Journal of Engineering Science *Vol. XXV, no. 3 (2018), pp. 74 - 84*
Fascicle *Architecture, Civil and Environmental Engineering* *ISSN 2587-3474*
Topic *Energy Efficiency and New Building Materials* *eISSN 2587-3482*

DOI: 10.5281/zenodo.2557324
CZU 691.5:666.9

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IMPACT OF GRANULOMETRIC COMPOSITION ON MINERAL BINDER HYDRATION PROCESSES

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Received: September, 28, 2018
Accepted: November, 11, 2018

Abstract. This article presents the research results of the impact of granulometric composition on gypsum binder hydration processes. When the amount of finely ground gypsum in the gypsum binder is increased by up to 15%, the maximum hydration temperature rises by 10°C and the hydration process intensification occurs with the reduction in time required to reach the maximum hydration temperature.

Keywords: *granulometric composition, hydration, gypsum binder, fractions.*

1. Introduction

Granulometric composition of the raw binder directly affects hydration processes and binder structure formation, size and porosity changes as well as crystal morphology [1 - 3].

Direct impact of particle size distribution of gypsum binder on the phase composition, rheological, physical and mechanical properties and microstructure of calcium sulfate dihydrate, and thus, it makes sense to study the impact of particle size distribution of gypsum binder on the hydration and structure formation processes, and therefore, on physical and mechanical properties of gypsum [4 - 6].

2. Research objective

To explore the impact of particle size distribution of gypsum binder on both hydration and structure formation processes and physical and mechanical properties of gypsum.

3. Research techniques and materials

In this research, we have investigated gypsum binder composites. The basic components of the composite are *G5-H-II and G5-H-III Grade* gypsum binders *(*DSTU Б В.2.7-82:2010) produced in Ivano-Frankivsk (Ukraine). Compressive strength of the specimens is 5 MPa. The results of the X-ray diffraction analysis show that G-5 *H-II* Grade gypsum binder contains *G5-H-III* Grade gypsum binder (Figure 1-2). Further information on the refinement results is given in Figure 1 and Table 1 of the supplementary materials.

