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PHYSICOCHEMICAL SUBSTANTIATION OF EXISTING PHOSPHORITE PROCESSING METHODS

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Abstract: Using physicochemical methods of existing phosphorite raw material processing methods, the composition of Ca5F(PO4)3, CaSO4·H2O, CaCO3, SiO2, CaCl3b, CaF2, as well as MgSO4·H2O and other compounds was studied.

Keywords: EPC, Plast II, Francolite, gypsum, goethite, Energy-dispersive spectrum and quantitative composition of MOPC elements using a scanning electron microscope.

Acid processing of natural phosphates aims to convert the phosphorus pentoxide contained in the raw material into a water-soluble or plant-available form. Natural phosphates (apatites and phosphorites) contain phosphorus pentoxide primarily as calcium fluoroapatite $Ca_5F(PO_4)_3$ and partially as hydroxyapatite. The former is completely inaccessible to plants, while the latter is partially soluble in soil solutions. Depending on the acid used and the production method, acid processing produces water-soluble fertilizers (monocalcium phosphate and ammonium phosphates) or fertilizers containing phosphorus in a citrate-soluble form (dicalcium phosphate) [1].

The large-scale use of phosphorus fertilizers for agricultural production necessitates minimal costs for their production, transportation, storage, and application to the soil. Low acid consumption, complete utilization of raw materials, and intensive process implementation result in low production costs and capital investment, while the high quality of the resulting products (minimal or almost complete absence of ballast) ensures cost-effective transportation and soil application.

Sulfuric acid processing of natural phosphates is currently the most common method. Treatment of natural phosphate with sulfuric acid, taken in an amount corresponding to the formation of MCP, produces simple superphosphate and EPC, which is used to produce phosphorus-containing fertilizers [2].

$$Ca_5F(PO_4)_3+3{,}5H_2SO_4\rightarrow 3{,}5CaSO_4+1{,}5Ca(H_2PO_4)_2+HF$$

Fluorapatite is produced by decomposing natural phosphates with sulfuric acid in the presence of a recycled phosphoric acid solution. Sulfuric acid extraction, in its various forms, is the primary method for producing fluorapatite.

The essence of the method is that pre-prepared phosphate raw materials are decomposed with sulfuric acid, followed by filtration of the resulting pulp to separate the phosphoric acid released during the reaction from the precipitate, which consists primarily of calcium sulfate.

Reaction of fluorapatite decomposition with sulfuric acid:

$$Ca_5(PO_4)_3F+5H_2SO_4+5nH_2O=3H_3PO_4+5CaSO_4\cdot nH_2O+HF$$

In fact, decomposition occurs in the presence of EPA to ensure the mobility of the resulting pulp. Therefore, the decomposition process occurs not with sulfuric acid alone, but with a mixture of sulfuric and phosphoric acids:

$$Ca_5(PO_4)_3F+5H_2SO_4+nH_3PO_4+5mH_2O=(n+3)H_3PO_4+5CaSO_4\cdot mH_2O+HF$$

The number "m" indicates how many moles of water are present in the gypsum and can be 0 (anhydrous calcium sulfate precipitates), 0.5 (calcium sulfate hemihydrate precipitates), or 2 (calcium sulfate dihydrate precipitates), depending on the decomposition conditions.

Simultaneously, decomposition of other minerals contained in the phosphate raw material also occurs: calcite, dolomite, aluminum and iron silicates, and other components.

Calcium and magnesium carbonates and silicates react with sulfuric acid to form the corresponding sulfates.

$$CaCO_3+H_2SO_4=CaSO_4+CO_2+H_2O$$

$$CaO\cdot SiO_2+H_2SO_4=CaSO_4+SiO_2+H_2O$$

$$MgCO_3+H_2SO_4=MgSO_4+CO_2+H_2O$$

$$MgO\cdot SiO_2+H_2SO_4=MgSO_4+SiO_2+H_2O$$

Silicon dioxide reacts with hydrogen fluoride [41]:

$$SiO_2+4HF=SiF_4+2H_2O$$

Some of the SiF_4 is released into the gas phase, and some is converted into hexafluorometasilicic (fluorosilicic) acid [3]

$$SiF_4+2HF=H_2SiF_6$$

Silicon tetrafluoride is also formed by the interaction of H_2SiF_6 with silica:

$$2H_2SiF_6+SiO_2=3SiF_4+2H_2O$$

Hexafluorometasilicic (hydrofluorosilicic) acid reacts with the alkaline components of clay minerals, forming poorly soluble sodium and potassium fluorosilicates.

