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Production of composite materials based on phosphate mineral waste

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Abstract. Composite materials have features such as rapid construction. Some composite materials primarily include epoxy resins, methyl methacrylate-based polymers, initiators, and plasticizers. In addition, there are also some inorganic and organic composites. This type is generally more expensive, but since it uses organic polymers, it is difficult to guarantee its long-term performance, such as protection from aging, UV resistance, and sunlight. Cost is reduced by the inclusion of a large amount of phosphogypsum, and some metal oxides contained in phosphorites can chemically react with it, increasing its strength. Furthermore, silicates in ore can also react chemically with it, thereby improving its interfacial adhesion.

INTRODUCTION

Resources and energy are becoming increasingly scarce, so the use of local resources is becoming increasingly important. Slags, which are by-products of the processing of local phosphorite ores, are a promising source of elements necessary for the sustainable development of various industries, such as building materials, ceramics and glass. Alternative ways of using such local materials are also being sought.

Recently, the phosphorus industry has become one of the most promising and financially stable sectors of the chemical complex. At the same time, such development of the industry occupies vast areas in the form of large-tonnage waste generated by the phosphorus industry (phosphogypsum, granular phosphorus slags,) and has a negative impact on environmental components [1].

In order to combat the accumulated waste in the phosphate industry, a preliminary analysis of the main types of products of the phosphate industry (phosphate fertilizers, phosphoric acid, yellow phosphorus) was carried out.

The most important raw material reserve of the construction complex is the multi-ton waste of the phosphorus industry, the complex use of which allows the formation of rational structures of new composite materials as a result of physical and chemical interactions [2].

The development of a technology for obtaining building materials based on the complex processing of waste from the phosphorus industry is an urgent issue in the field of building materials.

Phosphogypsum is a waste product in the production of phosphoric acid from phosphorite. This is a waste material containing various levels of impurities, including gypsum, which can be separated from phosphogypsum by various methods. Given the current production of phosphogypsum, its use, disposal or transportation are environmentally and economically efficient in all respects: environmentally and economically. Therefore, in recent years, the possibilities of processing phosphogypsum and its proper use have been expanding. Judging by the number of publications, interest in phosphogypsum as a source of secondary raw materials has increased significantly over the past decade. Initially, phosphogypsum was mainly used in the construction, cement, road construction, and agricultural industries. However, in the last 10-20 years, due to the increase in anthropogenic pressure on the environment and the resulting natural disasters, the attitude towards raw materials sources has changed. Phosphogypsum is considered a source of elements with many useful properties, including calcium, phosphorus, and rare earth elements, and is used as a mineral resource in technological processes, including [2].

More than 50 gypsum wastes can be listed in the national economy, of which phosphogypsum is the largest. Wastes are generated in various volumes, and phosphogypsum slags from them amount to several million tons. It is purposeful to express the aspects of using chemical industry wastes as secondary resources as follows: obtaining binders based on phosphogypsum and other gypsum-containing wastes. In this area, the innovative technologies for the preparation of binders (modified phosphogypsum, sulfomineral cements, etc.) Similar scientifically based technologies have been introduced in Russia, Lithuania, Armenia, Bulgaria and other countries. In Bulgaria, the production of products by extrusion without washing phosphogypsum, and in Belarus, the technologies for the preparation of polymer phosphogypsum are noteworthy [3].

In Uzbekistan, fundamental changes have occurred in all sectors of industrial production. Including in the construction industry. Due to the growth of industrial, civil and residential buildings, the demand for construction, cement and gypsum-based finishing building materials has increased sharply. Gypsum-based materials are most often used for interior decoration. Their advantages are relatively low production of lime and cement, fuel consumption in the production process, sufficiently high strength, rapid hardening and rapid strength gain. It consists mainly of a gypsum binder, to which various fillers, extenders and modifiers are added.

Currently, considerable experience has been accumulated in the production of gypsum binders from industrial by-products. The schemes for the production of binders are diverse and usually include preliminary processing of raw materials (washing, neutralization of acid in the liquid phase, etc.). Given that the largest amount of all by-products is phosphogypsum, its processing into a binder is the main solution of the research work.

