MODERN TECHNOLOGIES OF COMPLEX PROCESSING OF PHOSPHATES

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ABSTRACT
Apatite is mineral - common name for a number of related minerals of the apatite group with the common formula Ca₅(PO₄)₃(F, OH, Cl). Varieties (mineral species in the group) - fluorapatite (F - up to 3.8), chlorapatite (Cl - up to 6.8), hydroxylapatite, carbonate-apatite (with content of carbonate group СО₃²⁻). It often contains manganese, iron, strontium, aluminum, rare earths impurities. Kola apatite concentrate is a promising and raw material for complex processing, allowing producing, in addition to the basic product – phosphoric fertilizers, strontium, rare earth elements and fluorine compounds. In creation of the complex phosphates processing technology it should be taken into account that apatite minerals are the main source of phosphorus in the modern industry, and its processing technology must ensure maximum extraction of this very element. As it was shown before, this can be achieved, in particular, with synthesis of glassy and melted phosphate fertilizers, used efficiently in the modern agriculture. The technology of extraction of rare earth elements from apatite concentrate must be viewed as an important additional process, contributing to complex processing of apatites.

Keywords: apatite, phosphorite, apatite concentrate, phosphate fertilizers.

INTRODUCTION

Chemical composition of apatite
Content (in %): CaO -53-56; P₂O₅-38-41; F - up to 3.8 (fluorapatite); Cl - up to 6.8 (chlorapatite); manganese, iron, strontium, aluminum, thorium, rare earths, carbonate group - СО₃²⁻ (carbonate-apatite) impurities, etc. often occur.

By crystal-chemical features the apatite supergroup is divided into five groups: apatite group, hedypahne group, belovite group, britholite group and ellestadite group. So, officially the word “apatite” is not the name of a mineral. It serves as the name of the supergroup (apatite supergroup) and the group of minerals. Apatite is one of the most widespread accessory minerals. In magmatic rocks apatite can be one of the first to begin crystallizing, and continue until completion of crystallization, often already at the intercumulus stage. Crystal druses often occur in miarolas in granite pegmatites, in sedimentary rocks - in the form of rounded grains. Typical mineral of carbonatites and lamprophyres. In these rocks apatite can be a xenocryst, and can come both from the mantle, and from crustal rocks, or can crystallize directly from the melt.

Apatite is one of the most widespread biominerals. Its microcrystals are present in teeth and bones of vertebrate animals and man. Apatite is established in all forms of life - bacteria, invertebrates and plants. Biogenic apatite is usually hydroxyl apatite and contains a lot of CO₂ - up to 6%. The main difference of biological apatite from Earth crust apatite consists in their chemical compositions. It is established that in biological apatite a part of Ca²⁺, (PO₄)³⁻ or (OH)⁻ ions is replaced with other ions. For example, Ca²⁺ can be replaced by Sr²⁺; Mg²⁺; Na⁺ or K⁺; phosphate ions are partially replaced with carbonate ions, and (OH); fluoride, chloride or carbonate-ions are present as additional anions. On the average human and mammals’ bones contain 60-70% of calcium phosphates (the value changes depending on the age and state of health).

Phosphorite is a sedimentary rock, the main component of which is cryptocrystalline or microcrystalline calcium phosphates from the apatite group. The bottom P₂O₅ content limit in phosphorite is assumed conventionally as 12%.

The most widespread phosphatemineral of phosphorites is fluor-carbonate-apatite (francolite), the main peculiarity of which is that a part of phosphorus(PO₄³⁻) in the elementary cell is replaced with carbon(CO₃²⁻) with formation of a continuous isomorphous series from fluor-apatite to kurskite. Besides carbon, other isomorphous replacements are frequent in phosphate minerals of phosphorites; calcium -with strontium, sodium, etc.; fluorine- with OH⁻, Cl⁻, CO₃²⁻ group, etc.; PO₄³⁻ anion - with O₂⁻ anion.

