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Development of composition of fine-grained concrete based on ash-and-slag wastes for additive technology of manufacturing small architectural forms

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Abstract. Developing a fine-grained concrete composition for additive technologies is an important scientific and practical task, since traditional building mixtures are unsuitable for 3D printers, and special solutions are practically absent in mass production. This study aims to develop a composition of fine-grained concrete for additive technologies using local resources and ash and slag waste of the Ust-Kamenogorsk thermal power plant, which contributes to the expansion of the raw material base used in this area. The work was carried out taking into account the analysis of the literature review, which made it possible to identify key aspects and directions in the development of concrete mixtures for additive technologies. This article discusses the possibility of using ash and slag waste in concrete as a filler. Ash has a grain size comparable to river sand, so it can be used as a new material to replace fine filler. To obtain the mixture, 5 experimental mixtures and one reference sample were prepared. The optimal composition is considered to include 30% of M500 Portland cement, 40% of sand, and 30% of ash and slag. The physical and mechanical characteristics of this composition are as follows: the mobility of the mixture is 5.81 cm, and the setting completion time is 4 hours 19 minutes. The results of the sample tests confirmed that the created fine-grained concrete compositions are suitable for extrusion on construction 3D printers. The possibility of creating a composition based on local ash and slag waste for additive technologies used in producing small architectural forms was experimentally confirmed.

Keywords: additive technologies, 3D-printer, ash and slag waste, fine-grained concrete, mixture mobility, extrusion, water retention capacity, adhesion strength of layers, frost resistance.

1. Introduction

The use of additive technologies in the construction industry allows the implementation of architectural projects of any complexity and reduces the amount of industrial waste, the housing shortage, materials, energy, and labor costs for construction. Currently, a wide range of materials is used for additive technologies: various polymers and rubbers, powders of steel, titanium alloys, nickel, aluminum, and copper, as well as tool and structural ceramics, biocompatible and nano-reinforced composites [1].

Cement-based materials that take a long time to harden cannot meet the performance requirements of 3D printing. The composition must have thixotropic properties: reduce viscosity under mechanical impact and restore it at rest [2].

A pressing issue in the design of concrete mixtures is to ensure a set of required material properties using available man-made raw materials. The economic efficiency of using ash and slag waste from coal-fired thermal power plants to produce fine-grained concrete was confirmed by science and practice. In addition, ash and slag waste from thermal power plants is one of the most

common man-made wastes in the country and therefore represents a virtually unlimited and inexpensive local resource. When assessing the suitability and possibility of using ash, special attention should be paid to compliance with the requirements of the interstate standard [3].

In the work [4] it was found that the molding of the studied sand-cement mortar by the extrusion method (3D printing) [5] leads to an increase in the total pore volume by 10%, the volume of open capillary pores by 22%, the volume of conditionally closed pores by 9%, microporosity by 8%, a decrease in the open non-capillary volume by 65% compared to traditional casting samples of similar composition with further compaction. This leads to a decrease in compressive strength by two times compared to the injection molding method with further compaction, and an increase in water absorption by 22%. Based on the results obtained, directions for improving raw mixtures for 3D printing were determined.

Ash and slag are more susceptible to the effects of cyclic wetting and drying than standard aggregates, therefore fine-grained concrete prepared using ash and slag materials exhibits more active water-absorbing properties. For this reason, finished building structures made of fine-grained concrete are coated with special protective solutions that prevent moisture from penetrating into the product and protect it from the effects of external environmental factors [6]. Without special coatings, structures made of ash and slag fine-grained concrete cannot be durable. However, the application of such coatings requires significant labor costs and financial resources.

Control of the properties of concrete mix and hardened concrete is an integral part of the construction process. However, with the use of 3D printing technology in construction, some methods for assessing the properties of concrete mix and concrete will have their characteristics associated with the formation of the structure and properties of concrete mix and concrete under conditions of laying and strength gain in thin layers. The composition of the construction mixture was selected based on the technological requirements of 3D printing equipment and ensuring the required characteristics of the mixture [7]. The paper substantiates the main problems of quality control of concrete when using additive technology, and proposes methods for determining strength characteristics taking into account the features of 3D printing.

This paper [8] presents the results of experiments that allow us to continue developments in the field of optimization of construction mixture compositions in experimental construction using 3D printing. As a result of testing the concrete mixture, it was found that the density is 1940.3 kg/m³, setting time: start - 3 hours 20 minutes, end - 4 hours, mobility by cone immersion, 3.40 mm, strength (28 days): under compression - 30.4 MPa, under bending - 4.7 MPa. The data indicate that the resulting mixture has the necessary rheological properties and optimal setting time and can be used for the construction of buildings and structures using 3D printing.

