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Research of the Process of Obtaining Monocalcium Phosphate from Unconditional Phosphate Raw Materials

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Abstract: The article presents methods for processing low-grade phosphate raw materials from the Chilisay deposit using a circulation method to produce mineral fertilizers and feed monocalcium phosphate. A study was conducted on the process of obtaining high-quality monocalcium phosphate, and optimal parameters for the decomposition of low-grade phosphate raw materials were determined. Based on the research, it was established that for the decomposition of phosphate raw materials, phosphoric acid with a concentration of 36–42% P_2O_5 should be used; the recycle phosphoric acid rate should be 540–560% of the stoichiometric amount required for the formation of monocalcium phosphate (MCP); the decomposition temperature should be 95–100 °C; the decomposition duration should be 40–50 min; the filtration temperature of the insoluble residue should be 85–90 °C; the crystallization temperature of MCP should be 40–45 °C; and the crystallization duration should be 85–90 min. For the sulfation of the mother solution and the production of recycle phosphoric acid, sulfuric acid with a concentration of 86–93% H_2SO_4 should be used; the sulfuric acid rate should be 95–100% of the stoichiometric amount required for the decomposition of dissolved $Ca(H_2PO_4)_2$. After drying the wet residue, monocalcium phosphate was obtained with the following composition: P_2O_5—55%, Ca—18.01%, H_2O—4.0%, F—0.01%, As—0.004%, Pb—0.002%. The obtained monocalcium phosphate is used in agriculture as a mineral fertilizer and feed monocalcium phosphate.

Keywords: phosphate raw materials; phosphoric acid; mineral fertilizers; monocalcium phosphate

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1. Introduction

Kazakhstan possesses vast reserves of unconditional phosphate raw materials for the production of mineral fertilizers and feed-grade monocalcium phosphate [1,2]. The Chilisay deposit in the Aktobe region contains large reserves of ore amounting to 1.13 billion tons, with a P_2O_5 content of 16.51–19.36% [3,4]. The estimated resource volume is 1.128 billion tons of ore with a P_2O_5 content of 10.28% (or 116 million tons of P_2O_5). Currently, three known deposits are being developed: Chulaktau, Aksay, and Zhanatas, with combined reserves reaching 1.5 billion tons [5].

Kazphosphate LLP (Kazakhstan, Taraz city), specifically Mineral Fertilizer Plant, produces mineral fertilizers such as simple superphosphate, ammophos, sulfammophos,

nitroammophos, and feed defluorinated phosphates (feed tricalcium phosphate with 27% P_2O_5) for agriculture by processing standard phosphate ores (21–25%).

The Chilisay phosphorites are characterized by a variable mineral composition. Their quality varies significantly depending on the content of harmful impurities, which reduce the technological parameters of the products.

The enrichment of phosphate ores has been extensively studied in the literature. Various enrichment schemes have been explored, as well as laboratory and semi-industrial tests for processing Chilisay phosphorites [6–8]. However, due to high costs and the inefficiency of enriching low-grade phosphate raw materials, this technology is not used in production. To address the challenges of processing unconditional raw materials and improve efficiency, a circulation technology for processing Chilisay phosphorites is proposed. This eliminates enrichment costs and allows for the production of pure mineral fertilizers and feed-defluorinated monocalcium phosphate.

Recently, methods for enriching sandy and shelly phosphorites have been developed [9]. However, for phosphorites containing a low amount of monomineralic grains, even with fine grinding, these methods are ineffective [10].

In [11], a method for decomposing phosphorites from the Karatau and Chilisay deposits using potassium bisulfate was proposed. Experimental data describe the kinetics of phosphorites decomposition using 5–25% $KHSO_4$ solutions at temperatures of 25, 50, and 70 °C with a significant excess of the costly potassium bisulfate reagent.

Studies [12,13] suggest the possibility of producing feed defluorinated phosphates from low-grade phosphorites of Karatau and Chilisay using corrective additives in the form of acidic phosphates. A mechanochemical method for producing fertilizers with a high content (up to 100%) of citrate-soluble P_2O_5 was proposed, including the use of humic compounds [14] and a method for the extractive processing of low-grade phosphate raw materials [15,16].

Currently, research is being conducted on the technology of processing low-grade phosphorites using humate compounds, which promote rapid plant growth and improve soil fertility [17,18].

Particular attention is given to the comprehensive processing of technogenic waste [19,20]. Kazphosphate's Novo-Dzhambul Phosphorus Plant and Mineral Fertilizer Plant have accumulated approximately 7.0 million tons of industrial waste—slag, dust, and phosphogypsum. These waste materials increase by 10% annually, polluting the atmosphere and causing environmental damage in the regions where the plants are located [21].

In this context, the problem of utilizing solid and liquid industrial waste and unconditional phosphate raw materials into mineral fertilizers is highly relevant.

Phosphorites ($Ca_3(PO_4)_2$) and apatites—fluorapatite ($Ca_3(PO_4)_2 \cdot CaF_2$) and hydroxyapatite ($Ca_5(PO_4)_3OH$)—are used as raw materials for the production of mineral fertilizers. Phosphate ores are sedimentary rocks cemented by calcium phosphates [22–24].

During the preparation and processing of these ores (crushing, grinding, screening, transportation, etc.), losses exceed 40%. Fine fractions, constituting 35–44% of the mined ore, accumulate in waste dumps [25–28].

Enriched apatite and phosphate concentrates are used to produce mineral fertilizers and phosphorus [29–31]. Studies have examined the potential use of low-grade phosphorites from the Zhanatas deposit and phosphate-siliceous shales during agglomeration roasting with oil refining waste [32].

