.517
Si–O–Si	1,091.71	86.493	0.941	1,246.02	1,083.99	4.237	–1.281
CO ₃ ^{2–}	1,427.32	89.387	1.358	1,442.75	1,288.45	3.823	0.210
CO ₃ ^{2–}	1,450.47	89.854	0.359	1,589.34	1,446.61	2.951	–0.456
Organic matters	2,927.94	99.586	0.840	2,951.09	2,885.51	–0.015	0.121

The absorption water contained in the test sample is characterized in the temperature range from 90°C to 170°C by endoeffects. When the heating temperature increases to 200°C and above, the crystal transition of quartz occurs. Dehydration of clay compounds occurs in the temperature range of 520–570°C, and at temperature values of 700°C and above, carbonate compounds decompose. Exothermic effects in the temperature range of 940–980°C lead to crystallization of aluminate compounds [21]. According to the derivatogram, the duration of the analysis is 90 min, and there was a loss of 8.44% of the mass of the raw material.

The initial processing of the low-grade phosphorite sample was performed using a Struers device, followed by an examination of the sample micrograph using a metallographic microscope. The obtained results are depicted in Figure 5.

The analysis of the studied sample revealed the presence of white-shiny calcite and yellowish dolomite minerals. These minerals are commonly found in sedimentary metamorphosed rocks and are difficult to distinguish due to their similar properties, such as three-sided perfect mineral fusion along the rhombohedron. However, dolomite is harder than calcite and has a higher density [22–24]. The results also

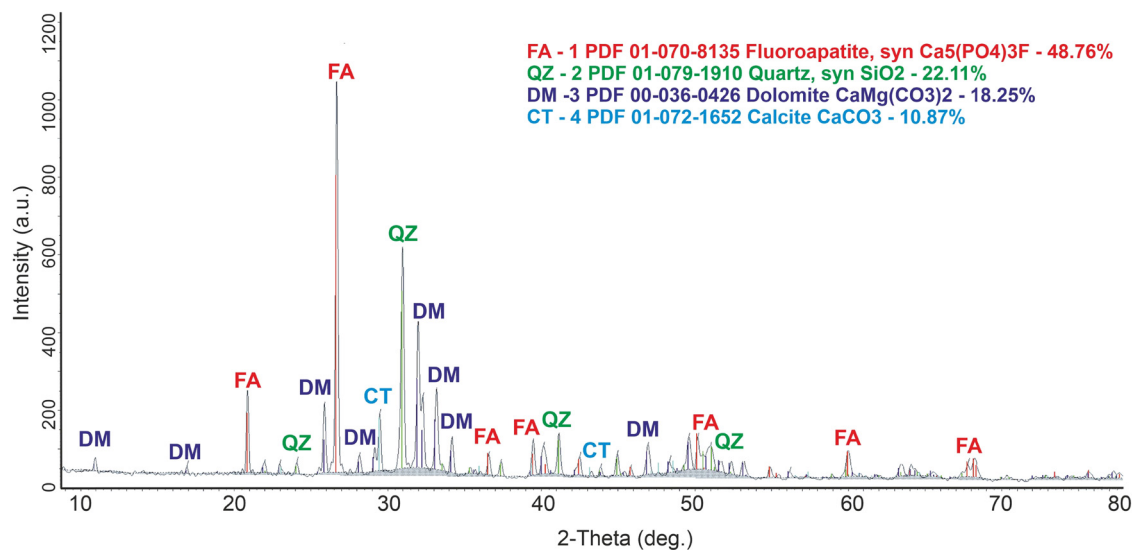


Figure 3: X-ray diffraction peaks of low-grade phosphorites.

