Composite Gypsum Binders with Silica-containing Additives

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Composite Gypsum Binders with Silica-containing Additives

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Abstract. New types of fine mineral additives are proposed for designing water-resistant Composite Gypsum Binders (CGB); these additives significantly differ from traditional quartz feed: wastes from wet magnetic separation of Banded Iron Formation (BIF WMS waste), nanodispersed silica powder (NSP), chalk. Possibility of their combined use has been studied as well.

1. Introduction

Optimization of structure formation is the basis for increased efficiency of composite gypsum binders. Analysis of scientific and technical literature has shown that using microdispersed silica additives (microsilica, etc.) with the composite gypsum binders allows obtaining efficient composites with a stable structure, which harden without dangerous destruction. There are tens of billion tons of waste from BIF WMS in Russia; they are a unique silica-containing feed allowing controlling the structure formation in gypsum-based composites, but currently they find little use.

Of special interest is nanodispersed silica powder (NSP), which has never been used in CGB previously. Its introduction as an active mineral additive allows not only controlling the structure formation in gypsum-based composites, but significant expanding the feed base as well.

Thus, a timely task is production of efficient CGBs by using a proper ratio of components: gypsum binders, portland cement, multi-component mineral additives to lower $Ca(OH)_2$ concentration in the liquid phase of the hardening system by formation of low-basic calcium hydrosilicates and other poorly-soluble compounds that compact the structure and prevent ingress of water into the hardened composite.

2. Materials and methods

The following materials were used to obtain efficient CGBs: gypsum binders (GB) – β-modifications of G-5BII (G-5) and α-modifications of GVVS-16(G-16), portland cement CEM I 42.5H (PC) и multi-component fine mineral additives from new types of feed resources:

– WMS waste, with different polymineral composition, containing over 70% of quartz in different modifications.

– nanodispersed silica powder (NSP), containing up to 99.72% of SiO_2, produced by separation from natural hydrothermal vents in volcanic areas following a two-stage process scheme: membrane concentration, cryochemical vacuum freeze drying of silica colloid solutions with the average grain size ranging from 5 to 100 nm, specific area of 100000-400000 m^2/kg, an average zeta potential of nanoparticle surface of -25.0-56.0 mV;

– technical dispersed chalk, grade MTD-2 with oversize product for no.014 sieve not exceeding 0.8%, containing at least 96% of $CaCO_3$;

– superplasticizer (SP) SikaPlast 2135, on the basis of lignosulfates and modified polycarboxylates.

To conduct a thorough analysis of properties of the feed components and the CGB structure, both standard methods and modern physical and chemical analytic methods were employed: laser granulometry, differential microcalorimetry, optical and raster electron microscopy, X-ray phase analysis, etc.

3. Designing a rational composition of a CGB modified with silica-containing additives

Activity of CGBs is influenced by fineness and particle size distribution of their components, which alongside with their chemical composition determines a degree to which they participate in the gypsum cement stone structure formation, starting from the earliest stages of hydrate and structural formation. Of special interest are studies aimed at determination of particle size distribution of CGB components as factors, influencing the strength of the hardened composite.

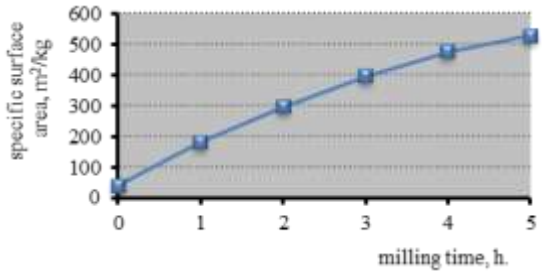
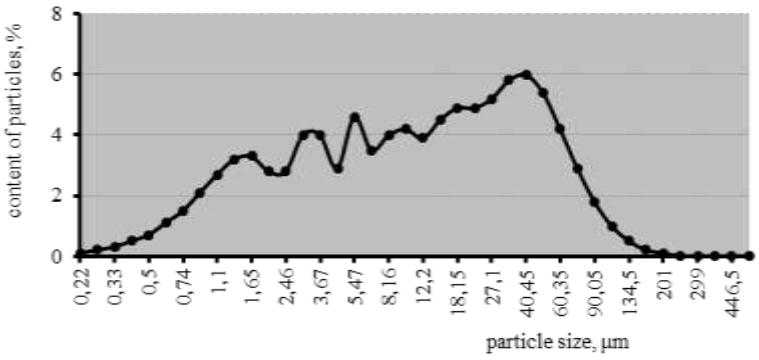


Figure 1: Milling kinetics of the WMS waste

The studies determined possibility and efficiency for application of nano- and micro-dispersed mineral additives (WMS waste, NSP and chalk) to ensure the high performance characteristics of the CGB.

