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PROSPECTIVE OPPORTUNITIES TO REDUCE ENERGY CONSUMPTION FOR GYPSUM BINDERS PRODUCTION

ПЕРСПЕКТИВНІ МОЖЛИВОСТІ СКОРОЧЕННЯ ЕНЕРГОСПОЖИВАННЯ ПРИ ВИРОБНИЦТВІ ГІПСОВИХ В'ЯЖУЧИХ

Summary. *The article analyzes the technologies of gypsum binder production and selects the most effective production method. The processes of dehydration and hydration of various modifications of gypsum are researched, in which the preservation of temperature gradient allows to obtain a semi-aqueous form of calcium sulfate throughout the entire volume of the gypsum binder particle. A mathematical model of heating of a spherical particle, which was obtained by using the Fourier's method, is presented, with the help of which the optimal size of gypsum particles for firing is calculated.*

Key words: *gypsum, temperature gradient, crystalline hydrate, coolant flow, temperature redistribution.*

Анотація. *У статті проаналізовано технології виробництва гіпсового в'яжучого та обрано найбільш ефективний спосіб виробництва. Досліджено процеси дегідратації та гідратації різних модифікацій гіпсу, в яких збереження температурного градієнта дозволяє отримати напівводну форму сульфату кальцію по всьому об'єму частинки гіпсового*

в'яжучого. Наведено математичну модель нагрівання сферичної частинки, отриману за допомогою методу Фур'є, за допомогою якої розраховано оптимальний розмір частинок гіпсу для випалу.

Ключові слова: *гіпс, градієнт температури, кристалогідрат, потік теплоносія, перерозподіл температури.*

Perspectivity of this or that material is determined by its influence on the system man – material – environment, as the unity of geochemical environment and life is inseparable and is the most important condition for the existence of nature and man. One of the negative consequences, from the point of view of ecology, was the increase of anthropogenic radiation background due to the intensification of industrial development in the second half of the twentieth century, which caused the movement of a huge amount of natural radionuclides (uranium, thorium and their decay products). The level of their concentration on the Earth's surface has sharply increased due to the extraction of a number of minerals during their extraction from the subsoil and subsequent processing. Various construction materials, including facing materials and products, contribute to the increase of anthropogenic radiation background. Thus, according to the World Health Organization, the annual radiation dose in buildings is comparable to the dose received during X-ray diagnostics.

It is no less relevant that in the conditions of market economy in the construction industry there is a tendency to develop energy-saving technologies on the basis of cheap local raw materials. In terms of ensuring the economy of material and energy resources, and even more so – strict environmental requirements gypsum materials and products based on them are in a more preferable position compared to other building materials. This is due to the wide availability of natural gypsum raw materials and gypsum-containing waste, simplicity and environmental friendliness of production of gypsum binders and products based on them. Besides, gypsum is not toxic, no CO_2 is emitted during

its processing and binders produced from it, unlike cement and lime, are not allergens and do not cause silicosis. And also they practically do not contain inert radioactive gases (radon ^{222}Rnand thoron ^{220}Tn) and radioactive nuclides (radium ^{226}Ra, thorium ^{232}Th, potassium ^{40}Ka) of natural origin, the presence of which adversely affects the physical and moral – psychological health of people [1-4].

Gypsum is close to human skin in terms of acid and vapor diffusion resistance. When it hardens, it regulates the humidity in the room, creating a favorable microclimate. Products made of gypsum "breathe" like wood, while not rotting, as it is not a medium in which biological bacillary processes can develop.

Gypsum is characterized by increased fire safety, low heat and sound conductivity. This property positively affects the operation of gypsum coatings, walls and buildings in general.

Of all types of gypsum binders, the α-form of construction gypsum is of the greatest interest, as it with sufficiently high strength belongs to low-temperature and the least energy-consuming types of binders. However, to date, the technology of obtaining this type of gypsum has a number of significant drawbacks.