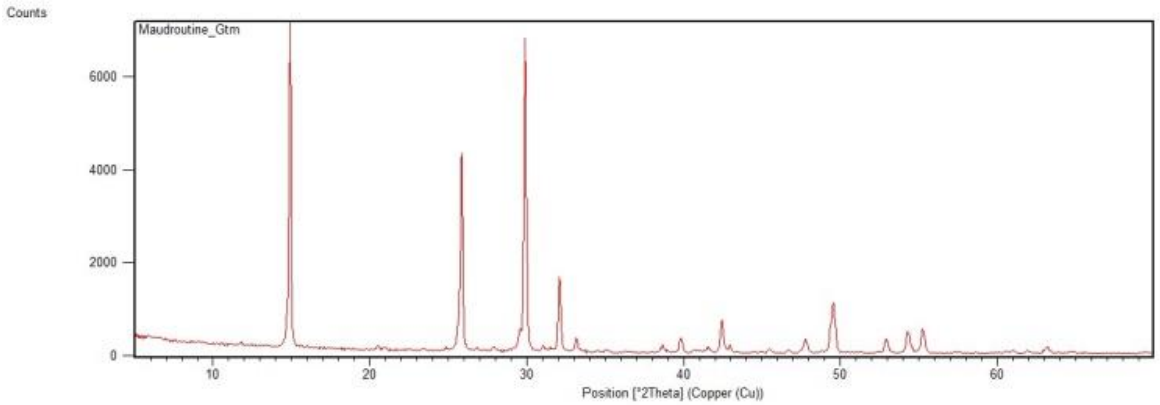
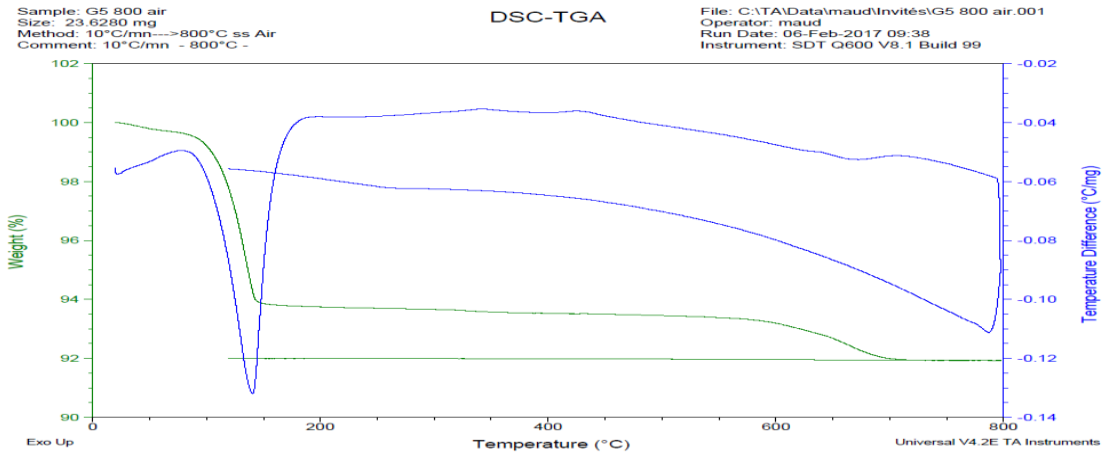
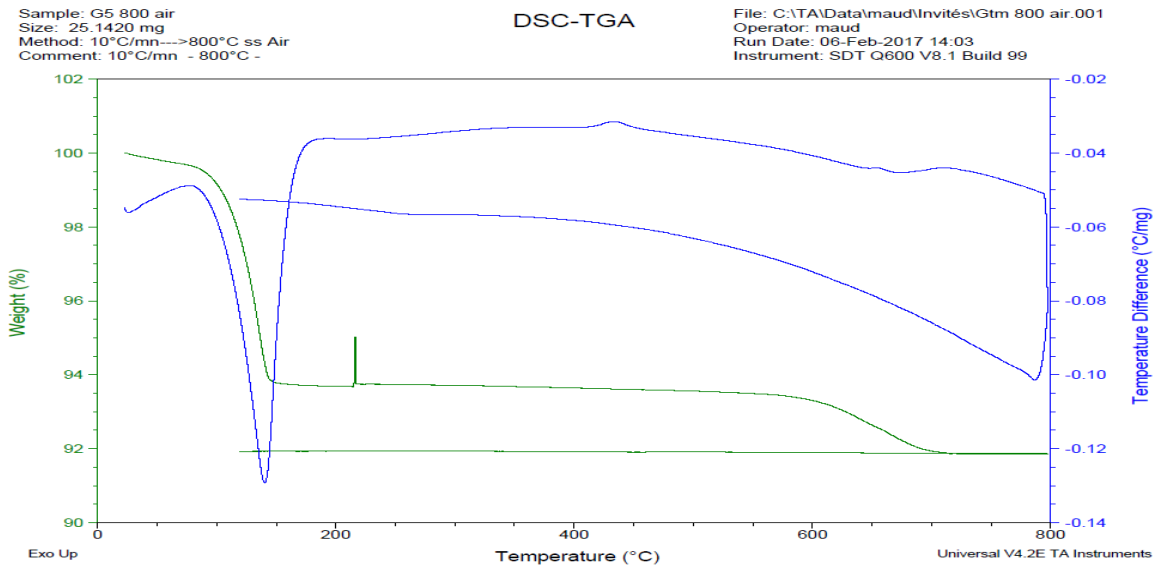


Figure 1. Rietveld refinement of X-ray diffraction of gypsum binder.

Differential thermal analysis curves for both unground and finely ground building gypsum are given in Figure 2 a and b.



a)



b)

Figure 2. Differential thermal analysis curves for building gypsum:
a – unground; b – finely ground.

Different compositions of specimens were prepared to explore the impact of additives.

Homogeneous paste of gypsum was prepared manually by admixing hemihydrate G4 Grade gypsum and water. The amount of water required to produce paste of standard consistency was 50 wt% and was determined in the previous tests for this kind of gypsum binder. In the specimens containing additives, Taurit and silica were added to G4 Grade hemihydrate gypsum binder and thoroughly mixed followed by water addition to obtain the paste of standard consistency. Mixing gypsum binder compositions with various additives is given in Table 1.

