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ENERGY-EFFICIENT CEMENT-SLAG MIXTURES FOR 3D-PRINTING

ЕНЕРГОЕФЕКТИВНІ ЦЕМЕНТНО-ШЛАКОВІ СУМІШІ ДЛЯ 3D-ДРУКУ

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The article presents a set of experimental-static models of the properties of fine-grained concretes on a cement–slag binder and quartz sand with the addition of a hardening accelerator made on a 3D printer. The influence of the factors of the composition of the mixture and the effects of their interaction on the studied properties of concrete was established. By analyzing the models, the influence of the factors of mixture composition on the studied properties was ranked. The nature and degree of interrelation of individual properties of concrete are shown. The relationships between structural strength and setting time, as well as various strength indicators of concrete produced on a 3D printer, were established for different values of mixture composition factors.
The use of a binder containing 30… 40% of ground-granulated blast-furnace slag and of hardening accelerator–sodium sulfate in the amount of 1…2% by weight of the binder allows obtaining energy-efficient mixtures suitable for 3D printing.

У статті наведено комплекс експериментально-статичних моделей властивостей дрібнозернистих бетонів на основі цементно-шлакового в'яжучого з додаванням прискорювача тверділня, виготовлених на 3D-принтері. Встановлено вплив факторів складу суміші та ефекти їх взаємодії на досліджувані властивості бетонних сумішей та бетону. Проаналізовано вплив факторів складу суміші на досліджувані параметри. Показано характер і ступінь взаємозв'язку окремих властивостей бетону. Встановлено залежності між міцністю конструкції та часом друку, а також різними показниками міцності бетону,

виготовленого на 3D-принтері. Використання в'яжучого, що містить 30…40% меленого гранульованого доменного шлаку та прискорювача твердіння – сульфату натрію в кількості 1…2% від маси в'яжучого дозволяє отримати енерго-ефективні суміші, придатні для 3D-друку.

Keywords:
Portlandcement, blast furnace slag, 3D construction printer, additive technologies, superplasticizer, hardening accelerator.
Портландцемент, доменний гранульований шлак, 3D будівельний принтер, адитивні технології, суперпластифікатор, прискорювач твердіння.

Introduction. The development of new technologies in the construction industry in the near future will make it possible to fundamentally change the views and approaches to the traditional methods of erecting buildings and structures, as well as solve a number of environmental and economic problems. The most urgent problems include reducing the cost and impact on the environment and increasing the speed of construction without losing quality. A rational solution to these problems is using the additive method construction of buildings and structures. This technology involves using a special 3D printer to apply a plastic concrete mixture layer by layer and building the walls by extrusion.

State of the issue and research objectives. 3D printers allow using extrusion molding of structures to provide high-speed robotic construction of objects, including complex shapes, with minimized consumption of materials [1-3].

Most often, fine-grained concrete mixtures with the required strength, frost resistance, high adhesion and cohesion properties and curing speed are used for this purpose [4].

At the present stage of construction development in Europe, the introduction of resource-saving technologies while ensuring high-quality building materials and structures is relevant. Structures based on Portland cement, which in turn is the most energy-intensive component of concrete and mortar, are widely used in construction, so it is advisable to develop technologies that significantly reduce its usage while maintaining or improving the quality of concrete and mortar. One such direction is the wide application in construction practice of composite cements, in which a significant part of the clinker is replaced by active mineral additives of man-made origin, in particular blast furnace granulated slag [5, 6].

The actual problem in the design of concrete mixes is to provide a set of necessary material properties while using available man-made raw materials. When using 3D printing, they must ensure normal extrusion of the mixture by the printer's printhead, the necessary structural strength sufficient for laying the subsequent layers, and the adhesive strength for reliable bonding of the layers to each other [7]. As a result of curing, the mixture should achieve the necessary design parameters established for concrete [4].