The research work [9] recommends using standard sand concrete M300 based on Portland cement grade 500 for printing. In the laboratory of the V.S. Gryzlov State University, studies were conducted on the main characteristics of sand concrete M300 (B22.5). Based on these studies, minimum requirements for the properties and characteristics of mixtures for the manufacture of building structures using the additive technology method were determined.

The grain size of fly ash is comparable to river sand, which allows its use as an alternative material to replace fine aggregate. Studies have shown that ash has a porous structure, which can help reduce concrete shrinkage [10], [11]. However, to our knowledge, the use of significant amounts of fly ash and slag as a replacement for both fine and coarse aggregate to produce fine-grained concrete has not been the subject of research. Therefore, this study focuses on the mechanical and physical-technical properties of concrete. Ash and slag waste from the Ust-Kamenogorsk thermal power plant was selected as the material under study.

2. Methods

Development of compositions of construction mixtures for additive technology, research of their properties, and testing were carried out based on recommendations of the relevant standards.

The ash and slag waste of the Ust-Kamenogorsk thermal power plant was used in the study. Ash-and-slag mixture (ASM) for preparation of fine-grained concrete (FGC) should meet the requirements of [3], [12], which were used to study their following properties: grain composition, specific surface area of fine-grained ASM mixture, bulk density, grain density, humidity. The chemical composition of ash and slag was determined according to [13], and the content of free calcium oxide - by [14]. The total specific activity of natural radionuclides in ash and slag was determined by gamma-spectrometric method according to [15].

For the study, the following characteristics of the construction mix and cured fine-grained concrete to be tested were identified:

1. The mobility of the mix;
2. Timing of the beginning and end of the setting of the mix;
3. Compressive strength of the hardened mortar (concrete);
4. Water retention capacity of the mixture;
5. Water absorption.
6. Bond strength of the cured mortar layers;
7. Average density of the hardened concrete;
8. Frost resistance.

Tests of the construction mixture and hardened samples of fine-grained concrete were carried out following [16], [17]. The mobility of the mixture was determined by the slump of the cone molded from the concrete mixture following [18], [19]. The water retention capacity of the mixture was determined by the water content in the sample after testing following the recommendations of [20].

Compressive strength and adhesion strength of hardened samples were determined according to [21], [22]. Compressive strength on standard consistency prism samples of size 160x40x40 mm was determined on a machine to determine the strength according to [23]. The adhesion strength of hardened concrete was assessed by the force of separation of the sample from the base - a concrete slab, applied to the sample through a metal disk with an anchor.

Frost resistance of hardened concrete was determined according to [24], [25]: the number of freeze-thaw cycles - up to 400; samples of 100x100x100 mm were frozen for 2.5 hours at a temperature of minus (18 ± 2) and thawed at a temperature of (20 ± 2). The average density of hardened concrete was determined according to [26] by the accelerated method using a Le Chatelier device.

3. Results and Discussion

The chemical composition of ash and slag wastes from Ust-Kamenogorsk Thermal Power Plant according to the test results is given in Table 1.

Table 1 – Chemical composition of ash and slag

Test	Chemical composition, %								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	SO ₃	Na ₂ O·K ₂ O	Impurities
Ash and slag	51.27	22.49	9.32	2.95	1.69	0.95	0.93	4.67	5.63

The specific effective activity of radionuclides (A_{eff}) was 287.74 Bq/kg (less than 370 Bq/kg), i.e., ash and slag waste according to this indicator can be used to manufacture building structures for any purpose. The fraction of ash and slag particles was 0.63 mm, the bulk density was 1107 kg/m³, i.e., less than the limit of 1200 kg/m³ [3].

Manufacturers of 3D printers [5] and the study [4] recommend using standard sand concrete M300 (B22.5) based on Portland cement M500 for building mixtures. Therefore, for the experiment, a reference sample recommended by manufacturers, and five experimental samples, with part of the sand composition replaced with ash and slag from 10 to 100% were developed (Table 2). The adopted water-cement ratio for sand concrete M300 was 0.37, which is also recommended by [5].