To obtain CGB of a required quality, the specific surface of the WMS waste shall not exceed 600 m^2/kg; thus, in this study its milling was performed in a laboratory pebble mill for a period of 270 minutes until attaining S_{sp}=500 m^2/kg (Figure 1).

The analysis of the particle size distribution of the mineral additives used has shown: fine milled WMS waste with S_{sp}=500 m^2/kg have a heterogeneous particle size distribution with a polymodal distribution of particles sized from 134.5 to 0.22 micron, with three evident peaks in the average and small particle regions (8.16…0.74 micron) with quite high weight ratio (up to 40%) and a well-developed surface roughness, thus facilitating compaction of the hardening matrix microstructure (Figure 2).



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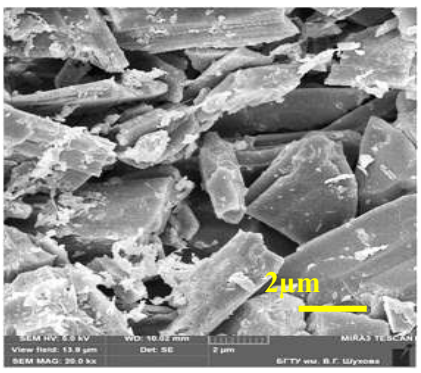


b

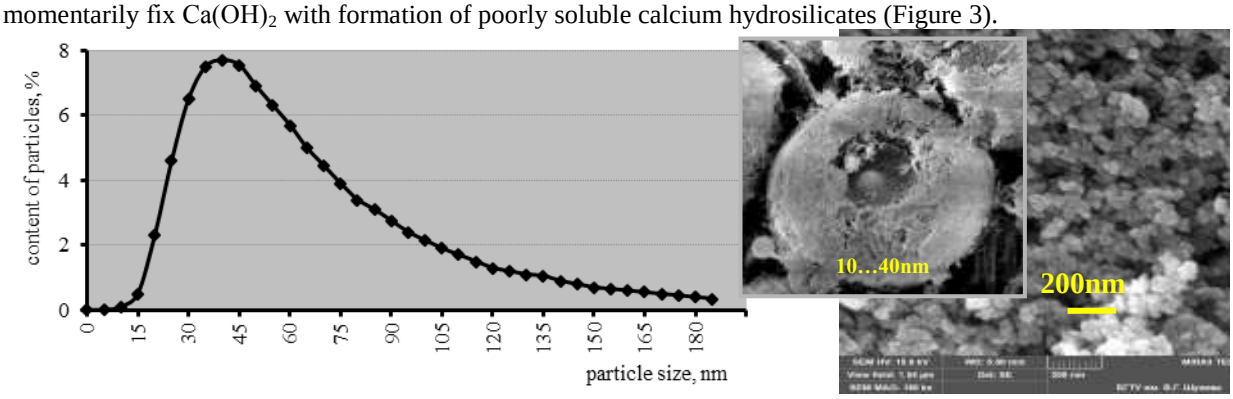
Figure 2. WMS waste particle size distribution (a) and surface morphology (b)

Crystalline structure defects and the total specific surface area value confirm their high fineness and reactivity (Table 1).