For additive manufacturing of building elements, it is important to use suitable materials that are low-energy-intensive and thus have a lower carbon footprint [8]. It remains a topical direction of using in additive technology such an active mineral additive in cement mixtures as granulated blast-furnace slag, produced in large quantities by the metallurgical industry [9]. As many studies and practical experience have shown, this material remains one of the most effective in composition with Portland cement.

Blast-furnace slag not only interacts with calcium hydroxide and promotes the formation of an additional amount of hydrosilicates in the cement stone, it also increases the carbonization coefficient of cement concretes and mortars, which has a positive environmental impact on the environment [9].

Compositions of building mixtures including granulated blast-furnace slag and providing a set of necessary properties for 3D printing cannot be considered sufficiently developed.

The aim of this work was to determine the effect of the composition of fine-grained concrete for 3D printing on a cement–slag binder. The main tasks of the work were to obtain mathematical models of the properties of fine-grained concrete based on cement–slag binder and, on their basis, analyze the effects of technological factors..

Materials and Methods of Research

Concrete mixes for 3D printer should provide their necessary formability during extrusion from the printer's head to achieve a given strength of layers (structural strength), as well as the adhesion ability of concrete with an acceptable setting time of the mixture without cracks and other defects.

In order to study the properties of extruded mixtures, a laboratory printer was designed and constructed [4]

To obtain the mixtures, the used materials were Portland cement CEM I 42,5R (EN 197-1), ground-granulated blast-furnace slag. Quartz sand with fineness modulus 2.1 was used as an aggregate. The hardening accelerator Na_2SO_4 and the naphthalene-formaldehyde superplasticizer SP-1 were added to the mixtures. Preliminary experiments on a laboratory printer found that the optimal content of superplasticizer is 0.3% of the mass of cement–slag binder. A further increase in its content leads to a decrease in the structural strength of the mixture and, accordingly, the need to increase the duration of layer-by-layer molding. The chemical composition of Portland cement and granulated blast-furnace slag are given in Table 1. The mineralogical composition of the clinker was as follows: C_3S—57.10%; C_2S—21.27%; C_3A—6.87%; C_4AF—12.19%. The specific surface area of Portland cement was S = 300–320 m^2/kg (EN 196-6). The quality factor of blast-furnace granulated slag is determined by the ratio:

$$K_a = \frac{CaO + Al_2O_3}{SiO_2 + TiO_2} \quad (1)$$

It fluctuates for slag of most cereals at metallurgical enterprises in the range of 1.2…1.7. The used slag according to the value of K_a, which determines the hydraulic activity, can be considered ordinary. For this, the value of K_a = 1.35.

The content of the glass phase in the slag was 75 – 80%, its specific surface S = 320 - 350 m^2/kg (EN 196-6), density - 2.9 g/cm^3, bulk density - 1340 kg/m^3, intergranular voidness - 45.9%, intragranular porosity - 15.5%.

Table 1

Chemical composition of raw materials*

Material	L.O.I.	Oxide content, %							
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	TiO_2
Clinker	-	21.80	5.32	4.11	66.80	0.95	0.63	0.42	-
Blast-furnace slag	0.59	39.51	6.47	0.14	47.19	3.12	1.76	-	0.25

* The chemical composition of Portland cement based on the used clinker was distinguished by an additional SO_3 content due to the introduction of gypsum in the amount of 3.1%.

Results and Discussion

In order to select the optimal parameters of the mixture composition, algorithmic experiments were performed in accordance with the typical plan B_3 [10]. Plan B_3 is a statistically valid three-level plan of experiments that provides for the need to test 17 series of samples while varying the studied factors within the established range, with the subsequent calculation of the coefficients of the regression equations for the studied parameters and a statistical assessment of their adequacy. The planning conditions for the experiments are given in Table 2.

Table 2

Experiment planning conditions.