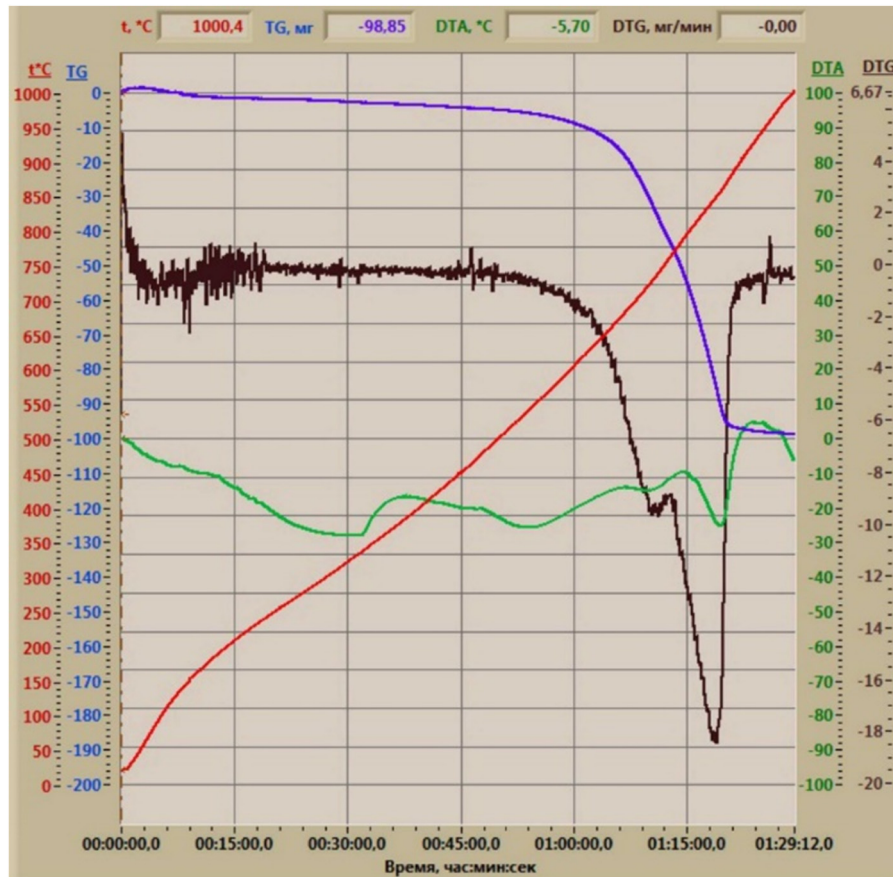
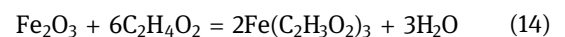
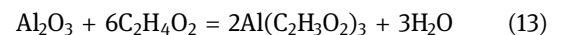
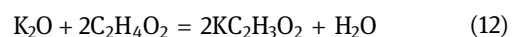
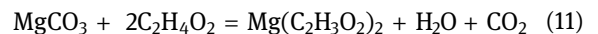
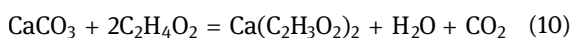
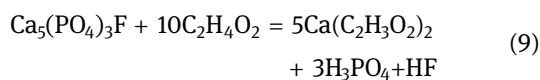


Figure 4: Derivatogram of low-grade phosphorites.

showed the presence of quartz, a trigonal mineral with a refractive index of 1.544, a hardness of 7, and a density of $2.6 \text{ g}\cdot\text{cm}^{-3}$. Quartz is commonly found in sedimentary rocks in combination with dolomites and has a cellular fracture and no mineral integration property [25]. The SEM analysis also revealed the presence of aluminosilicate minerals, such as muscovite, on a small scale, with an elastic and monoclinic syngonic classification, a refractive index of 1.6, and layered and lamellar crystal types [26].

4.2 Chemistry and thermodynamic analysis of the selective leaching process

The reactions of the interaction of phosphate raw materials and the compounds contained therein with acetic acid take place according to the following equations:



The reaction in Eq. 9 of fluorapatite and acetic acid proceeds with the release of calcium acetate, phosphoric

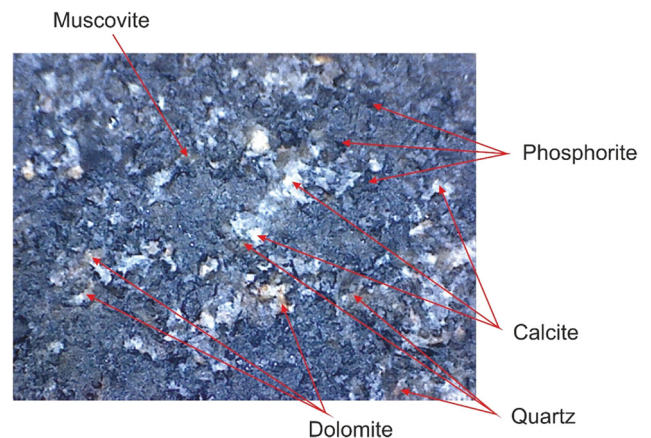


Figure 5: Mineralogical composition of low-grade phosphorites.

acid, and hydrogen fluoride, which pass into the gas phase. As a result of the interaction of calcium and magnesium carbonates with acetic acid, an exchange reaction occurs, where acetate salts, water, and carbon dioxide are released as a product. Since potassium and aluminate compounds are present in the phosphate raw materials in the form of nepheline, their interaction with acetic acid occurs with the formation of potassium acetate and aluminum products. The proposed chemical reactions are based on known data.