Table 1. Indicators of the WMS waste specific surface area

Characteristic	WMS waste
Specific surface area as per PSKh-2, m^2/kg	500
Specific surface area measured with Sorbi-M instrument (4-point BET method), m^2/kg	2920

Nanodispersed Silica Powder (NSP) has a polymodal distribution for particles ranging from 5 to 100 nm. The spheric form of its particles with a porous-net structure and hollows in the central part, as well as flakes with a thickness of 0.1-0.2 micron, determine their high pozzolanic activity and a unique property to momentarily fix $Ca(OH)_2$ with formation of poorly soluble calcium hydrosilicates (Figure 3).



a b

Figure 3: NSP particle size distribution (a) and surface morphology (b)

Finely dispersed chalk has an intermittent grading for particles sized 14.85…0.74 micron and 165…27.1 micron with evident peaks on the graph, thus facilitating compaction of a hardening CGB matrix (Figure 4). The porous microstructure and the spatial structure of partially damaged ring and tube chalk formations formed from regular segments sized 1…2 micron with numerous active centers in the fissure zone increase its reactivity, thus facilitating increased strength of the CGB; this is supported by studies of physical and mechanical properties.

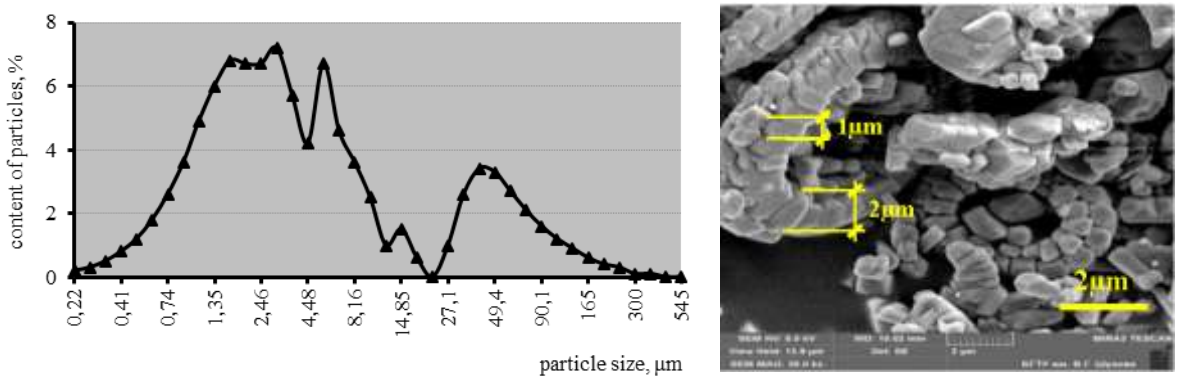


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Figure 4: Chalk particle size distribution (a) and surface morphology (b)

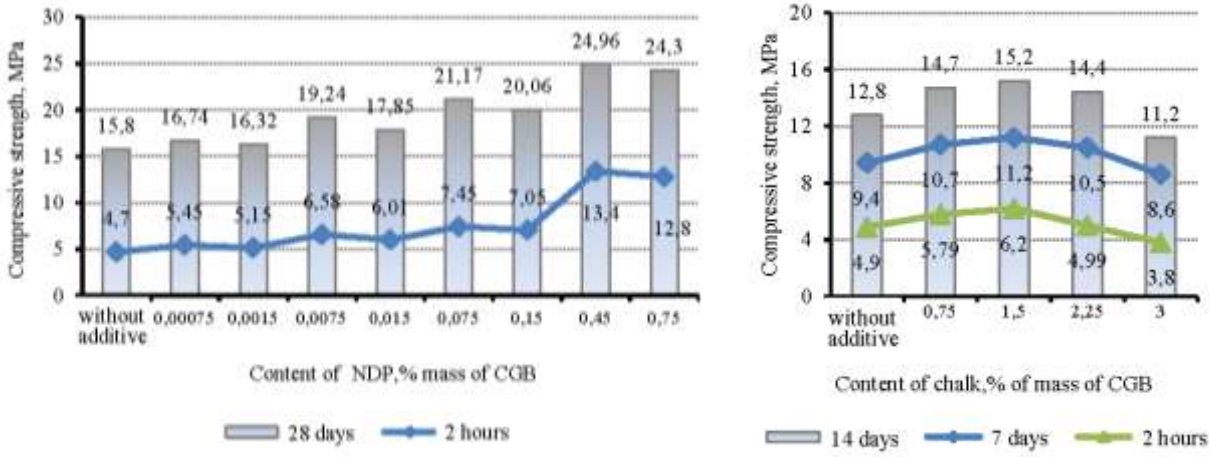
By way of trial, the amount of NSP in CGB was selected in such way that five days later the CaO concentration in water suspensions of calcined gypsum, potrland cement and active mineral additives (WMS waste + NDP) does not exceed 1.1 g/l, and seven days later it is less than 0.85 g/l, as per TU

