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Nurtayeva, Arailym
Department of Ecology, Mukhtar Auezov South Kazakhstan University

Baisbay, Omirbek
Department of Chemical Technology, Mukhtar Auezov South Kazakhstan University

Issayeva, Raziya
Department of Ecology, Mukhtar Auezov South Kazakhstan University

Iztleuova, Aigerim
Department of Ecology, Mukhtar Auezov South Kazakhstan University

他

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Investigation of Production Wastes Upon Roasting Mechanically Activated Phosphorite and Utilisation of Fluorine Compounds

Arailym Nurtayeva[1,*], Omirbek Baisbay[2], Raziya Issayeva[1], Aigerim Iztleuova[1], Zhangeldi Kurganbekov[1]

[1]Department of Ecology, Mukhtar Auezov South Kazakhstan University, Shymkent, Republic of Kazakhstan
[2]Department of Chemical Technology, Mukhtar Auezov South Kazakhstan University, Shymkent, Republic of Kazakhstan

*Author to whom correspondence should be addressed:
E-mail: arailymnurtayeva529@gmail.com

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Abstract: The purpose was to investigate the process of formation and characteristics of fluorine compounds in the production waste upon roasting mechanically activated phosphorite, as well as the development of effective methods and technologies for their utilisation. The present study employed the analytical method, the classification method, the functional method, the statistical method, the synthesis method, structure-functional method, method of deduction. During the study, the composition of waste products from the roasting of mechanically activated phosphorite was analysed. Proper treatment of fluoride compounds is critical to preserving the environment and ensuring general well-being. These substances are toxic and can harm ecosystems and human health. Fluoride compounds generated during firing can have a negative impact on biological systems, and therefore, the effective disposal of these substances is becoming an integral part of the industrial production of phosphate rock and mineral fertilizers. The waste was found to contain significant amounts of fluoride compounds, including gaseous and solid forms. This confirms the need to develop methods and technologies for their utilisation.

Keywords: ecosystem; atmosphere; soil; water resources; pollution

1. Introduction

The study of production waste from the roasting of mechanically activated phosphorite and the utilization of fluoride compounds are important and relevant tasks in the field of environmental protection and sustainable development. The process of roasting mechanically activated phosphorite, which is a key source of phosphorus for fertilizer production, can produce a variety of wastes, including fluoride compounds. These compounds have toxic properties and can adversely affect the environment and human health. Therefore, understanding the mechanisms of the formation of fluoride compounds and developing effective methods and technologies for their utilization are becoming an integral part of industrial processes. Studying this subject will not only reduce pollution of water resources, soil, and atmosphere but also prevent potential adverse effects on ecosystems and human health[1-2]. Moreover, the results of the study will be useful for developing and implementing more environmentally friendly waste treatment methods in fertilizer production, complying with environmental legislation, and promoting sustainable development in the industry.

The problematics of the study of waste production in the roasting of mechanically activated phosphorite and the utilisation of fluoride compounds is the need to address several key issues[3]. It is required to investigate the mechanisms of the formation of fluoride compounds in the roasting process and to identify the main sources of their formation. It is also necessary to assess the toxicity and the extent to which these compounds affect the environment and human health to determine the optimal parameters and constraints for their disposal. The development of efficient methods and technologies for the utilization of fluoride compounds is required. This involves finding optimal reagents and processes that can convert toxic compounds into less harmful or stable forms and ensure that the disposal process is highly efficient and economically viable. Aspects of the economic and social feasibility of various methods of fluoride utilization need to be considered. This includes assessing the costs of implementing and supporting such practices, as well as assessing their impact on the workforce and local communities. Finally, it is important to consider legislative and regulatory aspects related to waste management and environmental protection. The study should consider the requirements of environmental legislation and quality standards for the disposal of fluorinated compounds and ensure compliance with relevant regulations. Thus, the problem of the research includes the study of the mechanisms of formation of fluorine compounds, the development of effective methods and technologies for their utilization, as well as consideration of economic, social, and legislative aspects related to this topic.

The article by O. Nishita et al.4) focuses on the use of biological processes for industrial wastewater treatment, which offers a sustainable alternative method to traditional chemical methods. It highlights the various bioremediation methods, their effectiveness in removing different contaminants, and the overall environmental benefits compared to standard approaches.

The study by Y. Chernysh et al.5) focuses on the challenges and opportunities associated with the recycling of phosphogypsum, a major waste product from fertilizer production. It analyzes the environmental issues associated with phosphogypsum disposal, examines different methods of recycling it, including its use in construction materials and agricultural applications, and provides recommendations for sustainable approaches to managing this waste.

The study by M. Smol et al.6) uses a life cycle assessment (LCA) method to assess the environmental impact of an integrated technology for recovering phosphorus from sewage ash and using it in fertilizer production. The study analyzes the resource consumption, greenhouse gas emissions, and other impacts of the process, providing valuable insights for optimizing sustainability in fertilizer production and waste management.