Kazakhstan's mineral fertilizer producers are fully supplied with primary raw materials and are annually increasing their exports to foreign markets [33,34]. Additionally, improving the physicochemical properties of mineral fertilizers can significantly enhance

their effectiveness and prevent losses during application [35,36]. It also improves the consumer properties of granular mineral fertilizers [37,38].

The quality of phosphorus-containing fertilizers receives special attention. The application rate of fertilizers largely depends on the composition and structure of the soil, particularly in semi-sandy and sandy soils [39]. In such cases, encapsulating fertilizers allows for effective control of nutrient release, aligning with plant needs and delivering the necessary substances at the optimal time [40].

The use of modified polyelectrolyte derivatives based on polyacrylonitrile (PAN) in the production of superphosphate and double superphosphate not only improves the operational properties of mineral fertilizers but also increases the yield of agricultural crops [41–45]. Additionally, they form a thin film on the surface of complex fertilizer particles [46,47].

The study determined standard thermal effects during changes in the system's enthalpy, standard changes in system entropy, and Gibbs energy in the range of 333–363K during the decomposition of Cottrell dust with sulfuric acid, which reacts chemically with potassium-calcium phosphate [48–51].

Thus, the production of high-quality monocalcium phosphate from unconditional phosphate raw materials remains insufficiently studied, with little information available in scientific sources. Research and production of high-quality defluorinated monocalcium phosphate from unconditional phosphate raw materials are relevant and of scientific interest.

To obtain high-quality monocalcium phosphate, determine optimal parameters for the decomposition of low-grade phosphate raw materials, and increase product yield, it is necessary to: study the composition of phosphate raw materials; develop a circulation technology for phosphate processing; reduce foam formation; and determine the optimal parameters for MCP production, including phosphoric acid concentration and rate.

2. Research Methodology

In accordance with the logic of scientific research on this topic, the authors have chosen a methodology for conducting the study. It is a combination of theoretical and experimental methods, which make it possible to reliably study such a complex problem of processing low-grade phosphate raw materials by the circulation method using phosphoric acid.

Phosphorite samples No. 1 and No. 2 were used to study the elemental and mineralogical composition. Elemental analysis was performed on a JSM-6490LV scanning electron microscope (JEOL Ltd., Tokyo, Japan) with an INCAPentaFET-x3 energy dispersive X-ray microanalysis system (Oxford Instruments, Abingdon, Oxfordshire, UK). X-ray diffraction analysis was carried out using the automated diffractometer DRON-3 with $Cu_{K\alpha}$-radiation and a β-filter. Conditions for recording diffraction patterns were: U = 35 kV, I = 20 mA, recording θ-2θ, and detector 2 deg/min. Semi-quantitative X-ray phase analysis was performed using diffraction patterns of powder samples via the method of equal-weighed portions and artificial mixtures. Quantitative ratios of crystalline phases were determined. Diffraction patterns were interpreted using data from the ICDD card index: powder diffraction data base PDF2 (Powder Diffraction File) Release 2022 and diffraction patterns of minerals free of impurities.

The processes of acid decomposition of phosphate raw materials, dissolution, and crystallization of monocalcium phosphate under the influence of temperatures and excess phosphoric acid were studied. The experiments were conducted using a laboratory thermostatted installation. Chilisay deposit phosphorites and phosphoric acid were used in the studies.

During the experiment, the calculated phosphorite sample was decomposed using a calculated amount of phosphoric acid. To obtain monocalcium phosphate from the Chilisay phosphorite, a mixture of extraction and thermal phosphoric acid was used in a 2:1 ratio, with a H_3PO_4 concentration of 50–58% (36.2–42.0% P_2O_5). Sulfuric acid with a concentration of 93% was used to sulfate the solution and obtain gypsum.

The consumption rate of phosphoric acid, with a fivefold excess, was calculated based on the content of CaO, MgO, Fe_2O_3, and AI_2O_3 in the phosphorite, amounting to 80.16 g H_3PO_4 per 100 g of the phosphorite.

Figure 1 shows the spectral analysis of Chilisay deposit phosphorites. It is evident that the elemental analysis of phosphorite differs in the content (sample No. 1) of the following elements: P, Ca, Mg, Fe, Si, C.

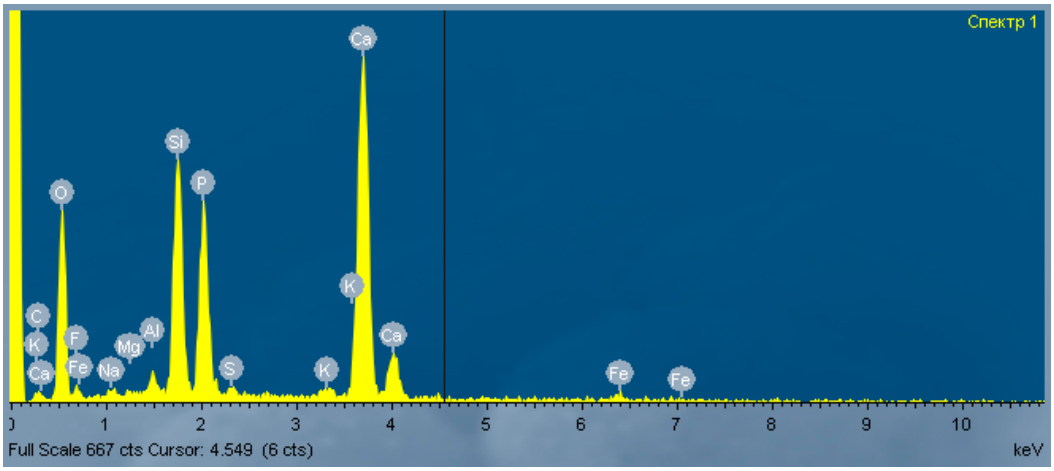


Figure 1. Energy dispersion spectral analysis of Chilisay deposit phosphorites.

