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Application of Microfillers in Energy-Saving Compressed Gypsum Composites

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This paper presents the results of comparative studies of the effect of highly dispersed fillers on the mechanical and structural characteristics of pressed composites based on gypsum. As microfillers, powders of metakaolin and the ash were introduced into the composition of the gypsum mixture. The active component in the form of metakaolin affects the structure and properties of pressed stone. The average median grain size of metakaolin predetermines an increase in packing density due to the filling of voids between larger particles of gypsum with a highly dispersed phase. The effect of increasing the density of the modified composite has been established. Studies of water absorption of stone with the addition of metakaolin have established an increase in water resistance and a decrease in water absorption of a modified composite. The results of studies of gypsum with ash additive confirm the effectiveness of the introduction of the ash in terms of strength and density. As in the case of metakaolin. Gypsum with the addition of ash has not only increased density and, as a result, high performance, but also high creep resistance. Based on the results of the microstructural and spectral analysis of pure and modified stone, a comparison was made of the elemental composition of the original stone and the modified composite on the grain surface and in the contact zones of gypsum particles with particles of fillers. They confirm the participation of additives in the formation of crystallites of the composite and the mechanical compaction of its structure.

1. Introduction

Gypsum-based materials and products currently deserve special attention from specialists in many industries. They are distinguished by high environmental friendliness, manufacturability and safety. The construction industry is showing additional interest in their increased comfort, increased sound insulation and thermal insulation.Of interest are methods for obtaining gypsum products directly from calcium sulfate dihydrate, excluding the most time-consuming and energy-consuming technological stages: firing of raw materials and drying of the resulting materials (Buryanov et al., 2020).Currently, various methods are being considered for obtaining products based on calcium sulfate dihydrate - natural and technogenic. They are based on the hydration and non-hydration mechanism of formation of crystallization contacts in the structure of gypsum stone. Obtaining crystallization structures directly from gypsum according to the scheme of hardening without hydration competes with many modern technological approaches. In the production of energy-saving gypsum composites, CO_2 and other toxic substances are not released into the environment, energy costs are sharply reduced. This makes this method even more attractive. Products can be obtained by pressing or vibrocompression. This method of obtaining building materials is very relevant. It allows in the shortest possible time to obtain a durable stone based on waste and by-products of industry (Ovcharenko et al., 2019). The pressing effect plays an important role. Due to the occurrence of shear forces and repacking of particles, the total cross section of the area of crystallization contacts increases (Chernishovet al., 2020).

However, the process of hardening of binder systems can also be controlled by introducing modifying additives with high activity (Samchenko et al., 2020). For example, the pozzolanic activity of calcined clays is associated with the dehydration of metakaolin (Samchenko et al., 2017).High-calcium fly ash is more active. Different granulometric composition and different morphology led to different effects of ash microspheres on the

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workability of mixtures (Zhang et al., 2021).The introduction of an ash component can reduce the heat of hydration, optimize particle packing, and maintain workability (Yang et al., 2021).The possibility of obtaining high-strength materials based on gypsum dihydrate and additives is confirmed by studies of the physical and mechanical properties of energy-saving compressed gypsum composites (Petropavlovskaya et al., 2021). Promising is the use of nanosized particles, whose high physicochemical and mechanochemical activity has a modifying effect on the processes of hydration and structure formation when creating mineral binders and concretes with high technical and operational characteristics: it changes the size and morphology of crystals, the state of the interfacial surface, porosity, etc. (Shuldyakov et al., 2020). Studies of the physicochemical processes of hardening of such systems (without hydration hardening) have received significant development. In the present work, the effect of aluminum-containing additives with the inclusion of nanosized particles on the mechanical and structural characteristics of unfired gypsum-based composites was studied.