The study by A. Ghosh et al.7) examines the environmental aspects of scandium mining, a critical element used in various industries. They evaluate the stages of the process of extracting scandium from its ores, identify the main environmental issues associated with each stage, and suggest potential strategies to minimize the environmental impact of scandium mining.

As argued by A.M. Aubakirov8), to reduce the adverse impact of pollution sources it is necessary to apply modern technologies and methods of emissions cleaning). For instance, gas cleaning systems such as scrubbers or filters are used to reduce emissions of gases containing hydrogen fluoride. Desulphurization of gas emissions is used to reduce emissions of sulfur compounds. It is also important that emissions are regularly monitored and controlled to ensure that they meet regulatory requirements. The study by R.A. Isaeva et al.9) emphasizes that fluoride compounds formed as a result of phosphorite roasting are a serious pollutant of water and soil resources, and therefore their utilization is an urgent task from the standpoint of environmental safety. B.K. Batyrbekova et al.10) point out the importance of investigating the formation processes and chemical properties of fluoride compounds to develop effective methods of disposal, minimize their impact on the environment, and ensure the safety of workers and the public. A.A. Kadirbaeva et al. 11) emphasize that the utilization of fluoride compounds is a complex task requiring an integrated approach including chemical, physical, and technological methods, and research in this area is necessary to determine the most effective ways of waste treatment. According to M.K. Aldabergenov and A.A. Sarbasov12), the production of organomineral fertilisers in Kazakhstan has prospects and can play a significant role in the development of agriculture in the country. Organomineral fertilizers are a combination of organic and mineral components that help improve soil fertility and increase crop yields13-14). The authors M. Olejarczyk et al.15) emphasize that the study of waste production and utilization of fluoride compounds is of great social importance, as it allows protecting of human health, reducing disease risks, and maintaining the quality of the environment for current and future generations.

The above viewpoints represent general ideas about the relevance, issues, and significance of the study on waste production upon roasting mechanically activated phosphorite and the utilization of fluoride compounds but are not direct quotations from particular studies or publications. The purpose of this study was to investigate current trends in the development of the phosphate industry in Kazakhstan, as well as to identify scientific and industrial strategies and approaches required for the efficient processing of phosphate rock.

The research objectives can be summarized as follows:

- to analyze the current trends in the development of the phosphate industry in Kazakhstan;
- to determine the content and chemical composition of rare earth elements (REEs) in phosphogypsum samples obtained from phosphate acid production, including elements such as cerium, lanthanum, neodymium, promethium, and others;
- to evaluate the efficiency of different methods of REE extraction from phosphogypsum using various solvents and extractants, including the determination of optimum extraction conditions;
- to optimize processes for maximizing REE recovery while minimizing energy and resource consumption;
- to study the possibility of using the obtained REEs in the production of various products, such as catalysts, magnets, and optical materials;
- to evaluate the properties and potential applications of these elements in various industrial sectors.
- to assess the economic feasibility of the processes and products under study.

2. Materials and Methods

This study was conducted through the application of methods that reveal the theoretical and practical content of the object. The analytical method helped determine the content and concentration of fluoride compounds in the production waste from the roasting of mechanically activated phosphorite. The analyses provided accurate data on the types and quantities of fluoride-containing substances, allowing the selection of the most effective methods and technologies for their disposal.

The statistical method was used to interpret the obtained data on the production waste from the roasting of mechanically activated phosphorite and the fluoride compounds contained therein. The statistical method helped identify relationships and dependencies between different parameters and determine the degree of influence of each factor on the content of fluoride compounds. By applying the functional method, various aspects of waste production in the roasting of mechanically activated phosphorite and utilization of fluoride compounds were investigated. The functional method helped evaluate the efficiency of different recycling processes and technologies and suggested optimal solutions to minimize the environmental impact.

The structure-functional method helped in the study of waste products resulting from the roasting of mechanically activated phosphorite and the utilization of fluoride compounds considering their structure and functional characteristics. This method identified the interrelationships between system components and determined their impact on overall process performance. The method of deduction helped in carrying out a logical review of the data on waste production in the roasting of mechanically activated phosphorite and the utilization of fluoride compounds. By applying the synthesis method, more efficient and safer firing processes for mechanically activated phosphorite with minimal formation of fluoride compounds were investigated and developed. For instance, the use of innovative catalysts or modification of firing conditions helped reduce the formation of fluoride compounds or their conversion to less hazardous products.

The theoretical component of the study was covered, including the basic principles and concepts underlying the processes of roasting mechanically activated phosphorite and utilization of fluoride compounds. Using a structural-functional approach, the relationships between waste structure and functional properties were investigated, providing an in-depth understanding of the processes occurring in the system. This research contributes to the development of effective methods of waste management. Additionally, experiments and data analysis were carried out to validate the theoretical assumptions and provide practical recommendations for the design and optimization of waste management processes. An important result of the study was the development of effective methods for the treatment of industrial wastes based on the knowledge gained about the structure and functional properties of these wastes. The gained in-depth understanding of mechanically activated phosphorite roasting and fluoride recycling allows the development of innovative and sustainable recycling methods that can reduce environmental impact and ensure efficient use of resources. These results are of great significance for industrial enterprises working with phosphate rock and society in general, striving for sustainable development and environmental protection.

