Obtaining gypsum products from gypsum dihydrate in a microwave field

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Abstract. The increasing requirements for environmental protection make the development of energy-efficient technologies for building materials urgent, combining a number of stages in the production of materials into one technological redistribution using more efficient methods of their heat treatment. The article discusses the possibility of obtaining gypsum products from two-water gypsum stone, bypassing the production of gypsum binder, using microwave heating as the most effective and convenient of the existing heating methods, which does not require direct connection of external electrodes to the internal electrodes of the mold, to which the material can burn, rendering the electrodes unusable. Due to the combination of the processes of binder production (dehydration of ground gypsum dihydrate with the elimination of 1.5 water molecules) and the finished product (the reaction of semi-aqueous gypsum with water to form a monolith of gypsum dihydrate) in one apparatus, the total production time of the product is greatly reduced, starting from the extraction of quarries.

1. Introduction
In connection with the increased requirements for environmental protection, it is advisable to develop new building materials using energy-efficient technologies and saving fuel and energy resources. Gypsum binder, used to manufacture a wide range of products, requires fuel to produce it. In this regard, the issue of replacing the binder with a component that requires significantly lower energy costs is relevant.

There are two modifications of calcium sulfate hemihydrate:
- \( \beta\)-CaSO\(_4\) \( \cdot \) 0.5H\(_2\)O (\( \beta\)-gypsum, stucco), which is characterized by a fine-crystalline structure with a high specific surface area and inhomogeneity of the mineral composition over the grain volume; the removal of water from calcium sulfate dihydrate during its production occurs in a vapor state, in non-pressurized devices connected to the atmosphere - a gypsum boiler, a rotary kiln, a mill for combined grinding and roasting, a fluidized bed furnace, a pipe dryer [1];
- \( \alpha\)-CaSO\(_4\) \( \cdot \) 0.5H\(_2\)O (\( \alpha\)-gypsum, high-strength gypsum), which is characterized by a coarse-crystalline structure with a small specific surface area and greater homogeneity of the mineral composition over the grain volume; removal of water occurs in a drop-liquid state, in sealed apparatus, closed from the atmosphere - an autoclave, a self-steamer, a damper [2, 3].

Existing methods for the production of gypsum binders require a significant investment of time for the dehydration of gypsum: \( \beta\)-gypsum - 2.5-3 hours at a temperature of 160-180 °C, \( \alpha\)-gypsum - 6-8 hours at a temperature of 124 °C [4]. Heating by means of microwave (ultra-high-frequency radiation) can reduce the isothermal holding time by 18-24 times. This allows you to reduce the use of fuel and
energy resources at times and do without the use of solid and liquid fuels. Due to the combination of the processes of binder production (dehydration of ground gypsum dihydrate with the elimination of 1.5 water molecules) and the finished product (the reaction of semi-aqueous gypsum with water to form a monolith of gypsum dihydrate) in one apparatus, the total production time of the product is greatly reduced, starting from the extraction of quarries [5].

Nowadays, there are a huge number of options for heat treatment of building materials. Most often, convective heat exchange is used in the manufacture of products, where heated steam serves as a heating unit. This method of heating materials on a cement binder leads to the formation of microcracks, which worsen its main parameters, such as frost resistance, water permeability, strength and crack resistance. In the technology of building materials, a difficult choice often arises: high mobility of the raw mixture and low basic parameters of the product or low mobility of the raw mixture and higher basic parameters of the product. Another drawback is that the post heating materials at factories occupies a large area. Now more and more often in production they use electric heating with the help of electrodes. In many ways, this method is superior to convective heating of the material. However, it has disadvantages:
- the complexity of the production of forms with large electrodes to which the material burns from time to time;
- the impossibility of using this method in conveyor technology, which makes senseless the advantage in the speed of heating the product.

What is Microwave? Microwave (ultra-high frequency radiation) - radiation represented by electromagnetic waves of the following characteristics: oscillation frequency 300 MHz - 30 GHz, wavelength 1 m - 1 mm. This type of wave is similar to the following types of electromagnetic radiation:
- radio waves (30kHz – 30MHz, 10m – 10 km);
- infrared (thermal) radiation (10^{12} – 1,5• 10^{14} Hz, 2 microns – 760 nm);
- visible light (1,5• 10^{14} – 3• 10^{16} Hz, 760 nm – 400 nm);
- ultraviolet radiation (10^{16} – 10^{18} Hz, 400 nm – 50 nm);
- X-ray radiation (10^{18} – 10^{20} Hz, 50 nm – 0,001 nm);
- gamma radiation (10^{20} Hz, less than 0,001 nm).