The most widespread forms of occurrence of phosphate substance are microconcretions (grains,oolites, spherolites), cryptocrystalline aphanitic phosphate (“microsphorite”), isotropic and decrystallized phosphate cement of nodular phosphorites, phosphate, building up body fossils (mainly, shells), a part of which originally consisted of calcium phosphate (shell phosphorites), and another part formed as result of replacement of carbonates with phosphate (biomorphoses). Mineralogic nature and petrographic peculiarities of phosphate substance produce a material effect on physical and chemical properties of phosphorites, their solubility, technological peculiarities, etc.

Besides calcium phosphates phosphorites include non-phosphate minerals: principal ones - dolomite, calcite,
quartz, calcic, glauconite; accessory ones - clay, aluminosilicate, ferrous minerals (pyrites, iron hydroxides), organic substances. Uranium, rare earth elements (ceric group lanthanides), strontium, more rarely Pb, V, Sc, Zr, Se impurities, etc. are present in lower concentrations.

Apatite fields

The world apatite reserves are concentrated in the fields of Khibiny tundras (Kola Peninsula). Oshurkovo and Seligdar, as well as other fields rich in apatite are located in Buryatia and Yakutia. Apatites are found in Kokchetav, Akmolinsk and Kustanai regions (Kazakhstan). In Ural (Ilmen mountains) apatite is concentrated in deep-seated alkaline magmatic rocks and pumice-oligocytic formations. Big contact origin apatite crystals occur in Baikal region. From foreign ones, the fields of Morocco, Vietnam, China, Tanzania can be mentioned. All active reserves of apatite ores of Russia, represented by the developed apatite-nepheline ores mined in nepheline syenites (Khibiny field group), apatite-magnetite ores in carbonatites, technogenic apatite-baddeleyite washery refuses (Kovdor field), reserve fields of apatite-staffelite ores (Kovdor massif) are concentrated in Murmansk region. [2, 3]

Total reserves of apatite ores (converted to P2O5) of Murmansk region make about half of all reserves of phosphoric ores of Russia, and their share in production output exceeds 90 %. The reserve balance of apatite ores of Murmansk region accounts 13 fields, whereof there are 10 fields of apatite-nepheline ores of Khibiny group, 2 fields of complex apatite-containing ores (Kovdor field of magnetite and apatite ores and Kovdor apatite-staffelite fields), 2 sections (Alluaiv and Sengisiyok) of apatite-lorapite ores of Lovozero field. The balance also accounts complex apatite-containing ores of wet magnetic separation tailings of the tailing pit of Kovdor technogenic field.

The balance reserves of apatite-nepheline ores of Khibiny massif are the largest in Russia [4]. OJSC “Apatite”, operating based on them, has 4 mines within it: Kirovsky (Kukisvumchorr and Yukspor fields), Rasmvumch (Apatite Circus field and pit part of Plato Rasmvumch field). Partomchhor and Oleniy Rucheck fields are mined by CJSC “North-Western Phosphorous Company”. Kovdor field of complex apatite-containing ores is developed by OJSC “Kovdor GOK”.

Application

Apatite and phosphorite are cold the “bread” stone - they are applied for production of phosphate fertilizers. Phosphate minerals are used in the chemical industry (for production of phosphorus, phosphoric acid and other compounds) and in the ceramic industry. The so-called phosphoric glass, transmitting ultraviolet rays, is made of phosphoric fertilizers production wastes. Glass grades, trapping infrared heat rays, are also produced. Application of phosphoric glass allows manufacturing special purpose glasses, used in high temperature productions. Some grades of phosphoric glass withstand heating up to 800-900 °C.

Phosphate glasses became the basis for development of new types of effective, environmentally safe fertilizers and ameliorants. Low chemical stability and biological activity of phosphate glasses allow using them in agriculture as a promising, non-toxic material, having typical kinetic dependence solubility on temperature and availability of ferments near the fertilizer grains. Such a peculiarity leads to the fact that dissolution of these fertilizers always coincides with the vegetative phase. Released useful components, contained in fertilizers, promote growth, and do not pollute environment, as it often happens, when usual superphosphates are used. Efficiency of application of glassy phosphate fertilizers reaches 90-95%, unlike traditional fertilizers, where the factor of its use by plants does not exceed 50%.

