Technical properties of activated gypsum

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Abstract. The influence of the activation of the building gypsum in the vortex layer apparatus on the specific surface, the setting time, the heat release, the change in the mineralogical composition, and the strength of the gypsum stone are presented in the article. The measurements were carried out by standard methods. It has been found that the processing of the gypsum binding material in the fluidized bed results in its mechanical activation, which (assuming the optimum processing conditions), in its turn, results in a 200 percent increase in the gypsum’s specific surface area, as well as in a 47 percent increase in heat emission during hydration. Assuming the optimum ABS-processing conditions, there is a 44 percent increase in compression strength, and a 50 percent increase in the flexural strength. It takes 2-10 minutes less for the gypsum paste setting.

1. Introduction

It is acknowledged that physical processing methods of substances are often accompanied by an increasing intensity of physico-chemical processes at the interphase boundary. Such methods are known as mechanoactivation [1].

The influence of mechanoactivation on the physico-chemical properties of mineral binders and the performance properties of derived artificial stones obviously depends on the type of binder. The mineral binders, whose initial structure formation is attributed to the flow of both topochemical and crystallization processes (e.g. Portland cement) feature the onset of mechanoactivation and significant positive effects when treated by a vortex layer apparatus [2]. This is mainly due to the increase in the intensity of interphase interactions, which naturally affects the parameters of a structure (yielding a finely-crystalline structure of an artificial stone with a large number of contacts) and the properties of a cement stone [3].

The determination of how the vortex layer apparatus treatment affects the properties of mineral binders, whose initial structure formation occurs by the Le Chatelier crystallization mechanism (e.g. of gypsum) is of scientific and practical interest both for establishing mechanoactivation advantages, and for determining the operating modes of apparatuses that improve the performance properties.

The crystal lattice of gypsum has a layered structure. Water molecules are layer-by-layer distributed between bilayer packets of CaSO₄, which is characterized by perfect cleavage in this direction. Moreover, each water molecule binds the ion Ca²⁺ with two ions O²⁻, with one of them found in the next layer. Arranged between the layers, water molecules are thus better separated from the gypsum crystals [4].
In the gypsum industry there is no need for preliminary mechanical activation of the raw materials. Mechanical treatment is used mainly for phosphogypsum [5-6] or for gypsum binders made using heat treatment [7]. The possibility of obtaining an unburnt anhydrite binder by short-term grinding of natural gypsum-anhydrite stone together with a complex hardening activator in the vortex layer apparatus was reported [8]. This paper focuses on examining how the treatment of gypsum grade G-5 (β-hemihydrate) by the vortex layer apparatus affects the setting time of gypsum paste and the physical and technical properties of gypsum stone.

2. Research methods
Gypsum grade G-5 BII (β-hemihydrate) as per GOST 125-79 produced by CJSC "Samara Gypsum Combine" was used for the research.

The specific surface was determined by the air permeability method using the PSKh-9 instrument. The setting time of the gypsum paste, the compressive strength and bending tension, and the content of hydrated water were assigned as per GOST 23789-79.

Optical images of gypsum samples after treatment by the vortex layer apparatus were made using the digital optical microscope Levenhuk D870T (8 Mp, trinocular type).

X-ray photographs were taken by an automatic X-ray diffractometer D2 Phaser (produced by Bruker AXS GmbH). The obtained diffraction spectra were processed by the DIFFRAC.SUITE software package. Phases were identified with invoking the diffraction data base ICDD PDF-2 Release 2013 via the DIFFRAC.EVA-v3.1 software package. The quantitative calculation of the phases was carried out using the Rietveld method via the DIFFRAC.TOPAS-v4.2 software package.

The portland cement was treated in the vortex layer (ABC) apparatus model 297 produced by LLC Regionmetrans. Fig. 1 shows a typical configuration of the vortex layer apparatus.

![Figure 1. A typical configuration of the vortex layer apparatus with a rotating electromagnetic field: 1 - the inductor magnetic circuit; 2 - the three-phase winding of the inductor; 3 - the non-magnetic cylindrical body of the apparatus working area; 4 - the ferrimagnetic bodies; 5 - the treated material; 6 - the casing.](image)

When ABC treated under the action of shock effects from ferromagnetic bodies, not only the specific surface of the binder increases, but also more defective particles occur. In this case, the degree of this transformation of the particles' substance depends both on the ABC energy density and on the intensity and force of the substance particles and the ferromagnetic bodies colliding. The mode of grinding of building gypsum in ABC was taken from preliminary experimental studies. Thus, the treatment time was 3 min, the electromagnetic field rotation frequency was 70 Hz, the ferrimagnetic body diameter vs. length ratio was 0.12, and the ferrimagnetic body weight vs. grinding material weight ratio was 0.65 [9,10].