In the process of selective leaching under the action of acetic acid, carbonate, potassium, and aluminate compounds contained in phosphate raw materials are involved. They are present in the solution in the form of acetate salts during the exchange reaction, and in the insoluble part of the pulp, the phosphate part, compounds of silicon, iron, and calcium fluoride remain. Acetic acid, due to its chemical properties, is a monocarboxylic acid, belongs to the number of proton polar solvents. This, in turn, is based on the fact that acetic acid contains a hydrogen ion capable of splitting in the form of a proton H^+ ; acetic acid has a $pK_a = 1.8 \times 10^{-5}$. In other studies [27–32], these data have been substantiated and presented. The results of the thermodynamic analysis of these chemical reactions and their mechanisms are presented in Table 4.

Based on the above, it can be said that the reaction of fluorapatite and acetic acid does not proceed from a thermodynamic point of view. Reactions 10 and 11, where interactions of carbonates with acid are described, occur at low temperatures; increase in temperature leads to a decrease in the Gibbs energy. The decomposition of potassium and aluminum oxides in acetic acid can be explained by the fact that these compounds are present in the phosphate raw materials in the form of a nepheline mineral. Nepheline is a mineral, sodium/potassium aluminosilicate $(Na,K)AlSiO_4$ [26], formed in rocks. In studies conducted by the Academy of Sciences of the USSR

[33], it was found that nepheline is partially soluble in acetic acid. Thermodynamic probability of the interaction of calcium and magnesium carbonates, potassium, and aluminum oxides with acetic acid in phosphate raw materials occurs according to the following scheme: $CaCO_3 > MgCO_3 > Al_2O_3 > K_2O$. Obviously, this information complements the data on the thermodynamic probability of these reactions. The reaction of iron oxide with acetic acid also has positive Gibbs free energy values and therefore does not proceed.

4.3 Experimental data of the selective leaching process

The results of experimental studies on the enrichment of low-grade phosphorites with acetic acid are presented in Tables 5 and 6 and in Figure 6.

It was found that an increase in the reaction temperature during the enrichment of phosphorites affects the increase in the reaction rate and the level of acetic acid (α) consumption. Thus, with increasing temperature and time, the indicators of P_2O_5 and P_2O_5DI also increase. However, at $40^\circ C$ and 20–30 min, the amount of phosphorus(v) oxide increases and reaches a maximum value at 40 min; subsequently, this indicator decreases or remains unchanged at 50 min. This phenomenon can be explained by the fact that the establishment of equilibrium in these values or calcium (magnesium) acetates formed as a result of the interaction of dolomite and acetic acid inside the pulp inhibit the further course of the process. To verify this fact, the Pilling–Bedworth ratio can be used [34], according to the following equation:

$$PB_{ratio} = 2 \frac{M_{Ca(CH_3COO)_2}/d_{Ca(CH_3COO)_2}}{M_{Ca_5(PO_4)_3F}/d_{Ca_5(PO_4)_3F}} \quad (15)$$

Table 4: Thermodynamic analysis of the selective leaching process

Reaction no.	Gibbs free energy ΔG (kcal)										
	Temperature ($^\circ C$)										
	0	10	20	30	40	50	60	70	80	90	100
(1)	80.82	83.10	85.52	88.08	90.77	93.36	96.01	98.78	101.67	104.68	107.8
(2)	−0.85	−0.79	−0.70	−0.59	−0.46	−0.30	−0.12	0.08	0.31	0.56	0.84
(3)	−8.25	−7.79	−7.40	−7.06	−6.75	−6.48	−6.23	−6.00	−5.80	−5.61	−5.44
(4)	−100.90	−100.90	−100.92	−100.96	−101.01	−101.07	−101.13	−101.20	−101.27	−101.34	−101.41
(5)	−14.05	−10.45	−7.01	−3.68	−0.45	2.70	5.79	8.84	11.83	14.79	17.70
(6)	37.60	40.04	42.47	45.01	47.62	50.30	53.05	55.87	58.76	61.72	64.74

Table 5: Experimental data on the enrichment of low-grade phosphorites with acetic acid