2. Materials and methods

2.1 Materials

In the work, gypsum waste from ceramic industries (Russia, Moscow) was used as the main raw material. To increase water resistance and shield the effects of water, as structuring additives-modifiers in comparative experiments, metakaolin (Tables 1 and 2) produced by Synergo (Russia) and acidic hydro-removal ash (Russia, Moscow) (Table 3) were used. The choice of additives was due to their high pozzolanic activity. The chemical composition of metakaolin is represented by silicon oxide SiO_2, wt. % (51, 4), aluminum oxide Al_2O_3, wt. % (> 42) and iron oxide Fe_2O_3, wt. % (0.8), PPP - < 1, wt. %.The mineralogical composition of metakaolin is given in Table 1.

Table 1: Mineralogical composition of metakaolin

Name of clinker mineral	Content, wt. %
Amorphous kaolinite	90.0
Mica	3.0
Quartz	4.0
Cristobalite	< 1

The average amount of silicon dioxide, aluminum oxides was: $SiO_2$55.72 % (against 51.4 % according to the passport); Al_2O_3 44.28 % (against 42 % according to the passport), iron oxide was not detected (according to the passport 0.8 %). The chemical formula of metakaolin used in the work is: $Al_2O_3 \cdot 1.26\ SiO_2$.
Physical and technical properties of metakaolin are shown in Table 2.

Table 2: Physical and technical characteristics of metakaolin

Characteristic	Indicator
Humidity, %	< 0.5
Bulk density, kg/m^3	410
Density, kg/m^3	2,500
Specific surface, m^2/kg	1.670
Loss on ignition, %	2.5
Pozzolanic activity, mg $Ca(OH)_2$/g	> 1.000

Aluminosilicate hydroremoval ash was introduced as an additional disperse modifier. She was enriched. The chemical composition after enrichment is shown in Table 3. The basicity modulus (the ratio of the sum of calcium and magnesium oxides to the sum of aluminum and silicon oxides) is 0.049. The ash amorphous modulus tends to unity. The enrichment of the ash and its separation into fractions made it possible to isolate a fraction with an average particle size of 10 μm (the granulometric composition is shown in Figure 2).

Table 3: Chemical composition of fractionated ash

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, %											
Iron-containing	0.2	1.5	8.4	21.7	0.6	3.4	0.4	1	58	0.2	0.05	0.8
Aluminosilicate	0.6	1.6	21.5	57.8	2.1	2.3	0.9	0.1	4.6	0.4	0.1	3.2
Carbon	–	–	–	–	–	–	–	–	–	–	–	52.8

2.2 Methods

1. The main physical and mechanical characteristics of modified gypsum stone were studied in the work: compressive strength, average density, total and open porosity. They most adequately reflect the effect of additives on the properties of the resulting modified gypsum stone. Physical and mechanical characteristics

were determined by standard calculation and calculation-experimental methods. After molding, the samples were stored indoors under humid conditions until testing. For testing on a hydraulic press, the samples were installed on the press supports in the least favorable conditions.

