Transformation of non-firing technology issues for construction composite production from particulates using phosphogypsum

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Abstract. This paper presents the research results of the structure formation process of construction composites with the simultaneous extraction of a non-radioactive rare-earth metals concentrate in a non-fired technological process from a chemical production waste, phosphogypsum, which is being accumulated in dumps for years and causing damage to the environment. The article provides the results of the initial material studies by the X-ray fluorescence method, differential thermal calorimetry, and spectrometry on such aspects as radioactivity, chemical composition, dehydration energy. A flow chart of the energy-saving non-firing technology for the direct production of wall materials with a simultaneous extraction of the rare-earth metal concentrate from phosphogypsum is presented. When leaching the phosphogypsum, the concentrate, containing non-radioactive rare-earth metals, was obtained. It has been shown that phosphogypsum can be used as a construction material without restrictions on radioactivity. Laboratory research and verified technology proved the phosphogypsum exhibits astringent properties that provide the production of wall materials by non-firing method with the simultaneous extraction of the rare-earth metal concentrate. The developed technology makes it possible to separate strategically important rare-earth metals from the phosphogypsum while reducing the cost of production of wall materials by 2 ... 3 times.

1. Introduction

Currently, the construction industry has faced the problem of developing effective wall products and materials used in road construction. The technology of wall materials is associated with the high cost of their production, due to the significant costs of endothermic structure formation reactions. Replacing the processes of increasing the internal energy of bond formation by heating with the entropy change by the thermodynamic method results in non-firing technologies for the production of construction materials and products from recycling of anthropogenic particulates. A promising direction for the production of piece wall materials seems to be the technology using isothermal pressing with a wide raw material base that allows the use of local, non-deficient, natural and

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anthropogenic raw materials, industrial waste and by-products, which is a simpler technology, allowing one to organise their production with the minimal investment. The problem of phosphogypsum utilization is one of the most significant global environmental problems [1-4] and it can be solved by means of using new technologies in the construction industry in such areas as road construction, gypsum production and anhydrite binders and fillers for the construction mixtures. The economic efficiency of the direct use of phosphogypsum or its products instead of traditional natural raw materials in the construction industry in various areas has the following indicators: road construction - 5.4%; gypsum binder production - 2.5%; production of anhydrite binder when used in construction - 3.9%; filler production - 21–53% [5]. There are several ways to use phosphogypsum: as one of the components of the binder in production; in the manufacturing of fillers [6], in the production of drywall without the use of paper and fibers [7], in the manufacturing of wall products, for example, bricks using a firing technology [8]; in the manufacture of Loess [9], in the construction of motorways; in non-fired technologies for producing wall materials and paving slabs. Non-radioactive rare-earth metals are extracted from phosphogypsum [10-13]. There is an autoclave method for processing phosphogypsum into gypsum binder, when phosphogypsum with the moisture content of up to 55% is fed from the sulfuric acid production workshop to the receiving hopper of the workshop for processing it into the gypsum binder. The resulting gypsum binder reaches 40 - 50 MPa in strength, its water demand is 30 - 36% [14]. Water-resistant anhydrite binders are obtained from phosphogypsum wastes by firing them with the addition of aluminosilica materials, which in sand solutions achieve compressive strength of dry samples of up to 10 - 15 MPa [15]. To obtain solutions from phosphogypsum with high strength indicators, high-performance grinding in a vibratory mill is used [16,17]. Composite waterproof gypsum binder for the road industry is also obtained by co-milling with a finely ground mixture of refining slag and calcium sulfate dihydrate gypsum [18]. Phosphogypsum can be used in the production of construction materials as a basis for crystallization structures, not the binder, which opens up the prospects for its large-scale application in industry [19,20]. With casting technology, it is impossible to bring gypsum dihydrate particles to the required distance, therefore, the authors offer their own method of forming such systems. There is a technology for producing cladding plates from phosphogypsum by pressing water pastes with simultaneous drainage of water [21,22]. A cheaper and less resource-intensive method is also known. The compression of rigid mixtures containing 70 - 80% of phosphogypsum, 20 - 30% of gypsum, and anhydrite or sulfate-slag binder, under the pressure of 5 - 20 MPa makes it possible to obtain products with a compressive strength of 5 MPa or more, which makes it possible to widely use the resulting mixture for the production of construction blocks and road construction elements [23,24].

The authors of this paper made an attempt to transform the key aspects of the non-firing technology for construction wall and road materials.

The following assumptions were used as the theoretical basis of this research:

- water films at the phase interface lead to the emergence of proppant pressure, the value of which is determined by the forces of interaction of diffuse layers of the electric double layer of colloidal systems of dispersed materials and the concentration of charged hydrated particles;
- process water is adsorbed in the form of films on the surface of hydrophilic particles with intensive mixing of the components of the initial mixtures;
- when heating a raw material to the temperature of 65 ... 70 °C and regulating the pH of water extracts from 2 to 8, the effect of aquating of the water films in thickness occurs;
- water film thickness depends on the features of the raw ingredients and the value of the dehydration energy;
- the ability of particulates to structure formation during pressing is predicted by the value of dehydration energy, automatically determined by the thermal method of differential scanning calorimetry.