Immediately after mixing with water, the specimens were casted into a 40×40×160 mm mold. In 2 hours, the specimens were unmolded and the tests were conducted to evaluate compressive and bending strengths. Six specimens of different compositions were used for each test; the respective average values are given in the paper.

Water resistance coefficient was defined as water-saturated state to dry state compressive strength ratio.

The research of granulometric composition was conducted using Cilas 990 Laser Particle Size Analyzer

Conductivity measurements

The phase composition of the resulting products was estimated using X-ray diffraction: the values were estimated at room temperature with Cu Kα radiation on a PANalytical X'pert Pro diffractometer equipped with an X'Celerator detector in the 2θ range from 5° to 70° (step 0.033°, time/step 50s). To prepare the specimens the powder was sieved with a 63 μm mesh. Phase identification and Rietveld Refinement were performed with an X'Pert HighScore Plus.

Thermal analyses were performed using Q600 SDT TA Instruments. The temperature was modified from RT up to 800 C at a heating/cooling rate of 10ºC/min under dry air flow (100 mL·min^{-1}) with α-Al_2O_3 used as a reference.

The electrical conductivity of the β-calcium sulfate hemihydrate suspension was measured at room temperature (20 ± 1°C). The β-hemihydrate suspension was prepared by adding 50 ml of distilled water to 2.5 gm of G5-H-II or G5-H-III Grades or their mixture with further continuous agitation. The readings were taken at the same time intervals (277C, 303C, 284C).

Changes in the microstructure of the composites were observed by SEM. SEM images were carried out on a JEOL JSM 6510 LV W-filament microscope operating at an accelerating voltage of 15 kV.

4. Research results

Data representing the granulometric composition of G5 Grade building gypsum showed the following: 90% of particles sized less than 80 μm; ca. 50% of particles sized less than 20 μm; and ca. 10% of particles sized less than 3 μm (Figure 3). The maximum value corresponds to 55 μm on the differential particle size distribution curve, the percentage of particles of smaller diameter is 65%. The percentage of particles sized up to 10 μm is 30 wt%. Particles sized up to 3 μm (10%) are the main particles that influence the specific surface area value. High surface energy of such particles is due to their high dispersibility. It is small fractions which are the first ones to undergo the hydration process.

