

The Role of Mineral Fillers in The Process of Structure Formation in Model Systems $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ - Microfiller - H_2O

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ABSTRACT

The influence of fillers on the processes of structure formation in the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ - Microfiller – H_2O system was studied.

It is shown that with an increase in the concentration of the microfiller, the strength of coagulation contacts filler-filler becomes predominant and, in accordance with the nature of the introduced filler, the integral strength either increases (finely ground quartz sand) or drops sharply (kaolin).

Keywords:

gypsum, binders, calcium sulfate, dihydrate, quartz sand, marble, kaolin

All types of gypsum binders consist of semi-aqueous gypsum or anhydrite. Their production is based on the ability of dihydrate gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the process of heating partial or complete dehydration.

Calcium sulfate is the basis of all gypsum binders, which are usually obtained by heat treatment of dihydrate calcium sulfate at different temperatures. Depending on the temperature and heating conditions, various modifications of calcium sulfate are obtained, differing in the content of crystallization water, density, shape and size of crystals, heat of hydration, heat capacity, solubility, optical and other properties.

Therefore, in order to clarify the mutual influence of the components, we set up a series of experiments to study the role of mineral fillers (finely ground quartz sand, marble, kaolin) on the

processes of hydration and structure formation in the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ system.

As is known, the production of gypsum binders based on gypsum minerals is based on its firing, leading to dehydration of its constituent components - dihydrate calcium sulfate and clay part, and on the subsequent hardening of the resulting products [1-7].

The removal of any amount of water from the structure of dihydrate calcium sulfate is accompanied by the destruction of the crystal lattice and the formation of lower hydrates with a new crystal lattice. The formation of the following phases has been proven – $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$; CaSO_4 III, CaSO_4 II, CaSO_4 I [8].

At present, it has been established that after mixing and mixing the gypsum dough, a small induction period follows, after which crystal nuclei appear from the supersaturated solution. When the

size of the embryos reaches more than the critical size, crystal growth begins, accompanied by recrystallization [9].

The rate of nucleation is proportional to the relative supersaturation, and the growth rate of crystals is proportional to absolute supersaturation.

The conversion of hemihydrate to dihydrate proceeds without intermediate stages, while the transition of soluble anhydrite (anhydrite 111) to dihydrate is always carried out through the hemihydrate. Insoluble anhydrite (anhydrite 11) is converted to dihydrate one step [10].

Analysis of the literature data shows that many issues related to the mechanism of hydration of hemihydrate, soluble and insoluble anhydrites, the processes of nucleation and growth of dihydrate crystals, and many issues related to the mechanism

of hydration remain unclear and they continue to be the subject of discussion. Despite the fact that, in comparison with Portland cement, monomineral gypsum binders, which have high solubility and a well-defined crystal structure of hydrate phases, serve as a convenient object of study.

Using the example of dihydrate calcium sulfate and its dehydration products, we [11] studied the processes of hydration by sorption of water vapor at the McBain-Bakr vacuum-sorption unit.

The study of sorption-desorption isotherms on dihydrate calcium sulfate showed that isotherms do not have a fundamental difference from other hydrophilic low-disperse non-porous sorbents, they are reversible, confirming that in this case adsorption is not complicated by side processes.