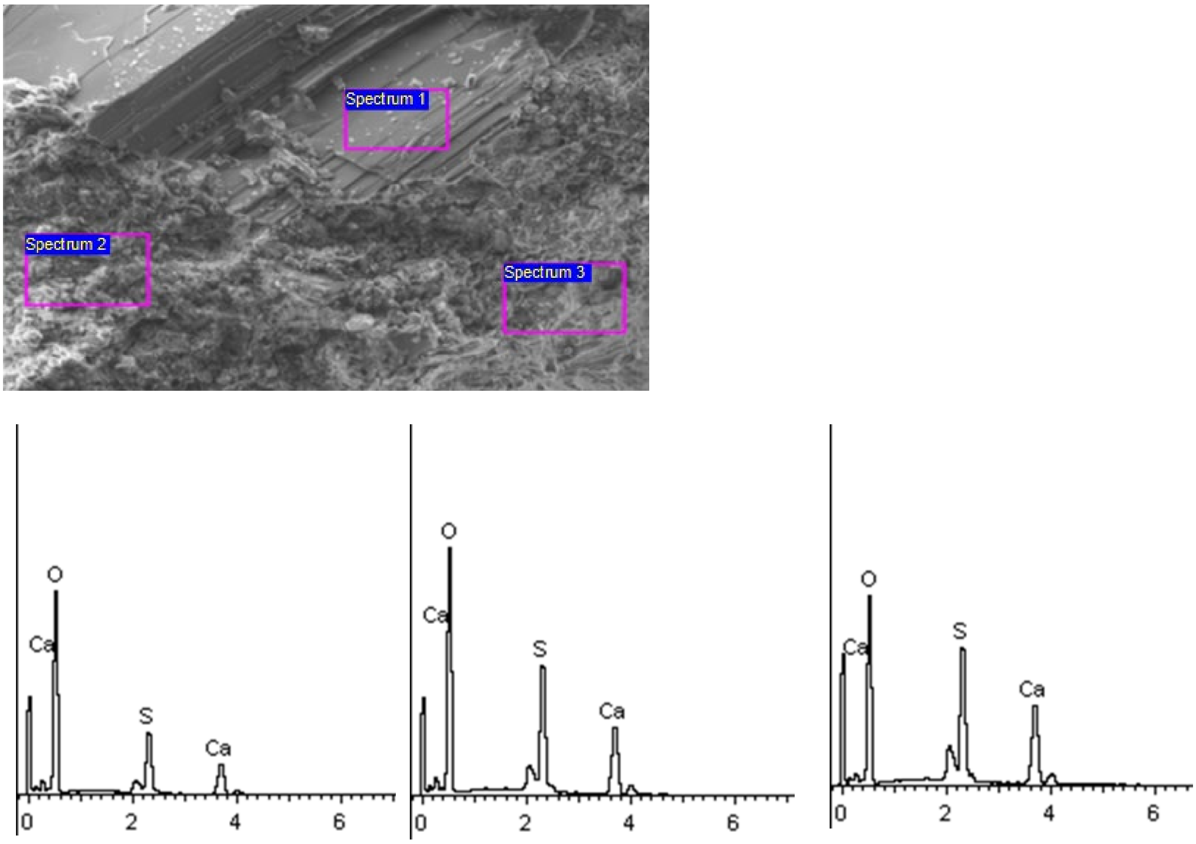
2. Structural features of gypsum dihydrate crystals and compositions based on it were evaluated by electron microscopy using an electron scanning microscope of the shared use laboratory of Tver State University.

3. Results and discussion

The results of studies on the average density and strength of the gypsum composite modified with metakaolin / ash confirmed the possibility of their use in the non-hydration hardening system.

An increase in the percentage of metakaolin from 1.3 to 1.4 % at W/T=0.07 makes it possible to increase the ultimate strength and water resistance of the tested specimens by 25 %. The optimal strength value corresponds to the content of metakaolin in the studied range - 1.3 %.

It has been established that the maximum values of ultimate compressive strength of an unfired composite of various compositions are observed at W/T=0.06. It was found that during pressing, the critical values of moisture during pressing are optimal from the point of view of the highest degree of compaction of finished products.



spectrum 1 spectrum 2 spectrum 3

Figure 1: The microstructure of an additive-free non-fired stone of non-hydration hardening based on gypsum dihydrate with spectra

Table 4: Quantitative indicators of the chemical composition of the additive-free non-firing gypsum composite, in weight %

spectrum	O	S	Ca	total
spectrum 1	76.78	11.81	11.42	100.00
spectrum 2	69.52	14.86	15.62	100.00
spectrum 3	64.39	16.52	19.09	100.00
mean	70.23	14.39	15.38	100.00

Table 5: Quantitative indicators of the chemical composition of the non-firing gypsum composite without use, in atomic %

spectrum	O	S	Ca
spectrum 1	88.02	6.75	5.22
spectrum 2	83.59	8.91	7.50
spectrum 3	80.23	10.27	9.50
mean	83.95	8.65	7.41