Mainly α-gypsum is produced in pressurized hermetic apparatuses (autoclaves, self-sealing apparatuses, dampers) or in apparatuses for dehydration of calcium sulfate dihydrate in liquid media (boilers). The main disadvantage of these technologies is the high consumption of fuel and electricity with low efficiency. This is explained by the fact that firing is carried out either at high pressure (0.4-3.0 MPa) or a large amount of time is spent (from 5 to 15.5 hours).

Gypsum is also produced in plants with a vibrating wave-shaped grate, which is fired with high-temperature gases or superheated steam. However, efficient firing is only possible if all particles are of the same size, which is impossible to achieve in practice.

In the above methods, water is removed from gypsum raw material in a liquid-drop state, but since gypsum is steamed in a humid environment, calcium dihydrate is formed on the surface of the particles due to the high hygroscopicity of gypsum, therefore, the pieces of initial gypsum should be large, because the use of small fraction leads to the formation of a large amount of secondary dihydrate, and as a result – a decrease in the quality of the product firing. The steaming of large-sized pieces consumes too much time, heat and fuel energy resources, which negatively affects both economic and environmental aspects.

The most effective method, in terms of firing rate, is the method of gypsum firing with hot gases in a pipe-dryer at the installation of the company "Babcock – BSH" [1]. The main disadvantage of this method is that in a cylindrical reactor firing proceeds unevenly because of the large difference in the velocity of the coolant across the cross-section of the reactor-tube. In addition, the firing process takes place at normal pressure. In such conditions water from particles of initial calcium sulfate dihydrate is removed in the form of vapor, which leads to destruction of a large number of crystals and the structure of the crystal lattice is loosened. This is due to the fact that in the gaseous state, 1 mole of water (18 g) occupies V=22.4L/mol. 18 g of water in the liquid state occupies V=18ml, i.e. the volume ratio at atmospheric pressure is 1244. Consequently, gypsum is of low quality with low strength of stone after its hardening.

Thus, gypsum binders obtained by thermal treatment of calcium sulfate dihydrate have, depending on the temperature and heating conditions, various modifications of semi-aqueous and anhydrous calcium sulfate, differing from each other in density, shape and size of crystals, heat of hydration, heat capacity, optical properties and others.

Calcium sulfate hydrates belong to a rather wide class of compounds united by the common name – crystallohydrates. Each crystallohydrate represents a phase of absolutely definite composition. Even partial loss of water

by crystallohydrate leads to destruction of its crystal structure and formation of a new phase – crystallohydrate with less water content or anhydrous form of calcium sulfate.

Two solid phases always coexist in the process of crystal hydrate dehydration [5; 6]. In the presence of a gaseous phase (water vapor), such a system is monovariant. Therefore, at a given temperature, the vapor pressure in the system is quite definite and can change only at the disappearance of one of the solid phases.

Crystal hydrate is dehydrated if the water vapor pressure in the surrounding space is less than the pressure corresponding to the equilibrium of crystal hydrate with anhydrous salt or low hydrate. If the water vapor pressure is greater than the equilibrium pressure, the crystalline hydrate is dehydrated, i.e. it changes to a crystalline hydrate with a high water content. Processes of dehydration of crystalline hydrates have specificity depending on thermal-physical conditions, which was the subject of the present research.

The processes of dehydration of crystalline hydrates are referred to the processes of thermal dissociation. They are characterized by the presence of a temperature critical point, above which there is a significant intensification of dehydration. The latter indicates that the mechanism of dehydration before and after this point is significantly different [5]. To understand the processes of dehydration of hydrate forms of calcium sulfate, the dissociation equilibrium diagram of these compounds is of considerable interest (Fig. 1).
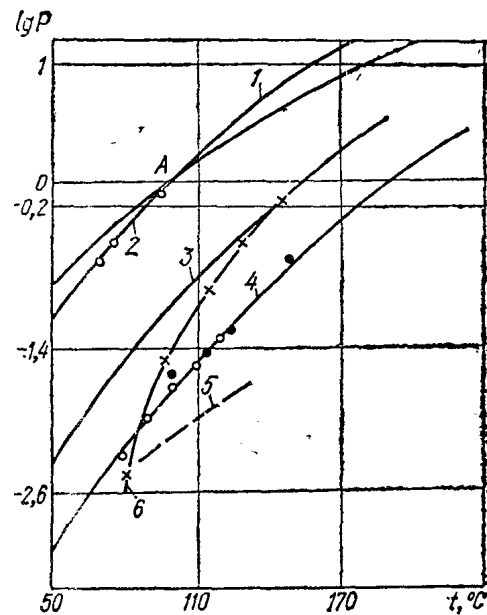
Figure 1. Dissociation equilibrium for calcium sulfate crystalline hydrates:

