Influence of modifying composition of gypsum binders on the structure of composite materials

V G Klimenko ¹

¹ Belgorod State Technological University named after V.G. Shukhov, Kostukov St., Belgorod, Russia, 308012, Russia

E-mail: Klimenko3497@yandex.ru, klimenko.vg@bstu.ru

Abstract. At present, the modern society utilizes composite materials in various branches of the national economy. The properties of such materials depend on their composition and structure, and may considerably differ from the properties of source materials. In turn, texture and structure of crystals, their packing order, size and level of sophistication affect the structure of materials. This is particularly demonstrated by hydration curing materials on the basis of gypsum and magnesia binding materials, as well as portland cement. Structuring control is one of the key problems of composite materials. Gypsum binding materials with various modification composition are suggested as a model system to study the influence of texture and structure of materials on their properties. One of them is the construction gypsum – an anhydrite binder and a multiphase gypsum binder (MGB). Scanning electron microscopy (SEM) was chosen as the main method of study. It is found that gypsum crystals that are formed during hydration and curing of gypsum binders with various modification composition have different texture and structure. It prevents from getting the optimal packing of a material. It is justified and confirmed that the MGB consisting of several modifications of calcium sulfate allow choosing the best material composition due to the combination of crystals having different size and form. Besides, MGB contains significant amounts of insoluble anhydrite that reduces the water-gypsum ratio of a binder and compacts its structure. Considerable attention is paid to microfillers, which significantly affect the texture and structure of materials based on gypsum binders. Iron ore concentrate of the Lebedinsky GOK generally consisting of magnetite, as well as impalpable flour cullet waste of sodium and potassium glass were used as microfillers in the given study. Ultra- and nanodispersed powders at their introduction to gypsum and anhydrite compositions change the size and morphology of crystal newgrowths and ensure the formation of ordered, denser and uniform fine-crystalline structures of composite materials, which leads to the reduction of structure imperfection, porosity and increase in contact areas of crystalline hydrates increasing physical and mechanical performance of gypsum materials. Efficient composite construction materials are obtained on the basis of MGB and microfillers.

1. Introduction

The initial form of gypsum crystals differs a lot. They can be tabular, columnar, prismatic, filamentary and needle or twinned thus forming the so-called ‘dovetails’. Quite often they result in bizarre foliated, columnar, scale aggregates – fibrous, dendritic (tree-like), skeletal, radially fibrous, rose-cut, anholites. There is a lot of factors influencing textural and structural characteristics of calcium sulfate. The most critical of them are the following: preparation conditions (temperature, pressure, pH medium, water-gypsum ratio of a binder (W/G), presence of electrolytes); nature of a curing activator
of insoluble anhydrite (CaSO₄ II); ultra- and nanodispersed fillers; superplasticizing admixtures, various additives. The size of pores and their diameter distribution is also an important parameter.

Chemical additives change not only the solubility of anhydrite and gypsum, but also exert significant effect on the nature of crystallization of newgrowths during hydration of anhydrite binders [1, 2]. Calcium sulfate dehydrate, crystallizing during anhydrite hydration, is similar to prismatic crystals extended along the growing axis. The presence of ZnSO₄-7H₂O additive in the anhydrite solution leads to rapid growth of CaSO₄·2H₂O crystals. The length of such crystals is more than that of gypsum obtained from pure anhydrite. The introduction of K₂SO₄ additive into the anhydrite binder leads to spontaneous crystallization of needle gypsum spheroliths. NaNO₃ and KCr(SO₄)₂·12H₂O additives do not strongly affect the form and size of gypsum crystals formed during hydration of anhydrite binders [3]. Gypsum set-retarding admixtures have strong impact on gypsum crystal habit [4]. In turn, the crystal habit influences the properties of gypsum materials. The crystal habit also depends on modification composition of gypsum binders. Thus, quite coarse prismatic gypsum crystals are formed from α-CaSO₄·0.5H₂O during hydration, and characteristic forms representing extended thin crystal beams coming from one center are formed from β-CaSO₄·0.5H₂O. According to Yu. B. Potapov [5], the addition of hard-burned free lime into phosphogypsum dihydrates leads to repacking of their particles and allows increasing the density and strength of composite materials on its basis without additional grinding. After mechanochemical activation, the phosphogypsum particles have lamellar irregular shape, unlike prismatic extended form of initial well-structured phosphogypsum crystals.