Table 2 – Composition of samples

Sample	Components of the mixture, %		
	Cement	Sand	Ash and slag
Reference	30	70	0
No.1	30	60	10
No.2	30	40	30
No.3	30	20	50
No.4	30	10	70
No.5	30	0	100

The physical and mechanical characteristics of the samples obtained as a result of the tests are given in Table 3.

Table 3 – Physical and mechanical characteristics

Indicators	Unit	Sample					
		Reference	No.1	No.2	No.3	No.4	No.5
Mixture mobility	cm	5.75	5.77	5.81	5.84	5.91	5.94
Beginning of setting	h, min	3.15	3.18	3.18	3.21	3.25	3.27
End of setting	h, min	4.20	4.18	4.19	4.25	4.28	4.32
Normal density	mm	17	17	19	22	23	23
Water retention capacity	%	91.5	91.5	91.7	91.8	92.1	92.3
Compressive strength after 28 days	MPa	31.2	31.2	31.1	30.8	29.4	28.3
Adhesion strength	MPa	3.89	3.87	3.78	3.44	3.12	3.05
Frost resistance	cycles	75	75	76	76	77	77
Average density	kg/m ³	1980	1993	2027	2085	2150	2194
Water absorption	%	4.8	4.82	4.87	4.95	5.01	5.12

The analysis of the data presented in Table 3 allows us to formulate several main conclusions about the influence of ash and slag particles on the physical and mechanical properties of mortar for 3D printing.

The addition of ash and slag increases the mobility of the mixture (Figure 1). This is because ash and slag particles have glazed surfaces, reducing their friction against each other. The glazing of particles explains the reduction in the total viscosity of the mixture containing ash and slag, compared to standard sandcrete, and the increase, although insignificant, of the setting period of concrete (Figure 2).

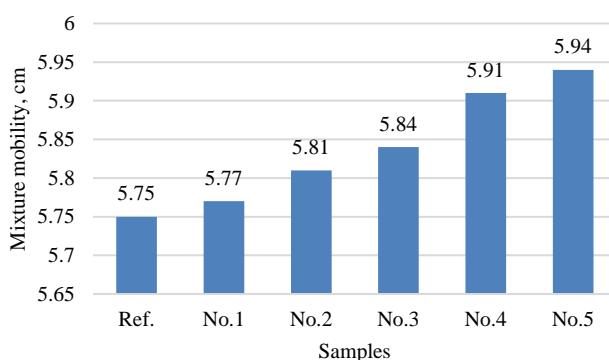


Figure 1 – Mixture mobility

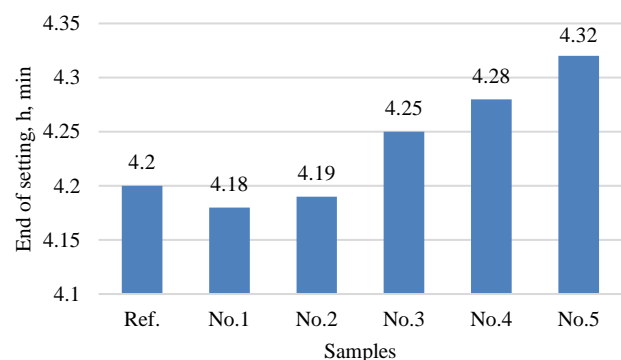


Figure 2 – End of setting time

The normal density of the mixture grows as the share of ash and slag in its composition increases (Figure 3). This phenomenon is probably because ash and slag particles have a small

specific surface area and finer grinding than sand, and therefore more effectively fill the cement pores.

The introduction of ash and slag into the composition of the mixture increases its water retention capacity (Figure 4), while the setting time increases insignificantly. The increase in water retention capacity is due to the fact that water is absorbed on the surface of ash particles. Absorption prevents the movement of water and its escape to the surface, which, in turn, leads to a decrease in water separation and delamination of concrete prepared with the addition of ash and slag, compared to the standard solution [18]. (10) For the same reason the water absorption of concrete increases (Figure 5).