In summary, the purpose of this sequence was to provide recommendations for optimizing the roasting of mechanically activated phosphorite and the utilization of fluoride compounds based on the results obtained.

3. Results

Surface-active additives, water-soluble acrylic polyelectrolytes (AWPs), which have proven themselves in solving analogous practical issues, were used to intensify liquid-phase abrasion of phosphorite. This relatively simple and energy-efficient method is implemented by applying pulsed energy directly to the material to be processed. The distinctive feature of the effects of AWP K-9 influence under study on the grinding process is that they are observed only at the joint action of a surfactant and a certain stress state. By itself, lowering the specific free surface energy does not lead to the development of new surfaces – it only facilitates the action of mechanical stresses[16).

Figure 1 shows the results of a study where the effects of firing temperature and surfactant additive concentration on the residual fluoride content of phosphorite as well as on the assimilable P_2O_5 content were investigated.

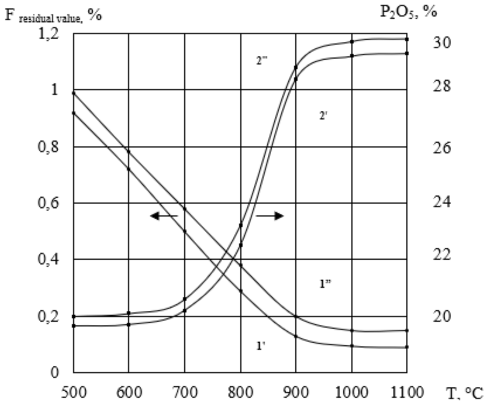

Fig. 1: Relationship between roasting temperature, surfactant additive concentration and residual fluorine content in phosphorite (1), and the content of assimilable P_2O_5 (2)

Note: T:L ratio=1:5, roasting time – 50 minutes. 1^I, 2^I *– without additives;* 1^{II}, 2^{II} *– with 0.03% addition of K-9.*

As Figure 1 shows, after liquid-phase abrasion in the vibratory mill, it is possible to reduce the roasting temperature to 900°C, which was over 1300°C under static conditions. Therewith, the transition point of β-modification of tricalcium phosphate into α-modification can be reduced to 820-850°C. This is explained by the fact that in liquid-phase abrasion of phosphorite upon the impact of grinding bodies there is an increase in temperature up to the value from 1400 to 1500°C, after which there is a sharp cooling to the temperature of the surrounding liquid phase, which is from 40 to 60°C. Due to this effect of instantaneous heating and rapid cooling, the formation of the A-modification of tricalcium phosphate can be consolidated. Thus, liquid-phase abrasion allows combining the melting of phosphorite at temperatures of 1400-1500°C and preservation of the α-modification of tricalcium phosphate by hardening it under rapid heating and cooling. In abrasion of phosphorite, its crystal lattice is broken, resulting in the removal of fluorine from the material. Fluorine is a chemical element with the symbol F and atomic number 9. It is a highly reactive and corrosive gas that is part of the halogen group on the periodic table. Fluorine is used in various industrial applications, including the production of fluoride compounds for dental care, in the manufacture of certain chemicals, and in the nuclear industry. The fluorine remaining in the solid phase after mechanical activation is no longer bound to the phosphorite crystal lattice and can therefore be extracted by roasting at a temperature of around 900°C.

Phosphorite decomposition is accompanied by decarbonisation (at 850-950°C) and defluorination (at 1300-1550°C). When the temperature reaches 2000°C, the solid phase changes to a liquid phase. Depending on the rate of melt cooling, the composition of soluble forms of phosphate changes in the melt structure[17)]. Therewith, the composition α and β-modifications of tricalcium phosphate are qualitatively changed. Knowledge of the dependence of the amount of assimilable and non-assimilable P_2O_5 on the cooling rate makes it possible to determine the optimum conditions for feed phosphate production. Experimental results and infrared spectroscopy data show that abrasion of phosphorite suspension results in defluorination, increase of its reactivity and conversion of tricalcium phosphate from β-modification to assimilable A-modification[18)]. These changes are not so much related to the increase in specific surface area as to the increase in defectivity of fluorocarbonapatite crystals. The change in the symmetry of the phosphate ion caused by the increase in defectivity is considered to be the main process that facilitates the subsequent thermal decomposition of phosphorite and determines the digestibility of the defluorinated tricalcium phosphate.

