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Study of the Properties of Concrete with Gypsum-Ash Binder

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It is known that the increasing demand for cement production is linked to the increasing world population, and the rapid development of construction technology. As a result of these factors, cement plants are causing a massive environmental problem by emitting CO_2 into the atmosphere. This significant air pollution may contribute to global warming. The search for alternative eco-friendly materials is an urgent need. Fly ash is a by-product in the form of powder produced by burning pulverised coal in power plants in huge quantities. Having no useful application, it is an organic waste, causing problems in landfilling. It is a pozzolanic material high in alumina and silica, which in the presence of water, acquires the cementitious properties of a renewable secondary cement-based material. When it is added to different types of binder, a new type of binder can be formed due to the mutual influence of fly ash on the nature and speed of the processes. The aim of the study was to develop a composition based on fly ash with a high content of free calcium oxide to replace cement with an alternative binder in the production of structural materials. For this, it was made a series of composite samples of different properties to obtain multilevel reinforcement. These samples showed high compressive strength (up to 90 MPa), indicating the synergistic effect of the composite components and their proper selection in building structures.

1. Introduction

Structural defects in building materials have different sizes and refer to the levels of their scaly structure. The consequence of the defectiveness of building composites is the localization of stresses with a concentration at the crack tips. (Korotkikh, 2011). In modern composites, the suspension of crack development at the macro level is provided primarily by reinforcing bars. However, the question of the strength of the matrix, i.e., how the micro- and nanolevels of the composite are reinforced, remains open. The approach to reinforcement at the nanoscale varies greatly depending on the selected binder. Among binders, gypsum materials are promising materials due to their cost-effectiveness, environmental friendliness, fire resistance, simplicity of technology and low energy intensity of production. But they are characterized by low structural plasticity and require additional reinforcement (Petropavlovsky, 2020). First of all, at the micro and nano level. For this, various methods can be used, including self-reinforcement with crystals (Petropavlovsky, 2020) or formation of a close-packed structure (Yu et al., 2022). Fly ash can be used as a component to ensure the densest packing of particles in the composite (Nguyen Hong-Ha et al., 2023). It is formed during the combustion of solid fuels in power plants and consists mainly of fine particles. Spheroidal ash particles can be located in the pore space between gypsum crystals and increase the degree of filling the structure with a solid phase. In addition to the role of ash as a mechanical agent, it is possible for it to participate in chemical transformations in the process of structure formation. An important role will be assigned to the composition of the ash - chemical and mineralogical. The chemical composition of ash and slag from the combustion of the most common energy fuels is determined by the chemical and mineral composition of burning rocks and combustion technology (Ogorodnikova et al., 2005). The change in the composition and properties of ash will be additionally influenced by the method of collecting ash (Larionova, 2018). Studies have been carried out to evaluate the chemical fractions of trace elements in coal combustion residues (Deming Khan et al., 2021). The researchers concluded that the composition of the volatile may include Hg and Cd. Then the ash cannot be used in gypsum composites for residential construction due to the relatively high environmental impact of these

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substances. Fly ash can carry a potential risk of residential pollution. This will negatively affect the people living there. The likelihood of developing severe illnesses may increase (Amran et al., 2021). The use of gypsum binder as an environmentally friendly binder in this case is mostly leveled. However, the enrichment of the ash and its separation into individual components allows increasing the uniformity and purity of each ash component (Petropavlovskaya et al., 2022). The use of fly ash, according to many researchers, has a number of undeniable advantages - an increase in corrosion resistance and performance properties, a reduction in the cost of the final composite (Petropavlovskaya et al., 2022). The possibility of producing building bricks from waste gypsum and fly ash has been studied (Sithole et al., 2023). The researchers concluded that since the gypsum was partially replaced by 0 to 40 % fly ash, the strength of the composite material decreased due to the low reactivity of the fly ash. At the same time (Panda et al., 2020), they state in their work that the addition of fly ash reduces the water demand of the mixture (water-cement ratio), reduces the total cost of production, and gives composites higher strength than a pure binder. The authors of another work (Sadique et al., 2013) investigated the possibility of ash activation and concluded that the activation of calcium-rich liquid ash can be very effective when using combined mechanical activation and agitation. The activation of fly ash in self-reinforced compositions based on gypsum binder is very promising (Petropavlovsky, 2020). In the case of nano-reinforcement of a gypsum binder with ettringite, aluminate, and alkaline components are used. By controlling the pH of the solution, as well as the quality and quantity of components, including ash, thin strands of ettringite crystals can be obtained that reinforce the gypsum matrix. Such control of crystal formation in the composite is the most subtle and complex setting and is carried out after selecting the material composition of the composite. In the present study, the aim of the work is to obtain a high-strength self-reinforcing gypsum composition with improved performance properties based on fly ash. The introduction of fly ash will possibly increase the structural plasticity of the composite due to a more active flow of the process of self-reinforcing with ettringite whiskers and obtaining a compacted structure of gypsum stone. This will make it possible to use the resulting composite in the production of critical structural materials. To do this, it is necessary to study in more depth the determining factors of self-reinforcement of the gypsum composition with the inclusion of a solid phase of highly basic ash.