Table 1 shows the results of the spectral analysis of sample No. 1.

Table 1. Results of spectral analysis of sample No. 1.

	O	F	Na	Mg	Al	Si	P	S	K	Ca	Fe
Spectrum 1	43.11	2.12	0.64	0.45	0.94	11.88	8.71	1.26	0.59	28.59	1.71
Spectrum 2	44.14	1.98	0.86	0.48	1.01	9.50	10.98	1.89	0.45	27.30	1.41
Spectrum 3	44.78	2.29	0.48	0.43	1.18	10.73	9.02	0.97	0.73	27.51	1.88
Average	44.01	2.13	0.66	0.45	1.04	10.70	9.57	1.37	0.59	27.80	1.67
Standard deviation	0.81	0.64	0.18	0.08	0.12	0.61	0.49	0.14	0.17	0.71	0.31
Maximum	44.78	2.29	0.86	0.48	1.18	11.88	10.98	1.89	0.73	28.59	1.88
Minimum	43.11	1.98	0.48	0.43	0.94	9.50	8.71	0.97	0.45	27.30	1.41

From Figure 2, it is evident that the intensity of sample No. 1 confirms the presence of SiO_2 (quartz) in the composition, with characteristic diffraction maxima d = 4.25496, 4.03464, 3.34257 Å. Diffraction maxima d = 3.34257, 3.04923 Å correspond to CaF_2 (fluorite), diffraction maxima d = 2.78867, 2.76934 Å correspond to $Ca_5(PO_4)3F/CaF_2{\cdot}3Ca_3(PO_4)_2$ (fluoroapatite), diffraction maxima d = 2.69039 Å correspond to Fe_2O_3, and diffraction maxima d = 3.24215 Åcorrespond to $KAlSi_3O_8$ (potassium feldspar).

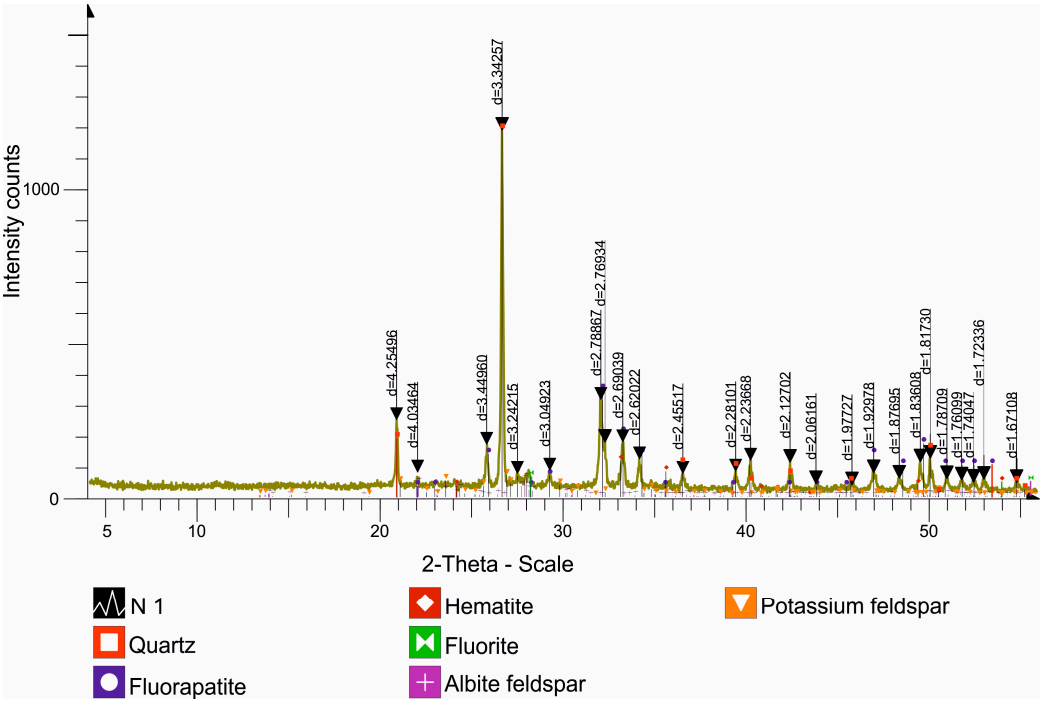


Figure 2. Diffraction pattern of sample No. 1.

The content was calculated for the main phases. Possible impurities, the identification of which cannot be unambiguous due to their low content and the presence of only 1–2 diffraction reflections or poor crystallization of compounds. The results of semi-quantitative X-ray phase analysis of crystalline phases of sample No. 1 are shown in Table 2.

Table 2. Mineralogical composition of phosphorite (sample No. 1).