How is heating carried out in a microwave field? To ensure the possibility of heating, the presence of polar dielectrics in the substance is necessary. One of the most common polar dielectrics is water. If a permanent magnet or other source of magnetic field is brought to the compass needle, it will turn its north pole to the south pole of the magnet, i.e. opposite to the action of the field of this magnet. Polar molecules behave in a similar way with respect to an external electric field. And in a microwave field, a high-frequency change in the directions of the external field occurs, so a polar molecule with the same high frequency turns against the direction of action of this field. At the same time, during the turns, the molecule touches neighboring molecules that vibrate in the same way, which causes an increase in the kinetic energy of molecular motion and, accordingly, an increase in temperature in the dielectric substance. Non-polar dielectrics are weakly affected by the electromagnetic field. Such materials will be heated in a microwave field only if they are mixed with polar dielectrics. For example, metal powder or water already indicated above. This means that the presence of polar dielectrics is mandatory in masses heated in microwave ovens. In a molecule of gypsum dihydrate it is
- these are 2 water molecules (CaSO_{4} • 2H_{2}O). Whether there is enough crystallization water for heating in a microwave is to be investigated [6].

The scientific novelty lies in the fact that by combining the production of a gypsum binder and directly a product from it in one form-apparatus, the need to use an energy-consuming binder is eliminated. Instead, they use dihydrate gypsum from quarries, which, during heat treatment, directly in the sealed form of the product at temperatures above 100 °C turns into a hemihydrate, while releasing water in an amount corresponding to 1.5 water molecules according to the chemical reaction equation (1) [7,8,9].

\[
\text{CaSO}_{4} \cdot 2\text{H}_{2}\text{O} = \text{CaSO}_{4} \cdot 0,5\text{H}_{2}\text{O} + 1,5\text{H}_{2}\text{O} \quad (1)
\]
Then, the resulting system, when the temperature drops to 40 °C, sets and hardens with the formation of a secondary dihydrate according to reaction (2).

\[
\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} + 1.5\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}
\]  

(2)

An aspect of scientific novelty is the use of a microwave field for heat treatment of gypsum masses, which will allow organizing conveyor production of products, since the source of microwave radiation does not require direct contact connection to the mold with the raw product [10, 11, 12].

The practical significance of this work lies in the fact that gypsum products manufactured using this technology are devoid of an intermediate stage - the production of a binder. And the use of a small amount of water, necessary exclusively for heating the mixture under the action of microwave radiation, makes it possible to increase the strength of products in comparison with existing porous gypsum products.

2. Materials and Methods

As mentioned above, the amount of water in the material affects the intensity of its heating. Therefore, it is necessary to investigate the effect of water on the intensity of heating and physical and mechanical properties of gypsum samples.

The following materials were used in the work:
- Gypsum two-water ground, Kamsko-Ustinsky mine, residue on sieve No. 02 - 8.45% (average fineness of grinding), hygroscopic moisture content 0.5%, content of crystallization water 16%, residue on sieve No. 02 - up to 10%;
- The following equipment was used in the work:
  - microwave microwave oven Candy MGD 1771 M with a power of 700 W, a frequency of 2.45 GHz;
  - glass cylindrical forms made of tempered glass for the manufacture of plaster samples;
  - pyrometer RGK PL-12;
  - hydraulic press Controls 50-C8455.

3. Results

Samples were prepared with different water content (0, 5, 10%). The consumption of raw materials (gypsum dihydrate, water) of materials and the characteristics of gypsum-water mixtures before molding and after its completion are shown in Table 1.

Table 1. Consumption of materials and characteristics of gypsum-water mixtures measured during the manufacture of samples.

| The amount of added water, % of consumption gypsum | 0 | 5 | 10 |
|--------------------------------------------------|---|---|----|
| Gypsum consumption, g                            | 200 | 200 | 200 |
| Water consumption, g                             | 0 | 10 | 20 |
| \(\rho_{\text{uncons. mix}}\), kg/m\(^3\)        | 1040 | 840 | 750 |
| \(m_{\text{mold.mix}}\), g                       | 183 | 186 | 196 |
| \(V_{\text{mold.mix}}\), cm\(^3\)               | 122 | 122 | 122 |
| \(\rho_{\text{comp. mix}}\), kg/m\(^3\)         | 1500 | 1525 | 1607 |

Note to Table 1:
- \(\rho_{\text{uncons. mix}}\) – density of unconsolidated mixture, kg/m\(^3\);
- \(m_{\text{mold.mix}}\) – weight of the molded mixture, g;
- \(V_{\text{mold.mix}}\) – volume of the molded mixture, cm\(^3\)
ρ_{comp. mix}, density of the compacted (molded) mixture, kg/m³

Analyzing table 1, we notice that the density of the compacted (molded) mixture increases with an increase in the content of added water (Fig. 1).

Figure 1. Change in the density of the compacted (molded) mixture \( \rho_{\text{comp. mix}} \) depending on the content of added water \( W \).