Phosphorus, phosphoric acid and phosphorus compounds, released, from apatite ores, are also applied in cattle breeding, food industry, military art, medicine. There are more than a hundred of branches of national economy, where these substances are used.

Processing

Kola apatite concentrate is a promising and raw material for complex processing, allowing producing, in addition to the basic product - phosphoric fertilizers, strontium, rare earth elements and fluorine compounds [5, 6]. Despite obvious environmental expedience of complex apatite processing, at present there is the only industrial scheme, providing for extraction of rare earth elements, strontium as by-products and fluorine recovery, based on decomposition of apatite by nitric acid (Figure-1).

Decomposition of apatite is implemented in the cascade of several reactors or a multi-section reactor. The process chemistry is reflected by the following equations:

\[
\text{Ca}_5(\text{PO}_4)_3\text{F} + 10 \text{HNO}_3 = \text{Ca(NO}_3)_2 + 3 \text{H}_3\text{PO}_4 + \text{HF}
\]

6 \text{HF} + \text{SiO}_2 = \text{H}_2\text{SiF}_6 + 2 \text{H}_2\text{O}

\[
\text{SiF}_4 + 2 \text{HF} = \text{H}_2\text{SiF}_6
\]

Main decomposition process parameters: duration 1.5 hours, nitric acid rate 110-115 % from the stoichiometric one, temperature 50-55 °C, apatite penetration degree 99%. In the above-described apatite decomposition conditions, the most of strontium nitrate is slaked out from the solution and turns out to be in a solid phase today with insoluble residue from apatite. It is separated by filtration, which is usually preceded by condensation. Extraction of strontium in concentrate makes ~ 60 % towards content in apatite. Strontium nitrate is well-soluble in water, and its restricted solubility is explained by the salting-out effect of compounds, containing nitrate-ions. Growth of HNO3 concentration from 5 to 46 % leads to reduction of strontium nitrate content in solution from 39.55 % down to 1.15 %.

After separation of strontium concentrate the solution is fed to calcium nitrate crystallization, which is
implemented in three stages in crystallizers by “freezing” at 10, 0 and -15 ºС respectively. At that ~ 90 % of Ca(NO₃)₂·4H₂O is released into a solid phase. Released calcium nitrate tetrahydrate crystals are separated from the mother solution by filtration with their subsequent flushing with nitric acid at -10 ºС. The flushing solution, containing mainly nitric acid, as well as phosphoric acid and sodium nitrate, is fed to the apatite decomposition stage.

After separation of Ca(NO₃)₂·4H₂O the mother solution comes to the stage of fluorine separation in the form of Na₂SiF₆ sediment. Soda, as well as various intermediate products, forming in production and being the source of sodium-ions, for example, the cycling solution of sodium fluoride, can be used as a precipitation agent. Duration of precipitation makes 60-90 minutes, temperature of the reaction mass amounts to 20-40 ºС. The suspension formed with a solid to liquid ratio = 1:25 comes to the settling tank. The surface active agent (for example, polyacrylamide) is added to the suspension for more effective clarification. Fluorine yield in the condensed product makes 77 %. The condensed product from the settling tank with a solid to liquid ratio = 1:5 comes to the drum vacuum filter. Sediment from the filter is subjected to double countercurrent water flushing with subsequent filtration. Base material content in the dried product makes about 90 %.