Infrared spectroscopy is a technique used in chemistry to identify and analyze the chemical composition of substances. It works by measuring the absorption, emission, or reflection of infrared light by a sample. Different chemical compounds absorb infrared radiation at specific frequencies, allowing scientists to determine the types of bonds and functional groups present in a substance. Infrared spectroscopy analyses were performed to identify the role of liquid-phase mechanical activation of phosphorite in defect accumulation, promoting fluorine removal and increasing specific surface area. Based on the results of these analyses, it can be assumed that the defects formed in the structure of fluorocarbon apatite are primarily localised in the coordination complexes that bind Ca_{II}^{2+} ions to the surrounding oxygen of the O_{III} tetrahedron of RO_4^{3-} and the F ion. This statement is associated with the decrease in the intensity and disappearance of the 1100 cm^{-1} absorption band, caused in the first approximation by vibrations of the $P\text{-}O_{III}$ bond. At mechanical activation of phosphorite in liquid-phase medium (T:L=1:5), when much higher dispersity was achieved than in samples obtained in media with less liquid phase, the decrease of the 1100 cm^{-1} band and even more so its disappearance was not observed[19)]. This suggests a rather complex nature of the defect accumulation process during mechanical activation. Long-term preservation of reactivity of activated fluorocarbonatapatite suggests the possible existence of a mechanism of fixation of formed defects upon adsorption of macromolecules of polyelectrolyte K-9. Adsorption is a process in which molecules or atoms adhere to the surface of a solid or liquid material. It is different from absorption, where a substance is taken up and incorporated into the bulk of another substance. Adsorption is commonly used in various applications, such as in the removal of pollutants from air and water using adsorbent materials like activated carbon. The infrared spectroscopy spectra of activated phosphorite showed absorption bands at 1430, 1465, and 880 cm^{-1}, which can be attributed, respectively, to the valence and strain vibrations of CO_3^{2-}-ion in the apatite structure at its substitution of the RO_4^{3-} – tetrahedron. A derivatograph is a scientific instrument used for thermal analysis, particularly in materials science and chemistry[20)]. It is used to study how a material's properties change with temperature. A derivatograph typically measures parameters such as weight loss, expansion, and other thermal characteristics as a sample is heated or cooled. Derivatograph data support the position that CO_3^{2-} and H_2O are obtained structurally bound after mechanical activation of phosphorite. Water is released over a wide temperature range of 100÷510°C, and CO_2. The total weight loss of the activated sample was 5.3%, whereas that of the original sample was only 0.25%.

Thus, during mechanical activation of phosphorite, there is a significant and rather complex increase in the defectivity of the fluorocarbon apatite structure with the inclusion of water and polyelectrolyte macromolecules, very significantly changing the composition and properties of phosphorite towards increasing its reactivity[21)]. In the abrasion of phosphorite, the distances between ions of its crystal lattice change and their transition to new positions. These changes result in “strained” chemical bonds, many of which are subsequently broken. It is due to these polymorphic transformations that the deco fluorination of phosphorite begins already at the stage of mechanical activation[22]. This statement is based on the results of investigating the surface of mechanically activated phosphorites using a Cam Scan MV2300D SEM scanning electron microscope.

As the micrographs presented in Figure 2 show, the samples of mechanically activated phosphorite under study do not change their sizes during the roasting process, and the shape of the particles stays close to spherical. The surface of the original sample particles has a “loose”, cellular structure with a considerable number of microcracks (tiny cracks that are not visible to the naked eye)[23]. Phosphorite particles heat-treated at 900℃ have a smoother surface. A relatively small number of rather large pores with rounded outlines are observed. The obtained data testify to the compaction of the structure of activated phosphorites during roasting. Microcracks usually form at weak points in the crystal lattice. Nevertheless, the formation of microcracks is not the final destruction of the crystal lattice, because when the load is removed, if destruction has not occurred, the microcracks merge and practically disappear. During adsorption, molecules of AWP K-9, penetrating by two-dimensional migration along the newly formed surfaces and lowering their surface energy in the formation of these surfaces, facilitate the development of micro-slits – surface defects, prevent their re-closure under the action of adhesion forces after removal of external influence.

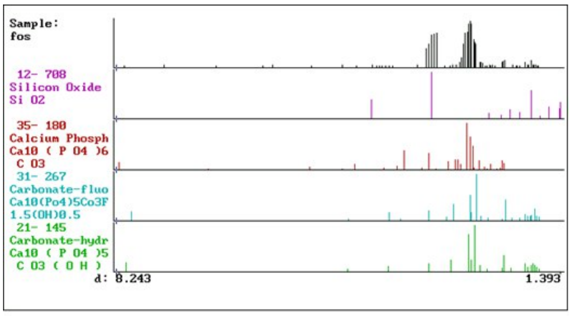

Fig. 2: Surface microstructure of phosphorite mechanically activated with the addition of surfactant K-9: (a) before roasting; (b) after roasting at 900°C

The adsorption of surfactants results in a more intensive development of microslits. The surfactants form a two-dimensional gas on the surface where they are adsorbed and, under the pressure of this gas, penetrate the mouths of the microcavities, tending to widen each microcavity. Thus, they contribute to external deforming forces and promote phosphorite dispersion. Dispersion is improved not only by the pressure of the two-dimensional gas, but by shielding the adhesion forces that act between opposing microslit surfaces when foreign matter penetrates the formed microslits. During mechanical activation at its various stages, the main accompanying fluorocarbonatapatite minerals play a positive role in building up the reactivity of phosphorite[24]. Therewith, apart from the reasons related to the physical properties of minerals, mechanochemical interactions involving minerals of such complex multiphase systems as phosphate ores should play a significant role.

