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Formation of the Structure of Ash-Gypsum of Non-Hydration Hardening

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The article presents a model of non-hydration hardening of dispersed systems - mineral binders (without the stage of hydration) and the results of studies of gypsum stone with ash filler from the standpoint of the formation of the optimal structure of the material of non-hydration hardening, as well as its density and strength. The model assumes the use of binary mixtures of dispersed components with different dispersions. The study was based on data on the granulometric composition and dispersion of gypsum powders and aluminosilicate microspheres. It was isolated from the ash-slag mixture - waste from a thermal power plant. The aluminosilicate microsphere contains not only microsized spherical particles of the amorphous phase but also nanosized grains in a sufficient amount. This makes it possible to control the particle packing density. Experimental verification of the optimization of the granulometric composition of a binary dispersed system based on gypsum and ash microspheres was carried out. Based on the results, the optimal content of the filler in the composition of the non-hydration hardening structure was established. It is shown that filling with highly dispersed particles affects the performance properties of the resulting modified stone.

1. Introduction

Binders that harden without a hydration step (non-hydration binders) require certain prerequisites to be maintained in the system. These conditions should ensure the formation of crystallization contacts in the structure of calcium sulfate dihydrate (Buryanov et al., 2020). One of these conditions is the optimization of the grain composition (Petropavlovskii et al., 2021). It determines the nature of the resulting structure (Petropavlovskii et al., 2021). The dispersion and granulometric composition of the non-hydration binder determine the internal structure of the topological space. This certainly affects the basic physical-chemical and physical-mechanical properties of the binder. Denser packing of binder particles in a dispersed system of calcium sulfate dihydrate is achieved by combining mixtures of different particle sizes in the compositions. This makes it possible to increase the strength of the non-hydration type structure.

Also, the strength of non-hydration curing systems will depend on the individual strength of the binder particles. Important factors of non-hydration hardening will be the number of contacts and the average strength of an individual contact between the particles of the binder (Kharkhardin et al., 2003). The number of contacts is determined by the sizes (average diameters) of the particles and the way they are arranged - packing. Packing of particles as a topological set is determined by the main geometric characteristics of the dispersed system. They depend on the nature of material grinding (Zommer et al., 2021). The differential and integral size distribution of particles in a dispersed system (Korolev et al., 2007), the mean geometric diameter, mode, and other characteristics of dispersed systems are important for modeling the topological space of disperse systems, not only the non-hydration type of hardening.

Mathematical description of the size distribution of particles in the composition of solid-phase disperse systems has been studied by many researchers. Many different equations have been proposed for particle distribution functions of binder systems (Petropavlovskii et al., 2021).

Thus, knowledge of the law of distribution of particle sizes in the composition of gypsum or cement-dispersed systems makes it possible to solve various theoretical and applied problems:

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•It is reasonable to extrapolate the composition of dispersed systems of mineral powders over the entire required range of particle sizes (mainly in the smallest fractions) (Lesovik et al., 2020);
•According to the weight distribution, calculate the distribution of particles over their surface, number of particles, volume, etc.;
•It is reasonable to choose average indicators characterizing powders (Korolev et al., 2007);
•Make technical calculations more accurately;
•Simplify the study on models.

Today, there is considerable interest in obtaining a quantitative, mechanism-based description of the behavior of deformation and compaction of dispersed systems, suitable for numerical modeling (Kharkhardin et al., 2015). The Rosin-Rammler-Sperling-Bennett (Rosin-Rammler for short) formula is most widely used to describe cement dispersed systems (Buryanov et al., 2020). However, many works theoretically and experimentally prove the inapplicability of the Rozin-Rammler equation to highly dispersed compositions. The logarithmically normal distribution law of A.N. Kolmogorov has great advantages for describing the distribution of highly dispersed systems (Buryanov et al., 2020).

But gypsum systems in the series of binders stand apart. Gypsum highly dispersed systems include not only individual mineral «primary» particles. They may contain a fairly large volume of aggregates. They are formed under the action of cohesion during the grinding process. Moreover, the aggregates are quite stable and are characterized by a sufficiently high dry strength (Petropavlovskii et al., 2021).

The influence of such aggregates and the particles themselves on the properties of powders, including the ability to compact, is far from being the same. These differences should be even more pronounced when the system is multifractional, obtained by mixing powders with different specific surface areas to obtain the most dense packing of the material after pressing, which requires the use of numerical methods for the mathematical description of the formation of the structure of the dispersed system.

Due to the fact that the formation of the structure of non-hydration hardening has its own characteristics, the strength of the «quasi-basal» type gypsum stone, according to the theory of non-hydration hardening, is determined primarily by the number of contacts in the system formed between particles of different sizes (Buryanov et al., 2020).

