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Synthesis of Biopositive Composites Based on Gypsum Binder and Dispersed Additive of Unburned Coal

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Reducing the density of building composites improves a number of performance properties of materials. Reducing the thermal conductivity, weight, and thickness of building products provides a solution to problems of energy and resource conservation and leads to a reduction in the consumption of natural resources and energy. To solve these problems, the work explores the possibility of using one of the fractions of fuel ash containing predominantly unburned organic residues of solid fuel. The structural features of unburned coal after high-temperature treatment can contribute to the transformation of the structure of mineral composites. The synthesis of modified gypsum with the addition of unburned coal fraction additionally leads to a reduction in the volume of gypsum binder used by up to 30 %. The purpose of the work was to determine the optimal additive content of this by-product according to the criteria of density and porosity. The results obtained demonstrate the effect of changing the content of additives on the synthesis of modified gypsum. It has been established that gypsum modified is superior to the control composition in all aspects of structural changes. First of all, this was manifested in the porosity characteristics. The radical change in the pore structure is confirmed by research and analysis of the results obtained using the mercury porosimetry method. The total pore volume increased more than 4 times. The achieved results on density and porosity open up new broad opportunities in the field of creating bio-positive materials for green construction.

1. Introduction

Modern approaches in construction materials science are largely based on the results of the latest physical and chemical research. Until recently, unburned coal in the composition of ash and slag mixtures was considered one of the most negative components of waste from fuel power plants as components of building compositions based on mineral binders (Petropavlovskaya et al., 2023). In the composition of dry ash (Baeră et al., 2019) and hydraulic removal (Amat et al., 2017) at coal-fired power plants, according to many researchers, the coal content in fly ash can be (1-15) % (Rasskazova et al., 2018). Sometimes, the content of unburnt coal can reach 25 % (Delitsyn et al., 2012). The synthesis of building materials is traditionally based on the use of valuable natural resources (Petropavlovskaya et al., 2020).

When coal is burned in the boilers of coal-fired thermal stations, complex chemical processes can occur. High-temperature processing can result in the formation of crystalline and glassy phases (Pichugin, 2019). The quantitative content of these phases and the relationships between them are determined primarily by the genesis of the carbon fuel used, the method, the technological regime of combustion and, the method of waste removal, the so-called focal residues (Tanga et al., 2023). The crystalline phase is represented by primary minerals. They are contained in the mineral part of the coal used. In addition to primary minerals, new formations are present in the crystalline phase. They are formed during the combustion of fuel. In the process of high-temperature firing of primary minerals. Studies of crystalline phases reveal the presence of magnetite, hematite, quartz and mullite in them (Pichugin, 2019). Of the minerals that are new formations, calcium silicates, aluminates and aluminoferrites, similar to the minerals of cement clinker, are noted (Kosivtsov et al., 2021). Therefore, they are still considered the most valuable components of ash and slag waste (Tanga et al., 2023). The varied glassy ferroaluminosilicate phase is also important. Aluminosilicate and amorphous phases

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can be successfully used in the composition of cements and concretes with the replacement of part of the binder. This approach is driven by the need to solve the problem of reducing the carbon footprint in the production of mineral binders. First of all, Portland cement. In addition to replacing part of the cement, the creation of alternative binders also solves the problem. For example, high-strength and water-resistant gypsum modified binders.

Modification of traditional gypsum stone with nano- and microfillers makes it possible to increase the competitiveness of many non-cement composite binders. Carbon nanomodifiers (Pervyshin et al., 2017), microdispersed aluminosilicate additives or industrial dusts are introduced into gypsum compositions. Ash aluminosilicate microspheres are also used (Amran et al., 2022).

However, among researchers there is still a negative attitude towards unburned coal particles in the composition of mineral binders - gypsum (Chumachenko et al., 2017) and cement (Song et al., 2022). Even more negative than to free calcium oxide in the composition of the aluminosilicate microsphere of fly ash. By classifying particles of unburned coal (Petropavlovskaya et al., 2022) and isolating microdispersed fractions with particle sizes less than 50-70 μm, they can be used in the synthesis of effective mineral-based building composites.