$$(Na,K)_2O+H_2SiF_6=(Na,K)_2SiF_6+H_2O$$

Compounds of iron and aluminum sesquioxides dissolve to form the corresponding phosphates:

$$Al_2O_3+2H_3PO_4=2AlPO_4+3H_2O$$

$$Fe_2O_3+2H_3PO_4=2FePO_4+3H_2O$$

In this case, supersaturated solutions are formed, from which aluminum and iron phosphate hydrates are slowly released: $AlPO_4\cdot 2H_2O$ и $FePO_4\cdot 2H_2O$.

Impurities contained in natural phosphates complicate the decomposition process, impair its performance, and reduce the quality of the processed products. They lead to excessive sulfuric acid consumption and increased waste. Carbon dioxide gas is released during carbonate decomposition, forming a stable foam in the decomposition reactor. Magnesium, aluminum, and iron phosphates reduce the activity of phosphoric acid. Furthermore, some phosphoric acid is lost as hydrated iron phosphates and precipitated gypsum, degrading its quality and thereby complicating its further use.

During sulfuric acid decomposition of phosphate ore, magnesium compounds are converted into soluble magnesium sulfate and phosphate, preventing high levels of raw material decomposition and degrading the quality of the resulting acid.

Natural phosphates containing large amounts of acid-soluble magnesium, aluminum, and iron compounds are unsuitable for sulfuric acid decomposition. Iron-containing mineral impurities are particularly undesirable and harmful. For these reasons, iron-containing nodular phosphorites from the Yegoryevsky and Vyatka-Kama deposits are not suitable for sulfuric acid decomposition [4].

At 100°C, when a stoichiometric amount of EPC is involved in the process, the liquid phase becomes saturated with monocalcium phosphate. This achieves a decomposition rate of approximately 13%.

Subsequently, during the decomposition process, Ca(H2PO4)2 H2O begins to crystallize, and the liquid phase is an acidic solution saturated with monocalcium phosphate. Monobasic calcium phosphate then precipitates from the saturated solution, with the change in the composition of the liquid phase characterized by a solubility isotherm. Due to the precipitation of monocalcium phosphate, the reaction pulp thickens, and the degree of apatite decomposition reaches 60-65%.

Apatite dissolution isochrones were compared in partially neutralized EPC solutions (at varying degrees of neutralization and a temperature of 40°C) [46].

Under the given conditions, the rate of apatite decomposition, which also corresponds to the initial moment of dissolution (in the absence of a reaction product in the solution), decreases significantly as the first hydrogen ion of the EPA is neutralized. This slows down the achievement of equilibrium K_p values for apatite.

Under conditions of vigorous stirring (1000 rpm) with EPA solutions of different concentrations at an acid-to-apatite weight ratio exceeding 15-25%, saturation of the solutions according to the $CaO-P_2O_5-H_2O$ diagram is clearly not achieved [48]. The degree of apatite dissolution in 1 hour increases with increasing concentration of the initial acid only up to a certain limit (up to ~46% P_2O_5). As the acid concentration increases to 48 and 50% P_2O_5, the degree of decomposition decreases sharply. Under these conditions, the rate of process is determined primarily by the rate of crystallization of the solid phase from the supersaturated phase, since Supersaturation of the liquid phase is achieved quickly and is a consequence of the difference in the rates of dissolution and crystallization. In turn, the greater the supersaturation of the solution, the greater the driving force and speed of crystallization, and the smaller the size of the crystals that form.

Of interest [5] for the production of EPA are data on the solubility in the $CaO-P_2O_5-H_2O$ system in the temperature range of 0-152 °C. In the region of low P2O5 concentrations (0-30 mg/l), the solubility isotherm at 25 °C consists of three branches corresponding to solutions in equilibrium with $CaHPO_4H_2O$, $Ca_3(PO_4)_2$ 0,5 H_2O or $Ca_5(PO_4)_3OH$.