In order to improve the performance properties of non-hydration hardening systems, the influence of the granulometric composition of binders on the structure and properties of ash-gypsum stone was studied. The introduction of microsphere fillers is a promising and resource-saving direction in the development of materials science (Zommer et al., 2021).

2. Materials and methods

2.1 Materials

In the studies, dihydrate natural gypsum of the Samara gypsum plant and an ash microsphere were used (Figure 1, 2). The quantitative indicators of the chemical composition of the gypsum in weight % and in atomic % is given in Table 1, 2 respectively.

The microsphere was obtained in the factory from the ash and slag mixture - a waste from a thermal power plant in the Moscow region (Figure 3). Separation and froth flotation was used (Kosivtsov et al., 2021). The chemical composition of the ash aluminosilicate microsphere is given in Table 3. Losses on ignition in the composition of such ash products do not exceed 1.8 % (Chalov et al., 2021).

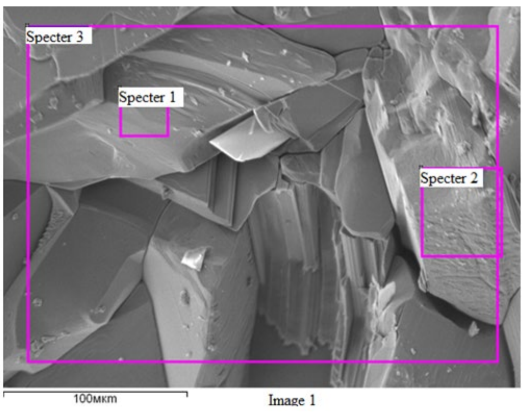

Figure 1: Microstructure of natural gypsum stone from the Samara region

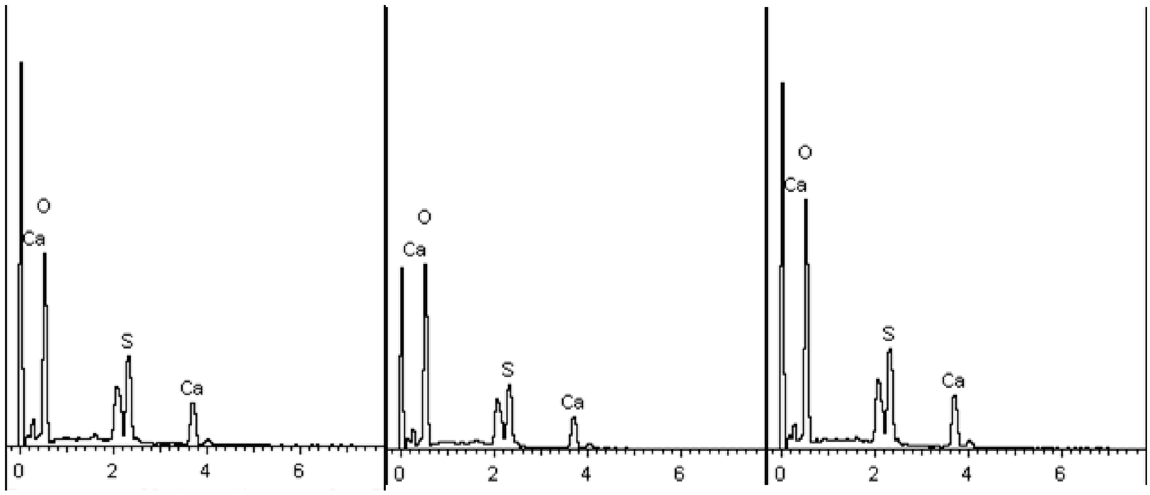

Figure 2: Spectra of natural gypsum of the Samara gypsum plant

Table 1: Quantitative indicators of the chemical composition of the gypsum, in weight %

spectrum	O	S	Ca
spectrum 1	52.82	11.13	12.60
spectrum 2	53.97	19.21	19.80
spectrum 3	59.41	14.21	13.50
mean	55.40	14.85	15.30

Table 2: Quantitative indicators of the chemical composition of the gypsum, in atomic %

spectrum	O	S	Ca
spectrum 1	60.72	6.38	5.78
spectrum 2	67.26	11.94	9.85
spectrum 3	69.77	8.33	6.33
mean	65.92	8.88	7.32