The important property of superplasticizing admixtures is their dispersing force on hydration product of binders [6]. According to theoretical views, surfactants increase the number of crystallization centers, limit the growth of crystals along an active boundary and hence increase their dispersion, which in turn leads to the increase in internal milling fineness. The superplasticizing admixture S-3 exerts dispersing and modifying effect on gypsum crystals that are formed during hydration of gypsum binders [7]. The introduction of at least S-3 0.5 wt.% leads to the reduction and change of crystals forms. Instead of a needle regular facet they become less accurately expressed and have denser packing. Surfactants change the gypsum form from fibrous to short-length prismatic habit. The Melflux 5581 F superplasticizer [8], which reduces the size of gypsum crystals to 5-7 microns, produces a similar effect. The prism edges become uneven, somewhat flattened.

Volzhensky A.V. [9] was studying the W/G influence on dispersion of gypsum binder hydration products, their quantity and strength during the compression of a gypsum stone. The differential thermal analysis (DTA) was used to define the size of gypsum crystals. It is shown that unlike the size of crystals, their form does not depend on W/G. The higher the W/G, the coarser the crystals. Some authors [10] note that the water-gypsum factor does not affect the form of gypsum crystals.

Thus, the ultimate strength of composite material structures is mainly defined by size and kinetics of supersaturation in the hardening system. More favorable conditions for crystal growth lead to higher decrease in the structure strength. To the contrary, the more favorable are the conditions for new crystal seeds, the lower are the tension and higher the strength. The modification composition of gypsum binders plays a key role in this process. The analysis of literature sources confirms the advisability of studying new methods that influence structural-morphological parameters of calcium sulfate in gypsum binders.

**Purpose of the study.** To define the influence of modification composition of gypsum binders and nature of microfillers on the structure of composite materials.

### 2. Materials and methods

The iron ore concentrate (IOC) of the Lebedinsky GOK was used as the raw material in the given study [11]. The G-4 gypsum of LLC Unistrom-Trading was used as the construction gypsum (CG). It had the following characteristics: \( R_{\text{com}} = 4-5 \text{ MPa}, R_\theta = 2.0-2.5 \text{ MPa}, \) setting time 8-13 min. The pH of water suspensions of construction gypsum (W/G=12.5) equals 7.4. Thermal insoluble anhydrite (CaSO₄ II) was obtained via compression of rock gypsum at 650 °C within 3 hours. The pH of its
water suspensions equals 11.2. K$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$ in the amount of 2 wt.\% were used as activators of anhydrite curing. Raw materials were grinded in a vibration mill. The strength properties of materials were determined on 2×2×2 cm samples on the 2nd and 7th day of curing. Before tests the samples were dried within 2 hours at 60 °C. The normal consistency was defined in accordance with GOST 23789-79. Scanning electron microscopy (SEM) was chosen as the main method of study. The study was carried out using high resolution scanning electron microscope TESCAN MIRA 3 LMU.

3. Main part
The main components of MGB include CaSO$_4$ II, soluble anhydrite (CaSO$_4$ III), construction gypsum (β-CaSO$_4$.0.5H$_2$O). At the initial stage, the structure of gypsum formed during hydration and curing of a monophase binder was studied. According to SEM results, the microstructure of hydration products β-CaSO$_4$.0.5H$_2$O represents thin fine prismatic crystals with extended form, which intersect with each other thus forming a friable felted texture with a large amount of pores (Fig. 1a). The crystals mainly have tabular and prismatic habit. The length of crystals reaches up to 8 µm, and the thickness makes 0.4-0.8 µm. The extended gypsum crystals can form beams growing from one center. The finely-crystalline gypsum structure is caused by high solubility of β-CaSO$_4$.0.5H$_2$O (6-8 g/l). In turn, high solubility of β-CaSO$_4$.0,5H$_2$O ensures the formation of a large amount of crystallization centers. This is also caused by high W/G (0.65). The amount of crystallization contacts in such structures is less than the coagulative ones.

Thus, considerable solubility of construction gypsum ensures the formation of a large amount of gypsum crystallization centers. At the same time, fine thin and extended crystals, sometimes crystal beams growing from one center, are formed.

The anhydrite binder is hydrated in a different way. CaSO$_4$ II, even in the presence of sulfate curing activators, is hydrated more slowly than β-CaSO$_4$.0.5H$_2$O. Its solubility is close to the solubility of gypsum, but it is less than the solubility of β-CaSO$_4$.0.5H$_2$O. Besides, first the CaSO$_4$ II crystals become covered by a network of cracks and split into small particles (Fig. 1c). Then, gypsum crystals, which form and size depend on pH medium and ion composition of the activator begin to grow from this mass. Thus, when (NH$_4$)$_2$SO$_4$ is used as an activator, coarse lamellar gypsum crystals, sometimes in the form of a ‘dovetail’ (Fig. 1d), are formed. Thin extended gypsum crystals are formed in acidic medium.

