Formation of the spatial structure of a condensed system of calcium sulphate dihydrate

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Abstract. At present, universal models of the structure of crystalline bodies are well known. Such models should describe the structure of solids at the micro level. They are presented in the form of geometric topological models. Spatial models are also used to describe the structures of mineral disperse systems that arise during their crystallization. The arrangement of system elements represented as non-deformable rigid spheres can be interpreted based on topology. Simulation in the study of condensed systems makes it possible to quickly process and analyze significant data arrays in the directional synthesis of complex dispersed systems.

1. Introduction

The study of the structure of disperse systems is one of the new promising areas of building materials science [1 - 3]. Moreover, the structure at various dispersion levels can be considered [4, 5]. Or on a number of levels. This more clearly describes the system, but at the same time managing it complicates [6]. Directional structure formation when obtaining the latest materials with desired properties by conducting numerous computational experiments is provided [1, 3, 4]. This is necessary to identify defining patterns. For this, mathematical models are used [7,8]. When implementing the process of structure formation in a mathematical model, the values of the output parameters or the ranges of their possible changes are set. External parameters are necessary to characterize the operating conditions of the process [9, 10]. When solving a direct problem, the model allows to calculate the output parameters from the set values of the external and internal parameters. When creating models of technogenic or natural processes, often a more complex inverse problem is solved. It is necessary to find its internal parameters in the given values of the external and output parameters. In engineering practice, the solution of the inverse problem corresponds to the so-called design calculation, often aimed at optimizing the internal parameters according to some optimality criterion [7, 9].
In modern approaches to modeling various processes, in addition to descriptive information to characterize the design scheme, special techniques and symbols of visual graphic images can be developed [7].

Structural mathematical models - topological and geometric, make up two levels of the hierarchy of mathematical models of this type. Topological models describe the totality of the elements of an object and the relationship between them. It is proposed to use this mathematical model of research to determine and clarify the relationship between elements. It displays the complex structure of an object.

First of all, in the case of using such an object, which consists of a large number of elements [7]. The geometric mathematical model supplements the information that is presented in the topological mathematical model. It may contain additional information about the shape and size of the object and its elements, about their mutual arrangement.

A geometric mathematical model usually includes a collection of, for example, equations of lines or surfaces and algebraic relations. They determine the belonging of the regions of space to the geometric body of the object or its elements. Such a mathematical model can be specified by the coordinates of some set of points. Using them, by interpolating a line or surface, you can build, which will limit the area. Such boundaries can also be set in a kinematic way: a line - as the trajectory of a point, and a surface - as a result of moving the line. It is possible to imagine the shape and size of the region as a set of typical fragments of a fairly simple configuration.

Functional mathematical models consist of relationships that are phase variables, i.e. internal, external and output parameters of the object are interconnected. Often the functioning of complex objects using the totality of its reactions to some known (or given) input actions can be described. This kind of functional mathematical model belongs to the type of black box. It only imitates the external manifestations of the functioning of an object. But it does not disclose or describe the processes that take place in it. The most widely used simulation mathematical models in the study of control systems for complex objects are [10, 11]. But in other areas of research, they are also used [11].

When modeling, it is also necessary to set certain relations that establish the conditions for the transition from the model to the object under study (the original). Such relations are called “scale” [9, 12].

The issues of applying topological and geometric approaches to the description of disperse systems in works on building materials science were also considered [5, 6, 13, 14]. Obtaining a denser package with regulation of the composition of disperse systems is associated [13].

The most relevant methods of mathematical modeling in the study of systems based on calcium sulfate dihydrate are. The formation of a crystallization structure in the "dihydrate - dihydrate" system occurs according to the contact condensation hardening scheme. This direction along with the hardening of gypsum binders based on hemihydrate of calcium sulfate (hydration) develops.

During contact-condensation hardening of calcium sulfate dihydrate, there is no hydration if there is no hemihydrate of calcium sulfate in the system [16]. The process of formation of primary contacts is due to the approach of particles of different sizes to a close distance [16]. In the system, intergrowth nuclei between particles of the dihydrate (coarse and fine phases) arise [17]. The hardening process of condensed systems is initialized.

The formation of phase contacts in a condensed system of calcium sulfate dihydrate is possible under the following conditions:

- availability gypsum particles at closely acting forces distance;
- the presence in the system of gypsum particles of different sizes;
- compliance in the system of chemical uniformity;
- the presence on the surface of the solvent particles in the form of thin layers. The concentration of the solution by the particle size is determined [1, 17].

In accordance with the structure formation mechanism of such systems between particles of gypsum, the formation of crystallization contacts can occur. Due to the interaction of gypsum particles of different sizes, this happens. Such a mechanism underlies the formation of the primary structure [17].
Currently, universal models of the structure of crystalline solids are well known. They are designed to describe the structure of solids. They are represented in the form of geometric-topological models. Spatial models are also used to describe the structures of mineral disperse systems. For example, to describe the calcium sulfate dihydrate structure.

2. Research methods
As the initial dispersed system, gypsum powder was used. Real raw mixtures of powders of calcium sulfate dihydrate were made. They had different dispersion. Powders on a jaw crusher were obtained. And then — grinding in a laboratory pebble mill. The composition of the powders by size was estimated by the analysis of variance using a Fritsch Particle Sizer ‘analysette 22’ laser analyzer (figure 1). The specific surface of the powders by the filtration method on a PSX-11 device was evaluated. Mixing during the preparation of gypsum raw mixes with a mixer was carried out. The study of physical and mechanical characteristics was carried out on sample cylinders 50x50 mm in size. Hardening of gypsum samples was carried out at normal temperature.