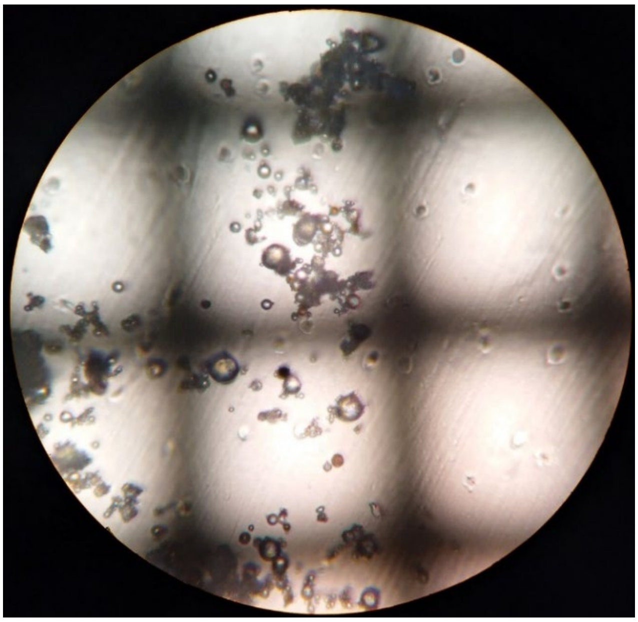

Figure 3: Micrograph of an aluminosilicate ash microsphere

Table 3: Chemical composition of the ash aluminosilicate microsphere

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	P_2O_5	SO_3	C
Content, %	0.6	1.6	21.5	57.8	2.1	3.7	0.9	0.1	4.6	0.4	0.1	1.8

The particle size distribution of the ash was studied using a laser particle analyzer. The powder contains a sufficient amount of particles corresponding to nano sizes. The particle distribution histogram generally corresponds to the normal law (there is one maximum, the curve asymptotically approaches the abscissa axis on both sides), but it is not symmetrical about the center, it is shifted towards small particles. The average particle size in the composition of the raw mixture is 3 μm. The particle scatter range is quite wide, from 0.3 to 100 μm.

The particle distribution histogram of the dihydrate powder is similar to the one above. However, the integral curve is flatter, the optimum is implicitly expressed, within the distribution range from 3 to 10 μm, the percentage of particles is quite constant. The maximum number of particles of 19.24 % corresponds to a size of 20 μm.

Studies of dispersed systems of non-hydration hardening were carried out using polydisperse powders of gypsum dihydrate and aluminosilicate microspheres.

In view of the fact that the optimal from the point of view of packing density is a bidisperse system composed of two polydisperse components, the characteristics of mixtures based on gypsum dihydrate and ash microspheres were studied in the work.

2.2 Methods

Powder mixtures were obtained by mixing fine powders in various combinations. Bidisperse mixtures were used in accordance with the accepted topological model (Figure 3). Powders of calcium sulfate dihydrate were obtained on a jaw crusher. And then - grinding in a laboratory ball mill. The size composition of the powders was evaluated by dispersion analysis using a Fritsch Particle Sizer 'Analysette 22' 9 laser analyzer. Mixing of raw mixes was carried out by a mixer. The study of the properties of ash-gypsum stone was carried out on cylinder samples 50x50 mm in size. The hardening of gypsum samples was carried out at normal temperature.

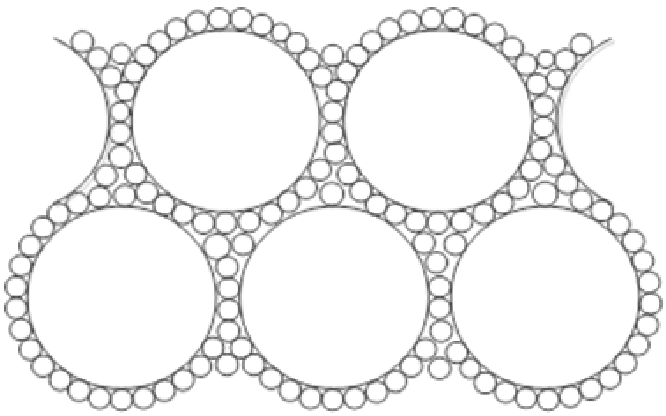

Figure 4: Fragment of an ideal model of the internal topological structure of a dispersed system of non-hydration hardening on a plane

3. Results and Discussion

The mathematical model was developed in order to solve the problem posed in the study. It describes the topology of the unit cell structure of a dispersed system of condensation hardening. A structure was created in which a smaller sphere is located in the gap between larger spheres. The spheres imitated particles of gypsum dihydrate and ash microspheres. The study of the topology of the dispersed system was carried out using a computer model of the non-hydration hardening system (Delitsyn et al., 2022). The creation of such a model was necessary to study the processes of packing spheres in an elementary cell at the lowest cost. A computer model of the structure of a dispersed condensation hardening system is shown in Figure 5. It is represented by large particles shown in the section and small ones. They are located over the entire surface of large particles, which are moved apart by the size of a small particle.

The conducted studies confirmed the positive effect of the dispersion of powders on the physical and mechanical characteristics of the resulting gypsum with an ash microsphere and materials based on it (Figure 6). The results obtained correlate with the results of other authors (Petropavlovskaya et al., 2018).