![Complex apatite processing scheme.](image)

The defluorinated solution is fed to the stage of rare earth elements separation. For this purpose, it is neutralized with ammonia or ammonia water to pH 1.4 at 80-90ºС. Under such conditions rare earth elements precipitate in the form of phosphates. The neutralized suspension from the last cascade comes to the filter press, where the sediment is separated from the mother solution and is flushed with water. The rare earth concentrate taken from the filter represents a product with 20 % humidity. Concentrate contains 25% of the total of rare earth elements (converted to oxides) 12.5% of CaO, 33% of P₂O₅, as well as iron and aluminum compound. With processing of 1 t of apatite about 30 kg of concentrate can be produced. Extraction of rare earth elements in concentrate makes ~ 75% towards content in apatite. After
separation of rare earth elements, the solution is fed for production of fertilizers.

When processing rare earth elements concentrate one shall ensure return of phosphorus, the share of which in concentrate makes about 3% from that contained in apatite, to the main process flow diagram.

Two basic schemes of concentrate processing are offered: according to the first of them concentrate is dissolved in nitric acid, and then oxalates of rare earth elements are precipitated with oxalic acid (unlike calcium, ferric, aluminum oxalates, oxalates of rare earth elements have restricted solubility even in relatively acidic solutions). For sufficient completion of precipitation of rare earth elements, the oxalic acid excess must make 200 \% from stoichiometric one. Then oxalate sediment is calcined at 900°C with production of total of rare earth elements oxides, containing 93-95 % of the basic product.

Rare earth elements concentrate can also be treated by alkali liquor with heating with production of sediment rare earth elements hydroxides and sodium phosphate solution. Sediment is then dissolved in acids (nitric or hydrochloric) and the solution of rare earth elements, free from earth elements hydroxides and sodium phosphate solution. Rare earth elements can be extracted from this solution by extraction or precipitation methods.

Brief description of the process of dry batch production for glassy fertilizers from ground phosphorite

The composition of glassy phosphate fertilizers is within the glass-forming range in K₂O – (Mg, Ca)O - P₂O₅ basis system and contains microelements additionally. The components ratio is selected so that as a result of synthesis in glass they are mainly in a metaphosphate form, which is the most digestible by plants.

This fact determines position of the composition near the glass-forming limit. That is why even slightest deviations from the operating schedule can lead to crystallization of the glass mass. Moreover, high volatility of phosphorus oxide (V) during cooking does not allow using traditional methods of batch preparation for glass-making. [7].

The need emerged to produce granulated (or pelletized) batch, which passed preliminary thermal treatment, in which basic components are in semi-volatile compounds due to some chemical processes, and volatile constituents of original raw materials (CO₂, H₂O, etc.) are already removed as much as possible. Such a result was achieved on the batch manufactured by OJSC “Phosphorite”.

Process flow diagram

Feed stock
- potassium carbonate (potash), (K₂CO₃)
- ground phosphorite (at least 26.5% P₂O₅) TU
- caustic magnesite powder
- extraction phosphoric acid (20-23% P₂O₅).

Batch production consists of the following stages:
- preparation of phosphate pulp;
- neutralization of phosphate pulp with alkaline suspension;
- batch granulation and drying;
- grading and cooling of the dried product;
- dust and gas cleaning; storage and shipment of the finished product.

Preparation of alkaline suspension

Pre-dissolved potash is pumped to the collector. Magnesium oxide is batched in the same collector, and the required quantity is determined by the set potassium to magnesium ratio. The produced suspension is fed to the speed ammonizator evaporator, using a horizontal centrifugal pump. The alkaline constituent batch is measured by an induction type flow meter and is regulated by an angle type valve.

Preparation of phosphate pulp

Phosphate pulp is prepared by the design ratio of ground phosphorite and phosphoric acid. Ground phosphorite is fed to a specially mounted receiving bin in the form of a funnel. Phosphoric acid is batched to the same tank and controlled, using a slot flow meter. A reaction of interaction of phosphoric acid and ground phosphate components occurs in the tank:

\[
\text{Ca}_5(\text{PO}_4)_3\text{F} + 7\text{H}_3\text{PO}_4 = 5\text{Ca(H}_2\text{PO}_4)\text{2} + \text{HF}
\]  

Besides basic reactions, there is interaction of calcium salts with free sulfuric acid, present in wet-process phosphoric acid:

\[
\text{CaO} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} = \text{CaSO}_4\cdot2\text{H}_2\text{O} + \text{Q}
\]

To prevent precipitation of coarse particles of suspension, use of air-lift agitators is provided for in additional to the mechanical agitator. Phosphate constituent pulp is conveyed to neutralization, using a horizontal pump.