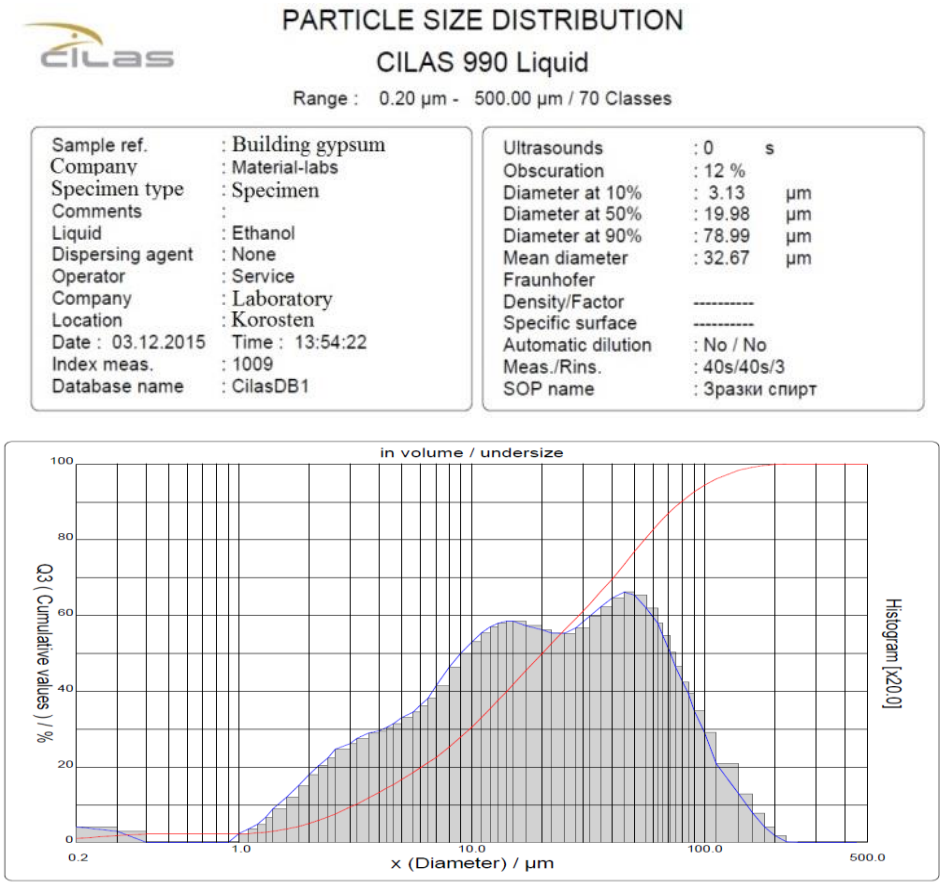


Figure 3. Differential particle sized distribution curve for building gypsum.

The research of the granulometric composition of finely ground gypsum showed the following results (Figure 4).

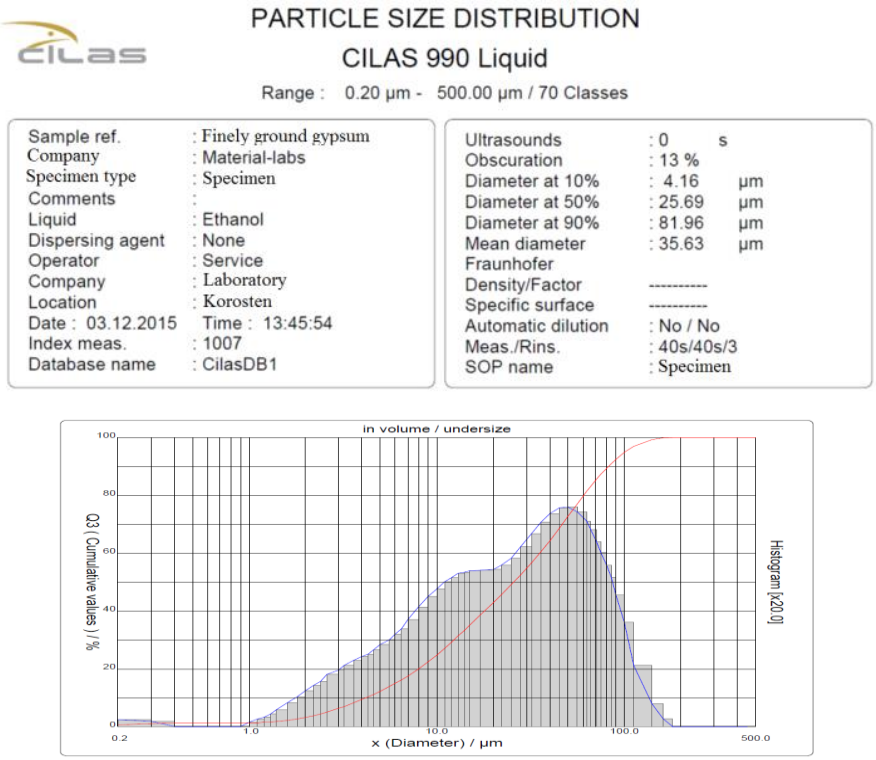


Figure 4. Differential particle sized distribution curve for finely ground gypsum.

90% of particles sized less than 82 μm; ca. 50% of particles sized less than 26 μm; and ca. 10% of particles sized less than 5 μm. The maximum value corresponds to 45 μm on the differential particle size distribution curve, the percentage of particles of smaller diameter is 76%. The percentage of particles sized up to 10 μm is 25%.

To assess the interphase region of gypsum [7], the surface energy coefficient was considered as the particles surface area to particles volume ratio (Table 1).

Table 1. Surface energy coefficient of building gypsum

Particle size	D_1, мкм	D_{10}, мкм	D_{55}, мкм	D_{45}, мкм	D_{90}, мкм
Particle diameter, μm	1	10	55	45	90
Surface energy, KPa, μm^{-1}	6	0,60	0,11	0,13	0,07

Reduced particle size leads to an increase in specific surface area. Surface energy coefficient [8] allows us to estimate the surface activity of each fraction. It is calculated by multiplying the surface activity coefficient by the content of each fraction.

Gypsum interphase region values are given in Table 2.

