Structure-forming role and properties of phosphogypsum in unburned technology of wall materials and rare-earth metals concentrate simultaneous production

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Abstract. The paper presents the theoretical aspects of the processes of structure formation of composites in the non-fired technology for producing building wall materials with the simultaneous extraction of a concentrate of non-radioactive rare-earth metals from phosphogypsum. The object of research is phosphogypsum – an environmentally-adverse chemical waste that accumulates in dumps over the years. The research results are illustrated with the X-ray fluorescence method, differential thermal calorimetry and spectrometry of the properties of phosphogypsum: radioactivity, chemical composition, dehydration energy, content of non-radioactive rare-earth metals. The effect of dehydration energy and pressure on the strength of the resulting building material is established. A flow chart of energy-saving non-firing technology for the direct production of wall materials with the simultaneous extraction of a rare-earth metal concentrate from phosphogypsum is presented. It has been shown that phosphogypsum can be used as a building material without radioactivity restrictions. It is proved that phosphogypsum exhibits astringent properties that provide annealing-free production of wall materials with the simultaneous extraction of a rare-earth metal concentrate. This technology allows for the selection of strategically important rare-earth metals from phosphogypsum while reducing the cost of production of wall materials by 2 - 3 times.

1. Introduction
Phosphogypsum is a large-tonnage waste of the chemical industry. On the territory of the Russian Federation, more than 300 million tons are already stored in its dumps. The problem of utilization of phosphogypsum is recognized by the world as a special agency of the United Nations Educational, Scientific and Cultural Organization [1-5]. Despite a significant amount of development in utilization of phosphogypsum, only 1.5% are used. At the same time, materials based on gypsum-containing components are in demand in the construction market; therefore, issues related to obtaining unburned building materials from waste phosphogypsum are relevant [6-13].

Rare earth metals such as cerium, lanthanum, neodymium, praseodymium are contained in phosphogypsum, which are used in the military-industrial complex [14-18]. World consumption of rare
earth metals is 110 thousand tons per year. Experts predict that by 2020, global consumption of rare earth metals will reach 200–220 thousand tons and will increase further. The main exporter of rare earth metals until 2010 was China (85% of world exports). Russia in the segment of rare-earth metals is currently an import-dependent country, since it does not have the capacity to separate the concentrates of rare-earth metals. Creation of phosphogypsum recycling facilities with simultaneous production of building materials and rare earth metals concentrate on the territory of the Russian Federation will ensure the environmental safety and comfort of living in the regions where phosphogypsum is stored in heaps. Moreover, it will allow the construction industry to offer efficient wall materials and provide partial import substitution in the market for rare earth metals. The Voronezh State Technical University is actively pursuing the development of energy-saving unburned technology for direct production of wall materials with simultaneous extraction of the concentrate of rare-earth metals from phosphogypsum [9-13].

We have formulated the following particular tasks in the development of this technology:

- the establishment of structure-forming properties of phosphogypsum;
- assessment of the energy of dehydration and press pressure on the strength of the resulting building material;
- development of methods for extracting a concentrate of rare earth metals from phosphogypsum;
- development of the concept of energy-saving unburned technology for producing wall materials with simultaneous extraction of rare-earth metals concentrate from phosphogypsum.

According to the provisions put forward by the authors [19-23], the structure formation of building composite materials is due to several significant factors. The first significant factor is the value of the wedging pressure of water films at the interface. It is known that when mixing the components of raw mixtures, water is adsorbed in the form of films on hydrophilic particles. The most important are the forces of interaction of an electric nature and the value of the disjoining pressure.

Since the maximum strength indices of the obtained materials depend on the value of the splitting pressure, this indicator should be evaluated at water film thicknesses of 10-7 m $> \Delta >$ 10-9 m (Figure 1).