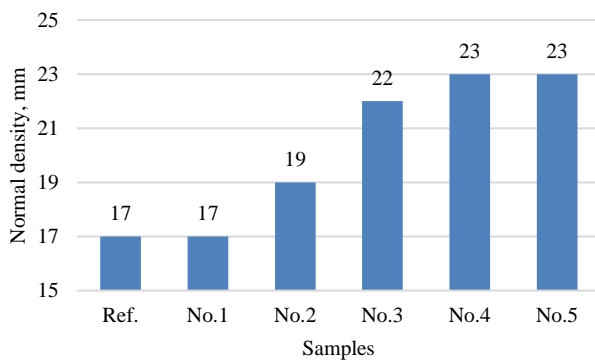


Figure 3 – Normal density

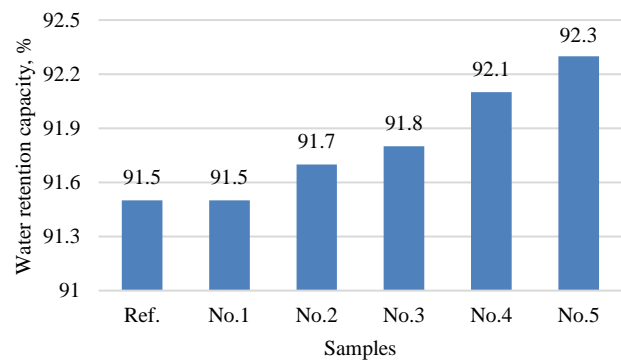


Figure 4 – Water retention capacity

Concerning the strength of modified samples, it can be noted that the addition of ash and slag to the mixture reduces the compressive strength values after 28 days (Figure 6), which is associated with an increase in the volume of water for mixing compared to the standard composition. Thus, in our experiment the water-cement ratio for sandcrete M300 is 0.37, and for ash-and-slag mixtures - in the range from 0.38 to 0.55.

The adhesion strength of layers also decreases with increasing ash-and-slag content in the compositions of experimental samples (Figure 6). Note that for small architectural forms, the reduction of strength values to the obtained values is not critical.

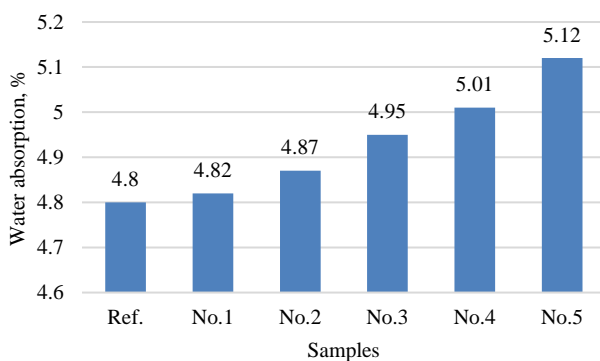


Figure 5 – Water absorption

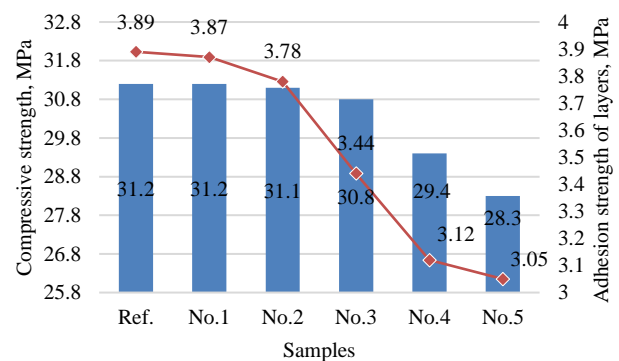


Figure 6 – Strength parameters of samples

Frost resistance of samples at an increase of ash and slag share in their compositions does not undergo significant changes (Figure 7).

The study showed that the introduction of ash and slag into the mixture increases the average density of samples (Figure 8). This phenomenon is due to the smaller specific surface area of ash microspheres compared to sand. The filling of voids between cement particles is denser, which leads to an increase in the average density of hardened concrete. Therefore, the surface of such a product does not contain large pores and will be smoother than a structure made of standard sandcrete.