Name	Formula	Concentration, %
Quartz	SiO_2	22.9
Fluorapatite	$(CaF)Ca_4(PO_4)_3/CaF_2{\cdot}3Ca_3(PO_4)_2$	36.7
Hematite	Fe_2O_3	2.1
Fluorite	CaF_2	5.7
Albite feldspar	$Na(AlSi_3O_8)$	4.4
Potassium feldspar	$KAlSi_3O_8$	3.9
Calcite	$CaCO_3$	23.9

From Figure 3, it is evident that the intensity of sample No. 2 confirms the presence in the composition of diffraction maxima d = 4.2526; 3.3411 Å, which correspond to SiO_2; diffraction maximad = 3.4476 Å, which correspond to $FePO_4$, diffraction maximad = 3.0372 Å, which correspond to $CaCO_3$: diffraction maximad = 2.7897 Å, which correspond to $Ca_5(PO_4)_3F$.

The results of semi-quantitative X-ray phase analysis of crystalline phases of sample No. 2 are shown in Table 3.

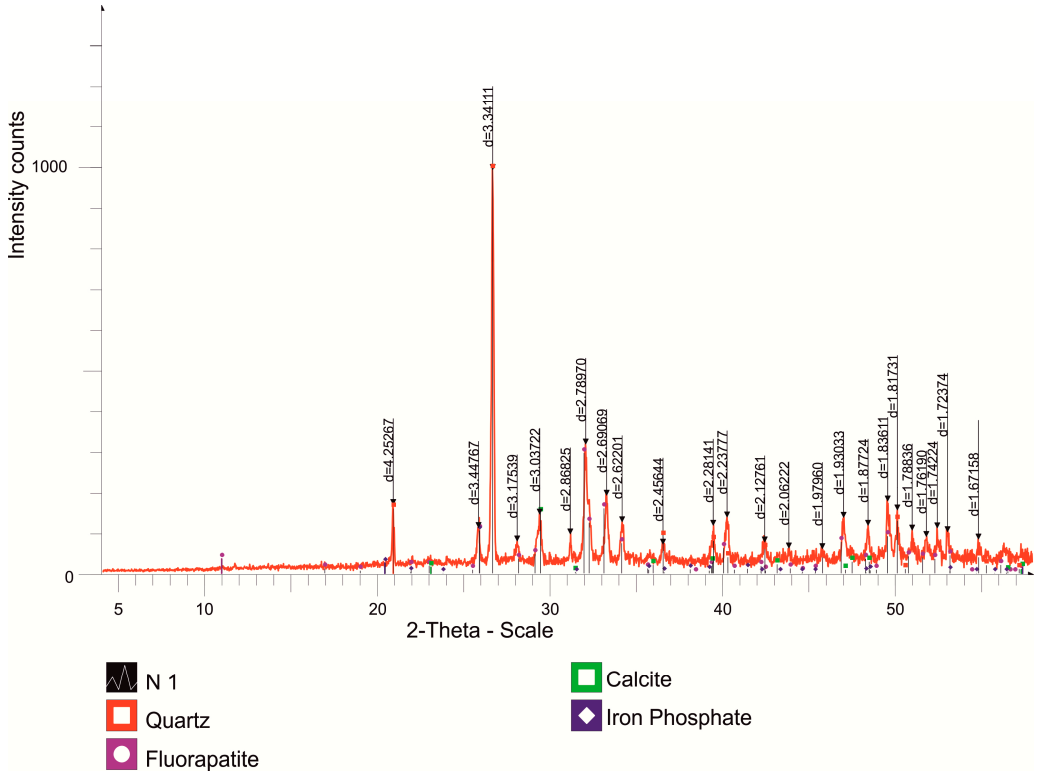


Figure 3. Diffraction pattern of sample No. 2.

Table 3. Mineralogical composition of phosphorite (sample No. 2).

Name	Formula	Concentration, %
Quartz	SiO_2	49.3
Fluorapatite	$Ca_5(PO_4)_3F$	36.7
Calcite	$CaCO_3$	7.4
Iron Phosphate	$FePO_4$	6.6

From the data in Table 3, it can be seen that the phosphate raw material mainly consists of quartz, fluorapatite, calcite, and iron phosphate.

The Chilisay deposit phosphorites are of the sandy type. They are mainly represented by quartz grains of various sizes (0.002–15 mm), cemented by calcium and iron phosphate. Feldspars, gypsum, and carbonates are present in smaller quantities.

The Chilisay phosphorites are characterized by variable mineral composition. Their quality varies widely depending on the content of harmful impurities that reduce the technological indicators of the products. Quartz is present in the form of well-rounded pebbles, large and angular small grains. The grains are mainly composed of pure quartz, the surface of some of them is covered with limonite or hydromica films.

Limonite is a product of the oxidation of iron-containing minerals (pyrite, glauconite, etc.), found in the pebble layer in the form of large accumulations or fine dust on the surface of glauconite, pyrite, and quartz. Organic matter in the Chilisay phosphorites is up to 0.8% and is associated mainly with phosphate matter and clay material.

The Chilisay deposit phosphorite (sample No. 1) was used for the experiment. The data on the chemical composition of the sample (Tables 1 and 2) were confirmed by other methods and are presented in Table 4. Methods for measuring the concentrations of all components except $SO_3$are in ST RK 2213-2012. ST RK 2213-2012 contains several methods for measuring Fe_2O_3 and Al_2O_3 concentrations [52]. In this work, a method described in

point 10.7 was used. Sample preparation for measuring Na_2O and K_2O concentrations was carried out according to point 10.13 of ST RK 2213-2012, but the measurement was carried out using an atomic absorption spectrometer contrAA 300 (Analytik Jena, Thuringia, Germany) with an acetylene-air flame. SO_3 content was measured using a method described in point 4.7.1 of GOST 8269.1-97 [53].

Table 4. Chemical composition of the Chilisay deposit phosphorite.