1 – saturation pressure for pure water; 2 – dissociation equilibrium for reaction $CaSO_4 \cdot 2H_2O \leftrightarrow CaSO_4 \cdot 0,5\ H_2O + 3/4H_2O$ (vapor); 3 – dissociation equilibrium for reaction $CaSO_4 \cdot 0,5\ H_2O\ (\alpha) \leftrightarrow CaSO_4 + 0,5H_2O$ (vapor); 4 – dissociation equilibrium for reaction $CaSO_4 \cdot 0,5\ H_2O\ (\beta) \leftrightarrow CaSO_4 + 0,5H_2O$ (vapor); 5 – dissociation equilibrium for reaction $CaSO_4 \cdot 0,5\ H_2O\ (\beta) \leftrightarrow CaSO_4 + 0,5H_2O$ (vapor) (β-semihydrate, previously dehydrated to 1 %); 6 – dissociation equilibrium for the reaction (according to Balarev) $CaSO_4 \cdot 0,5\ H_2O\ (\alpha) \leftrightarrow CaSO_4 + 0,5H_2O$ (vapor).

A large number of studies of moisture absorption capacity of alpha- and beta-forms of calcium sulfate semihydrates were conducted by a team of scientists under the leadership of H.-B. Fischer. It was found that soluble anhydrite as a result of aging (interaction of semihydrates with air moisture) passes at the first stage into semi-aqueous gypsum and at long storage periods under conditions of high air humidity into bi-aqueous gypsum [5-10].

The results of studies by Gordashevsky P.F., S. Novak, I. Ostradetsky, H.-B. Fischer [7; 8], which are confirmed by the above diagrams of calcium sulfate dissociation equilibrium, show that under certain conditions of the reaction the transition of soluble anhydrite into semi-aqueous gypsum is possible. For

realization of the reaction of transition of soluble anhydrite into semi-aqueous gypsum it is necessary to create appropriate thermodynamic conditions.

During the heat treatment of bi-aqueous gypsum, as a rule, there is an uneven distribution of temperature in each individual particle of raw materials. As a result, anhydrous gypsum (anhydrite) is formed on the surface of the particle. The scheme of heat flux impact on a particle of gypsum is shown in Fig. 2.
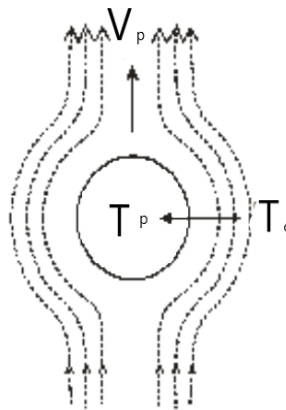

Fig. 2. Scheme of heat flux impact on the gypsum particle

The model of heating of a spherical particle was obtained by using the Fourier's method, under the assumption that the gypsum particles have the shape of a ball with radius r_0, their initial temperature is T_0 and the temperature of the coolant on the surface of the particle is T_1. Then the temperature distribution in the ball T(r,t) at time t is:

$$T(r,t) = T_1 + 2\frac{r_0}{\pi}(T_0 - T_1)\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} \cdot e^{-\left(\frac{n\pi a}{r_0}\right)^2 t} \cdot \frac{\sin\frac{n\pi r}{r_0}}{r}$$

where: a2 is diffusivity coefficient (a2 = λ/c·ρ);

λ is the coefficient of thermal conductivity;

c – specific heat capacity of gypsum;

ρ – density of gypsum.