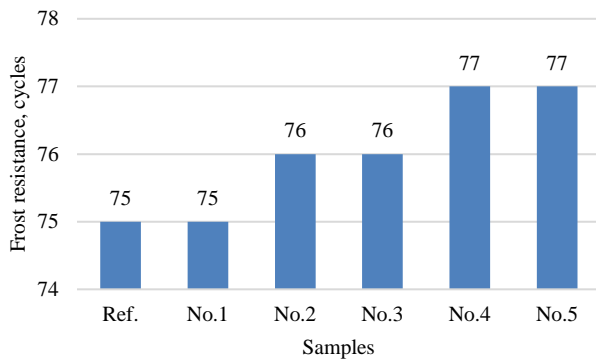


Figure 7 – Frost resistance

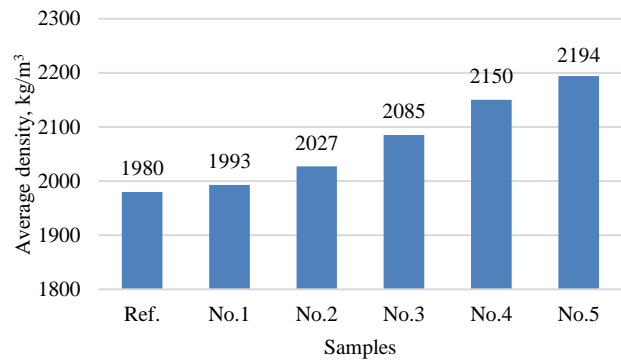


Figure 8 – Average sample density

Comparing the data in Table 3 and Figures 1-8 with the recommended values, we can draw several conclusions about the compliance of the experimental ash-and-slag fine-grained concrete compositions with them:

In terms of compressive strength, all compositions correspond to the recommended value. The highest compressive strength was obtained in the sample with the replacement of 10% of sand with ash and slag. Frost resistance of all samples corresponds to the normative. The highest index of frost resistance (77 cycles) was obtained in the samples in which the replacement of sand with ash and slag was 70% and 100. The water retention capacity of experimental samples corresponds to the recommended values.

Density corresponds to the normative value in samples with sand replacement with ash and slag more than 30%. Normal density is within the recommended values, but, as it seems, the optimal value is close to the value of the reference sample; it is obtained in samples with replacement of sand with ash and slag not more than 30%.

The setting time of experimental samples does not exceed 5 hours and is close to the indicator of the reference sample. Obviously, the shorter the setting time, the more preferable will be the composition of ash-and-slag concrete. The mobility of the mixture does not exceed the limit values, i.e., all compositions are suitable for extrusion.

In the course of the research, considerable attention was paid to the search for the recommended values of the indicators of construction mixtures for additive technology. Analysis of the data available in the special literature [7], [8], etc. allowed us to formulate the requirements to the compositions used for 3D printing of small architectural forms, in particular:

1. Compressive strength - not less than 22.5 MPa;
2. Frost resistance - not less than 70 cycles;
3. Water retention capacity - not less than 90%;
4. Average density - not less than 2000 kg/m³.

With regard to other characteristics (normal density, setting time, mobility of the mixture) it can be noted that in laboratory conditions it is difficult to determine their lower limit. The data of [9], [25], indicate that the normal density should be in the range of 10-25 mm, and mobility by cone immersion should be 5-8 cm. If the indicators do not meet these values, the concrete mixture is not suitable for extrusion.

According to [27], the optimum setting time is 2.5 hours. The termination of the setting should be no more than 5 hours [28], as too long curing will not allow the production of a building structure layer by layer.

Thus, replacing a portion of the sand with ash and slag provides a mixture suitable for use in additive technology for making small architectural shapes. The optimal composition of fine-grained concrete for 3D printing of small architectural forms is a composition containing 30% Portland cement M500, 40% sand, and 30% ash and slag. It should also be noted the high-performance characteristics of fine-grained concrete made with the addition of ash and slag: water resistance, fire resistance, and frost resistance.

4. Conclusions

Based on the results of the study, it is worthwhile to formulate several main conclusions:

Experimentally confirmed the possibility of developing a composition based on ash and slag waste of the Ust-Kamenogorsk Thermal Power Plant for additive technology for the manufacture of small architectural forms;

Tests of prototypes showed that fine-grained concrete compositions suitable for extrusion in a 3D construction printer were obtained;

The optimal composition is 30% Portland cement M500, 40% sand, and 30% ash slag. Physical and mechanical indicators of this composition: mixture mobility - 5.81 cm; setting end time - 4 hours 19 minutes; normal density - 19 mm; water retention capacity (9)- 91.7%; compression strength after 28 days - 31.1 MPa; adhesion strength - 3.78 MPa; frost resistance - 76 cycles; average density - 2027 kg/m³; water absorption - 4.87%.

The disadvantage of ash-slag concretes is their high water-absorbing capacity, therefore, finished building structures made of fine-grained concrete must be covered with special protective solutions that prevent moisture from penetrating inside and thereby increase the durability of the structure.

The main effects of modifying the composition of fine-grained concrete with ash and slag are economic (reducing its cost through the use of affordable and cheap technogenic waste) and environmental (reducing coal ash dumps Thermal Power Plant, which reduces their dangerous and harmful impact on the environment and human health).

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Galiya Rakhimova – concept, methodology.

Monika Kulisz – editing, resources.

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