At the same molar fraction of free EPA, the hydrogen ion activities of EPA solutions and saturated solutions of the $CaO-P_2O_5-H_2O$ system were compared. The hydrogen ion activity at 40°C is 1.7-3.9 times lower than that of the binary system. This indicates the destruction of the

H6P2O8 dimer, which determines the high activity of EPA solutions in the presence of calcium salt. It can be noted that the minimal relative differences in activity values at 40°C (70%) are characteristic of solutions with a molar content of 16% H3PO4, which corresponds to 36.8% P_2O_5 for the binary system and 40% P_2O_5 for the ternary system. i.e., the reactivity of such solutions, when considered as a function of hydrogen ion activity, is similar.

The constructed solubility diagram for the CaO-P_2O_5-H_2O system was compared with the results of experiments on the phosphoric acid decomposition of various types of CK phosphorites [6].

Based on experiments on the decomposition of highly carbonated CK phosphorites and phosphomeal, a byproduct of ammonium sulfate production via the conversion of phosphogypsum with ammonium carbonate salts, a nomogram was constructed to calculate the yield of dicalcium phosphate. At 40°C, with an increase in the CK rate from 100 to 110%, the yield of dicalcium phosphate increases by 2.45-2.75% in the case of decomposition of unenriched phosphate raw materials.

In recent decades, geological exploration work has discovered the largest granular phosphorite deposit in the Kyzylkum Basin in Uzbekistan, with twelve areas in Middle Eocene deposits showing the greatest potential. Kyzylkum phosphorites have no global analogues in their physicochemical characteristics, but their composition reveals some similarities with phosphorites from deposits in North Africa, the Middle East, and Afghanistan, which are quite common in Mesozoic-Cenozoic carbonate formations [7]. Active research into the chemical and mineral composition of the granular phosphorites of the Kyzylkum Basin began in the second half of the 1960s. Geologists have paid particular attention to the territory of western Uzbekistan, where a number of industrially viable types of phosphorite ores have been identified: granular (African type), nodular (Chilisay), and haly-gravel (Florida). Of the granular phosphorites, the following have been identified: Sardarinskaya (167 million tons), Karaganskaya (160 million tons) and eight more with estimated resources of 50-60 million tons.

Total reserves of granular phosphate rock are estimated at 10 billion tons of ore. In Uzbekistan, the Jeroy-Sardarya basin was recognized as the most promising, and a comprehensive development program was developed. The first start-up complex of the Kyzylkum Phosphorite Plant, costing $33 million and with a capacity of 570,000 tons of phosphate rock per year, was commissioned in 1998.

At the Dzheroyskoye deposit, of the several phosphorite horizons, the two uppermost layers, with a combined thickness of 1-1.3 m, are of practical interest. The overwhelming majority of samples from layer I contained 16-19% P_2O_5, while those from layer II contained 21-23%. According to petrographic data, the structure of phosphorites from the Sardar site is organogenic-oolitic-granular. The rock is cemented by carbonate cement with a minor admixture of clayey matter and consists of accumulated phosphate grains phosphatized by organogenic residues and approximately 70% phosphate oolites. Microscopic studies of granular phosphorite ores have shown a uniformity in their composition. Phosphate minerals make up 10-90% of the rock. Non-phosphate minerals are represented by calcite (20-50%), montmorillonite, hydromica and palygorskite, hydrohemitite (0.01-15%), gypsum (5-10%), quartz (0.1-70%), glauconite (traces), feldspars (0.1-0.3%) and halite.

Phosphorite ores of the Jeroy-Sardara Basin have the following phase composition (%): francolite – 56.0; calcite – 26.5; quartz – 7.5-8.0; hydromica minerals and feldspars – 4.0-5.0; gypsum – 3.5; goethite – 1.0; zeolite <1.0; organic matter – approximately 0.5.

According to their carbonate content, Kyzylkum phosphorites are characterized by a high carbon dioxide content, reaching 27% or more. Mechanical separation of the phosphate mineral and calcite is difficult because they intergrow finely in the phosphate ore.

Other traditional beneficiation methods (classification, washing, flotation, etc.) are also ineffective for this phosphorite. For example, mechanical enrichment of phosphorites from the Jeroy intergrowth using the flotation method yielded a combined concentrate with a yield of 35.6%, containing 22% P_2O_5; the P_2O_5 extraction coefficient into concentrate did not exceed 60.3% [8].

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