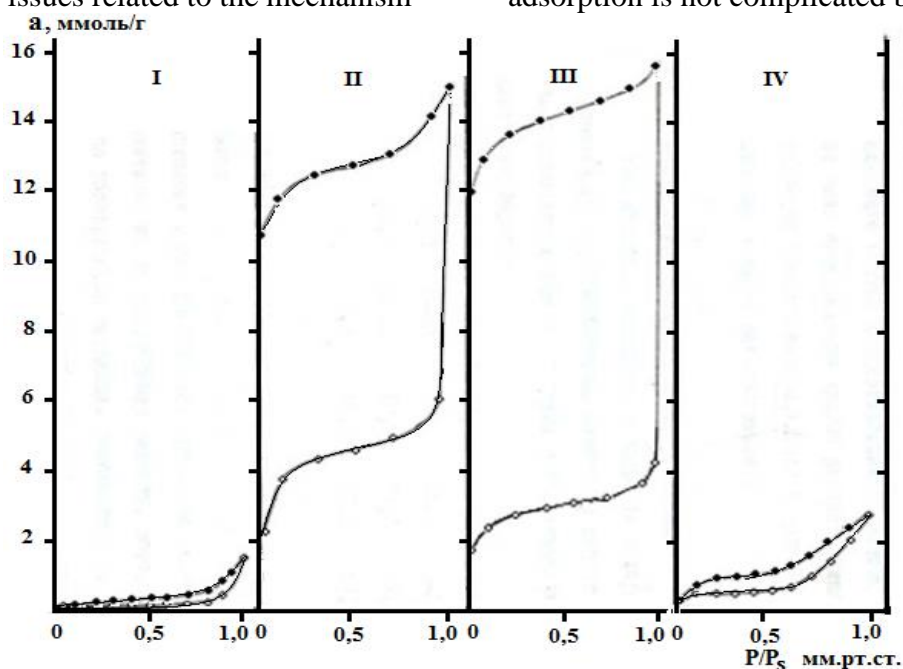


Рис. 1. Изотермы сорбции-десорбции паров воды на модификациях сульфата кальция. I- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, II- $\text{CaSO}_4 \cdot 0,5\text{H}_2\text{O}$, III- CaSO_4 раств., IV- CaSO_4 нераств.

In Figure 1 Isotherms of sorption-desorption of water vapor on dihydrate calcium sulfate and its dehydration products of semi-aqueous calcium sulfate after sorption at different elasticity of water vapor I- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; II- $\text{CaSO}_4 \cdot 0,5\text{H}_2\text{O}$; III- CaSO_4 , obtained at 300°C , anhydrite; IV- CaSO_4 , obtained at 700°C , insoluble anhydrite, S_{ud} , at different temperatures.

The nature of sorption-desorption isotherms on semi-aqueous calcium sulfate is significantly different from dihydrate and is close to the isotherms of hydrating sorbents by the presence of a large abnormal irreversible hysteresis loop. The

section of irreversibly bound water corresponds to the formation of 18.6% dihydrate during the isotherm removal, i.e. almost complete hydration, which is in good correlation with the thermogravimetry data, which showed the content of 6.21% hydrate water in the sample.

The appearance of dihydrate in the system using this method was recorded at P/P_s 0.75. The initial sections of the isotherm - the region of small and medium P/P_s can be associated with reversible physical sorption.

Isotherms on soluble anhydrite CaSO_4 obtained by dehydration of dihydrate calcium

sulfate at 300 °C have a similar appearance, differing only in smaller amounts of sorbed water in the initial region of P/P_s .

Isotherms obtained for high-temperature insoluble anhydrite are characterized by very low irreversible hysteresis and low sorption values in the region of small and medium P/P_s .

As the temperature rises and the crystal structure of the dehydration product changes, its dispersion is applied. Accordingly, the degree of hydration is also reduced, which for insoluble anhydrite is only 2.3% instead of 100 for CaSO_4 soluble.

Therefore, using the example of gypsum and its dehydration products of different composition and structure, the method of sorption of water vapor confirms the presence of a direct dependence of the hydration rate on the kinetics of dissolution of the initial phase.

The presence of a sharp inflection on the isotherm in the region of relative pressures close to unity and the appearance of dihydrate on the derivatogram in this region of water vapor elasticity suggests that the process of chemical hydration begins only after the appearance of condensed moisture in the system, that is, the appearance of liquid water.

Under practical conditions, hydration and the formation of the hydration structure are influenced by many factors, such as heat treatment of raw materials, water gypsum ratio (W/t), the introduction of additives, etc.

In our work on the topic "Study of the effect of mineral additives on the process of formation and properties of hydration structures in dispersed ganch systems", the main attention is paid to the study of the processes of hydration and structure

formation, the patterns of formation of nuclei and the growth of neoplasm crystals during the hydration of calcium sulfates in the absence and in the presence of mineral additives.

Consider the effect of mineral additives on the processes of hydration and structure formation in the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{H}_2\text{O}$ system.

As is known, calcium sulfate dihydrate is the final product in the $\text{CaSO}_4 - \text{H}_2\text{O}$ system and therefore it is not able to form hydration structures. It is considered for comparison with other modifications and clarification of the differences between its properties and the properties of secondary neoplasms.

The microfiller was administered in the following ratios to binders (binders) (%) 100-0, 90-10, 70-30, 50-50, 30-70, 10-90.0-100.