The development of new interpretations of the structure formation theory for artificial composites using non-firing technologies and production facilities for the recycling of anthropogenic products, in particular, phosphogypsum, with the simultaneous production of construction materials and a rare
earth metals concentrate on the territory of the Russian Federation, will provide environmental safety and comfort in the production regions where phosphogypsum dumps are formed. A technologically sound approach to the use of this material allows offering the construction industry technologically advanced and efficient wall materials in a new way, using the embedded capabilities for the extraction of rare earth metals, and provide their partial replacement. The study of the phosphogypsum properties is carried out at the Voronezh State Technical University, and on its basis the development of an energy-saving non-firing technology for the formation of wall materials and the extraction of rare earth metals from phosphogypsum is performed [25-28].

The following particular tasks were formulated for the development of this technology:
- definition of the structure-forming properties of phosphogypsum;
- assessment of the dehydration energy and pressure on the strength of the obtained construction material;
- development of the procedure for predicting the properties of raw materials for the structure formation processes of artificial construction composites using smart technologies;
- development of the technology for extracting rare earth metals from waste phosphogypsum and converting them into concentrate;
- scientific substantiation of the technology of energy saving in the low-temperature formation of materials for wall structures and the extraction of rare-earth metal concentrate from the raw materials.

As a result of the analysis of the obtained theoretical studies and laboratory tests, a technology is proposed for the direct production of construction composites by compressing of starting materials with preliminary mechanical and chemical activation of the surfaces of the raw material granules. This activation increases the internal energy of the original substance and promotes the recrystallization of phosphogypsum. Earlier studies [25-28] proved that when using the technological operation of compressing, a directed formation of an energetically effective crystal structure with 1-100 nm thick water films on its surfaces occurs.

Using the formulated theoretical provisions for the structure formation, the authors conducted field studies on the possibility of a direct production of construction products and the extraction of non-radioactive rare earth metals in the form of a concentrate from dump phosphogypsum of the chemical industry waste.

2. Materials and methods

In order to improve the reliability of the research, the phosphogypsum of the Voskresensk Chemical Plant was taken. The proportions of the chemicals in the studied phosphogypsum are presented in table 1 [12], this table does not contain the description of rare earth elements.

| Total moisture | pH   | P₂O₅ | F      | CaO   | SiO₂  | Fe₂O₃ | SO₃  |
|---------------|------|------|--------|-------|-------|-------|------|
| 42 – 45       | 2.5  | 0.8 –1.2 | 0.15 –0.55 | 35 – 42 | 0.2 – 0.6 | 0.2 – 0.3 | 0.3 – 0.7 |

Dispersed phosphogypsum was molded in the form of 5 × 5 cm cylinder samples on the testing machine hydraulic press MS-500 according to the non-firing technology for producing composite construction materials. The following factors were taken as the key factors affecting the strength of pressed samples of phosphogypsum:
- X₁ – dispersed phosphogypsum temperature, °C;
- X₂ – molding pressure, MPa;
- X₃ – pressing duration for the dispersed phosphogypsum, sec.

These factors are selected due to the fact that, according to the theoretical foundations of the experiment, the formation of the structure of compressed disperse systems (phosphogypsum) occurs
when the thickness of the water films between the contacting particles changes and due to the contact-condensation mechanism. In the latter case, it is assumed that joint crystallization planes of the particles of the raw material are formed, as in the technology for producing limestone brick and at some pressure application. All these factors are compatible and uncorrelated with each other. The limits of variation of the studied factors are given in Table 2. The selection of intervals for changing factors is determined by the technological conditions for producing artificial stone using the non-firing technology, and by the technical capabilities of the pressing process. The assessment criterion of the impact of various factors on the process of structure formation (Y) was the ultimate compressive strength of the obtained cylinder samples made of phosphogypsum, hardening under normal temperature and humidity conditions.

Table 2. The limits of input factor changes.

| Planning conditions | Factor change limits |
|---------------------|----------------------|
|                     | $X_1$, °C | $X_2$, MPa | $X_3$, sec |
| Basic level         | 60        | 15         | 360        |
| Top level           | 80        | 20         | 180        |
| Bottom level        | 40        | 10         | 10         |

The determination of the physicomechanical properties of the obtained phosphogypsum cylinder samples in the study was carried out on the basis of the requirements for experimental studies on the Instron 5982 universal electromechanical test system with an absolute error of the load value within ±0.5.

Dispersed phosphogypsum samples were heated in a baking oven to the required temperature, placed in molds and molded under compression pressure and the exposure time of dispersed phosphogypsum in a mold when loading was applied according to the specified limits of input factors change (Table 3).