Table 2. Values of interphase region of building gypsum and finely ground gypsum

Material		<1 мкм	<3 мкм	<10 мкм	10-20 мкм	40-50 мкм	50-60 мкм
Building gypsum	Particle diameter, μm	1	3	10	25	45	55
	Surface activity	6	2,00	0,60	0,24	0,13	0,11
	Fraction content	3	10	30	20	8,00	2
	Differential activity coefficient	18,00	20,00	18,00	4,80	1,07	0,22
Finely ground gypsum	Particle diameter, μm	1	3	10	25	45	55
	Surface activity	6	2,00	0,60	0,24	0,13	0,11
	Fraction content	3	20	26	17	9,00	8
	Differential activity coefficient	18,00	40,00	15,60	4,08	1,20	0,87

Particles sized up to 3 μm contribute significantly to the specific surface area.

It is commonly known that when studying refraction of light of supersaturated solutions [8] with a certain degree of supersaturation, there is a drastic change in optical properties of the solution. This is due to the formation of solid phase nuclei in the solution arising spontaneously at a certain temperature and concentration.

Optical density was measured in Expert -003 photometer intended for measuring optical density and spectral directional transmission coefficient of solutions and optically transparent objects as well as determining the concentration of a substance in a solution.

The principle of spectrophotometers is based on comparing luminous fluxes: the total flux (that passed the blank test) $\Phi_{0\lambda}$ and the flux Φ_{λ} that passed through the investigated media.

Spectral directional transmission coefficient T is calculated using the following formula:

$$T = \frac{\Phi_{\lambda}}{\Phi_{o\lambda}} \cdot 100\%,$$

Optical density (D) is calculated using the following formula:

$$D = -\lg\frac{\Phi_{\lambda}}{\Phi_{o\lambda}} = -\lg\frac{T}{100} = 2 - \lg T$$

Measured changes in the optical density of gypsum mortars are given in Figure 5.

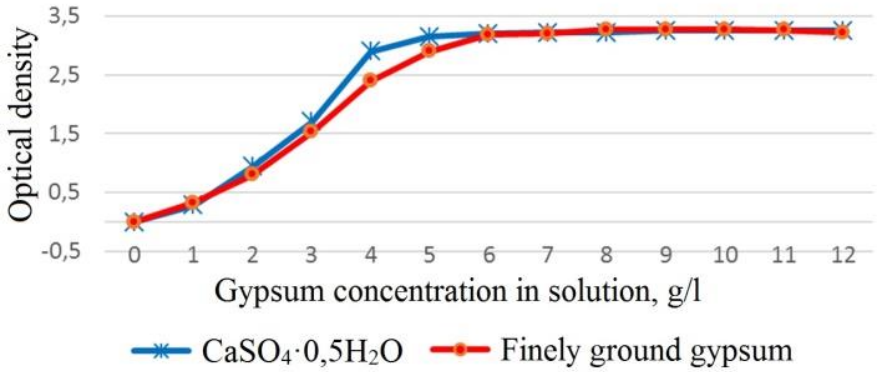


Figure 5. Changes in the optical density of gypsum mortars based on building gypsum and finely ground gypsum.

According to the given curves, the optical density of the unground building gypsum solution reaches the constant value at a lower concentration of the saturated solution. The graphical representation of the relationship between transmission coefficient and concentration does not represent the true picture, since the coefficient values are small and cannot be seen on this scale.

Data from Table 3 give a clearer picture of the distinctions.

Since dispersibility is one of the main factors affecting the hydration rate, high content of fine fractions results in high-speed dissolution and hydration of these fractions.

Table 3. Impact of gypsum concentration on the luminous transmission of gypsum mortar

Concentration	Transmission coefficient of gypsum mortars	
%	$CaSO_4 \cdot 0,5H_2O$	Finely ground gypsum
0	99,69	99,69
1	52,54	48
2	11,65	17,8
3	3,77	2,96
4	3,06	1,48

Table 3 Continuation

5	2,63	1,01
6	0,79	0,7
7	0,09	0,71
8	0,06	0,7
9	0,06	0,7
10	0,06	0,70
11	0,05	0,70
12	0,05	0,70

In the area of fine particles, a significant surface energy reserve can be observed, which provides active interfacial adsorption of gauging water molecules with spontaneous redistribution of the system components between the surface layer and the volume phase [7]. These particular factions dissolve faster than others. This is evidenced by an increased slope of the hydration temperature curve.