3. Results and discussion
The effects of the treatment time for building gypsum in ABC on the geometric dimensions of the gypsum particles are given in Table 1, on the mineralogical composition of the gypsum binder - in Table 2, on the setting time of the gypsum paste and the physical and mechanical properties of gypsum stone - in Table 4.
Table 1. Average particle size and specific surface area of building gypsum.

| S.No. | Treatment time, min | Specific surface, m²/kg | Average particle size, μm |
|-------|---------------------|--------------------------|--------------------------|
| 1     | –                   | 260.0±11.75              | 7.27±0.22                |
| 2     | 1                   | 365.0±16.45              | 5.15±0.15                |
| 3     | 2                   | 452.5±20.35              | 4.12±0.12                |
| 4     | 3                   | 518.0±23.35              | 3.61±0.09                |
| 5     | 4                   | 446.0±20.05              | 4.18±0.13                |
| 6     | 5                   | 389.0±17.15              | 4.82±0.15                |

A natural consequence for the ABC treated gypsum binder is the increased specific surface $S_{\text{spec}}$. Moreover, by analysing the data of Table 1, it is seen that $S_{\text{spec}} = (t)$ features the change kinetics of an extreme nature: the maximum $S_{\text{spec}}$ (growing $S_{\text{spec}}$ is almost 200%) is observed after ABC treatment 3 min long. The increasing temperature that accompanies the ABC treatment process leads to a change in the mineralogical composition of the building gypsum (Table 2).

It is clear from the analysis of the X-ray images that the initial and treated building gypsum are substantially different at the following intensities of diffraction reflections: $d = 6.01; 3.006; 2.803; 2.1377; 1.8453$ Å, which are typical for the $\beta$-modification of the hemihydrate gypsum (CaSO$_4$·0.5H$_2$O) and at $d = 3.74; 2.849; 2.3358; 2.223; 1.866$ Å, which are typical for the anhydrite (CaSO$_4$). The quantitative composition of the mineral phase of the initial and treated building gypsum is shown in Table 2, according to which the gypsum $\beta$-hemihydrate transforms into anhydrite when ABS treated. In this case, the $\beta$-CaSO$_4$·0.5H$_2$O content decreases 1.5-fold, and the CaSO$_4$ content increases 3.3-fold.

Table 2. Quantitative composition of the mineral phase of building gypsum.

| Phase description | Initial building gypsum | ABC-treated building gypsum |
|-------------------|-------------------------|-----------------------------|
| gypsum $\beta$-hemihydrate | 76.1 | 50.6 |
| Anhydrite | 11.1 | 36.6 |
| Dolomite | 6.7 | 6.7 |
| Calcite | 1.8 | 1.8 |
| Mica | 1.6 | 1.6 |
| Quartz | 1.1 | 1.1 |
| Microcline | 0.9 | 0.9 |
| Plagioclase | 0.6 | 0.6 |
| Gypsum | 0.1 | 0.1 |

The data obtained can be used in the estimate water demand for the production of CaSO$_4$·2H$_2$O. The amount of water to hydrate $\beta$-CaSO$_4$·0.5H$_2$O can be found by the formula:

$$W_{g.1} = \frac{27}{145} Q_1$$

and to hydrate CaSO$_4$ –

$$W_{g.2} = \frac{36}{136} Q_2$$

where $Q_1$ is the amount of $\beta$-CaSO$_4$·0.5H$_2$O; $Q_2$ is the amount of CaSO$_4$.

The calculation made according to the data of Table 2 shows that the total amount of water necessary for hydration of the initial gypsum binder is 17.1%, and for hydration of the treated gypsum,
19.1%, i.e. the difference is 2%. This result is very useful for calibrating experimental data on the content of hydration water in gypsum stone.

The change in the mineralogical composition leads to a regular change in the kinetics of chemical reactions, whose intensity can be estimated from the heat release kinetics (Fig. 2, a). It is expedient to analyse the heat release kinetics dependences by distinguishing individual stages, in particular, distinguishing three sections for the obtained dependences is thus expedient (Fig. 2, b). Each section is characterized by the parameters given in Table 3.