Then, the manufactured molds with mixtures were processed in a microwave oven according to a regime involving heating to a holding temperature range (120-150 °C) at an oven power of 300w, then the power was lowered to 100w and isothermal holding for at least 20 minutes in the indicated temperature range. The temperature was measured using a pyrometer as follows: every minute the oven was turned off and the temperature was measured at three points - at the top (closer to the lid), in the middle and at the bottom of the mold. If, during isothermal holding, the temperature at least at one point rose above 145 °C, then the mold was given time to cool down to a state where the maximum temperature on it dropped to 135 °C, then microwave heating at 100w was resumed. The mold heating mode is shown in Fig. 2-4.

Figure 2. Mode of heating the mold with plaster without added water (0%). The time to reach the isothermal holding temperature is 19 minutes. The duration of the isothermal exposure is 35 minutes.
Figure 3. Mode of heating the mold with gypsum-water mixture with 5% added water. The time to reach the isothermal holding temperature is 12 minutes. The duration of isothermal exposure is 28 minutes.

Figure 4. Mode of heating the mold with a gypsum-water mixture with 10% added water. The time to reach the isothermal holding temperature is 11 minutes. The duration of isothermal exposure is 28 minutes.

When analyzing the change in temperature during heat treatment of the molds, it is important to note that with an increase in the amount of added water, the mixture heats up faster. This dependence is nonlinear (Fig. 5).
Figure 5. Graph of the dependence of the time $\tau$ for the mixture to reach the isothermal holding temperature on the amount of added water $W$.

Gypsum specimens after cooling down to 40 °C. The volume and mass of the samples were measured, the density of the samples was determined immediately after stripping and after a week, because the sample was naturally dried (Table 2). The change in the density of the dried samples depending on the amount of added water (Fig. 6) has the same character as the change in the density of the molded mixture (Fig. 1). The appearance of the samples is shown in Figure 7.

| The amount of added water, % of consumption gypsum. | 0  | 5  | 10 |
|--------------------------------------------------|----|----|----|
| Sample volume, ml                                | 115| 115| 115|
| Sample weight immediately after stripping, g     | 172| 177| 194|
| Density of the sample immediately after stripping $\rho_1$, kg/m³ | 1496| 1539| 1687|
| Sample mass a week after stripping, g            | 172| 175| 182|
| Sample density in a week after stripping $\rho_2$, kg/m³ | 1496| 1522| 1582|
| Sample moisture $\omega$, %                      | 0  | 1.1| 6.2|

Samples tested for compressive strength. The test results are listed in Table 3 and a graph of compressive strength versus the amount of added water is plotted (Fig. 8).
Figure 6. Graph of dependence of the density of dried gypsum samples $\rho_2$ depending on the content of added water $W$.

Figure 7. Appearance of gypsum-water samples with 0%, 5% and 10% added water (pictured from left to right).

Table 3. Compression strength test results for gypsum-water samples.

| The amount of added water, % of consumption gypsum. | 0     | 5     | 10    |
|---------------------------------------------------|-------|-------|-------|
| Prepared sample weight, g                         | 133   | 131   | 140   |
| Sample height, mm                                 | 48    | 46.5  | 48.5  |
| Sample section diameter, mm                       | 48.5  | 48.5  | 48.5  |
| Sample cross-sectional area, mm$^2$               | 1847  | 1847  | 1847  |
| Breaking load F, kN                                | 4.8   | 14.2  | 10.9  |
| Compressive strength $R_{comp}$, MPa              | 2.6   | 7.7   | 5.9   |
4. Discussions and conclusions
An increase in the added water content increases the density of the molded mixture (and finished products) and reduces the heating time of the gypsum-water mixture to the isothermal holding temperature. The first can be explained by the filling of voids between gypsum particles with water, and the second - water consists of polar molecules that are highly active in the microwave field. It makes no sense to add more than 5% water to increase the heating rate. the heating time of the mixture in this case will increase by only 1 minute (Fig. 5).

It is important to note that in the samples with 5 and 10% added water, 3.9% and 3.8% of water remained, which may indicate the presence of water-binding impurities in the raw gypsum dihydrate, including calcium sulfate hemihydrate, which could be formed in the mill during grinding, because the temperature in the mill may rise above 100 ° C. The content of water of crystallization in raw gypsum is 16%. 2 situations are possible:
- Raw gypsum of the third grade and the amount of crystallization water in 16% corresponds to GOST 4013-2019;
- Raw gypsum contains calcium sulfate hemihydrate, which binds the missing 3.8% to 19.88%.

It is necessary to carry out a chemical and mineralogical analysis of gypsum dihydrate in order to unequivocally answer this question.

The dependence of the compressive strength of gypsum-water samples is parabolic. With an amount of added water of 5%, the highest strength value (7.7 MPa) is achieved. In the absence of added water, the strength is minimal (2.6 MPa). At 10% added water, the strength decreases (5.9 MPa). This can be explained by the fact that in the absence of water, dry gypsum is more difficult to tamp, gypsum particles slip through each other, in addition, they are separated by air and some of the particles are not close enough to each other to carry out contact homogenization, and with an excess of water, another pore structure that reduces strength. In general, low strength values correlate more with β-gypsum (stucco) than with α-gypsum (high strength gypsum).

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