In the paper [5], hydration processes were studied using acoustic resonance technique for dispersed systems along with DTA, X-ray diffraction analysis and infrared spectromicroscopy (IRS). According to received data, immediately after mixing with water, particles larger than 8 μm attach directly to water and the dihydrate is formed, which was proved by the X-ray diffraction data.

According to V. Korovyakov [9], there are two stages of gypsum stone structure formation. The first stage is a layer-by-layer stage: crystallizing dihydrate atoms attach to stage crystallization surface atoms, i.e., crystal growth occurs due to successively filled layers. The second stage is a normal stage: it occurs only if the surface is atomically rough. With this growth of gypsum crystals, crystallizing substance atoms attach to crystal atoms anywhere. This leads to normal displacement of the surface towards the atomically rough surface in the course of growth [9].

The authors of the papers[10-16] believe that if the liquid phase is highly supersaturated and the gaps are small, crystals grow too fast, so that the system fails to maintain supersaturation in the contact areas at the same level as outside the contacts, and besides intergrowth factors, a diffusing factor arises. During substance crystallization, a concentration gradient in the contact area is being built up reaching the maximum value at the entrance to the gap where newgrowths are formed leading to further formation of crystallization pathways. The ratio between the size of crystals and the area of contacts between them affects the strength of crystallization structures [8, 10]. In favorable conditions for the formation of new crystal nuclei and contacts between them (high supersaturation, high overall dissolution rate), stresses affecting (reducing) the structure strength decrease. Achieving the highest structure strength requires optimum crystallization conditions enabling the formation of crystals of sufficient size with minimum stresses occurring during crystal structure formation and growth. Therefore, both the optimum degree of supersaturation and crystallization rate should be achieved in the hardening

system. The optimum degree of supersaturation can be achieved by choosing the right ratio between particles of large and small diameter. Overall dissolution rate is controlled by the amount of fine fractions. Thus, ensuring continuous structure formation process over time creates the conditions in which stresses in a formed artificial stone during crystallization structure formation may lead to a lower strength of the material. Under certain structure formation conditions (supersaturation degree, material hardness, time of interaction), crystallization contacts are formed; these contacts increase the area, which in turn contributes to a higher material strength [8, 10].

Thus, it can be assumed that the prevalence of hydration or topochemical mechanism is related to binder dispersibility. Finer fractions get hydrated faster than others. Under uniform water distribution along the surface of the solid phase, water layer thickness decreases significantly with increasing specific surface area.

To determine the impact of finely ground gypsum on hydration processes certain building gypsum compositions (containing 5, 10, 15% of finely ground gypsum) were analyzed. Studies on the hydration process temperature variations showed that the addition of finely ground gypsum into gypsum binder leads to the hydration process intensification. When the amount of finely ground gypsum is increased by up to 15%, the maximum hydration temperature will rise by 10°C with the reduction in time required to reach the maximum temperature. However, it should be noted that the maximum hydration temperature of finely ground gypsum is higher than that of building gypsum but lower than that of the mixture of both gypsum types. Obviously, intensity increasing under two mechanisms should be considered.

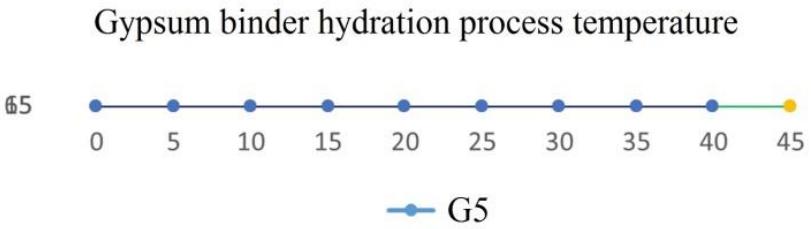


Figure6 Impact of the content of fractions of finely ground gypsum on the hydration temperature.

Impact of the content of fractions of finely ground gypsum on the hydration temperature is given in Figure 6. Variation of electrical conductivity during hydration of building gypsum of different granulometric composition is given in Figure 7.