EXPERIMENTAL RESEARCH

Hydrothermal treatment of fluorapatite at 1400-1500 °C leads to the isomorphic replacement of fluoride ions with hydroxyapatite:

$Ca_{10}(PO_4)_6F_2 + 2H_2O = Ca_{10}(PO_4)_6(OH)_2 + 2HF$

When heated, hydroxyapatite decomposes into tricalcium phosphate and tetracalcium phosphate:

$Ca_{10}(PO_4)(OH)_2 = 2Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O$

In the presence of silica, the process proceeds according to the following scheme:

$Ca_{10}(PO_4)(OH)_2 + 0.5SiO_2 = 3Ca_3(PO_4)_2 + 0.5Ca_2SiO_4 + H_2O$

In summary, the process can be represented by the equation:

$Ca_{10}(PO_4)_6F_2 + H_2O + 0.5SiO_2 = 3Ca_3(PO_4)_2 + 0.5Ca_2SiO_4 + 2HF$

Pre-granulation of powdered apatite concentrate with the addition of phosphoric acid eliminates the use of sand, reduces dust content in exhaust gases, and increases the rate of phosphate defluorination and the P_2O_5 content in the product. Adding phosphoric acid to natural phosphates instead of silica also significantly increases their deformation and melting temperatures. In the absence of SiO_2, the phosphoric acid standard corresponding to a molar ratio of $CaO:P_2O_5 = 3$ (mass ratio 1.18), the defluorination process can be represented by the following scheme: when mixing phosphate with acid.

$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O = 10Ca(H_2PO_4)_2\cdot H_2O + 2HF$

$CaCO_3 + 2H_3PO_4 = Ca(H_2PO_4)_2\cdot H_2O + CO_2$

When heating phosphate to 500-600 °C (in total)

$Ca(H2PO4)2\cdot H_2O = Ca_3(PO_4)_2 + 3H_2O$

When heating to 600-900 °C

$Ca_{10}(PO_4)_6F_2 + H_3PO_4 = 10Ca_3(PO_4)_2 + 6HF$

When heated above 900-1000°C

$Ca_{10}(PO_4)_6F + Ca_2P_2O_7 + H_2O = 4Ca_3(PO_4)_2 + HF$

The overall equation for the entire process is:

$Ca_{10}(PO_4)_6F_2 + H_3PO_4 = 10Ca_3(PO_4)_2 + 6HF$

Defluorination process mechanism. During the hydrothermal processing of fluorapatite, H+ ions and OH- ions formed during water dissociation penetrate the fluorapatite molecule if they do not carry solvate.

The use of phosphate fertilizers in livestock farming dramatically increases meat and milk production and provides an economic benefit of up to 20 times. On average, 1 ton of defluorinated phosphates can produce an additional ton of meat. The composition of feed and food phosphates is subject to strict requirements regarding the content of harmful impurities such as fluorine, arsenic, heavy metals, and others. Therefore, thermal phosphoric acid (TPA) is currently used to produce food products, some detergents, and a wide range of feed additives for livestock. However, its cost is high due to the significant energy consumption required for its production. Therefore, there is an urgent need to replace thermal acid with less expensive wet-process phosphoric acid (WPP), which must be pre-purified [4].

The stability of the solid-phase defluorination process depends primarily on the range between the intensive defluorination temperature and the melting point of the material being processed. The wider this range, the more stable the process will be without undermelting, which disrupts the normal defluorination process. To justify the selection of phosphoric acid addition rates and firing temperatures, the dependences of these firing temperatures for phosphorites were studied, taking into account possible variations in their composition.

A thermographic study of the chemical transformations occurring during firing allowed us to determine the temperature limits for additional chemical transformations for these phosphorites: when heated to 600°C, dehydration of monophosphates occurs, and in the temperature range of 600–1000°C, decomposition of fluorapatite with the release of CO_2 is observed. For phosphorite, these changes begin at 600°C and end at approximately 800°C. Analysis of the firing products at temperatures above 900°C, conducted using paper chromatography, revealed the presence of pyrophosphate, the formation of which under these conditions may be caused by a reaction between fluorapatite and calcium metaphosphate—a dehydration product of monocalcium phosphate—as this reaction results in a slight decrease in fluorine content. Significant pyrophosphate formation is observed at a calcination temperature of 1100°C, close to the melting point of metaphosphate. The onset of reaction between pyrophosphate and phosphate bases is observed only at temperatures above 1100°C.

RESEARCH RESULTS

We obtained feed phosphates from low-grade phosphate rocks. We first analyzed the physicochemical and thermodynamic properties of the starting components, followed by laboratory studies.

The study was carried out using a LABSYSEVOSTA derivatograph (SETARAMEVOLUTION, France) in the temperature range 30-1100^{0}C. The rate of temperature rise was 10 deg / min, and the weight of the sample was 360 mg. The chemical composition of solid phases, intermediate and end products of the reaction, the content of P_2O_5, was determined by the photocalorimetric method, and Ca^{+2}, Mg^{+2} by the complexometric method.