In the work explores the possibility of using as a modifier one of the fractions of fuel ash containing predominantly unburned organic residues of solid fuel - unburned coal. The structural features of unburned coal, which has undergone changes during high-temperature treatment, may possibly contribute to the transformation of the structure of mineral composites. The synthesis of a modified gypsum composite with a technogenic addition of a fraction of unburned coal additionally leads to a reduction in the volume of gypsum binder used. The purpose of the work was to determine the optimal additive content of this by-product according to the criteria of density and porosity.

2. Materials and methods

2.1 Materials

The research used gypsum binder – calcium sulfate hemihydrate α-modification. Gypsum binder is finely ground according to the classification of grain composition. The maximum residue on a sieve with a clear cell size of 0.2 mm does not exceed 2 %. This property has a positive effect on the characteristics of the resulting modified composites. Studies of the mineralogical composition of gypsum binder (Figure 1) showed the presence of impurities of anhydrite, dihydrate, celestite and quartz in the composition of the binder. The presented diffraction pattern (Figure 2) is typical for semi-aqueous gypsum with an insignificant content of calcium sulfate dihydrate and other impurities. In terms of impurity content, according to the analysis, the largest volume among impurities is occupied by anhydrite - 3.8 %. The used initial binder, according to the strength classification in accordance with the requirements of the GOST 125 standard, belongs to the G-16 grade. Gypsum has a compressive strength of 16 MPa. The bending strength is 6 MPa.

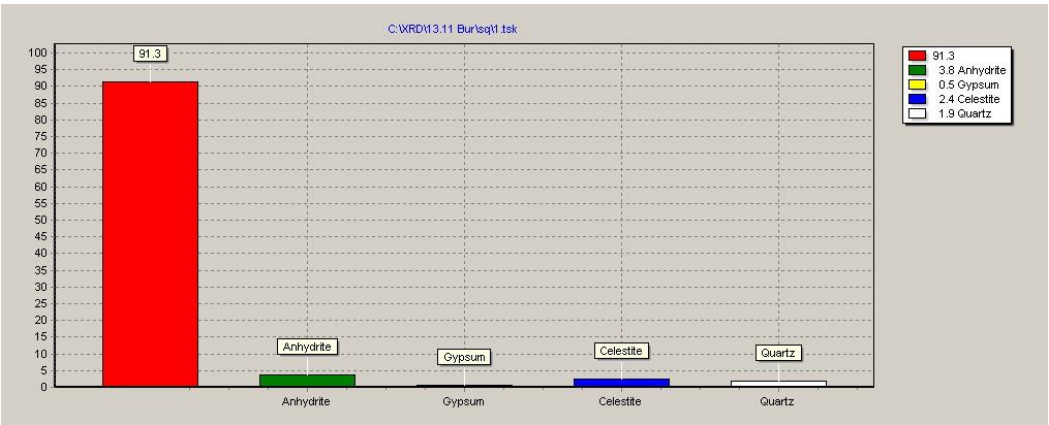

Figure 1: Phase composition of the original gypsum binder

The remains of unburned fuel from a thermal power station in the Moscow region were used as a modifier. Using the flotation and separation method, the ash residues of unburned brown coal were separated (Figure 3). Isolated unburned coal of the 0.005-0.07 mm fraction (Figure 4) was used in this study to improve the structure of the gypsum. The carbon content in unburned residues is 55.6 %.