Neutralization of phosphate pulp with alkaline suspension

Phosphate pulp is batched to the neutralization stage by a slot flow meter. Neutralization of phosphate pulp with alkaline suspension is implemented in the speed ammonizator-evaporator - SAE. A chemical reaction occurs in SAE between free phosphoric acid and potassium carbonate with formation of potassium phosphates. Free wet-process phosphoric acid is also bound with magnesium hydroxide with formation of acidic magnesium phosphate. The neutralization process of phosphoric acid in SAE can be represented by the following basic reactions:

\[
\text{CaO} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} = \text{CaSO}_4\cdot2\text{H}_2\text{O} + \text{Q}
\]
In addition to basic reactions, a number of by-reactions related to presence of fluorine, aluminum, iron components in phosphate pulp, develop with neutralization of acid with alkaline components. Iron and aluminum impurities form, mainly, neutral orthophosphate salts under the reactions:

\[
\begin{align*}
    \text{Fe}_2\text{O}_3 + 2 \text{H}_3\text{PO}_4 & \rightarrow 2 \text{FePO}_4 \cdot 2\text{H}_2\text{O} + \text{Q} \\
    \text{Al}_2\text{O}_3 + 2 \text{H}_3\text{PO}_4 & \rightarrow 2 \text{AlPO}_4 \cdot 2\text{H}_2\text{O} + \text{Q}
\end{align*}
\]

Hydrofluosilicic acid present in the reaction environment is neutralized by potash with formation of potassium silicofluoride:

\[
\text{H}_2\text{SiF}_6 + \text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{SiF}_6 + \text{CO}_2 + \text{H}_2\text{O}
\]

All the above-listed reactions are exothermic, but the thermal effect is insignificant, and the temperature in the unit is determined by the temperature of components fed to SAE. The temperature of pulp and vapor-gas mixture is measured in the circulation chamber and separation space of SAE.

The process of neutralization of phosphate pulp with alkaline suspension is controlled by pulp pH value, which is maintained within 3.0-3.5.

The finished pulp comes from SAE to the collector. The finished pulp represents a flexible suspension with viscosity of 24-25 Cps (with \( t = 600^\circ\text{C} \)) and density of 1.4-1.5 g/cm³ and is pumped with an ordinary centrifugal pump. The vapor-gas mixture from SAE and pulp collector is fed with a fan to the surface condenser for cooling and water vapors condensation, and residual gases are subjected to defluorination in the absorber. After the absorber scrubbed gases are emitted into the atmosphere by the fan via the exhaust pipe.

The finished pulp from the collector is fed by the centrifugal pump directly to nozzles of DGD (drum granulator-drier) of the granulation department.

**Batch granulation and drying**

Batch granulation and drying is implemented in DGD, which operating principle is that the finished pulp is dispersed to the rotating drum by means of mechanical nozzles on the screen of the dry product. The recoverable dried product and a part of dried particles in the spray cone are the granule formation centers.

The quantity of the returned dried product or process returnability mainly depends on the initial humidity of pulp, temperature of the heat carrying agent, productivity of nozzles and interior arrangement of the unit. The DGD unit is self-regulatory. With reduction of the recycle quantity, fed to the screen, a part of dispersed pulp particles does not contact the dry product and are dried with formation small particles, thus increasing the quantity of recycle in the system. With increase of the quantity of recycle most of dispersed pulp particles precipitate on the dry product screen and particle coarsening takes place.