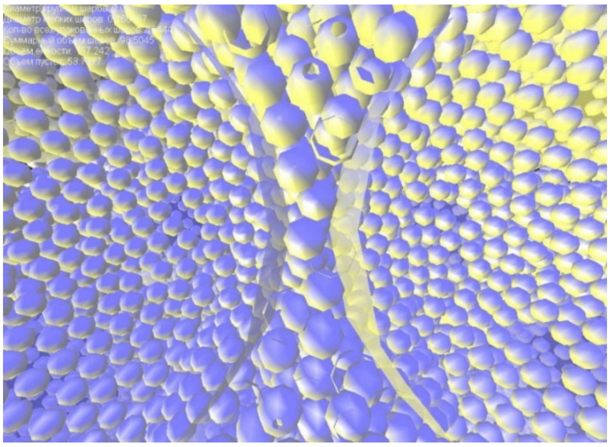

Figure 5: A fragment of a visualized model of the internal topological structure of a dispersed system of non-hydration hardening in volume (small particles are distributed over the transparent surface of large particles with a small geometric perspective)

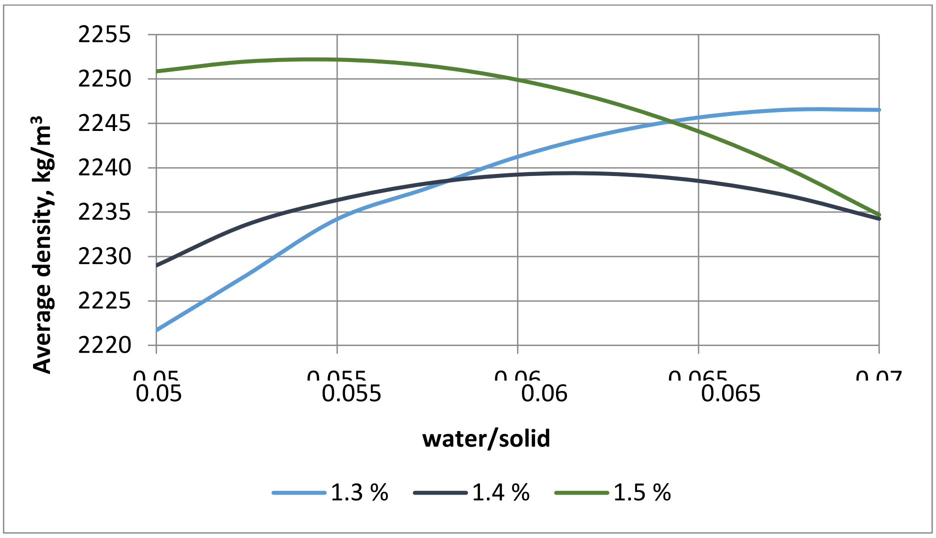

Figure 6: Influence of aluminosilicate microspheres on the average density at different water/solid

It has been established that the bidisperse system obtained by mixing powders of the ash component and dihydrate finely ground natural gypsum, to a greater extent meets the requirements for obtaining the optimal structure of non-hydration hardening (Figure 3). In the bidisperse system, there is a sufficient amount of both large and highly dispersed particles, according to the studies. The composition of the bidisperse varies from 0.3 µm to 100 µm. The granulometric composition of disperse systems using integral and differential distributions was investigated. The flatness of the integral curve of particle size distribution in the bidispere system confirms the presence of a fairly wide range of particle distribution. The histogram has two pronounced peaks corresponding to the maximum in the region of small and large particles. The ratio of particle sizes that characterize the peaks corresponds to the accepted model of non-hydration hardening. The maximum density – 2,252.1 kg\m^3 is achieved with the content of the aluminosilicate component of the ash - 1.5 %. Samples of ash-gypsum stone with water content - *water/solid* = 0.055 have the highest density.

Regulation of the composition of binary disperse systems consisting of powders of gypsum dihydrate and aluminosilicate microspheres makes it possible to increase the strength of the composite by optimizing the number of contacts between particles of different sizes, which is confirmed by high strength values of – 50 MPa. The optimal content of the aluminosilicate microspheres is reflected both in the strength and in the average density of the composite. The dense packing of gypsum particles and nanosized particles of the aluminosilicate microspheres predetermine the structure of the composite with high-performance properties.

4. Conclusions

Optimization of the granulometric composition of binary disperse systems consisting of powders of gypsum dihydrate and aluminosilicate microspheres made it possible to increase the density of the material by 12 % with an increase in strength by 29 %. The porosity was 1.58 %. Saving resources and energy in obtaining the material opens up prospects for its use in building technologies (Tkach et al., 2021). Approaches to the formation of the structure using the selection of the grain composition can be applied in the design of multicomponent binders with ash filler (Nguyen et al., 2021), fiber-reinforced concrete (Aleksandrova et al., 2022), and foam concrete (Lukpanov et al., 2022).

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