No.	Component	Content, %	Mineral
1	P_2O_5	19.96	Phosphorite
2	CaO	34.06	Feldspar
3	MgO	0.71	Hydromica
4	Na_2O	0.85	Glauconite
5	Al_2O_3	1.56	Glauconite
6	Fe_2O_3	2.32	Glauconite
7	SO_3	2.25	Pyrite, goethite
8	CO_2	14.36	Kurskite
9	F	2.13	Fluorite
10	K_2O	0.76	Glauconite
11	SiO_2	21.04	Kurskite

From Table 4, it can be seen that the phosphate raw materials contain mainly P_2O_5, CaO, SiO_2, and also carbonate compounds.

The Chilisay phosphorites, due to the peculiarities of their composition, contain a large amount of carbonates, within carbon dioxide reaching 4.56%, as well as glauconites. When decomposing this phosphorite, the formation of large volumes of very stable, difficult-to-destroy foam is observed due to the release of carbon dioxide.

$$CaCO_3 + 2H_3PO_4 \rightarrow Ca(H_3PO_4)_2 + CO_2\uparrow + H_2O \quad (1)$$

The solution to the foaming problem is proposed through the preliminary treatment of phosphate raw materials in bulk mass, with phosphoric acid, i.e., a decarbonization stage was introduced, preceding the stage of phosphorite decomposition, at which a significant part of carbon dioxide was released. At the decarbonization stage, the selection of optimal conditions (temperature value, norm, concentration of phosphoric acid) is carried out, under which it is possible to achieve the maximum decarbonization degree of the Chilisay phosphorite. At the next decomposition stage of decarbonized phosphorite, it is necessary to select the norm and concentration of phosphoric acid, as well as the decomposition time, which must be established by studying the decomposition process kinetics. The hot filtration stage (100 °C), where the insoluble residue is separated from the total mass of the monocalcium phosphate solution, is complicated by the organic matter content (resins and humic substances) in the phosphorite. The oily, finely dispersed layer of organic matter greatly complicates and increases the filtration time.

After monocalcium phosphate crystallization from the mother solution, the sediment is filtered, and the mother solution is returned to the head of the sulfation process to obtain phosphoric acid. When neutralizing free acidity in monocalcium phosphate, a neutralizing reagent is required. Calcium carbonate is used as a neutralizer according to GOST 5331-63, containing 88% $CaCO_3$. The reaction proceeds according to Equation (1).

At the first stage, decomposition was carried out in a thermostatted vessel equipped with a reflux condenser and a paddle stirrer, with a rotation speed of 200 rpm. The phosphorite was introduced in small portions into phosphoric acid with a concentration of 49.6–58.5%, heated to 95 °C. For 1 g of phosphorite, 4.5 g of acid was used.Then, the

reagents were mixed at this temperature for varying periods of time. The durations of the periods are discussed below.

At the second stage, after the decomposition was complete, the pulp was filtered on a heated vacuum filter through filter cloth (2 layers) at a negative pressure of 70 kPa, and the filtration time was measured. The sediment was washed with a certain amount of water heated to 75–80°C. The washed sediment was dried, weighed, and analyzed for the content of $P_2O_{5overall}$. and $P_2O_{5assimilated}$. The phosphate decomposition coefficient and the residue filtration rate were determined.

The filtrate, after separation of the insoluble residue, was placed in a thermostatted reactor equipped with a stirrer, cooled to a temperature of 40–45 °C, and maintained with slow stirring for 60–70 min. Then, the formed crystals were filtered on a vacuum filter. The sediment was weighed, analyzed for the content of P_2O_{5gen}, $Ca(H_2PO_4)_2$ and H_3PO_4, and treated with limestone to neutralize the free acid, then dried, weighed, and analyzed for the content of all forms of P_2O_5.

Spectral analysis of the obtained dry monocalcium phosphate was carried out using a JSM-6490LV scanning electron microscope (Figure 4). Results are shown in Table 5.

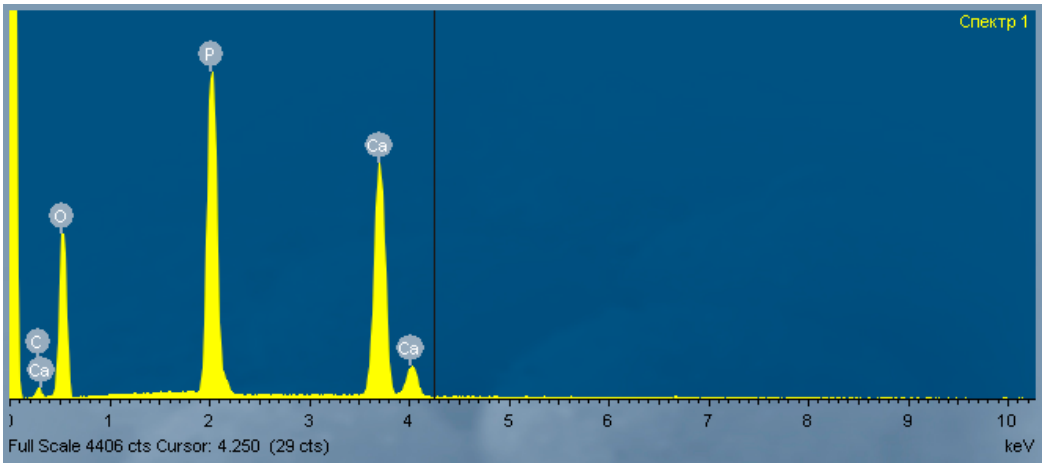


Figure 4. Energy dispersionspectral analysis of the obtained monocalcium phosphate from the Chilisay phosphorite.

