Structural–crystallographic and morphological properties of silicon composition of phosphate ore

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Abstract. In order to identify the prospects for complex processing of high-silicon phosphate by direct acid methods, the properties of the mineral raw material and its insoluble residue were investigated. Clarified literature data on the composition of the original sample. New data were obtained on the chemical composition, morphology, microstructure and optical properties of the siliceous component of the ore.

1. Introduction

Natural phosphate ores are represented by apatites and phosphorites. The minerals of the apatite group are expressed by the general formula 3Ca(PO₄)₂·CaX₂. The phosphate substance of phosphate ores is represented by fluorapatite 3Ca(PO₄)₂·CaF₂, fluorohydroxycarbonateapatite Ca₁₀P₅CO₂₃(F,OH)₃, francolite Ca₁₀P₅.₅C₀.₈O₂₃.₂F₁.₈OH, kurskit Ca₁₀P₄.₈C₁.₃O₂₂.₈F₂.ₐ(OH)₁.₂. The composition of phosphate ores includes minerals impurities: quartz, glauconite, calcite, limonite, dolomite, magnesian silicates, kaolin, pyrite, feldspar, etc. [1].

In terms of phosphate reserves Russia ranks fourth in the world. The peculiarity of the domestic raw material base is the predominance of apatite ores in its structure, locally concentrated on the Kola Peninsula. The high content of the target component of 39.4% in terms of P₂O₅ and the low content of impurities, including up to 1.5% of the insoluble residue represented by alpha-quartz, ensured the active exploitation of deposits and the supply of quality raw materials for the phosphoric industry. For this reason, phosphorite ores, which are of low quality, widely distributed in the territory of the Russian Federation, belonged to reserve reserves, and their direct reagent processing was considered ineffective. Operation of the Egoryevskoye, Vyatsko-Kamskoye, Polpinskoye deposits consisted mainly in the production of phosphate rock from them – a product of primary enrichment, which was used with low efficiency to increase soil fertility [2].

Nevertheless, the long-term development of a rich Khibinsky massif leads to its depletion, deepening of the developed quarries, flooding of the developed horizons and, as a result, increasing the cost of raw materials production. The remoteness of deposits from the main consumers of apatite (enterprises for its processing by acid extraction methods) contributes an additional, very tangible share to the increase in the cost of raw materials and end products based on it.

With a view of rational nature management, already from the end of the last century, the issue of engaging in the processing of substandard phosphate raw materials has become topical. There is an industrial experience of replacing the share of apatite with phosphate rock from the Kingiseppskoye and Egoryevskoye fields in the production of phosphoric acid and products based on it [3].

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In order to saturate the domestic market of the Russian Federation with affordable phosphorus-containing products, the prospect of direct processing of low-grade phosphate raw materials from the Bryansk region is estimated. The choice of the object of study is due to the presence of industrially significant reserves of phosphate raw materials, a developed network of highways and railways, the proximity of agricultural consumers, as well as the presence of an agricultural holding in the region [4]. It should be noted that the information on the chemical composition of phosphate ores of individual deposits, including the Polpinsky sample, available in literary sources was relevant in the eighties of the last century [1, 5], therefore, they require clarification, and the involvement in the processing of reserve types of raw materials requires further exploration.