2. Materials and methods

To investigate the properties of the composite, an aluminium sulphate solution and lime, high-strength gypsum G-16 produced by SAMARAGIPS and Beryozovsky region fly ash were used.

The main characteristics of gypsum on standard beam samples were determined according to the requirements of GOST 125-2018 Gypsum binders. Specifications and GOST 23789-2018 Gypsum binders. Test methods. A pH meter was used to determine the pH of the solutions. The tensile strength was evaluated using a laboratory hydraulic press.

2.1 Measurement of pH activity of extracts

In order to obtain preliminary data on the chemical activity of the components, pH measurements were taken on extracts of gypsum, quicklime, ash (all 1:3 by mass), as well as aluminium sulphate at the concentration stated above Table 2. The values obtained indicate a high reactivity of the ash and other components.

Table 1: Measurement of pH activity of extracts

Solution of	pH
distilled water	6.53
fly ash	12.11
gypsum	7.33
aluminium sulphate	3.59
slaked lime	12.01

Table 2: Chemical composition of high calcium ash from the Beryozovsky region fly ash

Content, wt.%								
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO		MgO	SO_3	R_2O
				all	free			
11.30	5.10	8.00	0.33	26.34	2.00	4.85	1.43	0.87
42.78	10.10	24.20	0.65	54.00	21.70	9.10	10.00	1.98

2.2 Measurements of fly ash characteristics

The specific surface area of the fly ash particles is 177 m^2/kg. The average particle size determined by air permeability is 12.2 μm. The true density of the ash is 2,780 kg/m^3. The bulk density of ash is 1,171.9 kg/m^3. The ash composition has been adopted according to (Kapustin, 2003). These data are shown in Table 2.

2.3 Experimental design

The effect of two factors on the properties of the composite was measured. A planned multi-factor experiment was used to gain an overall understanding of the influence of each component. The first variable, parameter X1 was taken as the mass ratio of ash to the mass of the dry phase. X1 took the following values: 20 %, 30 %, 40 %. For the second modifiable parameter, the ratio of sulphurous aluminium to liquid phase was taken. X2 took the following values: 6.25 %, 12.5 %, 18.75 %. The water-solid ratio was taken as 0.2. The amount of plasticiser was assumed to be 1 % of the weight of the dry phase. The final number of points was 9.

2.4 Preparing and testing the samples

The components in the designated proportions for each point were mixed in a steel bowl. The resulting mixture was poured into 2x2x2 cm steel master cube moulds. Once the samples had been set, they were marked with a coloured marker and stored under normal conditions for 28 days. On the 28th day, the geometric characteristics of the samples were measured with a calliper to an accuracy of 0.01 cm.
The specimens were then placed under the press and tested in uniaxial compression until completely broken. The maximum press load for each specimen was divided by the load transfer area. In this way, the maximum compressive strength values were obtained.
The fractured samples were placed in the ELVIZ-2C apparatus, which is designed to determine the moisture content in various samples by mass loss during drying. In the drying operation mode of 10 min, the samples lost moisture rapidly by changing their weight. The final values of the relative humidity of the sample were displayed on the instrument's display and entered by the researchers in tables.
Afterwards, the samples for each point were combined and ground to a powder. The true density was measured with a Le Chatelier apparatus: water was poured down to the zero mark, and the powder from the ground samples was poured into the funnel of the apparatus in equal portions until the liquid level in the apparatus rose above the mark with graduations. The true density was equal to the ratio of the mass difference of the powder to the displaced volume.

3. Results and discussion

3.1 General values

Table 3: Total values of the measurement results

No.	ratio to mass of solid phase			ratio to the volume of the liquid phase		R, MPa	average density, g/cm^3	total porosity, %
	Gypsum, %	Fly ash, %	Plasticizer, %	saturated lime solution	aluminium sulphate			
1	79	20	1	93.75	6.25	78.00	2.02	17.16
2	69	30	1	93.75	6.25	54.54	1.96	23.44
3	59	40	1	93.75	6.25	48.45	1.86	22.28
4	79	20	1	87.50	12.50	81.11	2.00	15.31
5	69	30	1	87.50	12.50	56.96	1.98	16.18
6	59	40	1	87.50	12.50	50.47	2.00	16.08
7	79	20	1	81.25	18.75	90.71	2.05	15.04
8	69	30	1	81.25	18.75	61.87	1.96	19.06
9	59	40	1	81.25	18.75	65.14	2.04	14.02

For each characteristic, intermediate values were calculated using the method of least squares. Taking these intermediate points into account, graphs showing the dependencies of uniaxial compressive strength, average density and total porosity were plotted.