Two processes occur simultaneously with drying of humid batch granules: moisture evaporation (mass exchange) and heat transfer (heat exchange). Water in the batch is mainly bound with salt by capillary forces (hygroscopic moisture). Up to 5-6 % of water is bound in the form of crystalline hydrates (crystalline moisture). So, the residual humidity of the product corresponds to the content of crystalline moisture in it. In the process of batch drying by flue gases with the temperature of 550-600°C moisture evaporates from the material surface comparatively quickly and moves slowly from internal layers of the material to its surface. This process continues until water vapor pressure in flues gases becomes equal to pressure of saturated water vapor over the dried material.

Granulation and drying time in DGD makes 35-40 minutes.

Stable work of DGD unit, as well as the quality of the finished product depends on the geometry of the pulp spray cone, its dispersiveness, liquid and uniform distribution along the spray cone section.

By its design the DGD unit represents a drum with the diameter of 4.5 m, length of 16 m, installed under the slope toward the material flow (angle of slope 3°). Drum rotation speed - 4.5 rpm.

The finished product is discharged continuously through the bottom hatch of the discharge chamber; flue gases are sucked off from the diametrically opposite coupling. In additional to water evaporation from the pulp in the process of drying fluorine-containing gases are emitted because of partial decomposition of salts, included in the composition of the batch under the following reactions:

\[
\text{K}_2\text{SiF}_6 + 2\text{H}_3\text{PO}_4 = 2\text{KH}_2\text{PO}_4 + \text{SiF}_4 + 2\text{HF}
\]

Flue gases outgoing from the DGD unit, containing water vapors, gaseous fluorine compounds, finished product dust, are subjected to scrubbing in the absorption system.

**Grading and cooling of the dried product**

The product is graded on double-deck unbalanced-throw screens. The commodity fraction of the product (1 to 4 mm) from the bottom sieve of the screen is fed for cooling to the spouting bed device (SB).

Cooling of the product granules occurs upon their contact with the atmospheric air, fed using the forced-draft fan through the collector to the tray, located in the bottom of the spouting bed unit cone. At that the product granules are in a suspended state, due to which contact of the hot material with the cold air is reached.

The finished product from the SB unit is fed to the band conveyor via the chute, which conveys it to the finished products warehouse.
Dust and gas cleaning

Flue gases outgoing from the DGD unit, containing gaseous fluorine compounds, moisture, product dust, are subjected to double-stage cleaning from pollutants before emission into the atmosphere.

The first stage is intended for scrubbing of effluent gases from dust, the second stage is intended for scrubbing from fluorine-containing gasses. Flue gases from the DGD unit with the temperature of 82-250 °C come to the gas scrubber, consisting of Venturi turbulent washer and two spray trap blocks. Scrubbed gases are discharged with a fan via the exhaust pipe into the atmosphere. The dusty air after the SB is subjected to wet cleaning from dust in the absorber with the bubble bed stabilizer and is emitted into the atmosphere with a fan.

Storage and shipment of the finished product

The granulated batch from the production block is conveyed to the bin by the system of band conveyors, wherefrom it is loaded to the railway cars. The technological cycle did not allow adding the required microelements in the composition of the granulated batch. Their content did not exceed 3.0 %. This induced the need to granulate microadditives at other production base with their subsequent mixing with the basic batch before feeding to the furnace, for melting of glassy fertilizers. [8].

CONCLUSIONS

In creation of the complex phosphates processing technology it should be taken into account that apatite is the main source of phosphorus in the modern industry, and its processing technology must ensure maximum extraction of this very element. As it was shown before, this can be achieved, in particular, with synthesis of glassy and melted phosphate fertilizers, used efficiently in the modern agriculture.

The technology of extraction of rare earth elements from apatite must be viewed as an important additional process, contributing to complex processing of apatite concentrate [9].

Combination of these two areas of use of phosphate raw materials can increase the processing efficiency considerably - maximum extraction of the valuable components from apatites can be achieved, with simultaneous reduction of the environment pollution with underextracted residues, which are removed to dumps and tailing pits, which is the typical problem of modern ore mining and processing mills.

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REFERENCES