| Object | The content of the component, % mass |
|--------|-------------------------------------|
| Khibiny apatite concentrate | P₂O₅ 39.4⁺ | CaO 51.5–52.0 | Fe₂O₃ – | Al₂O₃ – | MgO 0.2–0.4 | K₂O+Na₂O 0.8–1.0 | CO₂ – | SO₃ 3.0–3.1 | In.res. – |
| Phosphate raw materials of brand P (ordinary), Karatau | CaO 24.5 | Fe₂O₃ 36–39 | Al₂O₃ 1.0–1.7 | MgO 0.8–1.2 | SO₃ 3.5 | CO₂ 0.3–0.7 | K₂O 8.0 | Na₂O – | SiO₂ 2.2–2.4 | F 15–20 |
| Verkhnekamsk phosphate raw materials, primary concentrate | CaO 21.0–24.0 | Fe₂O₃ 34.0–38.1 | Al₂O₃ 3.7–4.8 | MgO 3.3–4.7 | SO₃ 1.8–2.3 | CO₂ 1.6 | K₂O 4.7–5.4 | Na₂O 1.0 | SiO₂ 2.5–3.0 | F 13–18 |
| Egorievsk phosphate raw materials, primary concentrate | CaO 20.4–23.3 | Fe₂O₃ 32.6–36.0 | Al₂O₃ 4.5–7.0 | MgO 4.0–4.6 | SO₃ 1.1–1.4 | CO₂ – | K₂O 4.1–7.4 | Na₂O 1.0 | SiO₂ 2.0–3.0 | F 18–19 |
| Kingisepp phosphorite, flotation concentrate | CaO 28.0 | Fe₂O₃ 39.0–42.0 | Al₂O₃ 3 | MgO 2.5 | SO₃ – | CO₂ 1.5–2.0 | K₂O 0.4 | Na₂O 2–2.2 | SiO₂ 5–20 |
| Polpinsky phosphorite, primary concentrate | CaO 19.5–21.5 | Fe₂O₃ 30.5–33.3 | Al₂O₃ 2.6–4.0 | MgO 0.5–2.3 | SO₃ – | CO₂ 3.4–5.0 | K₂O 1.1 | Na₂O 2.1–2.8 | SiO₂ 31–37 |

⁺ in GOST 22275-90, the content of P₂O₅ is not less than 39.0%. This is due to the gradual depletion of the field.

2. Experimental part
The object of the study was a representative sample of clod ore from the Polpinskoye field, which was subjected to grinding on a pilot plant, classification, and drying the powder to constant weight. Acid nitrate qualification “puriss.” (GOST 4461-77) and distilled water (GOST 6709-72), SiO₂ qualification “puriss. spec.” (GOST 9428-73, TU 6-09-3379-79) were used as reagents.

Physico-chemical studies were performed using a Nicole 380 FTIR spectrometer (ThermoScientific, USA), a Bruker D 8 Advance diffractometer (Bruker Corporation, USA), a KFK-3-01 photocolorimeter (ZOMZ, Sergiev Posad), a JEOL JSM-6510LV multifunction instrument (JEOL, Japan), ASAP 2020MP (Micromeritics, USA) adsorption analyzer of specific surface and
The initial sample with a particle size of 0.071–0.315 mm was subjected to decomposition with 0.1 M HNO₃ at a temperature of 25 ± 0.05°C in a reactor with an overhead stirrer. The process was completed upon reaching a decomposition rate of 99.7%, determined by the photometric method according to the ratio of the content of the extracted target component (P₂O₅_water) to its initial content in the raw material (P₂O₅_total) [6–9].

The reaction of the target component of phosphate rock with nitric acid is described by the equation:

$$\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3 + 20\text{HNO}_3 = 6\text{H}_3\text{PO}_4 + 10\text{Ca(NO}_3)_2 + \text{CO}_2 + \text{H}_2\text{O}$$

The resulting suspension, consisting of the reaction products and the insoluble residue, was separated by vacuum filtration. The precipitate was washed with distilled water, dried for 1 hour at 200°C, and then sent for research. The filtrate is supposed to be used to obtain phosphorus-containing products for livestock and agriculture.

3. Results and discussion

According to the results of chemical analysis, the investigated ore from the Polpinsky deposit is a low-grade phosphate raw material. The share of the useful component (P₂O₅) is 15.3%, the share of the main impurity (SiO₂) is one third of the mass of the sample – 32.9%, the content of other impurities is: CaO – 27.4%, MgO – 0.23%, Fe₂O₃ – 1.4%, Al₂O₃ – 1.2%, F – 0.008%, CO₂ – 4.0%.