In contrast to the additives of surfactants and electrolytes, which affect the solubility of calcium sulfates and change the amount of supersaturation in the liquid phase and thereby the kinetics of structure formation [12-15]. The paper investigated the role of microfillers on hydration and structure formation of dihydrate calcium sulfate, and quartz is the most hydrophilic of the fillers studied.

Dihydrate calcium sulfate is not capable of chemical hydration and does not form a hydration structure when interacting with water, but nevertheless, in concentrated pastes, a structure with low strength is formed over time due to sedimentation, recrystallization and drying. The low (2.05 g/l) solubility of calcium dihydrate also provides a low percentage of the appearance of secondary hydrates in the system due to recrystallization and, accordingly, an insignificant contribution to the overall strength of crystallization structure formation (Fig. 2.).

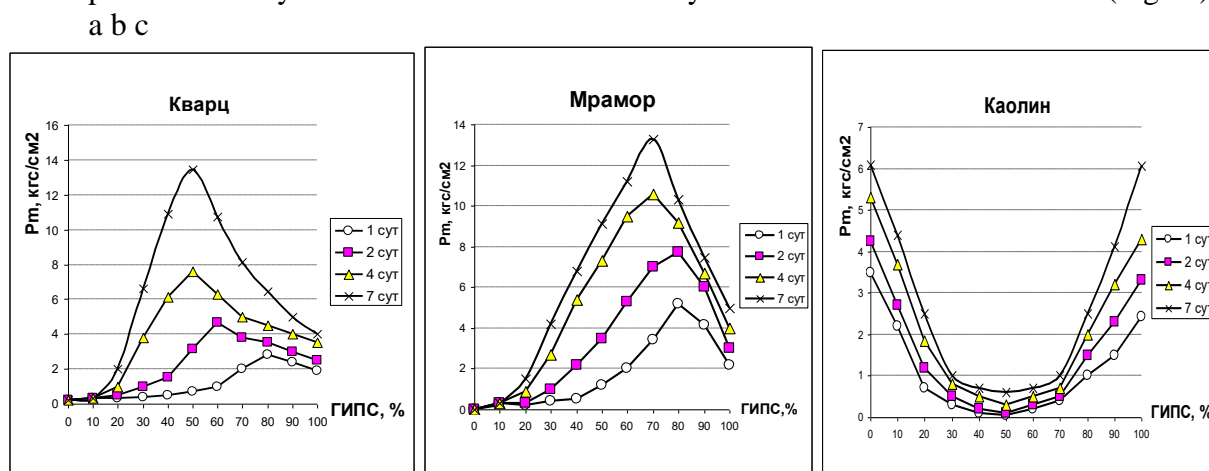


РИС 2. ВЛИЯНИЕ МИНЕРАЛЬНЫХ МИКРОПОЛНИТЕЛЕЙ НА ПРОЦЕССЫ СТРУКТУРООБРАЗОВАНИЯ В СИСТЕМЕ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{H}_2\text{O}$

As can be seen from the results of measuring the kinetics of structure formation (Fig. 2), a small plastic strength appears in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ aqueous pastes, explained by the recrystallization of the original product due to its low solubility (2.05 g/l), but mainly the strength is determined by coagulation contacts.

The role of the filler is clearly visible when comparing the strength of the freely formed sludge. As can be seen from Fig.2, the highest strength is noted in dihydrate pastes with sand at a ratio of 50:50, with marble at 70:30, and with kaolin at 50:50, the paste has the lowest strength.

The presence of microfillers in the suspension to a greater extent, the higher the cohesive ability of the embryos of the new phase - secondary hydrates in comparison with adhesion to the microfiller, prevents the hardening of the contacts, which causes the appearance of a minimum on the P m-C curves with large additives of the microfiller.

With an increase in the concentration of the microfiller, the strength of the coagulation contacts of the filler-filler becomes predominant and, in accordance with the nature of the introduced filler, the integral strength either increases (finely ground quartz sand) or drops sharply (kaolin).

Findings

The plastic strength in the pastes of dihydrate calcium sulfate shows that although the initial phase in this case is a ready-made hydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in the process of its contact with water, recrystallization of highly dispersed fractions of the powder takes place with the formation of secondary hydrates, causing the emergence of a hydration structure with crystallization hydrate-hydrate contacts.

It has been established that the higher the cohesive ability of the embryos of the new phase - secondary hydrates in comparison with the adhesion to the microfiller, prevents the hardening of the contacts, which causes a minimum on the P m-C curves with large additives of microfillers.

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