![Figure 1. Variation of the wedging pressure relative to the thickness of the water film for hydrophilic particles.](image-url)
\[ U(h, \varphi_m) = 2 \varepsilon_0 \varepsilon \left( \varphi_d + \varphi_m \right)^2 e^{-xh} - \frac{A}{12\pi h^2}, \]  

where \( \varphi_d \) – electric potential of the diffused layer, mB; \( \varphi_m \) – potential taking into account induction interaction and dispersion forces of intermolecular interaction, mB; \( \chi \) – inverse of the thickness of the diffuse layer, nm\(^{-1}\); \( h \) – particle spacing, nm; \( \varepsilon \) – dielectric constant of the dispersion medium; \( \varepsilon_0 \) – electric constant; \( A \) – Hamaker constant, J, which is related to the van der Waals constant \( A_B \) by the following equation:  
\[ A = \frac{\pi^2 N_A^2 A_B}{\nu_m}, \]  
where \( N_A \) – Avogadro constant; \( \nu_m \) – molar volume, 1 / mol.

At a temperature of 65 ... 70 ºС and a change in pH from 2 to 8, water films change their thickness, which contributes to an increase in water permeability (figure 2).

Figure 2. The relationship between the thickness of the boundary layer of water and pH on quartz particles.

The second significant factor is the energy of dehydration of dispersed materials.

It is known that dispersed materials with dehydration energy of more than 200 J / g can exhibit astringent properties [20-25].

In this regard, the most promising is the technology of direct production of building composites by pressing raw materials with preliminary mechanochemical activation of surfaces, which will contribute to the growth of the internal energy of the system and the start of recrystallization of phosphogypsum.

Earlier studies [19-22] proved that during pressing it is necessary to achieve directional formation of a structure with a water film thickness of 1–100 nm.

Based on the formulated theoretical positions, we carried out studies on the possibility of directly obtaining construction products while simultaneously extracting the concentrate of non-radioactive rare-earth metals from waste phosphogypsum.

2. Materials and methods

For research, phosphogypsum of Voskresensky chemical plant was used.

The radiological characteristics of the selected phosphogypsum were determined in the testing laboratory center of the Federal Public Health Institution "Center for Hygiene and Epidemiology in the Voronezh Region" on the MKS-01A "Multirad" spectrometer.

The chemical composition of the studied phosphogypsum, with the exception of rare earth elements, is presented in table 1.

Table 1. The chemical composition of the phosphogypsum of Voskresensky chemical plant (mass %).

| Total moisture | pH     | P\(_2\)O\(_5\) | F    | CaO   | SiO\(_2\) | Fe\(_2\)O\(_3\) | SO\(_3\) |
|---------------|--------|----------------|------|-------|-----------|----------------|---------|
| 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 subjected to extrusion according to the unburned technology for the production of composite building materials and the ultimate strength of the specimens under compression was tested immediately after pressing. The pressing and determination of the physico-mechanical properties of phosphogypsum was carried out in accordance with the requirements of standards on the Instron 5982 universal electromechanical testing system with an error of ± 0.5% at the Center for Collective Use of the Voronezh State Technical University.

The phosphogypsum leaching and the extraction of the concentrate of non-radioactive rare-earth metals were carried out according to the existing methods [26].

For this, pulp was prepared from the initial phosphogypsum with a 2% solution of sulfuric acid in the ratio T: J = 1: 1. The pulp was stirred for 20-30 minutes, then filtered. The resulting filtrate was evaporated in a porcelain bowl in a water bath, and the precipitate was molded in a hydraulic press to obtain defect-free samples of cylinders. The solution released as a result of pressing was added to a porcelain bowl and evaporation continued. The evaporation residue was washed with distilled water till neutral reaction with the medium, dried and prepared for an x-ray method for identifying rare earth metals.