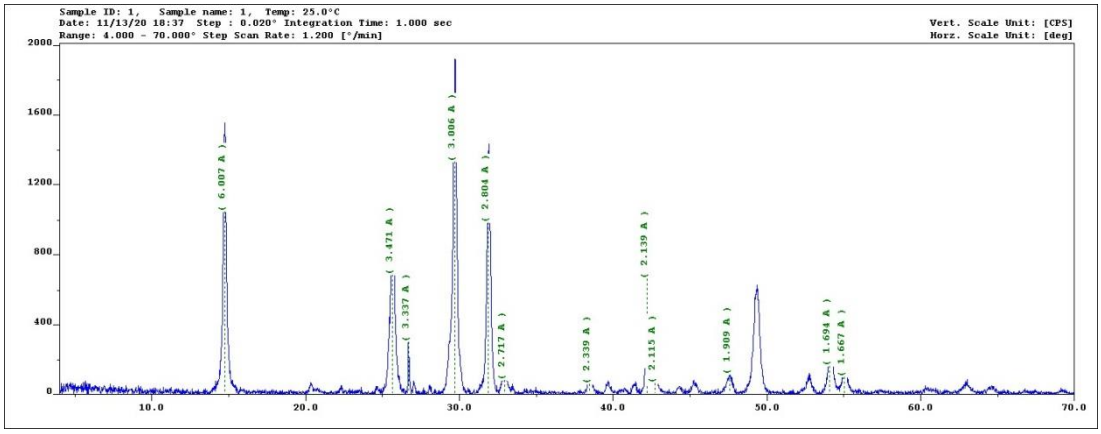

Figure 2: Registered diffraction pattern of the original gypsum binder

2.2 Methods

In this study, physical and mechanical properties were assessed using standard methods and equipment. The density of samples made on the basis of a modified gypsum mixture was determined on samples 20 × 20 × 20 mm. The samples were molded using the injection molding method. Hardening of gypsum composites was carried out under dry conditions. Strength characteristics were determined on a hydraulic press in accordance with GOST requirements.

The microstructure of the modifier and its features were studied using a DM200-2 QIDDYCOME digital microscope, as well as electron microscopy using a TESCAN Mira 3 scanning electron microscope. The features of the mineralogical composition of the materials were assessed by powder diffractometry using an ARL X'tra diffractometer. Also, samples of gypsum-based mineral binders were studied by thermogravimetry. The study was carried out on a Thermobalance device (Netzsch, Germany) with argon purging at 40 ml/min. The temperature program included two sections: the first – heating from 40 to 600 °C at a rate of 10 K/min, and the second – isothermal for 30 min.

3. Results and Discussion

Microstructural analysis of grains of unburned solid fuel after its high-temperature treatment in the volume of the furnace confirms the presence of high open porosity and developed surface (Figure 4). Unburned metamorphosed grains, in addition to the carbon fulleroid-like component, have a silicate part. It is fairly evenly distributed throughout the carbon nanomesh structure of unburned coal.

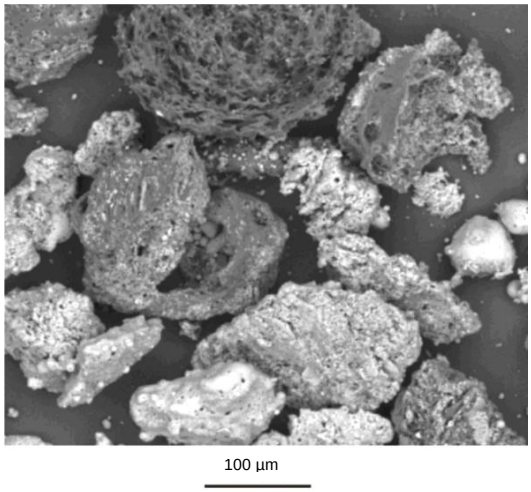

Figure 3: Particles of unburned brown coal in ash

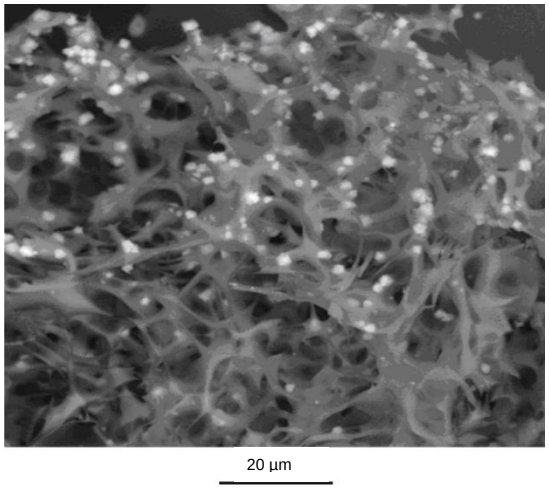

Figure 4: Microstructure of unburnt coal

Thermogravimetry results for gypsum composites showed that the control gypsum sample exhibited two mass loss peaks (Figure 5). They correspond to the loss of water of crystallization (Figure 5). The first peak, with a

maximum of 150 °C is associated with the loss of 1.5 mol of H_2O and the formation of calcium sulfate hemihydrate, and the second peak (190 °C) corresponds to the formation of anhydrite. At higher temperatures, the sample is thermally stable.