Temperature (°C)	Time (min)	pH	C (mol·L ⁻¹)	v (mol·L ⁻¹ ·min ⁻¹)	A (%)
20	10	3.452	0.00035318	0.18300	92.44
	20	3.487	0.00032583	0.09208	93.03
	30	3.515	0.00030549	0.06167	93.46
	40	3.528	0.00029648	0.04635	93.66
	50	3.533	0.00029308	0.03711	93.73
30	10	3.538	0.00028973	0.18569	93.80
	20	3.540	0.00028840	0.09287	93.83
	30	3.542	0.00028707	0.06193	93.86
	40	3.544	0.00028575	0.04646	93.89
	50	3.545	0.00028510	0.03717	93.90
40	10	3.567	0.00027101	0.18648	94.20
	20	3.570	0.00026915	0.09328	94.24
	30	3.584	0.00026061	0.06230	94.42
	40	3.597	0.00025292	0.04681	94.59
	50	3.611	0.00024490	0.03751	94.76

where 2 is the number of calcium acetate molecules; $M_{\text{Ca}(\text{CH}_3\text{COO})_2}$ is the molecular weight of calcium acetate; $d_{\text{Ca}(\text{CH}_3\text{COO})_2}$ is the density of calcium acetate; $M_{\text{Ca}_5(\text{PO}_4)_3\text{F}}$ is the molecular weight of fluorapatite; and $d_{\text{Ca}_5(\text{PO}_4)_3\text{F}}$ is the density of fluorapatite.

The value of PB_{ratio} is calculated to be 1.24 and, accordingly, it indicates that the acetate salts formed during the reaction have a significant diffusion resistance to the process under study, since this value lies within $2.5 \geq \text{PB}_{\text{ratio}} \geq 1$.

The revealed optimal regime parameters allow the enriching of low-grade phosphorites with acetic acid. In other studies on the enrichment of phosphorites [13,27,35–37], the duration of the acetic acid enrichment process is 40–60 min, and the process temperature is studied in the range of 20–70°C, with a process

duration of 40 min; at a temperature of more than 40°C, the indicators such as the amount of P_2O_5 and the output remain unchanged. The data obtained coincide with the data of studies on the enrichment of phosphorites and indicate the uniformity of the studies carried out.

4.4 Physico-chemical characteristics of enriched raw materials and assessment of their suitability for phosphorus production

This section presents the results of a study of the physicochemical properties of concentrates obtained during

Table 6: Technological indicators of the process of enrichment of low-grade phosphorites with acetic acid

Temperature (°C)	Time (min)	P_2O_5 (%)	P_2O_5 passed into solution (%)	E (%)	K	P_2O_5 DI (%)	Standard deviations for P_2O_5 DI
20	10	18.54	—	54.16	1.26	56.71	0.86
	20	18.86	—	54.96	1.28	57.77	1.02
	30	19.28	—	55.50	1.31	58.64	0.74
	40	19.13	—	55.42	1.29	58.45	1.04
	50	19.04	—	55.36	1.29	58.32	1.10
30	10	20.16	—	59.48	1.37	63.54	0.39
	20	20.73	—	59.79	1.40	64.33	0.91
	30	20.86	—	60.35	1.41	65.04	0.88
	40	20.82	—	60.53	1.41	65.20	0.71
	50	20.72	0.19	60.52	1.40	65.11	0.94
40	10	21.43	0.37	63.30	1.45	68.71	0.43
	20	21.85	0.41	63.28	1.48	69.06	0.97
	30	22.11	0.34	64.68	1.50	70.82	1.08
	40	22.21	0.37	65.27	1.51	71.56	0.69
	50	22.18	0.32	64.48	1.50	70.67	0.83