21-31-62-89 «Gypsum Cement Pozzolanic Binder». It was found out that additional introduction of NSP in the amount of 0.45%wt into CGB with WMS waste (for G-5, with a ratio of PC to WMS waste = 1:1), facilitates lowering CaO concentration in solutions to required limits (after 5 days it was 1.088 g/l; after 7 days it was 0.847 g/l) and increases stability of a hardened binder, which is supported by studies of their physical and mechanical properties (Table 2). There is an acceleration of an initial CGB hardening stage and an increase in its activity (by a factor of 2…3) and strength of hardened samples tested 28 days after (by up to 40%, see Figure 5-a).

Table 2. Changes in CaO concentration in CGB water suspension

No. item	Materials, g				CaO concentration in the solution, g/l, after:	
	Gypsum	Portland Cement	WMS waste	NSP	5 days	7 days
1	4	2.5	1.25	-	1.149	1.031
2	4	2.5	2.5	-	1.113	0.865
3	4	2.5	2.5	0.075	1.088	0.847
4	4	2.5	2.5	0.123	1.083	0.834

Addition of chalk (1.5%wt), serving as both crystallization centers and microaggregate, to the CGB allows increasing binder's strength (by 15…20%) during the early stages of hardening (Figure 5-b).



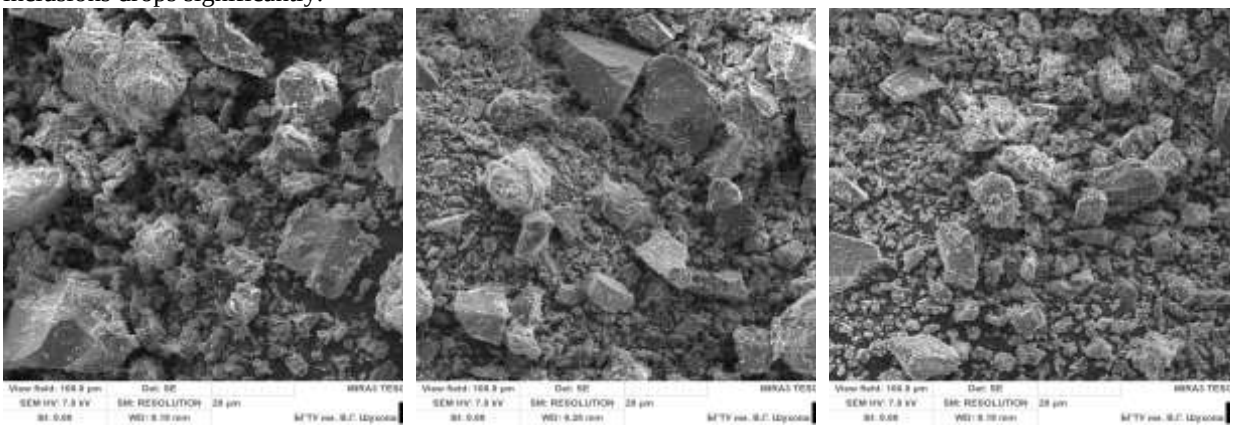
a b

Figure 5: Changes in CGB strength depending on NSP (a) and chalk (b) content

With the benefits of these results, the preparation of the CGB was performed in several stages.

First, a binder mineral modifier (BMM) was produced. For that end, the laboratory ball grinder was used to mill the WMS waste until $S_{уд}$=500 m^2/kg, and then it was ground (for 5, 10 and 15 minutes) together with the portland cement (in a 1:1 ratio) and chalk (1.5%wt of CGB) to determine the optimal preparation time. The studies have shown that when finish grinding the BMM components for 5 minutes, there is an increased content of large particles of the binary mineral additive with a well-developed rough surface, which is linked to destruction of rock-forming minerals in the WMS waste and chalk (Figure 6-a). Increasing the BMM finish grinding time to 10 minutes promotes a reduction in particle size and grain averaging due to gradual milling and breakage of chalk, portland cement and large polymineral particles of the WMS waste, serving as additional grinding bodies. A partial aggregation of the particles is observed (Figure 6-b). When finish grinding for 15 minutes, there is an increase in the BMM specific surface due to a finer grinding of chalk, portland cement and

