Influence of the polymeric additives on the process of calcium sulfatedihydrate crystallization

Yulia V. Ustinova[1,*]

[1]Moscow Polytechnic University, Bolshaya Semyonovskaya str., 38, 107023, Moscow, Russia

Abstract. The research is aimed to the clarification of the calcium sulfatedihydrate crystals growth and formation of in the presence of the different polymers based functional additives. The calcium sulfatedihydrate crystals have been synthesized both in the pure form and with the additives. The additives have included a super plasticizer based on a sulfonated melamine-formaldehyde resin (SMF), a methylcellulose (MC) and a redispersible polymer powder based on vinyl acetate, ethylene and vinyl chloride copolymers (VAEVC). The X-ray analysis and the electron microscopy have been applied to identify an influence of the polymer additives over the configuration and size of the calcium sulphate dihydrate crystals. The structural and strength characteristics of the gypsum materials have been also investigated.

1 Introduction

Nowadays many researchers analyse the influence of the various additives on the hydration hardening process of the inorganic binding materials. The establishment of the interconnection between the structure of the material and its properties brings to the effectively correction of the existing and development of the new technologies of obtaining of the materials with the established properties [1-6].

For instance, the introduction of sodium sulfide additives leads to the formation of an insoluble calcium sulfide. The last one can serve as a core for the formation of the hierarchical organized structures and promote clogging of pores, strengthening the structure of the anhydrite binder [7].

An addition of the nanomaterials to the Portland cement mortars could potentially enhance their properties as it is shown in [8-9].

The size, morphology and structure of the crystals of calcium sulfatedihydrate, forming in the process of hydration of semi-aqueous gypsum largely determine the properties of the construction materials [10-13].

It is shown in [14] that the crystals CaSO4·2H2O have a block structure. In a semi-aqueous gypsum containing an additive of microsilica, during hydration, areas of coherent scattering of a new phase with the smallest average dimensions are formed.

As it is shown in [15], the functional additives are widely spread in the production of dry mixtures on the basis of gypsum binders. They are presented by various classes of organic and inorganic substances. These additives are put in the dry mixture composition for the regulation of hardening terms, processes of curing and structuration of gypsum binders. Nevertheless, an impact of the functional additives on a microstructure of a calcium sulfatedihydrate is yet not rather studied.

Thus, the aim of the research is the investigation of the influence of the functional additives on a microstructure of a calcium sulfatedihydrate and the establishment of the interconnection between the structure of the material and its construction and technical properties.

2 Methods

A crystalline phase of the calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) has been obtained from the solution due to the supersaturation, which occurs as a result of a chemical reaction:

$$CaCl_2 + Na_2SO_4 + 2H_2O \rightarrow \rightarrow CaSO_4 \cdot 2H_2O \downarrow + 2NaCl \quad (1)$$

The synthesis of crystals of the dihydrate of calcium sulfate has been carried out by using the counter diffusion within 30 days.

Laboratory glassware has been used for the synthesis (see fig. 1).

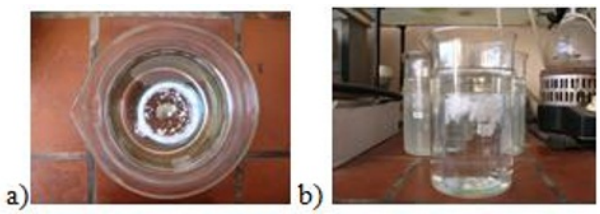

Fig. 1. Growth of calcium sulfate dihydrate crystals after 30 days after mixing the solutions: a) top view; b) side view.

*Corresponding author: ustinova.ju@gmail.com

The functional additives most widely applied in dry mixtures have been chosen for the research: a super plasticiser on the basis of a sulfonated melamine-formaldehyde resin (SMF), a methylcellulose (MC) and a redispersible polymeric powder on the basis of vinyl-acetic ester, ethylene and vinyl chloride copolymers (VAEVC).

The additives have been entered into the system with a sodium sulfate solution in the following concentrations (% of the mass of $CaSO_4 \cdot 2H_2O$): SMF – 1.0; MC – 0.5; VAEVC – 3.0; SMF + VAEVC – 1.0 + 3.0; SMF + MC – 1.0 + 0.5.

The methods of X-ray diffraction and scanning electron microscopy have been applied as the physical-chemical methods of a microstructure research. The X-ray diffraction has been performed on the X-ray diffractometer DRON-3M, CuK_2 radiation, Ni-filter. Shooting interval 2Θ = 8-70°.

A scanning electron microscope JEOL/EO, type JSM-6510, an increase of 50-500x, has been appliedto study the gypsum crystals morphology.