When unburned coal particles are introduced into the gypsum composite, the picture of the gravimetric study results changes (Figure 6). Two additional effects of mass loss appear (the first is 130 °C and the second is 450 °C) and also when the gypsum loses water. The first of the peaks that appears indicates a change in the structure and loss of crystallization water for gypsum by a different mechanism. The weight loss for three effects (138 °C, 157 °C, 189 °C) changed compared to the control composition (Figure 6).

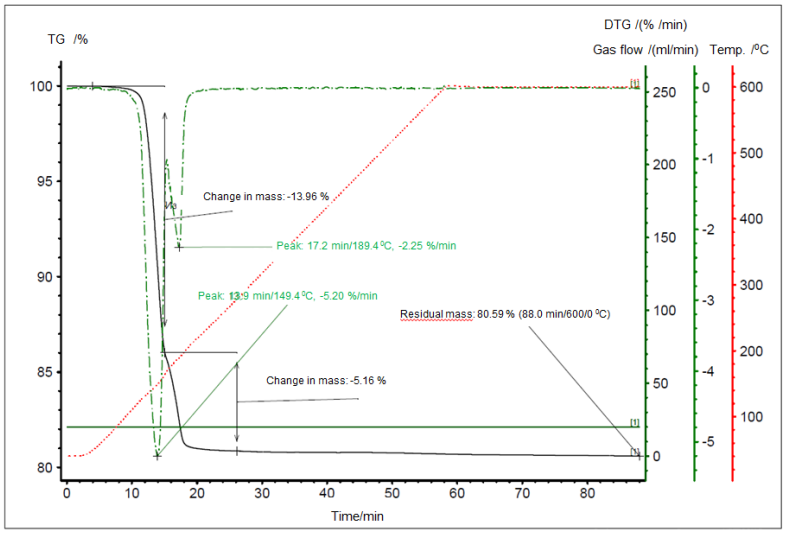

Figure 5: Thermogram of the control gypsum composition

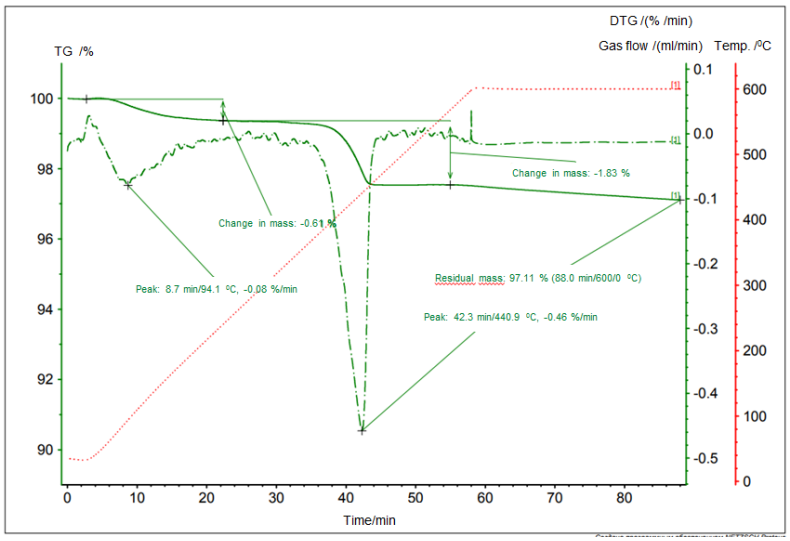

Figure 6: Thermogram of modified gypsum composition

A comparative analysis of the microstructure of the control (Figure 7) and modified gypsum stone (Figure 8, 9) shows a change in the habit of gypsum crystals. The structure of the stone (Figure 9) is represented by an accumulation of multidirectional gypsum crystals and particles of unburnt coal. A change in the pore space of the modified stone was established in comparison with the control composition. The microscopy data are confirmed by porosity studies. A transformation of porosity occurs. Pore distribution improves, average pore diameter decreases. If the average pore size for the control composition was 26.0398 μm, then for the modified one it decreased to 7.4162 μm. The total pore volume increased more than 4 times from 0.84 to 3.73 mm/g.