Table 5. Elemental composition of the obtained monocalcium phosphate from the Chilisay phosphorite.

Element	Percent by Weight
C	0.02
O	57.97
P	24.00
Ca	18.01

From Table 5, it is clear that monocalcium phosphate contains mainly calcium and phosphorus and is practically free of fluorine and other impurities.

Sulfation of the mother solution with sulfuric acid was also carried out in a thermostatted glass reactor equipped with a stirrer. The mother solution contains dissolved monocalcium phosphate, as well as iron and aluminum phosphates formed during the decomposition of phosphorite. During the process of sulfation of the mother liquor containing $Ca(H_2PO_4)_2$, $Mg(H_2PO_4)_2$, $FePO_4$, and $AlPO_4$, these salts decompose with 92.5–93% H_2SO_4 to form H_3PO_4, gypsum $CaSO_4 \cdot 2H_2O$, and sulfates $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$. In an acidic environment, the decomposition reaction of phosphate salts with sulfuric acid occurs very quickly—within 20 min—with the release of heat, causing the temperature of the solution

to rise to 60 °C. 20 min after mixing the reagents, the formed crystals of calcium sulfate and poorly soluble complex sulfate salts of metals that settled into the precipitate were filtered using a vacuum filter. The precipitate was washed with hot (75–80 °C) water, weighed, dried to a constant weight, and analyzed for the content of P_2O_{5gen}, P_2O_{5water}, F, Fe_2O_3, Al_2O_3, CaO, and SO_3. The thermodynamic data of the above-listed compounds formed have been previously studied and thermodynamic characteristics of entropy, enthalpy, and phase transition of substances are given in the source [54].

The filtrate obtained after separation of calcium sulfate was weighed, and the content of H_3PO_{4free}, H_2SO_4, MgO, Al_2O_3, and F was determined. It was then returned to the decomposition stage in the next cycle. Losses of P_2O_5due to the insoluble residue and gypsum were compensated by introducing an additional amount of phosphoric acid into the cycle.

The washing of the insoluble residue and gypsum in the second cycle was carried out first with the filtrates obtained after washing the insoluble residue and gypsum in the first cycle, and then with water. In the third and subsequent cycles, threefold washing of the insoluble residue and gypsum was carried out. In the third cycle, the first and second washings were performed using the filtrates obtained during the first and second washings in the second cycle, while the third wash was done with water. In subsequent cycles, the first and second washes of the insoluble residue and gypsum were carried out using the filtrates obtained after the second and third washes of the insoluble residue and gypsum in the previous cycle, with the third wash using water. The filtrate obtained after the first washing of the insoluble residue was added to the mother solution obtained after the separation of the crystals in the corresponding cycle. The filtrate from the first washing of the gypsum was mixed with the recycled phosphoric acid (the main filtrate) obtained after the separation of the calcium sulfate crystals in the same cycle. In this way, it was possible to regenerate the phosphoric acid fed into the phosphorite decomposition. The entire process is shown as a flowchart in Figure 5.

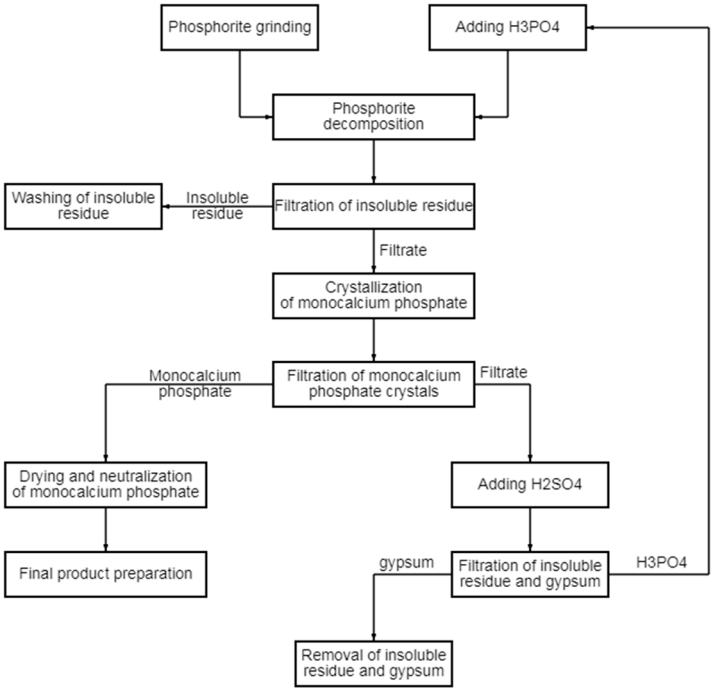


Figure 5. The process of obtaining monocalcium phosphate.

Based on the obtained research data, laboratory tests were carried out on the installation shown in Figure 6.