Table 6: Quantitative indicators of the chemical composition of the non-firing gypsum composite modified with the addition of metakaolin, at the age of 14 days of hardening, in wt %

spectrum	O	Al	Si	S	Ca	total
spectrum 1	62.08		0.07	16.87	20.98	100
spectrum 2	67.28		0.22	14.96	17.55	100
spectrum 3	57.56	17.92	18.81	2.88	2.82	100
spectrum 4	53.34		0.20	19.85	26.61	100
spectrum 5	60.00	7.16	6.98	11.78	14.08	100
spectrum 6	65.06	0.89	0.94	15.07	18.04	100

Table 7: Quantitative indicators of the chemical composition of a non-firing gypsum composite modified with the addition of metakaolin, at the age of 14 days of hardening, in atomic %

spectrum	O	Al	Si	S	Ca
spectrum 1	78.67		0.05	10.66	10.61
spectrum 2	82.18		0.15	9.12	8.56
spectrum 3	70.66	13.04	13.16	1.76	1.38
spectrum 4	72.10		0.16	13.39	14.36
spectrum 5	75.26	5.33	4.99	7.37	7.05
spectrum 6	80.48	0.65	0.66	9.30	8.91

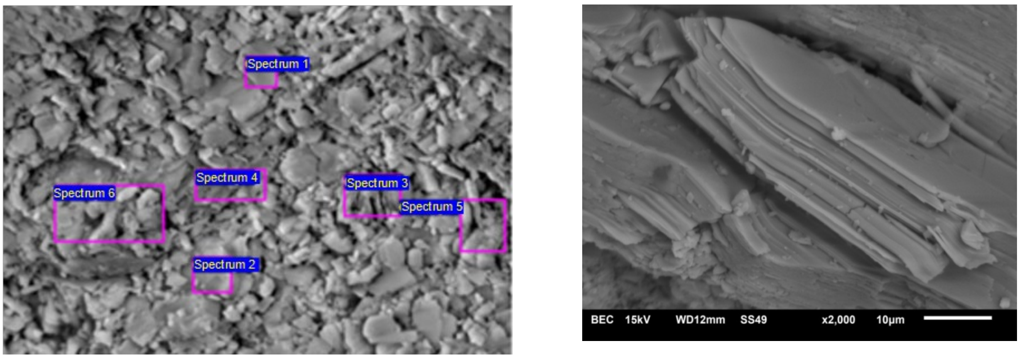


Figure 2: The microstructure of a modified non-firing composite based on gypsum dihydrate with the addition of metakaolin at the age of 14 days of hardening

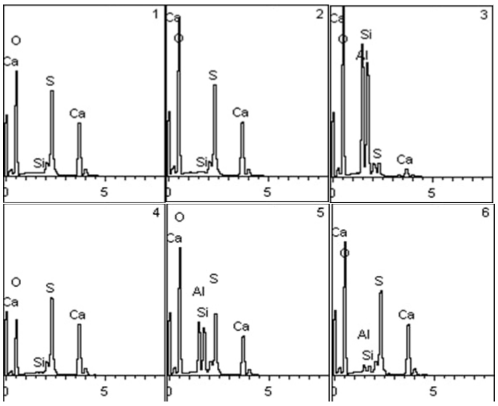


Table 8: Quantitative indicators of the chemical composition of the non-firing gypsum composite modified with the addition of metakaolin, at the age of 14 days of hardening in wet conditions, in wt %

Spectrum	O	Al	Si	S	Ca	total
Spectrum 1	65.11			15.66	19.23	100.00
Spectrum 2	57.26	0.72	0.62	14.83	26.57	100.00
Spectrum 3	54.14	0.54	0.75	17.76	26.81	100.00