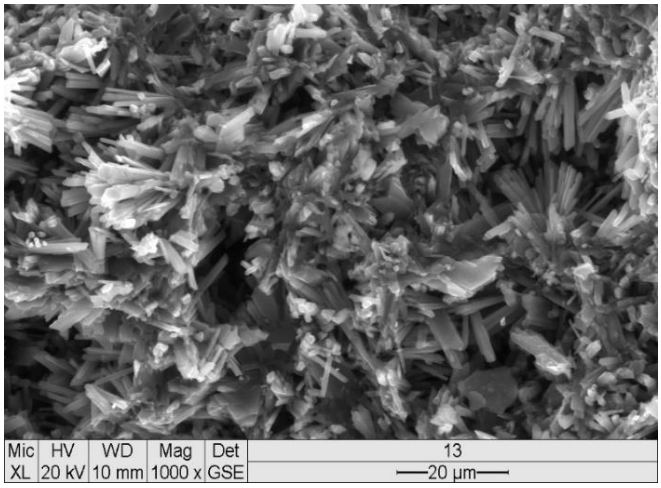

Figure 7: Microstructure of the original gypsum binder

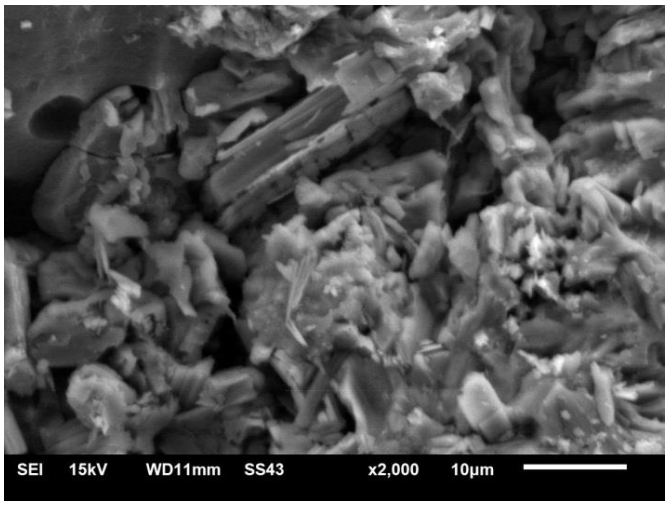

Figure 8: Microstructure of the gypsum binder

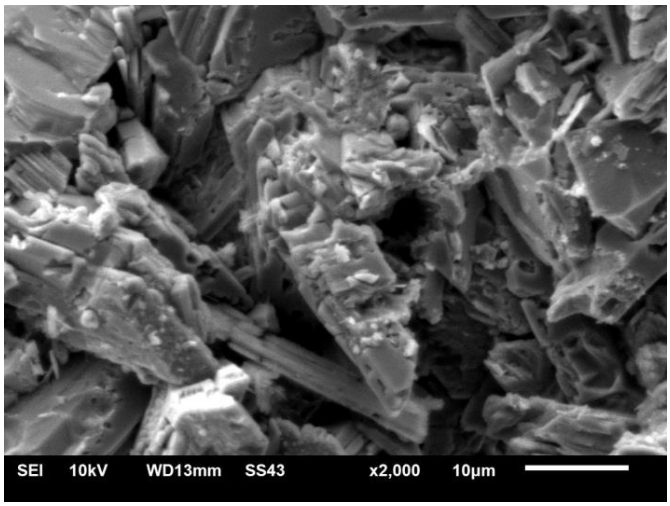

Figure 9: Microstructure of the gypsum binder

The structure of the stone (Figure 9) is represented by an accumulation of multidirectional gypsum crystals and particles of unburnt coal. A change in the pore space of the modified stone was established in comparison with the control composition. The microscopy data are confirmed by porosity studies. A transformation of porosity occurs. Pore distribution improves, and average pore diameter decreases. If the average pore size for the control composition was 26.0398 μm, then for the modified one, it decreased to 7.4162 μm. The total pore volume increased more than 4 times from 0.84 to 3.73 mm/g.

4. Conclusions

Based on the results of microscopic and thermogravimetric analysis and physical and mechanical tests, the role of metamorphosed particles of unburned coal as a modifier of the structure of the gypsum composite was confirmed. The synthesis of gypsum crystals occurs with the active participation of a modifier. The change in crystal morphology is confirmed by structural analysis data of the modified gypsum stone. The synthesis of a modified gypsum composite with a technogenic addition of unburnt coal fraction additionally leads to a reduction in the volume of gypsum binder used and has a positive effect on the natural balance and preservation of the environment.

Acknowledgements

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