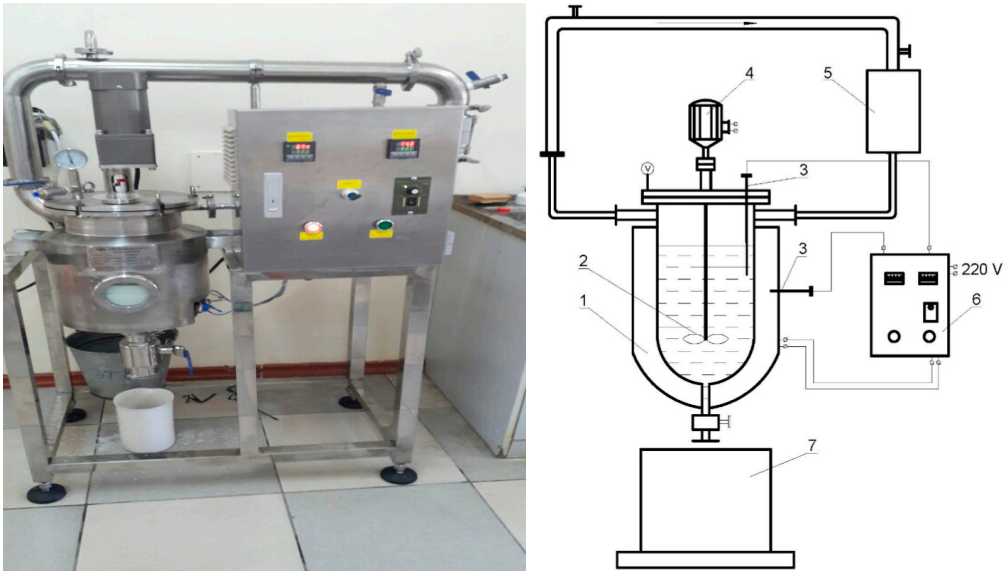


Figure 6. Laboratory installation for obtaining monocalcium phosphate from the phosphate raw materials.

Laboratory device (1) consists of a 0.01 m^3 reactor-mixer, where phosphorite and phosphoric acid are mixed with a stirrer (2). The reactor-mixer has a jacket, the temperature of which is regulated by a control panel (6). The temperature is measured by thermocouple (3). The stirrer is rotated by an electric motor (4). The evaporated liquid from the reactor is condensed in the condenser (5) and the condensate is returned to the reactor (1). After experiments, the pulp enters the collector (7) and is fed for filtration to separate the sediment from the mother liquor containing $Ca(H_2PO_4)_2$ and H_3PO_4.

3. Results

The kinetics of phosphorite decomposition at known rates and concentrations of phosphoric acid were studied under the following parameters: temperature of 80.95 °C and duration of reagent interaction of 1–50 min. Figure 7 shows the effect of duration on the decomposition coefficient of phosphate raw materials.

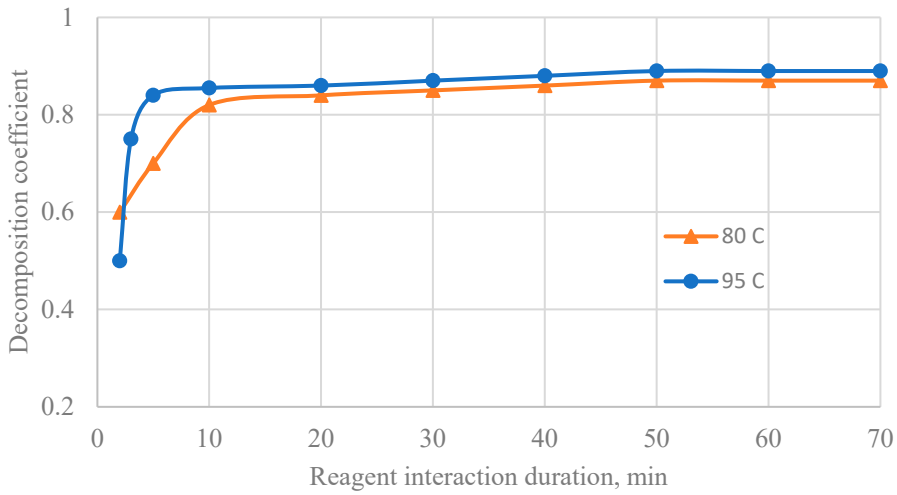


Figure 7. Phosphorite decomposition kinetics with afivefold excess of phosphoric acid.

The results of the studies shown in Figure 6 indicate that as the reagent interaction duration increases from 1 to 50 min, the decomposition coefficient also increases. The main part of the phosphorite decomposes in the first 10–15 min. With a further increase in

time, additional decomposition of the raw material occurs, and by 40 min, almost complete decomposition of the phosphorites (98%) is achieved. An increase in temperature from 80 to 95 °C causes an increase in the decomposition coefficient by only 0.05–0.07%. At a temperature of 95 °C, with the process duration of 30 min, the maximum achievable degree of decomposition is 98%, and remains the same—98%—at 40 min.

Almost complete opening of the phosphorite is achieved using a fivefold excess of phosphoric acid (540–560% of stoichiometry). Excess phosphoric acid allows monocalcium phosphate to be dissolved in the acid and for complete precipitation of silicon into the sediment. In this case, a solution of monocalcium phosphate is formed, unsaturated by CaO, and the sediment is mainly a silica-containing compound. Figure 8 shows the phosphorite decomposition rate from the process duration.