For example, quartz, as the hardest mineral, plays the role of an internal abrasive that promotes dispersion and activation, and mechanochemical interactions between it and phosphate matter and other minerals are not excluded. The carbonates, dolomite and calcite, undergo deep structural disturbances, as evidenced by the disappearance of dolomite and calcite lines on the X-ray diffraction spectra of the final samples and their analytical absorption bands (730, 715 cm^{-1}, respectively) on the Infrared spectroscopy. The difference of Aksai phosphorite ore fines from other formation phosphorites is apparently due to enrichment of fines, during crushing and sieving of ore, with clay minerals and, possibly, more reactive (less strong) phosphate component. Secondary phosphorites before and after mechanical activation are the most soluble. The reason for this is the nature of the phosphate matter and its lowest crystallinity and the significant content of quartz and clay aluminosilicates (kaolinite).

Comparison of the obtained X-ray radiographs with reference ones suggests that the following compounds are most likely to be present in the presented samples: carbonatapatite $Ca_{10}(RO_4)_6CO_3$ (database No. ASTM 35-180), fluorocarbonate hydroxyapatite $Ca_{10}(RO_4)_5CO_3F_{1.5}(OH)_{0.5}$ (ASTM 31-267), carbonate hydroxyapatite $Ca_{10}(RO_4)_5CO_3OH$ (ASTM 21-145), and quartz SiO_2 (12-708) (Fig. 3). The phase composition of phosphorites before and after roasting does not differ significantly. Phosphorites No. 4 and No. 6 (surfactant – K-4) stand out from all the samples under study, for which the intensities of the reflex peaks corresponding to $Ca_{10}(RO_4)_6CO_3$ and $Ca_{10}(RO_4)_5CO_3F_{1.5}(OH)_{0.5}$ are noticeably lower in comparison with the other samples, which may be a consequence of more intensive removal of fluorine and CO_2 in mechanical activation using surfactant K-4.

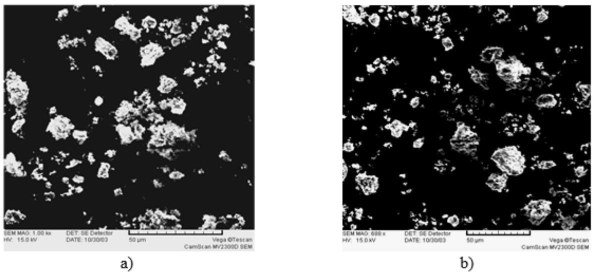
a) b)

Fig. 3: Comparison of phosphorite sample radiographs with reference radiographs according to ASTM fos – sample No. 1

During roasting of initial samples at 900°C, there is a regular decrease in the specific surface of powders by 3-4 times, which can be explained by the ordering of the substance structure due to healing of defects and microcracks, closing of micropores as a result of melting of fusible impurities. Therewith, the most noticeable densification of the structure during heat treatment is observed in the phosphorite sample obtained by activation with the addition of AWP K-4. The obtained results allow concluding that the increase in the degree of defluorination, transition of tricalcium phosphate from the non-assimilable β-modification into assimilable α-modification, as well as the increase in the solubility of tricalcium phosphate in weak hydrochloric acid is primarily associated with the destruction of the crystal structure of tricalcium phosphate and an increase in the defectiveness of crystals of fluorocarbonatapatite, rather than with an increase in the dispersibility of the material[21]. The change in the symmetry of the phosphate ion, the increase in defectivity is considered as the main process that facilitates the subsequent thermal decomposition of phosphorite and determines the digestibility of the defluorinated tricalcium phosphate (Fig. 4).

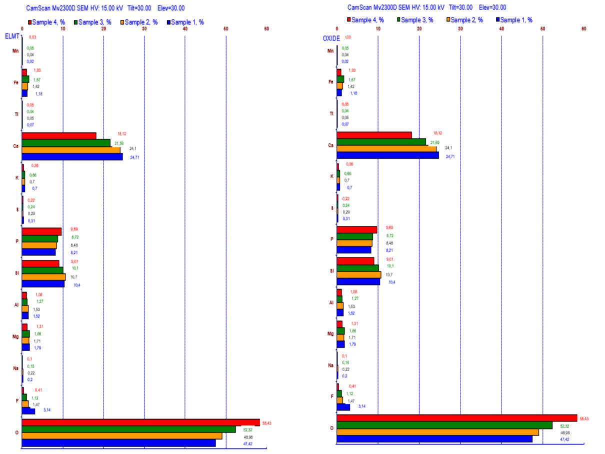

Fig. 4: Results of microprobe analysis on determination of elemental and oxide compositions of phosphorites

Note: blue – initial phosphorite; yellow – phosphorite after liquid-phase abrasion (T:L=1:5) without additives; green – phosphorite after liquid-phase abrasion (T:L=1:5) with addition of 0.03% AWP K-9; red – sample 3 after roasting at 900°C.