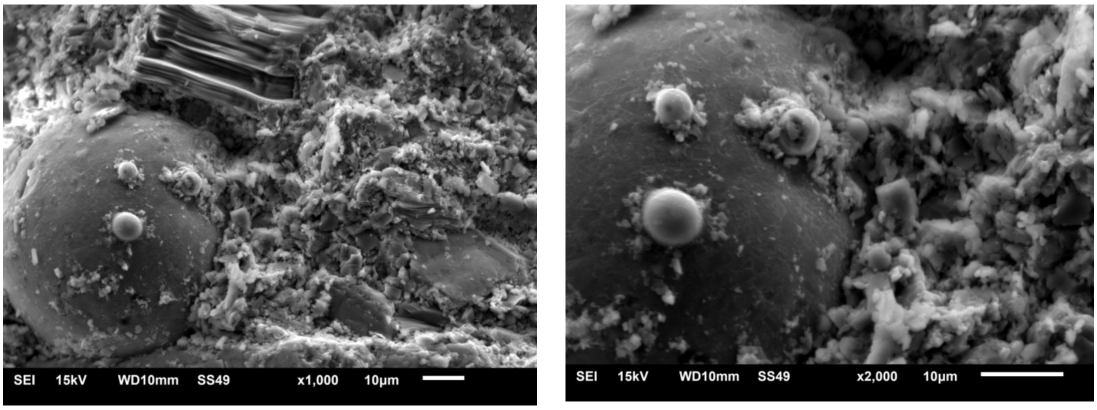


Figure 4: Microstructure of a modified non-firing composite based on gypsum dihydrate with the addition of ash at the age of 14 days of hardening in humid conditions

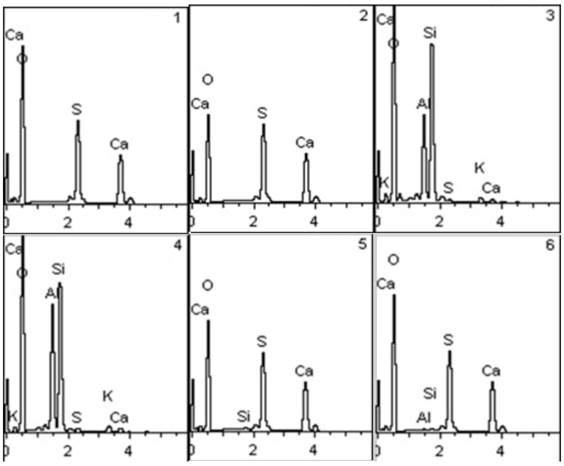


Figure 5: Spectra of a composite based on calcium sulphate dihydrate modified with an aluminosilicate additive

On the spectrum characteristic of the ash microsphere (Spectrum 3, Figure*5*), the percentage of aluminum is 7.93 %, while on Spectrum 6 it is only 0.07 %. However, Spectrum 6, along with aluminum and silicon, reveals a high calcium content and the appearance of K as an impurity, which affects the processes of gypsum stone structure formation, primarily the formation of its more defective structure.

Table 9: Quantitative indicators of the chemical composition of a non-firing gypsum composite modified with the addition of ash, at the age of 14 days of hardening in wet conditions, in wt %

Spectrum	O	Al	Si	S	K	Ca	total
Spectrum 1	68.70			14.28		17.03	100
Spectrum 2	61.04			17.31		21.65	100
Spectrum 3	61.95	11.15	23.75	0.46	1.52	1.16	100
Spectrum 4	59.47	15.68	21.31	0.66	1.69	1.18	100
Spectrum 5	64.08		0.35	15.75		19.82	100
Spectrum 6	66.62	0.09	0.19	14.84		18.26	100

According to the results of the microstructural and spectral analysis of pure and modified gypsum stone, a comparison was made of the elemental composition of the initial dihydrate and the modified composition both on the surface of the grains and in the zones of contact between calcium sulfate dihydrate particles of different sizes and contacts between dihydrate and ash particles.When analyzing the results in the composition of gypsum stone without additives, the absence of impurities in significant quantities was found. The elemental composition contains only elements representing calcium sulfates.When comparing the spectra of the original gypsum stone (spectrum 1, Table 9) and neoformations formed in the process of recrystallization of dihydrate particles (spectra 3, 6, Tables 9, 10), additional compounds of calcium hydroxide and aluminosilicates are detected.