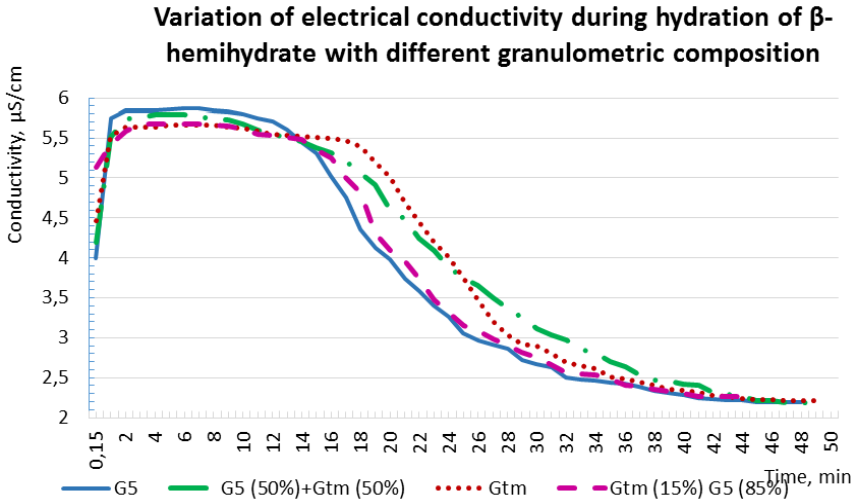


Figure 7. Variation of electrical conductivity during hydration of β-hemihydrate with different fraction sizes.

The results of measurements of electrical conductivity during hydration of calcium sulfate hemihydrate of different granulometric composition (Figure 7) showed that there are three main periods. Once the maximum value of electrical conductivity is reached, the first period comes in a very short time interval and is characterized by almost steady and constant maximum value. It corresponds to the maximum saturated state of the solution saturated with Ca^{2+} and SO_4^{2-}- ions. During the second period, calcium sulfate dihydrate is formed; this period is characterized by lower values of electrical conductivity.

And the third period is characterized by the minimum value of electrical conductivity, which indicates the end of the hydration process.

The analysis of the obtained results shows that G5 Grade requires more time to reach the maximum temperature; this is obviously related to the size of the particles and a longer time required for the solution saturation. The first induction period for finely ground gypsum is almost 1,5 times longer than for building gypsum; and on the contrary, the second period is characterized by a faster decrease in electrical conductivity, which indicates a higher rate of crystal formation if compared to building gypsum.

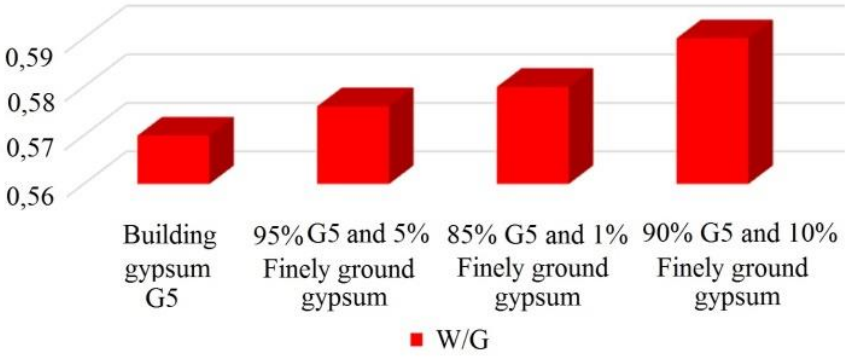


Figure 8. Diagram of impact of granulometric composition on water-to-gypsum ratio.

For the mixture of 50% of finely ground gypsum and 50% of G5 Grade gypsum, the second period involving crystal formation is longer.

Increased dispersibility of the system leads to an increase in the amount of water required for making a paste of normal density from 57% to 58.7% (Figure 8).

At the same time, increasing the amount of fine fractions in the binder adversely affects the strength properties, which is proved by the data from Diagrams 8-10.

Diagram of impact of fractional composition on the setting time of gypsum is shown in Figure 9.

Figure 9 shows that the finely ground gypsum without additives and coarse grind building gypsum are completely hydrated within 20 minutes; moreover, the degree of hydration of the modified gypsum of 50% and 100% is achieved in 50 and 70 min, respectively.