3.2 Compressive strength

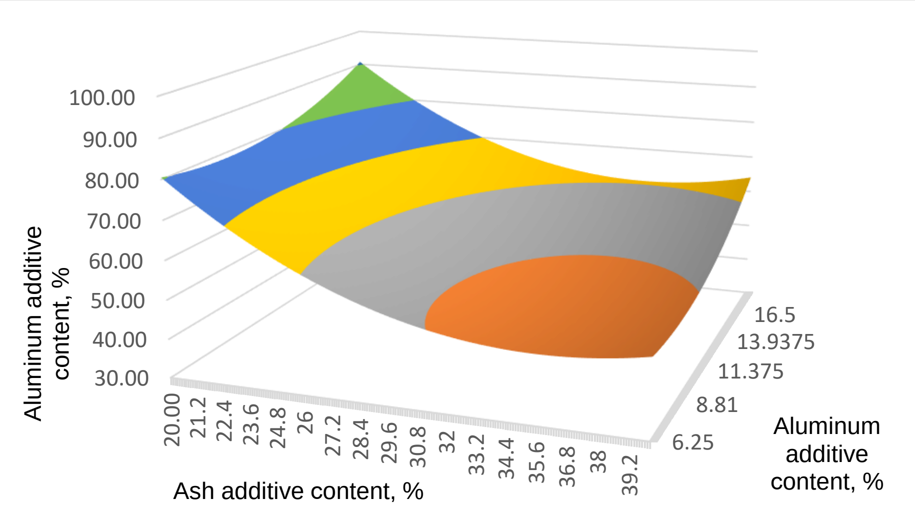

Figure 1: Dependence *of uniaxial compressive strength on changes in X1 and X2, MPa*

As can be seen in Figure 1, the graph has a simple concave shape. We can draw several conclusions from the graph. The compressive strength of the final composite is several times higher than the compressive strength of the pure gypsum specimens, indicating a positive, synergistic effect between the components.
The compressive strength of the samples increases as the amount of ash in the sample decreases. The compressive strength of the specimens increased significantly, nonlinearly, with increasing amounts of aluminium sulphate. In the area of the curvature close to the values of point 9 (i.e., X1 = 40 % and X2 = 18.75 %) a curvature was observed, which increased the compressive strength despite the increasing amount of ash. This may indicate a possible inflection point resulting from the interaction of aluminium sulphate and fly ash.

3.3 Average density

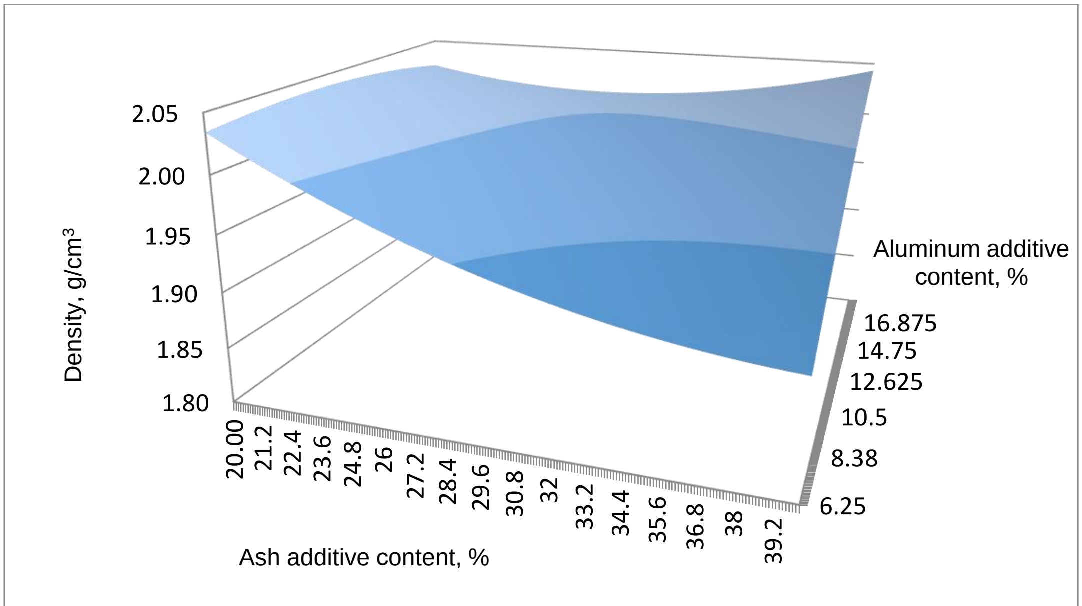

Figure 2: Dependence of average density on changes in X1 and X2, MPa

As can be seen in Figure 2, the density increases with increasing ash and aluminate phase content. The increase in density may be due to the provision of a plasticizing effect from the impact of Fly-ash together with a plasticizer. A compacted dispersed-reinforced gypsum structure is formed as a result of the interaction of all components present. The morphology of gypsum crystals changes. Additional structural bonds at the nano level are formed.