The experimental data of the thermographic study of the samples showed that there is a fundamental difference from the known processes at 740^{0}C and above. The derivatogram of the mixture phosphorite: potassium chloride: sand revealed additional endothermic effects associated with the melting of potassium chloride (770 and 800^{0}C) and the formation of potassium calcium and calcium silicate phosphates (above 102^{0}C).

The study of the charge, consisting of phosphorite and potassium sulfate, showed, as in the previous cases, at 110^{0}C there is an endothermic effect caused by the removal of hygroscopic moisture.

Endothermic effects in the temperature range 110-180-315^{0}C indicate dehydration of the present mineral salts at 410-770^{0}C - melting of potassium sulfate, dissociation of carbonate rocks, i.e. complete decomposition of calcite and other carbonate-containing minerals. At temperatures above 1000^{0}C, the phosphorite crystal lattice is rearranged and double potassium phosphates are formed [6].

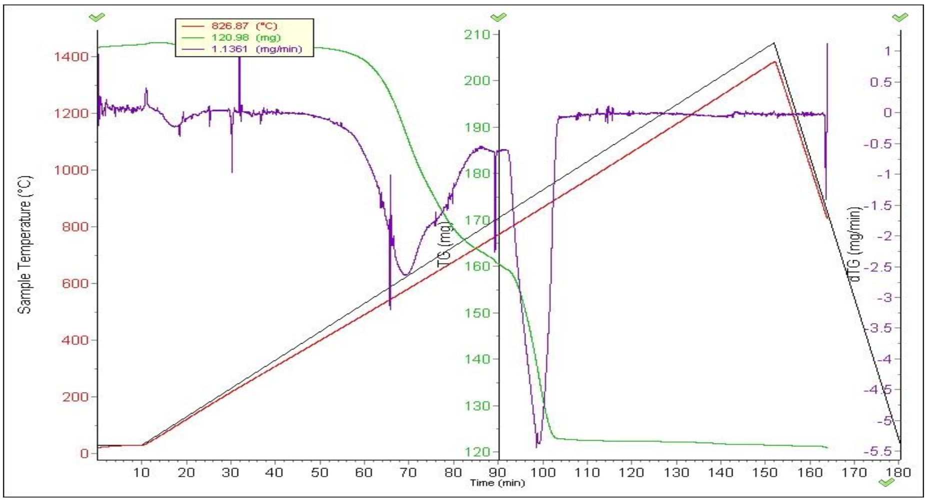

FIGURE 1. Derivatogram of phosphorite waste slurry.

The loss of mass is explained by the removal of crystallization water, as well as gaseous components CO_2, HF, SiF_4. The study of the reaction products obtained under conditions corresponding to the thermal effects on the derivatograms, as well as the kinetics of the process, made it possible to reveal the features of the mechanism of the main process and the accompanying chemical transformations, as well as the optimal parameters of the process.

During the preliminary assessment of the suitability of man-made raw materials for the production of building materials, it was necessary to ensure not only a satisfactory gross chemical composition and a minimum content of harmful impurities, but also their chemical and mineralogical homogeneity.

The rate of phosphate decomposition is directly proportional to the contact surface area between the solid and liquid phases. As grinding fineness increases, the surface area of the solid phase increases, thereby increasing the contact surface area between the phosphate and the liquid phase, thereby accelerating the decomposition process [8-10].

The decomposition of individual particles can be represented as follows: when exposed to acid, their surface becomes covered with microscopic, multifaceted depressions, which strengthen the surface area.

CONCLUSIONS

The utilization of phosphogypsum in the national economy contributes to reducing the anthropogenic impact on the environment by lowering the need for mineral extraction (such as gypsum and anhydrite) from the Earth's crust and minimizing the accumulation of chemically precipitated calcium sulfate in storage sites. Comparative studies of crop yields on various soils, both with and without phosphogypsum application, indicate that phosphogypsum can effectively serve as a substitute for natural gypsum, provided that both are applied in equivalent amounts based on their $CaSO_4 \cdot 2H_2O$ content.

Road construction projects frequently involve urgent repairs, especially during natural disasters (such as earthquakes, floods, snowstorms, etc.), which become more urgent. As a result, quick-repair building materials have emerged over the years. Currently, domestic quick-repair building materials primarily include inorganic and organic types. Inorganic materials are typically prepared using special cements (e.g., high-alumina cement, sulfoaluminate cement, etc.) or accelerator-treated Portland cement. These quick-repair materials are easy to manufacture and inexpensive, but typically have low strength and are incompatible with other materials.

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