The structure of an anhydrite stone is represented by gypsum crystals, six-sided lamellar anhydrite crystals and finely-crystalline mass of non-hydrated calcium sulfate.
The structure of MGB-based stone (Fig. 2a) is denser than that on the basis of the construction gypsum. It consists of coarse lamellar and thin fine extended gypsum crystals and fine crystals formed during anhydrite decay. Non-hydrated CaSO$_4$ II compacts the structure of a gypsum stone. The amount of hydrate water of optimum MGB structures lies within the range of 16-18 wt.%, which is less than that of gypsum (20.9 wt.%). Thus, about 20-25 wt.% of CaSO$_4$ II is not hydrated and acts as a filler. Based on the entire MGB mass, the amount of anhydrite filler makes 14-18 wt.%. Thus, this does not deteriorate the material properties but on the contrary improves them.

Microstructures of a basic MGB sample (Fig. 2a) and a sample with cullet additive (Fig. 2b) are fundamentally different. The structure of a basic composition contains a significant amount of fine non-hydrated CaSO$_4$ II crystals, which is confirmed by the amount of hydrate water (14.87%). On the contrary, the structure of the composition with the addition of a cullet represents twin perfect prismatic gypsum crystals, separate CaSO$_4$ II crystals and cullet grains. The amount of hydrate water in such samples is higher and makes 16.98 %. The initial rock gypsum contains 19.77 % of hydrate water. MGB modification with fine ground cullet waste reduces the amount of macropores in the material, which is in general agreement with literature data.

The consolidation of gypsum matrix structure was also carried out by introducing the following microfillers: iron ore concentrate of the Lebedinsky GOK (IOC) ($S_{sp} = 404-412$ m$^2$/kg) [11] and fine ground cullet wastes of sodium and potassium glass (CW) ($S_{sp} = 1181$ m$^2$/kg) [12]. Compositions on the basis of G-4 + 50% IOC (SGM-50) and anhydrite IOC (AM-50) binder +50% were studied.
Compositions on the basis of $\beta$-CaSO$_4$$\cdot$0.5H$_2$O are characterized by fast hydration and curing of a binder. At the same time, fine extended prismatic six-sided gypsum crystals extended along the growing axis are formed. IOC and fine ground CW particles (Fig. 3a) are captured in voids between crystals.

Such structurization mechanism is confirmed by the run of the strength change curve of a material on the basis of construction gypsum and IOC [11] and construction gypsum and finely-dispersed CW [12]. It is possible to introduce up to 30-40 % of fine ground additives into voids between gypsum crystals without breaking the crystallizational contacts. Further increase in the amount of an additive leads to the break of crystallizational contacts and decrease of material strength. Fine gypsum crystals cover filler particles closing its surface. This is confirmed by a gray color of a material on the basis of construction gypsum and IOC. Pure IOC has black color.
Compositions on the basis of anhydrite binders, activated by \((\text{NH}_3)_2\text{SO}_4\) and having alkaline reaction of the medium, lead to the formation of coarse crystals with layered and package structure similar to IOC in size. IOC particles settle down between and on gypsum crystals and worsen the formation of crystallization contacts (Fig. 3b). For this reason, the strength of composite materials on the basis of anhydrite binders decreases monotonously with the increase in IOC additive [11], and the color of samples turns intensively black. The microstructure of SGM-50 composition (Fig. 3a) represented by thin, fine prismatic extended crystals differs from the microstructure of AM-50 composition (Fig. 3b). There is a structural orientation of gypsum matrix on IOC surface leading to structure-breaking effect and increasing the material density and strength. The gypsum matrix changes its state from volumetric to filmy. Fine ground CW do not structure the anhydrite matrix acting as a filler of a composite material. The identity factor \((\text{Ki})\) that depends on the size of microblocks of gypsum structure is higher for AM material (0.37) than for SGM material (0.27). SGM has more fine-crystalline structure than AM. The area and intensity of \(\text{Fe}_2\text{O}_3\) reflexes on X-ray patterns at interplane distances of 0.2974 and 0.2536 nanometers are slightly higher for SGM material than for AM material. This confirms the change of parameters of a magnetite crystal lattice in gypsum magnetite compositions.

4. Conclusions
The microstructure of construction gypsum representing thin, fine prismatic and extended crystals differs from the microstructure of MGB and anhydrite binders. The structure of the latter ones contains significant amounts of uncrystallized mass filling the space between the growing gypsum crystals. The differences in binder microstructure are defined by various mechanisms of binder hydration. All these impacts the stress-strain properties of composite materials. The use of MGB instead of monophase binders and microfillers makes it possible to optimize the structure of composite materials.

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