3.4 Total porosity

As can be seen in Figure 3, porosity reaches its maximum values at an ash content of about 30 %. An increase in density can be caused by the formation at the micro- and nanolevels of reinforcing structural elements located in the voids of the crystalline intergrowths of the dihydrate.

The microstructure of the gypsum stone (Figure 4) of the control composition (initial for this study) and the optimal composition of the additive (Figure 5) were studied. The presence of an amorphous phase in the composition of gypsum stone with an ash additive contributes to a change in the morphology of gypsum crystals (Figure 5). A compacted fine-crystalline structure of the modified stone is formed.

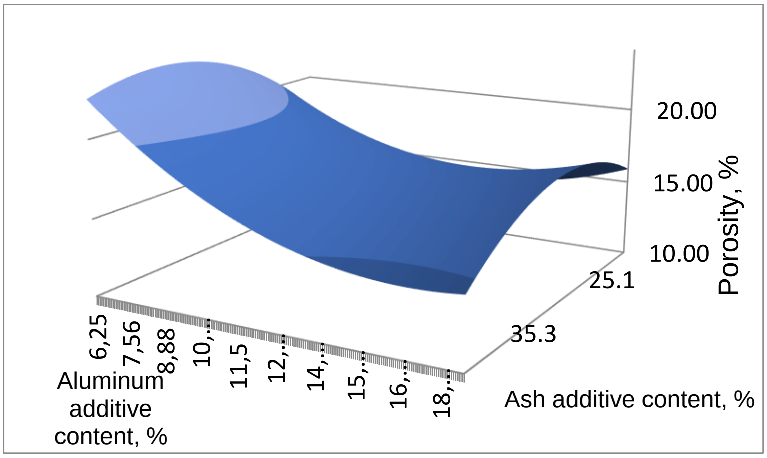

Figure 3: Dependence of 3.4 Total porosity on changes in X1 and X2, MPa

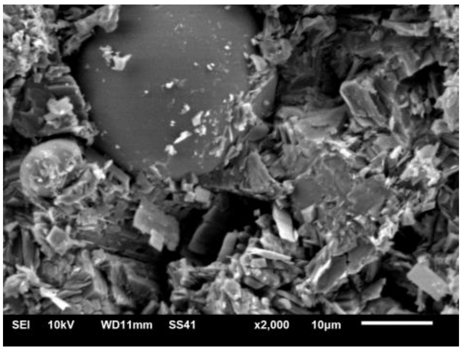

Figure 4: Microstructure of gypsum stone of control composition

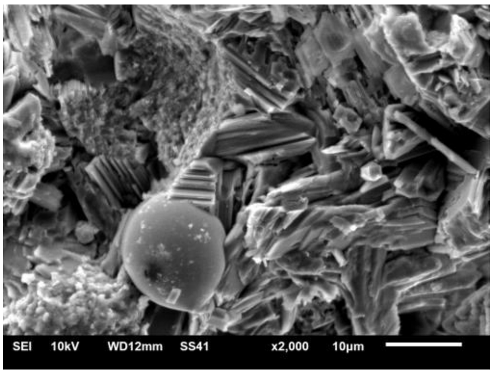

Figure 5: Compacted dispersed-reinforced gypsum microstructure with fly ash

4. Conclusions

The use of highly basic fly ash as an active mineral additive in self-reinforcing gypsum composite materials makes it possible to achieve high technical performance, primarily in terms of density and strength. A complex synergistic effect appears in the structure of the gypsum composite, apparently, at the stage of dissolution and crystallisation of a multi-component binder system based on calcium sulfate hemihydrate. This allows three times or more to increase the strength of the material. Reinforcement of the material at different scale levels improves all the main performance indicators. The resulting self-reinforced material with a strength of 91 MPa, a density of 2,050 kg/m^3 and a porosity of 15 % can be used to create building structures with innovative characteristics. The use of technogenic additives will increase economic efficiency and solve environmental problems in many regions. Further research will be carried out in order to obtain self-reinforced materials with high energy efficiency based on the developed composition of the composition.

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