The structural and strength characteristics of the gypsum binders have been tested according to the state standards (GOST).

3 Results and Discussion

The results of the X-ray analysis have shown that synthesized as in pure form and in the presence of the polymeric components crystals, correspond to the phase $CaSO_4 \cdot 2H_2O$ with the following typical peaks 7.63 Å; 4.283 Å; 3.065 Å; 3.799 Å, etc [16]. The layouts of the specified peaks practically don't change for all researched compositions. This fact demonstrates that molecules of polymeric components do not implement into the structure of a calcium sulfate dihydrate and the chemical composition of a product does not change. However - the relative intensity of peaks of the calcium sulfate dihydrate crystals with the additives differs from a control sample. So, for example, intensity of a peak of 4.283 Å for the calcium sulfate dihydrate crystals synthesized without components makes 12.08%; for the crystals of a calcium sulfate dihydrate synthesized in the presence of SMF – 15.16%; in the presence of MC – 8.48%; in the presence of VAEVC – 10.23%, etc. A change of intensity of peaks is more explicitly provided in the Table 1 and Table 2.

Table 1. Changes in the intensity of the $CaSO_4 \cdot 2H_2O$ peaks in the presence of the polymeric additives.

Peak	hkl index	d, Å	Intensity, %, for the investigated compositions			
			No add.	SMF	MC	VAEVC
2	020	7.63	100.00	100.00	100.00	100.00
3	021	4.283	12.08	15.16	8.48	10.23
4	041	3.065	14.43	14.82	15.89	15.38
5	040; 130	3.799	21.77	21.40	15.29	16.41

Table 2. Changes in the intensity of the $CaSO_4 \cdot 2H_2O$ peaks in the presence of the polymeric additive compositions.

Peak	hkl index	d, Å	Intensity, %, for the investigated compositions	
			SMF + VAEVC	SMF + MC
2	020	7.63	100.00	100.00
3	021	4.283	13.56	8.00
4	041	3.065	19.78	17.25
5	040; 130	3.799	32.30	15.75

Such a change in the intensity of the characteristic peaks is probably connectedwith the fact that the studied additives presented in the solution affect calcium sulfate dihydratecrystallization.

An analysis of the X-ray reflexes of the JCPDS database (33-0311) [16] has showed that the most peculiar granular forms for the synthesized $CaSO_4 \cdot 2H_2O$ crystals are pinacoid,inclined rhombic prismand vertical rhombic prism (see Table 3).

Table 3. The most peculiar granular forms for the synthesized $CaSO_4 \cdot 2H_2O$ crystals.

Peak number	hkl index	d, Å	Faceted form
2	020	7.63	Pinacoid
3	021	4.283	Inclined rhombic prism
4	041	3.065	Inclined rhombic prism
5	040	3.799	Pinaciod
5	130	3.799	Vertical rhombic prism

So, the data given in the tables 1, 2and 3has confirmed that the SMF additive promotes the growth of the 021 and 041 faces, and slightly inhibits the growth of the 040 and 130 faces. The growth of the 021, 040 and 130 faces suppresses, and the growth of the 041 faces increases in the presence of MC or VAEVC. The last one is poorly suppresses the growth of 021, 040, and 130 faces in comparison with MC. The growth of 041, 040 and 130 faces significantly increases, and the growth of face 021 is less intense in the presence of a complex additive on the basis of SMF+VAEVC. A complex additive on the basis of SMF+MC significantly suppresses the growth of 021, 040, and 130 faces.

The rate of a crystal germ formation can be significantly changed by the various additives, primarily surfactants, introducing into the solution. It is generally accepted that the action of surfactants is associated with their adsorption on the surface of submicrogerms, which hinders the further growth of crystal germs. In addition, they change the surface tension between the solution and the surface of the germ, increasing the work of a germformation.

The effect of polymer additives brings to the number of crystal germs decrease and their growth slowing and to the formation of an adsorption (molecular) film on the grains. The surface-active substances form due to the phenomenon of a selective adsorption of the film on the faces of the crystals growing out of the solution, and, mainly, on the facets with a large surface activity. These films hinder the rate of crystals growth, and also affect their shape, bringing it closer to the globular, by

reducing the growth rate in any direction. Since the rate of growth of crystals is often proportional to the surface tension, even very small additions of substances capable of changing the surface tension substantially affect the degree of wetting of the grains, the nature of the crystallization and the properties of the tumors.

There are some possible ways of adsorption of molecules of polymer additives on the crystal faces can be considered.