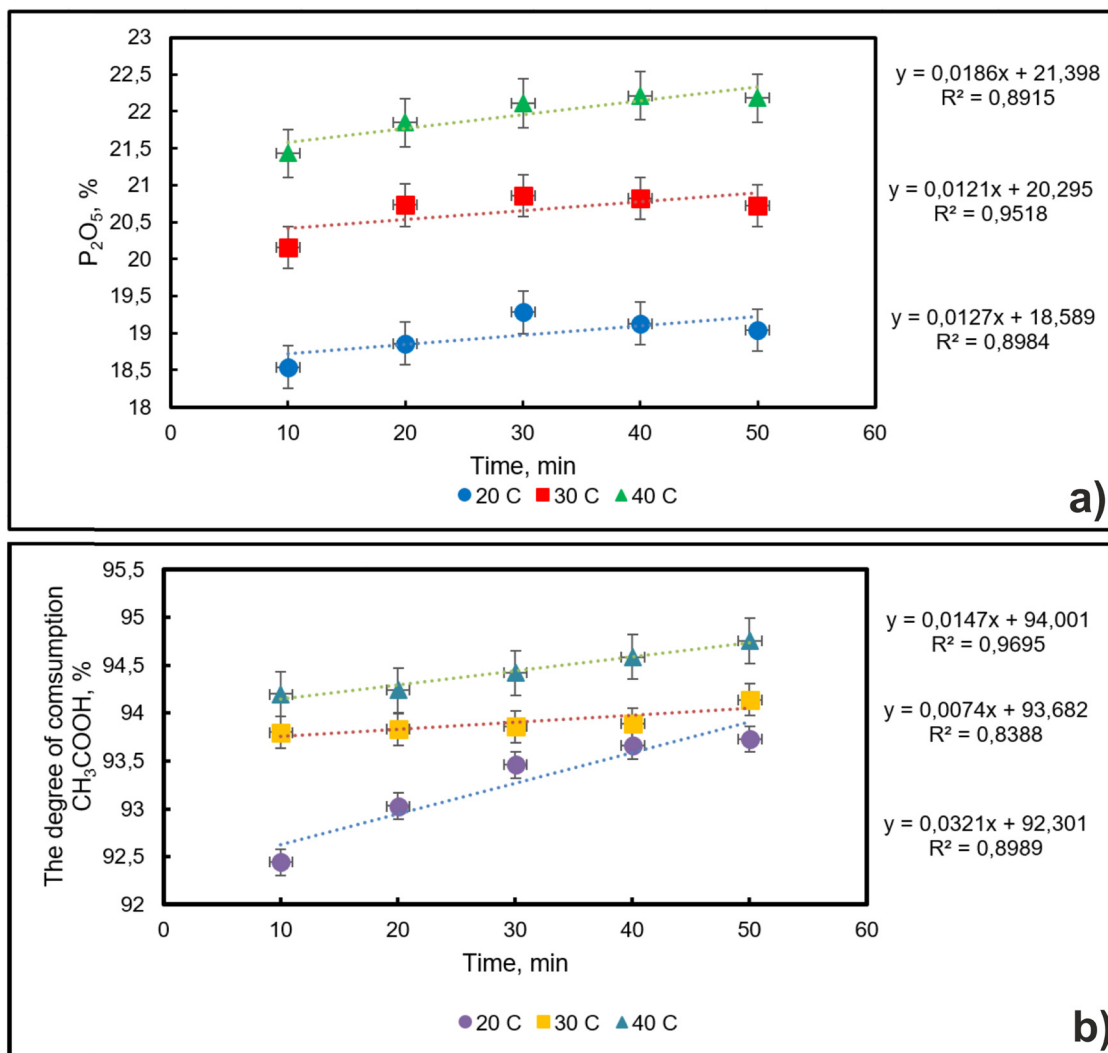


Figure 6: Acetic acid enrichment of low-grade phosphorites: (a) dependence of the increase in P_2O_5 on time; and (b) dependence of the acetic acid consumption level on time.

the enrichment of low-grade phosphate raw materials with acetic acid, as well as data on their suitability for the production of yellow phosphorus and phosphorus-containing fertilizers. The results of the chemical analysis of the enriched concentrate are presented in Table 7.

It can be seen from the table data that when the content of the main compounds in the composition of the enriched raw materials is compared with the results of the primary chemical analysis, a significant increase in the content of phosphoric pentoxide is observed in the enriched concentrates. Also, a decrease in the amount of magnesium and aluminum oxides indicates the course of the enrichment process with acetic acid. The phase composition of the enriched phosphorite is shown in Figure 7.

The phase composition is represented by the main compounds in the form of fluorapatite and silicon dioxide.

Compared with the phase composition of the feedstock, there are no carbonates or potassium- and aluminum-containing compounds in the final enriched product.