The capabilities of the method do not allow for recording the presence of several light elements, including hydrogen and carbon. Data on the chemical composition of phosphorites in terms of oxides were analyzed. The oxygen imbalance is distributed between carbon dioxide, which is part of natural carbonates, and water, which is part of hydroxyapatites and hydrated aluminosilicates. The analysis shows that the chemical composition of phosphorites is rather heterogeneous. The CaO/P2O5 ratio for different samples varies widely from 0.83 to 1.77. A comparison of pairs of samples before and after firing shows that the fluorine content decreases naturally during the roasting process. The decrease in oxygen imbalance indicates significant removal of carbon dioxide and bound water during heat treatment. Attention is drawn to the increased oxygen content and decreased calcium content in samples No. 3 and No. 4. Some parallel analyses of different samples of these phosphorites give comparable results, which does not give grounds to consider the data obtained as a local disturbance of the chemical composition. The kinetics of the a to b transition or, conversely, modification, occurs in the liquid state of phosphorite[25].

It can be assumed that the destruction of the structure of tricalcium phosphate under the influence of polyelectrolyte macromolecules is accompanied by changes in its coordination complexes. This is the reason for the change in the symmetry of the phosphate ion, a determining factor in the solubility of tricalcium phosphate. Changes may be occurring in the crystal lattice of fluorocarbon apatite, including the conversion of volatilized carbonates, sulfides, and fluoride compounds into a more resistant form that decomposes when exposed to heat. As a result of these studies, a significant intensification of solid-phase reactions due to preliminary mechanical activation of phosphorite was determined. Whereas in conventional heating, low-temperature stages are realized first, followed by high-temperature stages, in pulsed heating and abrupt cooling, high-temperature processes are mainly carried out. The use of acrylic polyelectrolytes during liquid-phase abrasion of phosphorite significantly increases the efficiency of de-fluorination and the content of the assimilable form of P2O5 in the resulting product. The main minerals accompanying apatite in phosphate ores play a positive role in increasing the reactivity of phosphate matter during mechanical activation at various stages.

Changes in the pH of the suspension and the fluoride content of the liquid phase during the test indicate the neutralization of the acid formed by the dissolution of fluoride by phosphorite salts passing into the solution during the abrasion process. To determine the maximum possible degree of phosphorite de-fluoridation and conversion of P2O5 into an assimilable form, an abrasion experiment was carried out for 3 hours[26]. The content of assimilable P2O5 – 23.2%, residual fluorine – 0.81%, which corresponds to the degree of de-fluoridation – 68% and the ratio of assimilable P2O5 to total P2O5 – 72.4%. The chemical composition of the liquid and solid phases, as well as the particle size distribution of the solid phase, were determined in the suspension treated for 3 hours and are presented in Tables 1-3.

Table 1. Chemical composition of the liquid phase of the treated suspension

S_{total}	F	CaO	MgO	Fe_2O_3	Al_2O_3
Res.	0.312%	0.072%	0.058%	0.024%	0.02%

Table 2. Chemical composition of solid phase of spent suspension

P_2O_5	CaO	Al_2O_3	Fe_2O_3	CO_2	F	IR	MgO	H_2O	Other
32.05 %	36.7 %	0.82 %	2.29 %	6.82 %	0.81 %	14.52 %	2.61 %	0.14 %	2.97 %

Table 3. Particle size distribution of the solid phase of the treated suspension

+0.4 mm	+0.315 mm	+0.2 mm	+0.16 mm	+0.1 mm	+0.063 mm	+0.05 mm	-0.05 mm
0.02 %	0.1 %	0.81 %	2.31 %	10.12%	54.21%	26.22%	6.21 %

The results of the chemical analysis of the treated suspension indicate the defluorination of phosphorite, the increase of P2O5 content in it, as well as the dissolution of salts, calcium, magnesium, aluminum, and iron in the liquid phase, which neutralize the acidic environment formed as a result of fluorine dissolution. This is evidenced by slight changes in the pH of the suspension during activation. The particle size distribution of the solid phase is represented mainly by fractions +0.063 and +0.05 mm, which corresponds to a specific surface of the obtained product of 86¸95 m2/h.

The initial phosphorite and the solid phase of the treated suspension were subjected to spectral and X-ray analyses. As a result of these analyses, it was found that in the initial phosphorite, phosphorus is in the form of fluorapatite, quartzite in the form of a-quartzite. The presence of dolomite (CaMg(CO3)2) was detected in both samples. The treated phosphorite shows a sharp deterioration of the crystal structure (absorption bands on the spectrogram are blurred) compared to the original phosphorite (absorption bands with pronounced peaks). There is also an increase in phosphate and a decrease in fluoride, dolomite, calcite, and quartz. On the X-ray and spectrogram appear peaks characteristic for the a-modification of tricalcium phosphate. During the operation of the phosphate slurry activation unit, 640 kg of phosphate slurry was produced. Solid phase, which was used for further processing into feed defluorinated phosphates. In this experimental batch, the content of total P2O5 was determined to be 33.21%, assimilable P2O5 to be 20.31%, and residual fluorine content to be 1.19%.