3. Results

The content of non-radioactive rare-earth metals in the sediment (table 2) obtained by leaching the concentrate was determined on an S8 Tiger X-ray fluorescence spectrometer (Bruker AXS GmbH, Germany).

| Table 2. The content of non-radioactive rare earth metals in the sediment resulting from the leaching of the concentrate. |
|---------------------------------------------------------------|
| Dysprosium   | Europium  | Cerium  | Neodymium | Lanthanum | Samarium | Gadolinium |
| 0,25         | 0,07      | 2,90    | 1,78      | 1,20      | 0,24     | 0,27       |

Differential scanning calorimetry was performed on an STA 449 F5 A-0082-M synchronous thermal analysis device (NETSCH, Germany) with the NETSCH Proteus software with an integrated monolithic scale system and highly sensitive DSC and DTA sensors. This study was carried out to establish the relationship between the energy of dehydration of samples and the press pressure.

The results of differential scanning calorimetry of pressed phosphogypsum Voskresensky chemical plant are presented in table 3.

| Table 3. Relationship between the energy of dehydration of phosphogypsum samples and press pressure. |
|---------------------------------------------------------------|
| Batch number | Press pressure, MPa | Dehydration energy, J/G | Compressive strength, MPa |
|------------|---------------------|-------------------------|---------------------------|
| 1          | 1,2                 | 296,0                   | 3,22                      |
| 2          | 2,4                 | 299,3                   | 4,14                      |
| 3          | 30,0                | 323,3                   | 26,49                     |
| 4*         | 35,0                | 370,4                   | 15,61                     |

*batch 4 was obtained by pressing phosphogypsum, from which a concentrate of non-radioactive rare-earth metals was previously isolated

4. Discussions

According to the results of measurements of the effective specific activity of natural radionuclides, phosphogypsum of the Voskresensky Chemical Plant is classified as class 1 materials in accordance with the Uniform sanitary-epidemiological and hygienic requirements for goods subject to sanitary-epidemiological supervision (control) and can be used as a basis for building materials.
The results of chemical analysis by the X-ray fluorescence method showed that the concentrate obtained after leaching of the phosphogypsum of the Voskresensky Chemical Plant contained non-radioactive rare-earth metals: dysprosium, europium, cerium, neodymium, lanthanum, samarium, gadolinium in the mass fractions indicated in the table. 3

As a result of differential scanning calorimetry of the pressed phosphogypsum, the first endo-effects with dehydration energy of more than 200 J/g were established. This indicates the presence of binding properties of the material under study according to the theory of structure formation of unburned building composites [20,23].

In addition, it was found that with an increase in the press pressure from 1.2 to 35 MPa for samples of phosphogypsum immediately after pressing, an increase in the energy of dehydration is observed. At the same time, the phosphogypsum samples that underwent the leaching of the rare-earth metal concentrate showed a decrease in strength by 40 ... 41%, despite an increase in the dehydration energy in comparison with the initial samples.

According to the theory of structure formation of unburned building materials [20,23], an increase in the strength of pressed phosphogypsum samples with an increase in the dehydration energy is explained by a decrease in the thickness of aqueous films. This effect is a consequence of an increase in crystallization contacts and a corresponding increase in the strength of intercrystallization bonds causing the formation of a monolithic structure.

Thus, the established endo-effects during the pressing of phosphogypsum provide direct production of wall materials with simultaneous extraction of the rare earth metal concentrate according to the concept of energy-saving unburned technology presented in two directions: Direct pressing to obtain wall materials and Leaching to obtain rare earth concentrates.

5. Conclusion

Energy-saving unburned technology of direct production of wall materials with simultaneous extraction of a concentrate of rare-earth metals from phosphogypsum as compared with conventional technologies for the production of wall materials and products does not contain an autoclaving stage. This is achieved by reducing the cost of production of wall materials from phosphogypsum by 2 ... 3 times while solving the problem of utilization of phosphogypsum. In addition to the economic effect, this technology provides an improvement in the environmental situation in regions where chemical waste products are stored in heaps for many years.

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