Thermoanalytical analysis of the starting material was carried out on an STA 449 F5 A-0082-M instrument (NETSCH, Germany) with the NETSCH Proteus software. The performed experimental study is aimed at establishing the correlation dependence of the dehydration energy of the obtained samples from phosphogypsum on the compressing pressure.

3. Results

For the reliability of the results obtained, the planning matrix for a full-scale experiment was designed, the results of which are presented in Table 3.

Table 3. The reference values of the n-implementations of experiments and the strength characteristic obtained.

| Experiment No | Implementation No | Physical strength, MPa (after 14 days of hardening) | Compressive strength, MPa (after 14 days of hardening) | Softening factor |
|---------------|-------------------|-----------------------------------------------------|-----------------------------------------------------|-----------------|
|               |                   | $X_2$, MPa | $X_3$, sec | $X_1$, °C |                                                   |                |
| 1             | 1                 | 10        | 10        | 40±5     | 1.92                                              | 0.39           |
| 2             | 4                 | 15        | 180       | 9.05     | 0.24                                              |                |
| 3             | 7                 | 20        | 360       | 40±5     | 9.14                                              | 0.49           |
| 4             | 10                | 10        | 10        | 40±5     | 3.18                                              | 0.25           |
| 5             | 13                | 15        | 180       | 5.3      | 0.39                                              |                |
| 6             | 16                | 20        | 360       | 4.47     | 0.50                                              |                |
| 7             | 19                | 10        | 10        | 3.72     | 0.42                                              |                |
| 8             | 22                | 15        | 180       | 7.76     | 0.27                                              |                |
The results of the thermoanalytical analysis of samples made of pressed phosphogypsum from the dumps of the Voskresensk chemical plant, and the physical and mechanical parameters are given in Figure 1 [12].

Figure 1. Dependence of the dehydration energy of phosphogypsum samples on compressing pressure [12], the lot 4 was obtained by pressing phosphogypsum, from which a concentrate of non-radioactive rare earth metals was preliminarily extracted.

To select the optimal composition of the mixture components, a set of sub-programs was used for mathematical modeling of the mixture composition from the initial components, Figure 2.

Figure 2. The strength of the obtained samples depending on the molding pressure, MPa, and the duration of the dispersed phosphogypsum exposure, sec.

Figure 3 shows the developed energy-efficient non-firing technology for the manufacturing of products from dispersed phosphogypsum.
4. Discussion
When conducting the studies according to the planning matrix, it was determined that the cylinder samples molded under conditions of the pressure of 20 MPa, the exposure time of dispersed phosphogypsum with a load of 360 sec and the temperature of the mixture and molds (40 ± 5) °C have the maximum value of the compressive strength of 9 - 10 MPa with a softening index of 0.49.

The analysis of the study results for pressed phosphogypsum by means of differential scanning calorimetry demonstrated the first endoeffects. The magnitude of the energy processes is expressed by the dehydration energy of the level exceeding 200 J/g. This level of dehydration energy indicates the presence of some physical process of binding properties, which is consistent with the theory of structure formation in the material under study within the technology of forming non-fired construction composites [26,28]. The obvious increase in the strength of the studied pressed samples of phosphogypsum is associated with the decrease in the thickness of hydration water films, while the growth in the strength of intercrystallization bonds is explained by the effect of the increase in the number of crystallization contacts in the material during pressing, causing the formation of the monolithic structure of a newly obtained product.

It was found that in the studied samples made of phosphogypsum, immediately after the increase in the compressing pressure from 1.2 to 35 MPa, the dehydration energy also increases by 5-9%. At the same time, in the samples of phosphogypsum that passed the technological procedure for leaching rare earth metals and despite the increase in the energy of dehydration, the decrease in strength by 40 ... 41% was found.

Laboratory tests and the proposed technology have proved the manifestation of the binding properties of phosphogypsum, providing for the implementation of a modern technology of the non-fired method for forming wall materials and the extraction of rare-earth metals concentrate. The proposed scientifically reasoned technology for the extraction of rare earth metals from phosphogypsum also makes it possible to reduce the production cost of wall materials by 2 ... 3 times compared to the production of limestone bricks.

Thus, the detected endo-effects during the phosphogypsum compressing provide the direct production of wall materials with the simultaneous extraction of the concentrate of rare-earth metals according to the concept of the energy-saving non-firing technology. Smart approaches will transform the key aspects of the theory of structure formation of non-fired artificial construction composites.

5. Conclusions
The energy-efficient non-firing technology for the direct production of wall materials with the simultaneous extraction of the rare-earth metal concentrate from phosphogypsum, as compared to the
conventional ones, does not include an autoclaving stage. This results in a 2 ... 3 times reduction in the production cost of the wall materials from phosphogypsum with the simultaneous solution to the problem of phosphogypsum disposal. In addition to the economic effect, this technology provides an improvement in the environmental situation in the regions where chemical production waste has been stored in dumps for years.

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