The results of IR spectroscopy of the analyzed sample in the region of 400–4000 cm⁻¹ (Figure 1) show that each spectrum is an overlap of overlapping bands that are associated with different types of vibrations of the main functional groups: H₂PO₄⁻, HPO₄²⁻, PO₄³⁻ (569, 605, 1044 cm⁻¹), SiO₂ (750–830 и 460–530 cm⁻¹); it is important to note that the band at 694 cm⁻¹ belongs to α-quartz), HCO₃⁻, CO₃²⁻ (694, 866, 1428, 1458 cm⁻¹), OH⁻ (3368, 3819 cm⁻¹), and the absorption bands at 463, 516, 694 cm⁻¹ and doublet 779–797 cm⁻¹ correspond to the silica and glauconite components of phosphate [10, 11].

According to the results of X-ray diffraction, the phosphate mineral of the ore under investigation has the structure of a hydroxycarbonateapatite [01-074-2680] hexagonal syngony with the unit cell parameters a = b = 9.38Å, c = 6.89Å. The main accompanying impurity is alpha-quartz [00-046-1045] trigonal syngony. Parameters of the α-quartz unit cell: a = 4.9133Å, c = 5.4053Å. Alpha-quartz is a stable at low temperatures polymorphic modification of SiO₂.

The ore particles of the initial sample in the range of 0.071–0.315 mm have a porous structure (Figure 2). This is characteristic of sedimentary rocks with close mutual germination of minerals.
the crystals of the main components of the ore, hydroxycarbonateapatite and α-quartz, are characterized by a cancerous fracture and imperfect cleavage [12, 13].

![Micrograph of polpinsky phosphorite particles at different magnifications](image1)

**Figure 2.** Micrograph of polpinsky phosphorite particles at different magnifications.

![Micrograph of particles of insoluble residue of polpinsky phosphorite at different magnifications](image2)

**Figure 3.** Micrograph of particles of insoluble residue of polpinsky phosphorite at different magnifications.

Using the X-ray fluorescence method of analysis, the elemental composition of the insoluble residue of the Polpinsky phosphorite and the reference SiO$_2$ sample (“puriss. spec.”) was investigated [14]. The results obtained indicate that the stoichiometric ratio of the elements in the sample under study (0.629) is preserved in comparison with the reference (0.621).

The optical properties of the insoluble residue (Figure 4) were estimated using the refractive index (GOST 9428-73, 15130-86); the obtained values of $n_e$ and $n_o$ were 1.555 and 1.538, respectively. According to the reference data, the optical identification characteristics of an alpha-quartz crystal are 1.553 and 1.544 [15, 16].

![Micrograph of α-quartz in determining the refractive index](image3)

**Figure 4.** Micrograph of α-quartz in determining the refractive index.
The isotherms of adsorption-desorption of phosphorite ore and its insoluble residue, obtained by the method of low-temperature (77 K) nitrogen adsorption (Figure 5 (a, b)) allowed us to calculate the values of specific surface area ($S_{sa}$) by the BET method, total pore volume ($V_p$) and volume distribution pore diameters (in the range from 1.7 to 300 nm) by the BJH method. For phosphate rock, $S_{sa}$ and $V_p$ were 8.03 $m^2/g$ and 0.0474 $cm^3/g$, respectively, and for $\alpha$-quartz – 11.48 $m^2/g$ and 0.0455 $cm^3/g$ [17]. An increase in $S_{sa}$ and a redistribution of pore size in the sample of the insoluble residue relative to the original sample of phosphate rock, which is associated with the extraction of the target component and soluble impurities in the solution, are noted.

For low-grade phosphate ore with a high proportion of silicon, complex processing seems appropriate, which consists in separating the suspension after the extraction stage by filtration into liquid and solid phases. The subsequent processing of the filtrate into soluble calcium and ammonium phosphates, and the precipitate (technical alpha-quartz) on glass is supposed to be carried out according to traditional technologies [18–20].

4. Findings
Specified literature data on the composition of high-silicon phosphate rock from the Polpino deposit. New data were obtained on the chemical composition, morphology, microstructure and optical properties of the siliceous component of the ore. The results of IR spectroscopy, X-ray diffraction, X-ray fluorescent analysis and polarization microscopy of the insoluble residue showed that it is alpha-quartz, its composition and optical parameters that determine its suitability for technological processing allow us to consider it as a raw material for the glass industry.

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