Technological Factors		Levels of Variation			Variation interval
natural view	coded	–1	0	+ 1	
Content of granulated blast furnace slag in the binder mixture (GBFS), %	X_1	50	40	30	-10
Na_2SO_4 hardening accelerator additive content (HA), % of the binder mass	X_2	0	1	2	1
Cement–slag binder content, kg/m^3, (Bnd)	X_3	300	400	500	100

The water consumption was varied to achieve the required workability by the standard cone slump method (8–10 cm), ensuring sufficient formability (extrusiveness) of the mixture. The suitability of mixtures for molding was determined by the time from the moment of mixing to the beginning of setting, at which it becomes impossible to further mold by the 3D printer.

After the processing and statistical analysis [19] of the experimental data given in Table 3, the regression equations which are shown in Table 4 were obtained, which can be regarded as mathematical models of the properties of the extruded concrete mixture and concrete on its basis.

Table 3

Experimental research results

№	Setting time, min	Structural strength after mixing and yardening, Pa			Tensile splitting strength, MPa		Compressive strength, MPa	
		10 min	25 min	40 min	3 days	28 days	3 days	28 days
1	35	5320	8513	15,160	6.6	9.3	19.7	32.7
2	60	3780	5679	10,700	4.5	6.7	10.8	21.2
3	85	3916	5482	9225	5.7	8.1	16.9	27.6
4	145	2730	4096	7000	3.9	6.1	7.8	19.5
5	70	4600	6916	12,300	4.9	6.6	13.8	19.4
6	95	3356	5034	9125	4.1	5	8.8	13.4
7	120	3426	5139	7480	4.4	6.1	13.1	17.1
8	160	2521	3781	6545	3.5	4.8	7.8	9.4
9	55	3637	5455	9375	4.3	7.7	12.9	21.7
10	85	3177	4765	7710	3.6	5.1	10.6	16.4
11	50	4020	6030	11,230	4.7	6.5	12	20.5
12	120	2900	4350	6970	4.0	6.5	12.7	18.5