Table 10: Quantitative indicators of the chemical composition of the non-firing gypsum composite modified with the addition of ash, at the age of 14 days of hardening in humid conditions, in atomic %

Spectrum	O	Al	Si	S	K	Ca
Spectrum 1	83.15			8.62		8.23
Spectrum 2	77.93			11.03		11.03
Spectrum 3	74.27	7.93	16.22	0.27	0.75	0.55
Spectrum 4	72.17	11.28	14.73	0.40	0.84	0.57
Spectrum 5	80.05		0.25	9.82		9.88
Spectrum 6	81.77	0.07	0.13	9.09		8.94

When comparing the spectra of the original gypsum stone and neoplasms formed during the recrystallization of dihydrate particles, compounds of calcium hydroxide and aluminosilicates are additionally detected. The spectral analysis confirms the formation of a fine-grained structure coupled with a structuring modifier - metakaolin, a reactive ash filler. A comparative analysis of the spectra obtained after 14 days of hardening indicates the active course of structure formation processes with the active participation of modifiers.

4. Conclusions

The conducted studies and the presented spectra confirm the possibility of obtaining a modified hardened structure of a stone of non-hydration hardening. The introduction of additives of different nature with sizes of different scale levels provides a multidirectional structure formation and an increase in the complex of operational properties. Materials based on the unfired system can be used as a basis for the design of structural materials

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References

Petropavlovskii K., Novichenkova T., Petropavlovskaya V., Sulman M., Fediuk R., Amran M, 2021. Faience waste for the production of wall products. Materials, 14(21), 6677.

Shuldyakov K., Trofimov B., Kramar L., 2020. Stable microstructure of hardened cement paste – a guarantee of the durability of concrete. Case Studies in Construction Materials, 12,00351.

Krivoborodov Y.R., Kuznetsova T.V., Samchenko S.V., 2018. Structural changes in refractory calcium aluminate cement concrete. Refractories and Industrial Ceramics, 59(12), 151-155.

Samchenko S., Zorin D., 2020. Influence of calcium sulphoaluminoferrite on the cement stone structure. E3S Web of Conferences. Topical Problems of Green Architecture, Civil and Environmental Engineering, 164(1), 14002.

Samchenko S., Zemskova O., Kozlova I., 2017. Ultradisperse slag suspensions aggregative and sedimentative stability. MATEC Web of Conferences, 106, 03017.

Ovcharenko G.I., Ibe E.E., Sadrasheva A.O., Viktorov A.V., 2019. Contact strength of C-S-H cement phase with additives. Technique and Technology of Silicates, 26(4), 98-101.

Chernyshov E.M., Akulova I.I., Goncharova M.A., Sergutkina O.R., Potamoshneva N.D., 2020. The problem of industrial waste utilization: concept, methodology and applied solutions. News of higher educational institutions. Construction, 8 (740), 70-91.

Buryanov A.F., Petropavlovskii K.S., Petropavlovskaya V.B., Novichenkova T.B., 2020. Formation of the spatial structure of a condensed system of calcium sulphatedihydrate. Journal of Physics: Conference Series. International Scientific Conference on Modelling and Methods of Structural Analysis, 1425(1),012194.

Yang S., Zhang J., An X., Qi B., Shen D., Lv M., 2021. Effects of fly ash and limestone powder on the paste rheological thresholds of self-compacting concrete. Construction and Building Materials, 281,122560.

Zhang J., Lv M, An X., Shen D., He X., Nie D., 2021. Improved Powder Equivalence Model for the Mix Design of Self-Compacting Concrete with Fly Ash and Limestone Powder. Advances in Materials Science and Engineering, 2021(9), 4966062.