WMS waste grains (the latter are largely represented by quartz of diverse genesis) and the number of large inclusions drops significantly.



a b c

Figure 6: Surface morphology, size and characteristics of BMM particles obtained by finish grinding for: a – 5 minutes; b– 10 minutes; c –15 minutes

The milled particles of the BMM components cover the larger aggregates or gather in separate agglomerations (chains and spheres); secondary aggregation of the particles is more pronounced (Figure 6-c).

The rational grinding time of the BMM components shall match the time when the particle aggregation starts during the dispersion, leading to a reduction in strength characteristics. Thus, the BMM finish grinding for 10 and 15 minutes is inefficient due to increased content of small particles and their secondary aggregation, promoting increased water-need of a cement mixture and increased energy costs. The joint grinding of the BMM for 5 minutes is the most practical, which is supported by the strength data (Table 3). The component ratio obtained was used as a foundation for calculation of the CGB composition (%wt): gypsum binder – 68.05, portland cement – 15, fine milled WMS waste – 15, Nanodispersed silica powder – 0.45, chalk – 1.5.

Table 3. Properties indicators of the Binder mineral modifier (BMM)

Grinding time, min	Specific surface, m^2/kg	Specific surface as shown by Sorby-M instrument (4-point BET method), m^2/g	Average Particle size, micron	Kp	Compressive strength, MPa, after	
					7 days	28 days
	357	2.3±0.2	5.4	0.29	22.3	36.2
10	392	2.6±0.2	5.1	0.30	21.5	34.3
15	439	2.9±0.2	4.8	0.31	19.8	31.2

At the next stage of the studies, the authors mixed the BMM together with a gypsum binder including β-hemihydrate of calcium sulfate (G-5) and α-hemihydrate of calcium sulfate (G-16) for 3 minutes, having the aim to increase the CGB efficiency. Grain size distribution, a practical ratio and its influence onto the physical and mechanical properties of the hardened CGB were determined (Figure 7).

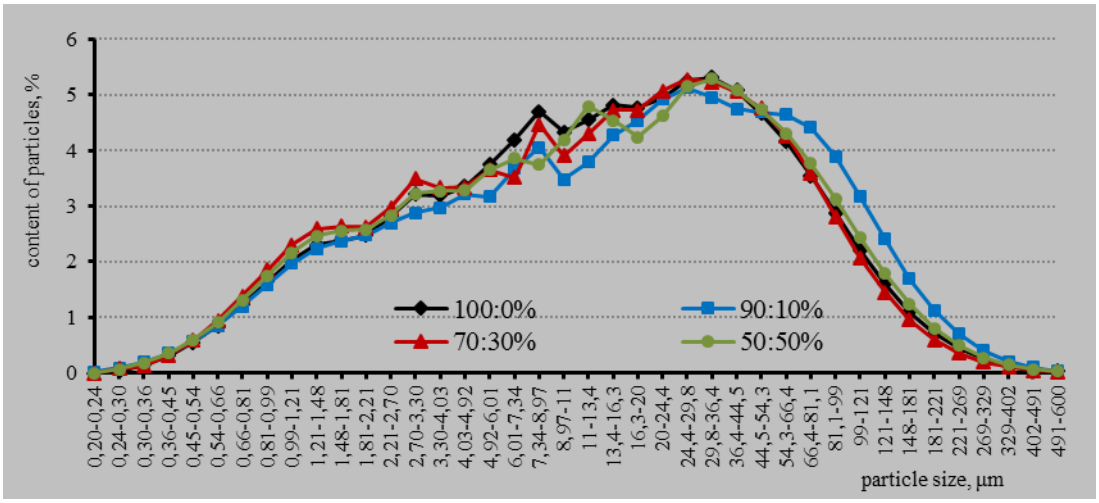


Figure 7: CGB grain size distribusion for different ratio of G-5 and G-16 in the gypsum binder

It was found out that the CGB, containing 70% of G-5 and 30% of G-16 in its gypsum binder shows the largest offset of the graph towards the reduction of fine fraction with four evident peaks: 1 – in the area of 13.4…16.3 micron particles; 2 – 7.34…8.97 micron; 3 – 4.92…6.01 micron and 4 – 1.81…3.3 micron. Increased content of 8.97…1.81 micron particles, which compact the structure, leads to a reduced volume of pore space between them, accelerated structure formation of the artificial gypsum cement stone and increased (by up to 20%) compressive strength limit at the early hardening stages with the values reaching 26.0 MPa 28 days after (Table 4).