Figure 1. Packing of a binary disperse system spheres of contact-condensation hardening.

3. Results
It was found that the distribution of particles in the composition of the powders corresponds to the normal distribution law. In addition, gypsum powders can consist not only of individual mineral source particles, but also of aggregates that are formed during the grinding process. The effect of such aggregates and the particles themselves on the properties of the powders is far from the same. These differences are even more pronounced with a multi-fractional system. Such a system is formed by mixing powders with different specific surfaces to obtain the most dense packaging of the material after pressing.

The problem was solved by creating a mathematical model that describes the distribution of solid particles in a unit volume (unit cell) subject to the formation of the maximum number of phase contacts.

Using the developed spatial model of a disperse system, mathematical dependences were derived: volumetric fillings (figure 2) on the total coordination number and total coordination number on the ratios of the diameters of the spheres of the bimodal system (figure 3).

In order to develop and confirm the operability of the mathematical model of hardening of condensed gypsum systems, this study was carried out. It describes the internal structure of a contact-condensation hardening composite based on two-water gypsum. Such a mathematical model allows you to control the process of structure formation of a dispersed system. It makes it possible to
accurately calculate the optimal particle size distribution of the raw material mixture of calcium sulfate dihydrate. To obtain composites of contact condensation hardening, this must be used.

Elements of the system are presented in the form of non-deformable rigid spheres. The arrangement of system elements can be interpreted based on topology and geometry. Simulation in the study of condensed systems makes it possible to quickly process and analyze a large number of calculated data in the directional synthesis of complex dispersed systems.

A common approach to the study of such systems is a three-dimensional reconstruction of the structure. Within the framework of such a model, the problem of finding the composition of the composite material reduces to the problem of the spatial packing of spherical particles in accordance with the hardening mechanism. The greatest number of phase contacts between hard spheres on the scale of the entire filled volume with a certain ordered arrangement of spheres will be achieved.

Topological characteristics are used to model the system. Structural topology determines the coordination of the nearest environment of a particle (sphere) in three-dimensional space by the coordination number and packing density in the system [6]. The coordination number is determined by the number of particles (spheres) that are in contact with the central particle (sphere) with respect to its immediate environment. Therefore, the number of spheres on the surface of the central sphere.

The maximum coordination number for the arrangement of spheres in the nodes of a face-centered cubic lattice or for dense hexagonal packing according to the required type of packaging (figure 1) is ensured.

The identification of mathematical patterns using the optimality criterion - the number of crystallization centers was carried out. A quantitative characteristic of the binary system was the ratio of the size of the gypsum particles. During the development of mathematical dependence and research, a spatial model was developed. The model allows you to approximate the structure of the material and calculate the necessary characteristics of the mixture in a conventional unit volume.

Contacts between gypsum particles of different sizes form a crystalline structure. They are called phase. The number of such crystallization contacts (active crystallization centers) is determined by the ratio of the sizes of the approaching particles and the quantitative content of particles of different sizes in the composition of the dispersed system. For this, binary mixtures of a certain type must be used. This will allow to obtain the maximum number of contacts of large and small particles in the package. According to the hardening mechanism, a small particle should be located in the gap between two large gypsum particles.

The dependence of the number of particles on the ratio of diameters (figure 3) has the form

\[ \sum B = f(m) = 43.98m^2 - 0.003m + 0.007, \]

where \( m \) – is the spheres size ratio in a binary system, \( \sum B \) – is the total coordination number.

4. Discussion

The obtained dependence shows that with an increase in the difference in particle sizes, the proportion of large particles increases. Such a system has coordination numbers that exceed the coordination numbers in systems with the same particle sizes. An increase in the total coordination number of particles of the system leads to an increase in the strength of structures based on binary mixtures of optimal grain composition. Designing the optimal particle size distribution of such a material allows one to increase the strength [15]. It is established that the compressive strength of dispersed systems by the strength of the particles of the material is determined by the number of crystallization centers between the particles of the solid phase and the compressive strength of an individual contact. The number of crystallization centers, in turn, depends on the size of the particles and the method of packing [15].
Figure 2. The effect of three-dimensional scaffolding by large particles in a binary system on the total coordination number.

Figure 3. The influence of the ratio of the spheres diameters in the binary system on the total coordination number.
The results of a computational experiment to optimize the internal structure using the obtained model (figure 4) showed that the optimal content of coarse powder is 30–40 %. The experimental data on the solubility and strength of gypsum composites obtained as a result of the study coincide with the calculations of the computer model. The validity and adequacy of the mathematical assessment of the process of structure formation of gypsum composites is proved. According to the research results, the optimal content of coarse powder is 30%; using the model, the optimum ratio of powders in the binary system is 30–40 %.

Figure 4. The influence of the ratio of the spheres size and volumetric fillings on the total coordination number.

An improvement in the gypsum stone structure with the optimum ratio of powders in the binary condensed system is confirmed by microscopic studies (figure 5).

Figure 5. Microstructure of a composite based on a binary mixture of optimal particle size distribution.
The structure of the condensed system is represented by large crystals, aggregates. The space between them is filled with aggregates and free dispersed particles of another dispersion level. This density increased the whole system.

5. Conclusions
Optimization of particle size distribution using mathematical modeling of the structures of condensed gypsum systems allows increasing the compressive strength of composites by increasing the number of phase contacts in a disperse calcium sulfate dihydrate system. This is confirmed experimentally. The compressive strength of the gypsum composite of the optimal composition is more than twice the compressive strength of the original samples. The increase in the dispersion of gypsum and the regulation of their particle size distribution are the main factors for obtaining high-strength gypsum stone. This can provide high quality materials and products based on it.

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