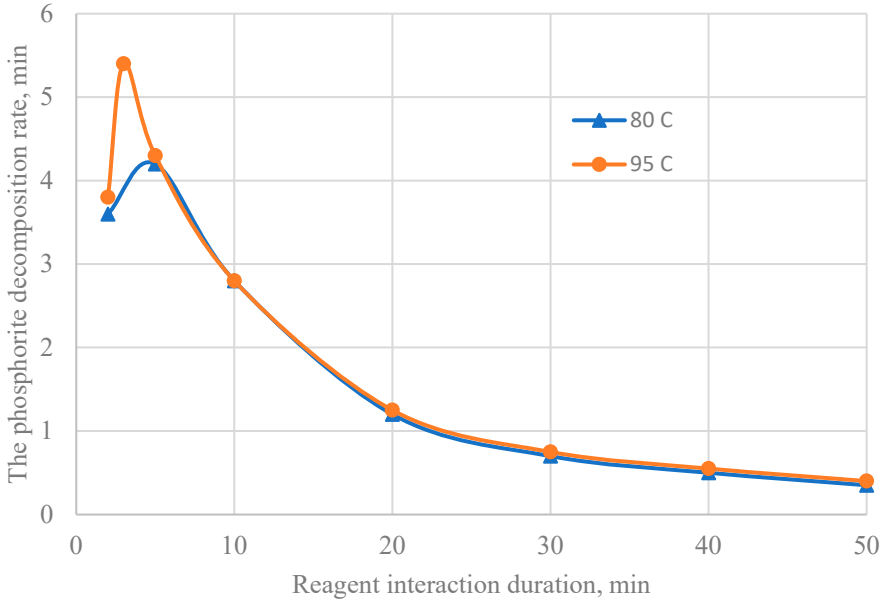


Figure 8. Change in phosphorite decomposition rate over time.

The highest decomposition rate is achieved in the first 5 min (4–5 g of phosphorite/min). The sharp decrease in the ore decomposition rate after 5 min is likely due to a decrease in the activity of hydrogen ions in the liquid phase due to the neutralization of the first hydrogen ion. At the same time, the temperature dependence of the degree and rate of decomposition is completely absent in the time interval from 10 to 50 min (Figure 8). The high rate of the process is ensured by the selected, theoretically substantiated conditions—decomposition with phosphoric acid containing 36.0% P_2O_5.

Thus, it was established that almost complete decomposition of the phosphorites is achieved with a reagent interaction duration of 40 min and a process temperature of 95 °C.

To conduct laboratory tests, phosphorite of the composition given in Table 4 was prepared. To obtain monocalcium phosphate from Chilisay phosphorite, a mixture of extraction and thermal phosphoric acid in a ratio of 2:1, with a concentration of 50–58% H_3PO_4, and 93% H_2SO_4 for sulfation of the mother solution were used. The decomposition temperature was 95–100 °C, and the decomposition duration was 40–50 min.

Based on the test results, the main parameters of the process for obtaining monocalcium phosphate from Chilisay deposit phosphorites were determined:

1. Concentration of phosphoric acid: 49.6% H_3PO_4
2. Norm of recycled phosphoric acid: 540–560% of the stoichiometric amount for the formation of MCP
3. Decomposition temperature: 98–100 °C

4. Decomposition duration: 45–50 min
5. Filtration temperature of the insoluble residue: 85–90 °C
6. Crystallization temperature of the mineral fertilizer (MCP): 40–45 °C
7. Crystallization duration: 85–90 min
8. Concentration of sulfuric acid for sulfation of the mother solution: 93% H_2SO_4
9. Norm of sulfuric acid: 100% of the stoichiometric amount for the decomposition of $Ca(H_2PO_4)_2$ contained in the solution, with the formation of gypsum and phosphoric acid.

4. Conclusions

(1) The elemental, chemical, and mineralogical composition of unconditional phosphate raw materials from the Chilisay deposit was studied. It was found that the phosphorites of the Chilisay deposit belong to the sandy type and consist of the minerals phosphorite, quartzite, fluorite, hematite, albite, and calcite.They contain the following substances: P_2O_5—19.96%, CaO—34.06%, MgO—0.71%, Na_2O—0.85%, K_2O—0.76%, Al_2O_3—1.56%, Fe_2O_3—2.32%, SO_3—2.25%, F—2.13%, SiO_2—21.04%.

(2) The influence of process duration on the degree of decomposition of phosphate raw materials and the decomposition rate of the raw materials was studied. It was found that with an increase in the interaction time of the reagents up to 50 min, the degree of decomposition increases, with the majority of the phosphorite decomposing within the first 10–15 min. With an increase in time, the decomposition of the raw material continues, and by 40 min, almost complete decomposition of the phosphorites is achieved, reaching up to 98%. The highest decomposition rate is achieved in the first 5 min (5 g of phosphorite/min), after which it decreases sharply. The sharp decrease in the ore decomposition rate after 5 min is due to the reduction of hydrogen ion activity in the liquid phase due to the neutralization of the first hydrogen ion.

(3) The study determined the following parameters for the process of obtaining monocalcium phosphate (MCP) from the phosphorites of the Chilisay deposit: phosphoric acid with a concentration of 36–42% P_2O_5; a recycled phosphoric acid rate of 540–560% of the stoichiometric amount required for the formation of monocalcium phosphate (MCP);a decomposition temperature of 95–100 °C; a decomposition duration of 40–50 min; afiltration temperature of the insoluble residue of 85–90 °C; a crystallization temperature of MCP of 40–45 °C. The obtained monocalcium phosphate has the following composition: P_2O_5—55%, Ca—18.01%, H_2O—4.0%, F—0.01%, As—0.004%, Pb—0.002%, and complies with the requirements of GOST 23999-80.

(4) Based on the obtained experimental data, a flowchart for the decomposition of unconditional phosphate raw materials from the Chilisay deposit was presented. The developed technology allows for the processing of low-grade phosphate raw materials, and the obtained monocalcium phosphate is used in agriculture as a mineral fertilizer and feed monocalcium phosphate. The results of this work are recommended for the commercialization of projects and the organization of feed monocalcium phosphate and mineral fertilizer production. The research was conducted under the BR21882181 project: "Development of technology for the production of highly effective materials based on mineral raw materials and technogenic waste".

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