Table 4. Compositions and principal properties of gypsum binders and CGB

No.	Composition of gypsum binders and CGBs on their basis, %wt:						B/Binder	Spread, m	Setting time min, sec		Compressive strength, MPa, on term			Kp
	GB		C	WMS waste	NDP	Chalk			start	end	2 hrs	7 d	28 d	
	Г-5	Г-16												
1	100	-	-	-	-	-	0.50	0.180	6-30	10-30	5.9	-	-	0.34
2	70	-	15	15	-	-	0.50	0.175	6-30	9-00	54	10.5	16.4	0.76
3	68.05	-					0.50	0.110	4-00	4-30	6.3	7.1	17.2	0.78
4	61.25	6.80					0.50	0.115	4-15	4-55	7.3	8.0	18.6	0.82
5			15	15	0.45	1.5	0.46	0.115	5-45	6-15	7.7	9.0	26.0	0.89
6	47.64	20.41					0.50	0.145	6-20	6-50	7.5	8.4	21.6	0.87
7							0.55	0.200	7-30	8-00	5.2	6.8	14.2	0.85
8	34.02	34.02					0.50	0.190	7-00	7-30	6.8	7.3	17.1	0.82

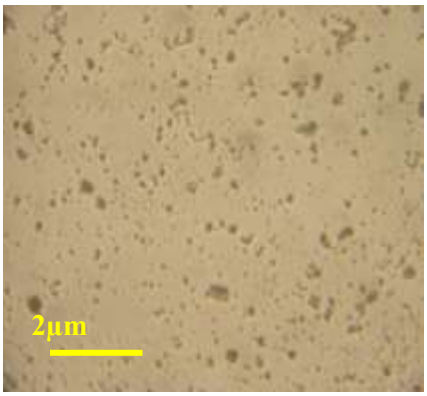


Figure 8. Distribution of the NSP particles in the water suspension

Further optimization of the CGB composition and structure was performed by addition of silica NDP (0.45%wt of CGB mass). The mixing (3 minutes) was performed with an amount of water necessary for preparation of the gypsum cement mixture with a laboratory ultrasound mixer (Figure 8), facilitating a uniform distribution of the CGB components and optimization of their grain size distribution, as well as accelerating the structure formation process. Then, the silica NDP suspension was mixed with a prepared CGB, including a practical amount of β-hemihydrate of calcium sulfate (G-5), α-hemihydrate of calcium sulfate (G-16) and the BMM. The mixing time of the gypsum cement mixture shall be at least 30 sec. The separate preparation of the silica NDP suspension solves the issue of CGB integrity in storage, as well as allows using standard equipment for CGB-based concrete mixes.

4. Conclusion

The attained level of physical and mechanical characteristics of the CGBs meets the requirements for binders applied in the construction: the water resistance coefficient is 0.82…0.89 with compressive strength values of up to 26 MPa. At that, a valuable property of the mineral additives (WMS waste and silica NDP) is their puzzonanic activity, which intensifies the hydration process of the clinker minerals, facilitating the process of fixing the $Ca(OH)_2$ appearing from hydration of C_3S, and optimizes the structure of the gypsum cement stone. The larger particles of the active mineral additive from the WMS waste serve as crystallization centers and as a microaggregate. Chalk particles serve as a microaggregate and as crystallization centers, facilitating hydration of aluminates and formation of different compounds with them during the early stage of hardening; they also increase early strength and improve performance characteristics of the hardened gypsum cement stone.

Joint addition of α- and β-hemihydrates of calcium sulfate (G-5 and G-16) promotes earlier formation of the structure in the gypsum cement stone.

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