The obtained data indicate that the process of transition of P2O5 into assimilable form goes with sufficient speed and effectively at the roasting temperature exceeding 900℃, already at 30 minutes of roasting the product containing 29.3% of assimilable P2O5 and 0.12% of fluorine will be obtained. Roasting at lower temperatures (800 and 700℃) does not give the expected result, but it does lead to a reduction in fluorine content, confirming the conclusions of laboratory studies on the mechanism of defluorination. Increasing the firing temperature up to 1000℃ leads to insignificant improvement of the product quality and cannot be justified from an economic standpoint. In this series of experiments, experiments were also carried out to determine the maximum possible degree of solid phase defluorination and conversion of P2O5 to an assimilable form. The roasting in this experiment was carried out at 900℃ for 2 hours. As a result, the content of assimilable P2O5 – 32.44%, and residual fluorine – 0.07%, which corresponds to the ratio of assimilable P2O5 to total P2O5 equal to 97.41%. Chemical X-ray diffraction and spectral analyses were performed on the obtained product (Table 4).

Table 4. Chemical composition of the obtained product

P_2O_5	CaO	Al_2O_3	Fe_2O_3	CO_2	F	IR	MgO	H_2O	Other
33.3	35.8	0.92	3.41	3.12	0.07	17.91	2.87	0.02	2.58

The results of analyzing the chemical composition of the resulting product indicate the defluorination of phosphorite and the reduction of water and carbon dioxide. X-ray structural and spectral analyses indicated a decrease in the dolomite content, strengthening of the crystal structure (more pronounced absorption peaks on the spectrogram), and almost complete disappearance of characteristic peaks of fluorapatite and b-modification of tricalcium phosphate. Thus, the obtained product fully meets the requirements of GOST 23999-80 for calcium phosphate fodder, and after grinding in the mill is a fine powder of grey color (with admixtures of calyx – due to the increased content of iron oxide), the aqueous solution of which has a weakly alkaline reaction, does not stick, is not hygroscopic, well dispersed. The volumetric weight of the product is 1.6 t/m3. The results of pilot tests have confirmed the possibility and efficiency of using the developed method of obtaining feed-defluorinated phosphates. The obtained results formed the basis for the initial data for the design of an industrial scheme for feed phosphate production with a capacity of 2000 t of 100% P2O5.

Mechanical activation of phosphorite, aided by surface-active additives, played a significant role in defluorination and increased reactivity, enabling the transition of tricalcium phosphate from non-assimilable β-modification to assimilable α-modification. The study's findings suggest that the defluorination process is intricately linked to the destruction of the crystal structure of tricalcium phosphate, accompanied by changes in coordination complexes and increased defectivity.

Furthermore, a fluidized bed process, as explored in related research, offers an innovative approach to recycling fluorine compounds efficiently. The findings emphasize the need for optimizing roasting temperatures and duration to achieve the desired defluorination while preserving other essential attributes of phosphorite.

Additionally, post-roasting, the utilization of fluoride compounds, as proposed in other studies, presents opportunities for reducing emissions and promoting environmentally sustainable practices. In summary, this research contributes to a deeper understanding of managing fluoride emissions in the phosphorite industry and offers insights into potential solutions for more sustainable processing.

4. Discussion

In study, have undertaken a comprehensive examination of the challenges and consequences associated with managing fluoride compounds generated during the roasting of mechanically activated phosphorite. In the context of existing literature on this subject, research not only aligns with but also extends the foundational knowledge concerning fluoride emissions in the phosphorite roasting process. One key facet of our investigation delves into the temperature-dependent relationship between firing temperature and the defluorination of phosphorite, drawing parallels with findings from previous research conducted by M. Smol et al.27). Specifically, aim to shed light on the intricate dynamics of fluoride compound release during phosphorite roasting, particularly when mechanical activation techniques are employed. Building upon the observations made by M. Smol et al.27), also contemplate the evaporation of fluorides and its implications for the quality of the resulting product.

Calcium phosphate is a key component for the formation and repair of the mineral matrix of bones and teeth, it helps to ensure good health for human beings28). The process of regeneration and biomineralization in the craniofacial complex requires the delivery of calcium phosphate to points of tissue damage or defects. This can be accomplished using various delivery systems such as nanoparticles, hydrogels, polymer-based matrices, or ceramics. Nanoparticles are an effective delivery vehicle for calcium phosphate because of their small size and large surface area29). They can be functionalized to provide a controlled and gradual release of calcium phosphate over a period of time. This allows for the gradual formation and growth of a new mineral matrix in damaged tissues. Hydrogels, in turn, have high water absorption capacity (can even contain more than 90% water) and can be filled with calcium phosphate30). They can be injected into damaged tissues in liquid form and solidify in situ to form gels. This provides direct delivery of calcium phosphate to damaged areas and promotes bone and tooth regeneration. Polymer or ceramic-based matrices are also used to deliver calcium phosphate to the tissues of the craniofacial complex. They can be designed with a specific structure and porosity to ensure optimal tissue interaction and promote tissue regeneration. Notably, calcium phosphate delivery systems must be biocompatible and safe for use in the body. They should provide a controlled release of calcium phosphate, preventing excessive accumulation or deficiency.