The first way is connected with an adsorption of polymer molecules on the faces possessing the greatest surface energy. It is noted in [1] that the values of the surface energy of the planes 010 (pinacoid), 120 (vertical orthorhombic prism), 011 and 111 (inclined orthorhombic prism) in the calcium sulfate dihydrate crystals are 240 ± 8, 480 ± 40, 640 ± 200 and 1540 ± 160 mJ / m^2, respectively. In this connection, it can be assumed that the polymer molecules are mainly adsorbed on the planes having the greatest surface energy values, i.e. on the planes 111 and 011 and, thereby, reduce the rate of crystal germ formation.

The second way is connected with an adsorption of surfactant ions on positively or negatively charged planes of crystals of $CaSO_4 \cdot 2H_2O$. A super plasticizer based on a sulfonated melamine-formaldehyde resin is classified as anionic surfactant. In an aqueous environment, this additive dissociates to form a negatively charged $R\text{-}SO_3^-$ group, where R is the organic radical of the sulfonated melamine-formaldehyde resin and positively charged Na^+ ions. It is obvious that the $R\text{-}SO_3^-$ group adsorbs on positively charged crystal planes and, thereby, reduces the rate of their growth. The presence of Na^+ ions in the aqueous environment does not affect the rate of a crystal germ formation, as well as the size and shape of the calcium sulfate dihydrate crystals. The aqueous environment is already saturated with Na^+ ions.

The electron microscope studies (see fig. 2) reveal that the synthesized crystals are prisms. The introduction of the test additives affects crystals' configuration. Thus, the SMF introduction promotes the crystals reduction, and the MC or VAEVC introduction allows the formation of more elongated crystals.

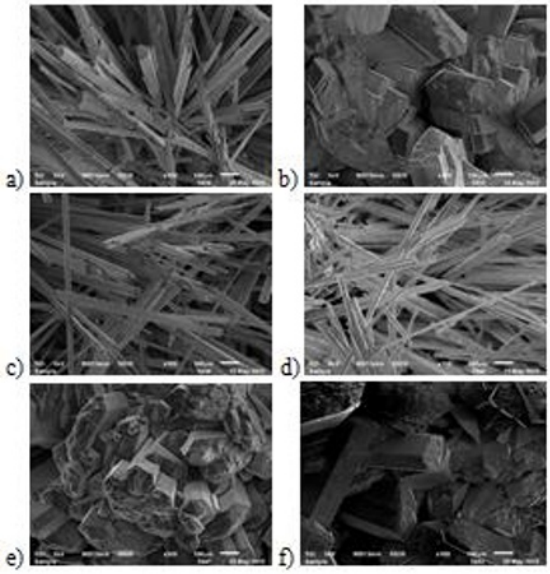

Fig. 2. Electron microphotographs of the synthesized crystals of the calcium sulfate dihydrate: a) no additive; b) with SMF additive; c) with MC additive; d) with VAEVC additive; e) with SMF + VAEVC additive; f) with SMF + MC additive.

As the Figure 2 shows, the length of $CaSO_4 \cdot 2H_2O$ crystals synthesized without additives varies from 1500 μm to 5 mm. The SMF additive reduces the crystal size, the crystal length is from 50 to 500 μm, and the diameter is from 100 to 550 μm. When MC is added, the crystals become narrower and crystalline splices appear. When VAEVC is added, the formation of narrower crystals is also observed.

The strength properties of bead specimens made of gypsum with the additives have been examined to study the influence of the microstructure of $CaSO_4 \cdot 2H_2O$ on the properties of materials based on gypsum binders. The results of the studies (see Table 4) have shown the flexural strength is 9.2 MPa and the compressive strength is 19.0 MPa for the control samples.

An addition of the SMF increases the flexural strength to 10.0 MPa, and decreases the compressive strength to 14.9 MPa. The increase in the flexural strength is explained by the slight elongation of the calcium sulfate dihydrate crystals in the presence of this additive. However, due to the fact that the size of the crystals is markedly reduced, there is no significant increase in the flexural strength. The compressive strength is reduced in comparison with the control sample also because the size of the crystals of the two-water gypsum in the presence of the SMF additive is reduced.

An addition of the MC provides the greatest upsurge in the flexural strength to 12.2 MPa in comparison to the control sample, and a slight decline in the compressive strength to 16.6 MPa. A noticeable growth in the flexural strength is due to the formation of the more elongated needle-like crystals in the presence of MC, while the size of the crystals remains practically unchanged. As a result, such crystals most likely perform the function of reinforcing fibers in a sample beam, thereby increasing its resistance to bending loads. However, the formation of such crystals does not provide an upsurge in the area

of contacts between the crystals, which leads to a reduction in the compressive strength.