If the particle path length is L and the coolant flow velocity is Vc.f., then the residence time (t) of particles of the fired material with diameter d (d = 2r$_0$) is determined by the dependence t = L/(V$_{c.f.}$ −V$_{p.v.}$). Substituting the value of *t* into the formula and setting *r* to zero, in the limit we obtain that the temperature in the center of the particle at the exit from the firing apparatus will be equal to:

$$T(0,t) = T_1 + 2(T_0 - T_1)\sum_{n=1}^{\infty}(-1)^{n+1}\cdot e^{-\left(\frac{n\pi a}{r_0}\right)^2 t}$$

The equation allows, at a given temperature in the center of the particle T$_{R=0}$ and time of its stay in the firing zone t, to determine the largest size of fired particles r$_{0max}$. The permissible value of factors is accepted from the condition of completeness of dehydration of two-water gypsum T$_{R=0}$ = 378-380 K and duration of firing of particles t ≤ 0.3 s. The results of calculations are shown in Fig. 3.

As can be seen from Fig. 3, the diameter of fired particles should not exceed 2.5-3.0 mm.
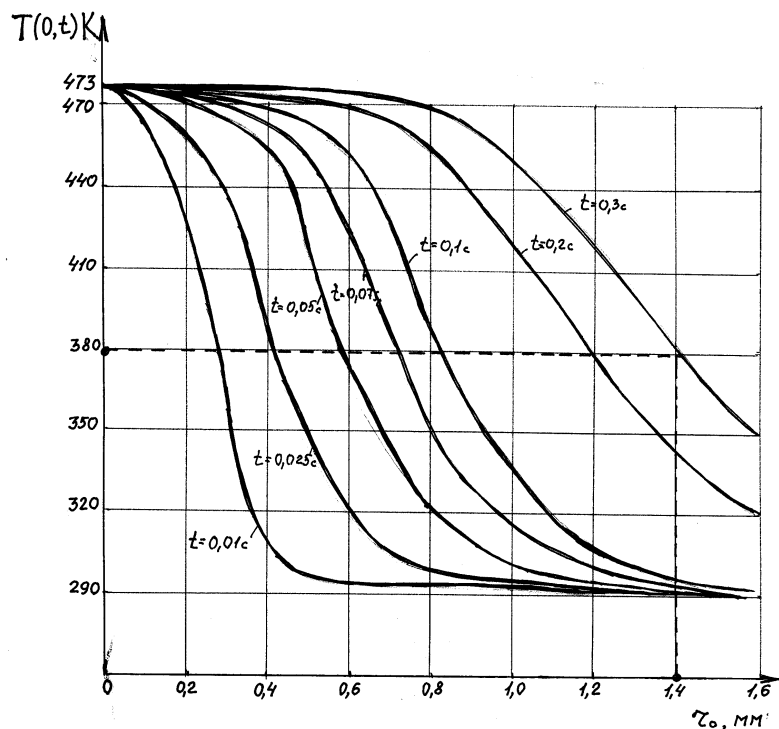

Fig. 3. Influence of particle diameter and time of their stay in the coolant flow on particle temperature

So, to obtain a quality product in the form of gypsum α-form, it is necessary to carry out the firing process in such a way that the gypsum particles consist of $CaSO_4 \cdot 0,5H_2O$ molecules throughout the entire volume. Therefore, the firing must be carried out in such a way that some of the material in the particle does not undergo dehydration. At preservation of a temperature gradient there will be processes of further dehydration of the central zone, and the allocated water will be absorbed by anhydrous gypsum passing into semi-aqueous due to diffusion of water from the center to the surface of the particle. For this purpose in the technological scheme should be provided a special post, where the temperature field inside the particle is equalized and the completion of semi-aqueous gypsum, which ensures the stability of properties of α-form of calcium sulfate semihydrate. Further development and improvement of gypsum binders production technology should be inextricably linked to the intensification of primarily thermal processes and the renewal of heating equipment operating on new scientifically substantiated firing modes.

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