![Figure 2. Heat release during hydration of the initial gypsum and the ABC-treated building gypsum (a) and the heat release dependencies analysis schematic (b).](image)

| Building gypsum kind | Heat release dependency section | Section I | Section II | Section III |
|----------------------|---------------------------------|-----------|------------|------------|
|                      |                                | $k_I$     | $Q$, J/kg  | $k_{II}$   | $Q$, J/kg  |
| Initial              |                                | 0.27      | 30.0       | 0.84       | 990.0      |
| ABC-treated          |                                | 0.33      | 135.0      | 1.17       | 787.5      |

According to the data of heat emission kinetics during the gypsum binding material's hydration, it can be concluded that the ABS-processed gypsum has a better water-contact performance: at each of the sections selected the values of a coefficient $k_i$ are better than those of the initial gypsum material. However, the total heat-emission values in the selected area are slightly higher in the initial gypsum: Initial gypsum binding material: 1,672.50 J/kg, and ABS-processed gypsum: 1,635.0 J/kg. The said is likely to be caused by different anhydrite content in gypsum binding materials in question (Table 2).

It is a known fact [11-13] that the hydration $\beta$ and modification of a hemihydrated gypsum results in the 19.3 J/mol heat-emission. Recalculating the heat-emission and gypsum content data $\beta$ (Table 2) it will be found that the hydrating of the initial building gypsum results in 3,186.8 J/mole heat-emission while the hydration of ABS-processed gypsum results in 4,685.3 J/mole emission which is 47 percent more. This is a convincing fact of boundary (binder – water) physical and chemical processes' intensification caused by the ABS-processing.

The said change in the gypsum binder particles geometry has an effect on the process of gypsum paste/block start structuring or the properties (Table 4).
Table 4. Setting time of the gypsum paste and strength of the gypsum stone.

| S.N o. | Treatment time, min | Standard consistency, % | Setting time, min | Ultimate strength, MPa, in: | Hydrated water content $W$, % |
|--------|---------------------|-------------------------|------------------|-----------------------------|-----------------------------|
|        |                     |                         | start | end | compression | bending |                         |
| 1      | –                   | 0.65 100%               | 7     | 25  | 52          | 28      | 38                       |
| 2      | 1                   | 0.66 101%               | 7     | 23  | 58          | 32      | 38                       |
| 3      | 2                   | 0.68 105%               | 6     | 20  | 65          | 37      | 39                       |
| 4      | 3                   | 0.69 106%               | 5     | 15  | 75          | 42      | 40                       |
| 5      | 4                   | 0.67 103%               | 6     | 25  | 47          | 16      | 36                       |
| 6      | 5                   | 0.66 101%               | 7     | 27  | 36          | 8       | 29%                      |

According to Table 4, ABS processing of gypsum for up to three minutes may reduce the setting time to 2–10 minutes. In addition, there is a slight increase in normal density of gypsum paste caused by increased specific surface area of gypsum (Table 1). A three-minute (maximum) ABS processing results in a significant increase in compression strength (44 percent) and in flexural strength (50 percent). ABS processing of the binding material for over three minutes results in the balling or granulometric heterogeneity of the said material. Thus, the ABS processing for 5 minutes led to the 30 percent decrease in compression strength and 71 percent decrease in flexural strength of gypsum.

Another fact that is characteristic to the change of a structuring rate post ABS-processing is an increased hydration water volume. So, the hydration water content had increased by 2 percent after the 3-minute ABS processing. The said amount matches the value as calculated according to Table 2. A decreased $W$ value resulted from the ABS-processing time increase (more than 3 minutes) is likely to be caused by anhydrite transformation into the insoluble modification.

4. Conclusions
It has been found that the processing of gypsum binding material in the fluidized bed results in its mechanical activation which (assuming the optimum processing conditions) results in a 200 percent increase in the gypsum's specific surface area, as well as in a 47 percent increase in heat emission during hydration. The latter is caused by the change in the gypsum binding material's content of minerals: It has been found that the $\beta$-CaSO$_4$·0,5H$_2$O content decreased 1.5 times, and the CaSO$_4$ content increased 3.3 times.

Assuming the optimum ABS-processing conditions, there is a 44 percent increase in compression strength, and a 50 percent increase in the flexural strength. It takes 2-10 minutes less for the gypsum paste setting. It has been found that the 3-minute ABS-processing results in a 2 percent increase of hydration water. A decreased $W$ value resulted from the ABS-processing time increase (more than 3 minutes) is likely to be caused by anhydrite transformation into the insoluble modification.

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