Table 4. Results of the study of strength properties.

Composition	Flexural strength	Compressive strength	Flexural strength / compressive strength ratio
No additive	9.20	18.97	0.48
SMF	10.03	14.94	0.67
MC	12.18	16.58	0.74
VAEVC	10.85	19.06	0.57
SMF + VAEVC	9.68	16.84	0.57
SMF + MC	10.70	15.78	0.68

An addition of the VAEVC does not practically affect the shape and size of the $CaSO_4 \cdot 2H_2O$ crystals. However, the flexural strength rises to 10.9 MPa, and the compressive strength grows insignificantly compared to the control sample and achieves 19.1 MPa. The increase in the flexural strength is due to the mechanical characteristics of the polymer film. However, at the same time, mortars of inorganic binders in the presence of redispersible polymer powders have a reduced compressive strength, which can be explained by the low resistance to compression of the polymer base and also by the air entrainment into the solution mixture [15].

The introduction of a complex additive based on SMF and VAEVC practically does not change the flexural strength, which is 9.7 MPa, and at the same time declines the compressive strength to 16.8 MPa. As it has been mentioned above, the decrease in compressive strength is due to the formation of the smaller crystals in the presence of the SMF-based additive.

The introduction of a complex additive based on SMF and MC increases the flexural strength to 10.7 MPa. This effect is associated with the formation of crystals of a narrower shape than the control sample. However, due to the fact that the SMF-based additive reduces the size of the crystals, and the MC additive promotes the formation of narrower crystals, the compressive strength decreases compared to the control sample to 15.8 MPa.

The ratio flexural strength / compressive strength has been also calculated to estimate the fracture toughness and reinforcing effect. The data presented in Table 4 allow judging the higher crack resistance of the compositions with the investigated polymeric additives as compared to the control composition. At the same time, the composition with methylcellulose shows the highest value flexural strength / compressive strength, which is 0.74.

The particles of the dispersed phase adhere as a result of their hydration with the formation of a porous solid phasein water-gypsum mixtures. Pores and other shortcomings are the defective structures of a gypsum stone, which determine its water permeability and low strength. Therefore, in scientific research it has been very important to assess the effect of the shapes and sizes of $CaSO_4 \cdot 2H_2O$ crystals synthesized in the presence of polymer additives on the structural characteristics of a plaster. The results are given in the Table 5.

Studies of structural characteristics (see Table 5) show that the change of the shape and size of $CaSO_4 \cdot 2H_2O$ crystals synthesized with additives based on a sulfonated melamine-formaldehyde resin, a methylcellulose and vinyl acetate, ethylene and vinyl chloride copolymers in gypsum binders does not affect the total pore volume and the nature of their distribution in the hardening product. Thus, in the presence of tested additives, a slight increase in the total porosity by 2 ... 5% is observed, the volume of closed pores rises, and the open porosity somewhat reduces.

Table 5. The structural characteristics test results.

Composition	Porosity, %			Density coefficient, %
	Open	Closed	Total	
No additive	37.15	1.88	39.03	60.97
SMF	35.76	7.42	43.19	56.81
MC	31.60	13.91	45.51	54.49
VAEVC	35.94	7.11	43.04	56.96
SMF + VAEVC	34.72	8.32	43.04	56.96
SMF + MC	32.64	10.07	42.71	57.29

4 Conclusions

1. It has been found that the additives such as a superplasticizer based on a sulfonated melamine-formaldehyde resin, a methylcellulose, a redispersible polymer powder based on vinyl acetate, ethylene and vinyl chloride copolymers influence the crystallization and properties of the plaster. Moreover, the superplasticizer based on a sulfonated melamine-formaldehyde resin has the greatest influence on the gypsum crystallization.

2. It is covered that the X-ray phase analysis method can be used to predict the shape and configuration of crystals.

3. The shape and size of the crystals of calcium sulfate dihydrate, formed during the hardening of the plaster, affect the physical and mechanical properties of gypsum products. Thus, in the presence of methylcellulose, the shape of the crystals of the two-water gypsum becomes narrower, approaching the needle-like form. As a result, such crystals are able to perform the function of reinforcing fibers in the hardening product, thereby increasing its resistance to bending loads. Accounting for such a factor is quite important in the development of materials based on gypsum binders with specified properties, because a regulation of the physical and mechanical properties of materials at the microstructural level becomes possible.

4. The results of the research can be applied in the manufacture of dry building mixtures based on gypsum binders and for the regulation of their properties.

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