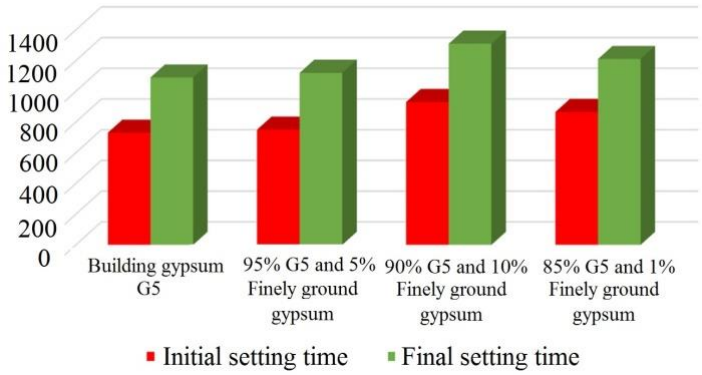


Figure 9 Diagram of impact of fractional composition on the setting time of gypsum.

Diagram of impact of granulometric composition on the strength of gypsum binder is given in Figure 10.

Figure 10 shows that the increased amount of finely ground gypsum fractions results in monotonically decreasing strength values. Ultimate compressive strength is reduced by

20% - from 4,5 MPa for the unground building gypsum to 3,8 MPa for the gypsum 10% of which was finely ground. Ultimate bending strength is reduced by 37,5% from 3,2 MPa to 2 MPa.

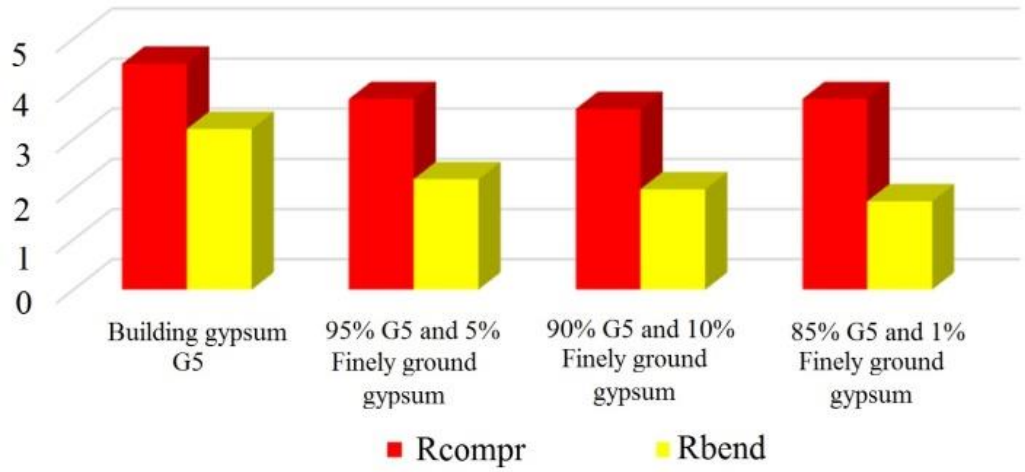


Figure 10. Diagram of impact of content of finely ground gypsum fractions on the strength of gypsum binder.

Conclusions

Conducted theoretical and practical research studies show the relationship between the particle-size distribution of gypsum binder grains, their phase composition, rheological, physical and mechanical properties and microstructure of calcium sulfate dihydrate.

Changes in the fractional composition allow you to influence the hydration processes and structure formation of gypsum binder, which makes it possible to change the properties of hydration products.

The findings of the conducted research prove that Grade G5 building gypsum requires a longer time to reach the maximum hydration temperature.

To achieve hydration process intensification we studied building gypsum compositions containing 5, 10 and 15% of finely ground gypsum binder.

Using 5, 10 and 15% of finely ground building gypsum results in maximum hydration temperature increase by 10°C and a shorter time to reach the maximum temperature. Moreover, the maximum hydration temperature of finely ground gypsum is higher than that of building gypsum but lower than that of the mixture of both gypsum types. It is related to an increased intensity under two mechanisms.

Moreover, increased dispersibility of the system leads to an increase in the normal density by 1,7%.

10% is the optimum recommended content of finely ground gypsum in binder.

An increased amount of finely ground gypsum by more than 10% in the binder content results in a decrease in both compressive and bending strengths by 20% and 37,5%, respectively.

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