The phosphate raw materials required for the production of electrothermal phosphorus in Kazakhstan are regulated by “ST RK 2213-2012-Karatau crushed phosphate raw materials: Technical conditions,” and indicators of raw materials necessary for the production of phosphoric acid “ST RK 2211-2012-Karatau fine-grained phosphate raw

Table 7: Chemical composition of enriched raw materials

P_2O_5	CaO	MgO	K_2O	Al_2O_3	Fe_2O_3	SiO_2
22.19%	32.40%	0.19%	0.08%	0.07%	1.76%	33.05%

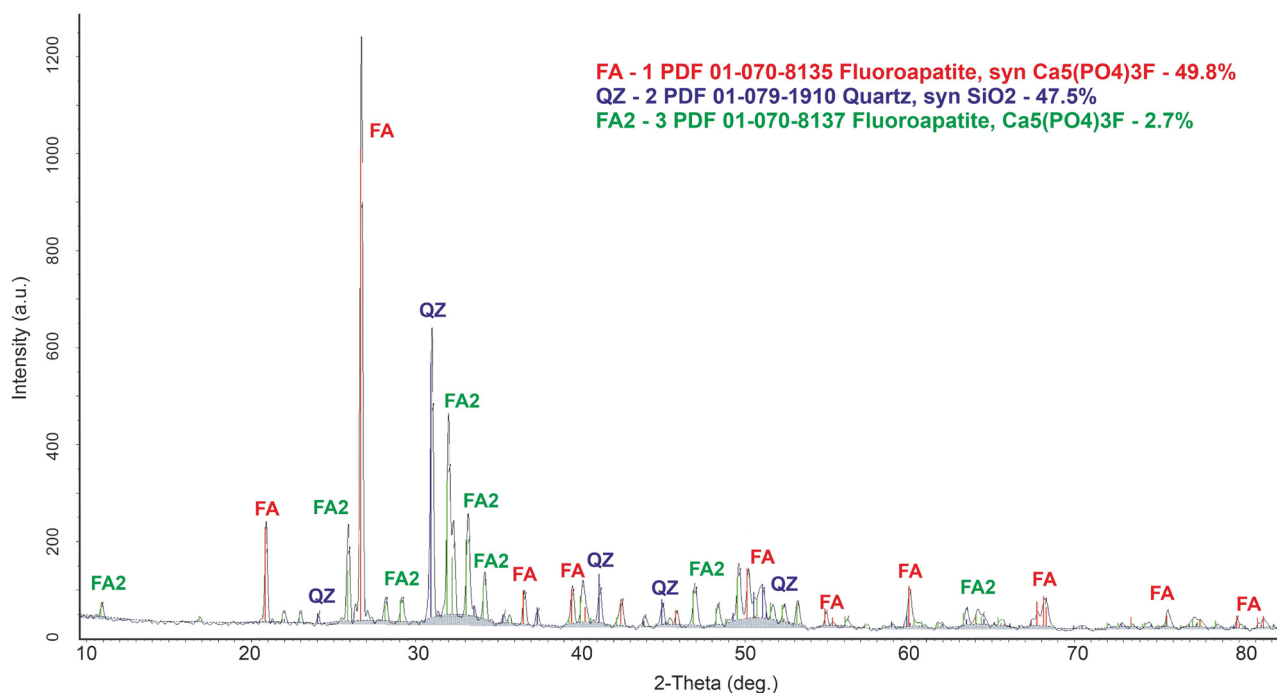


Figure 7: X-ray diffraction peaks of enriched phosphorites.

materials: Technical conditions.” The raw materials required for the production of electrothermal phosphorus are designated as FKT (Phosphorite Karatau for heat treatment), and the raw materials subjected to acid treatment are designated as FKE (Phosphorite Karatau for extraction).

Technical requirements for phosphate raw materials are based on technical capabilities and economic optimality during its mechanical, thermal, or extraction processing. The indicator with the greatest importance in phosphate raw materials is the content of phosphoric pentoxide (P_2O_5). At the same time, the concentrate enriched with acetic acid, according to the indication of P_2O_5 in the composition, corresponds to the grades FKT-1 and FKE-2.1.

5 Conclusions

The results of the studies indicate that the process of selective leaching with acetic acid effectively removes all carbonate compounds from concentrates and the following:

1. The concentration of phosphoric pentoxide increased from 14% to 22%.
2. The leaching process takes 30–40 min and takes place at a temperature range of 30–40°C. However, an increase in temperature results in the solubilization of phosphoric anhydride.

3. Along with carbonates, potassium and aluminum compounds also contribute to the leaching process. These compounds are present in the form of nepheline in the structure of phosphorites and are partially dissolved by acetic acid. This has been confirmed through thermodynamic analysis and experimental studies.
4. By removing carbonates and nepheline, phosphate raw materials can be utilized in the production of phosphorus through electrothermal sublimation and in the production of phosphoric acid through sulfuric acid treatment. This will increase the economic efficiency of these industries as the heat treatment process can be abandoned and the consumption of sulfuric acid can be reduced.
5. This study provides valuable information for the improvement of the processing of low-grade phosphorites and the efficient utilization of phosphate resources.

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