J.T. Holmes et al.'s31) fluidised bed fluoride recycling technique brings forth an innovative approach in managing fluoride emissions. The fluidized bed process is a method used in chemical engineering and industrial processes32). It involves suspending solid particles in a gas or liquid medium to create a fluid-like behavior. In a fluidized bed reactor or system, the particles become buoyant and exhibit properties similar to those of a fluid. This process is commonly used in various applications, including combustion, chemical reactions, and particle coating, due to its efficient heat and mass transfer properties. Comparing with our study, while they focus on the efficient recycling of fluorine, expand on the broader environmental repercussions and methods to curtail them. S.N. Kubekova et al.33) investigated mechanical activation's impact on defluorination, aligning closely with our research domain. Their emphasis on varying parameters like intensity and duration provides an essential foundation to our study, which delves deeper into the subsequent waste challenges.

T. Han et al.'s34) research on phosphorite decomposition via pyrolysis provides a comprehensive view on fluoride's evolution during roasting. The anaerobic conditions they describe seem to echo our findings of fluoride compound formations, justifying our emphasis on their management. In pyrolysis, phosphate rock is subjected to hot temperatures (typically between 900 and 1200°C) in the absence of oxygen or its insufficiency. This process is called anaerobic decomposition. Pyrolysis results in the decomposition of phosphorite into several components. Firstly, there is the formation of phosphorus gas (P_4), which is the main product of pyrolysis of phosphate rock. Phosphorus gas is highly reactive and can be used for further production of phosphorus compounds. Furthermore, pyrolysis produces other compounds such as phosphorus oxides (e.g., P_2O_5) and metal oxides contained in phosphorite35). These compounds can be further processed and used in various industrial processes. Notably, the thermal decomposition process of phosphorite requires control of conditions such as temperature, heating duration, and atmospheric composition. The optimum conditions may vary depending on the type of phosphorite and the products required36).

R. Li et al.'s37) exploration on the utilization of fluoride compounds post-roasting aligns with our conclusion's sentiment. Their focus on flue gases and technologies for reducing emissions resonates with our emphasis on environmentally sustainable methods.

5. Conclusions

The study of production wastes in the roasting of mechanically activated phosphorite and the utilization of fluoride compounds are crucial tasks for industry, ecology, and human health. Implementing effective methods for fluoride compound utilization supports sustainable industry development and reduces environmental harm. The roasting of mechanically activated phosphorite leads to fluoride compound formation due to the high fluorine content in phosphorite. This process involves the release of gaseous fluoride compounds and the formation of solid waste with fluoride content. Managing these different forms of fluoride compounds requires integrated approaches. Proper disposal of fluoride compounds is essential for environmental conservation and human well-being, as these compounds are toxic and can harm ecosystems and health. Developing efficient waste treatment and purification methods is necessary to mitigate these adverse effects.

Physicochemical methods may include absorption, neutralisation, or flotation of fluorides, while biological methods rely on the use of microorganisms capable of degrading fluoride-containing compounds. The selection of the best technology should consider cleaning efficiency, economic feasibility, and scalability of the process. An important aspect is the development of a control and monitoring system for fluoride emissions.

This entails the implementation of suitable monitoring tools and systems to measure and manage the levels of fluoride compounds in emissions. Additionally, it involves the establishment of regulatory frameworks and standards that, when followed, can mitigate pollution. Analyzing the industrial waste generated during the roasting of mechanically activated phosphorite is crucial for assessing the environmental and health consequences of this procedure. The fluoride compounds generated through roasting may possess toxic attributes and can have detrimental impacts on biological systems. Therefore, the utilization of these compounds is becoming an integral part of the industrial production of phosphate rock and mineral fertilizers. The application of efficient and environmentally safe methods of fluoride compound disposal is a necessity to minimize their adverse environmental impact.

The development and application of such methods will reduce the emission of fluoride compounds into the atmosphere and prevent contamination of soil and water. Furthermore, the utilization of fluoride compounds can contribute to the economic efficiency of production and improve working conditions. Further research and development in this area will play a significant role in finding innovative technologies and innovations for more efficient utilization of fluorinated compounds. Researchers and engineers are striving to find ways to treat waste that are environmentally friendly, efficient, and economically viable. The development of new recycling methods and technologies will reduce the environmental impact, reduce the consumption of natural resources, and promote sustainable development of phosphate rock and mineral fertilizer production.

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