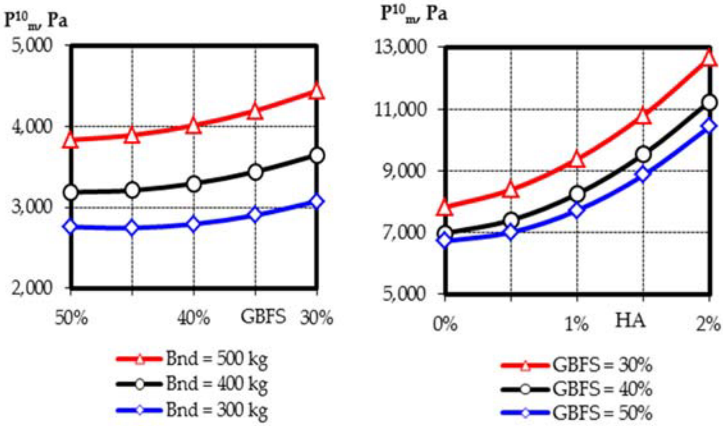
Table 4

Mathematical models of the properties of concrete mixture and concrete

Parameters	Mathematical Models	
Setting time, min	$T = 66{,}4 - 15{,}0 \cdot x_1 - 32{,}0 \cdot x_2 - 19{,}5 \cdot x_3 + 4{,}1 \cdot x_1^2 + 19{,}1 \cdot x_2^2 + 6{,}6 \cdot x_3^2 - 2{,}5 \cdot x_1x_2 - 2{,}5 \cdot x_1x_3 + 6{,}3 \cdot x_2x_3$	(1)
Structural strength after 10 min, Pa	$P^{10}_m = 3295 + 230 \cdot x_1 + 558 \cdot x_2 + 610 \cdot x_3 + 124 \cdot x_1^2 + 177 \cdot x_2^2 + 108 \cdot x_3^2 + 55 \cdot x_1x_2 + 72 \cdot x_1x_3 + 87 \cdot x_2x_3$	(2)
Structural strength after 25 min, Pa	$P^{25}_m = 4938 + 359 \cdot x_1 + 932 \cdot x_2 + 193 \cdot x_3 + 273 \cdot x_1^2 + 171\ x_2^2 \cdot x_3^2 + \cdot 198 \cdot x_1x_2 \cdot + 123 \cdot x_1x_3 + 247 \cdot x_2x_3$	(3)
Structural strength after 40 min, Pa	$P^{40}_m = 8258 + 830 \cdot x_1 + 2130 \cdot x_2 + 1350 \cdot x_3 + 296 \cdot x_1^2 + 853 \cdot x_2^2 + 283 \cdot x_3^2 + 280 \cdot x_1x_2 + 322 \cdot x_1x_3 + 560 \cdot x_2x_3$	(4)
Compressive strength at the age of 3 days, MPa	$f3_{cm} = 11{,}66 + 1{,}4 \cdot x_1 + 0{,}68 \cdot x_2 + 3{,}67 \cdot x_3 - 0{,}537 \cdot x_1^2 + 0{,}063 \cdot x_2^2 + 1{,}313 \cdot x_3^2 + 0{,}513 \cdot x_1x_2 + 0{,}963 \cdot x_1x_3 - 0{,}062 \cdot x_2x_3$	(5)
Splitting tensile strength at the age of 28 days MPa	$f^{28}_{tn} = 6{,}89 + 1{,}03 \cdot x_1 + 0{,}25 \cdot x_2 + 1{,}1 \cdot x_3 - 0{,}328 \cdot x_1^2 - 0{,}228 \cdot x_2^2 + 0{,}222 \cdot x_3^2 + 0{,}138 \cdot x_1x_2 + 0{,}213 \cdot x_1x_3 + 0{,}113 \cdot x_2x_3$	(6)
Compressive strength at the age of 28 days MPa	$f^{28}_{cm} = 20{,}74 + 4{,}7 \cdot x_1 + 1{,}51 \cdot x_2 + 4{,}88 \cdot x_3 - 1{,}01 \cdot x_1^2 - 0{,}56 \cdot x_2^2 + 0{,}69 \cdot x_3^2 + 0{,}06 \cdot x_1x_2 + 0{,}74 \cdot x_1x_3 + 0{,}21 \cdot x_2x_3$	(7)

Mathematical models allow quantitatively estimating the influence of varying factors (Figures 1 and 2), taking into account their possible interaction, on the studied properties, and to arrange them according to the degree of influence:

Setting time	HA > Bnd > GBFS
Structural strength after 10 min of curing	Bnd > HA > GBFS
Structural strength after 25 min of curing	HA > Bnd > GBFS
Structural strength after 40 min of curing	HA > Bnd > GBFS
Compressive strength at the age of 3 days	Bnd > GBFS > HA
Splitting tensile strength at the age of 28 days	Bnd > GBFS >> HA
Compressive strength at the age of 28 days	Bnd > GBFS >> HA



(a) (b)

Figure 1. Graphical dependences of structural strength (P) after 10 min (a) and 40 min (b) of mixture curing.

The structural strength of mixtures for 3D concreting based on blast-furnace granulated slag (GBFS) increases with increasing amount of binder, the minimum proportion of GBFS in the binder (30%) and the use of the maximum amount, within the composition's research hardening-accelerator additive (Figure 1). It should be noted that a more significant effect of the accelerator additive is observed also when the proportion of GBFS in the binder is minimal.

The analysis of the models (Table 4) shows that in the range of variation in the studied factors the compressive strength of 3D-printing concrete containing GBFS and hardening accelerator additive varies within 9.4–32.7 MPa. According to the obtained graphic dependences (Figure 2) with decreasing the proportion of GBFS from 50% to 40% of the binder and a gradual increase of the content of the binder from 300 kg/m3 to 500 kg/m3, it is observed an increase in compressive strength by 35–40% at the content of GBFS 40–50% and by 15–20% at the minimum slag content. The figures 2 show that the effect of hardening accelerator addition is also positive, which is more significantly manifested at the maximum binder content.

A joint analysis of the obtained mathematical models made it possible to establish their relationship Figures 3 and 4.

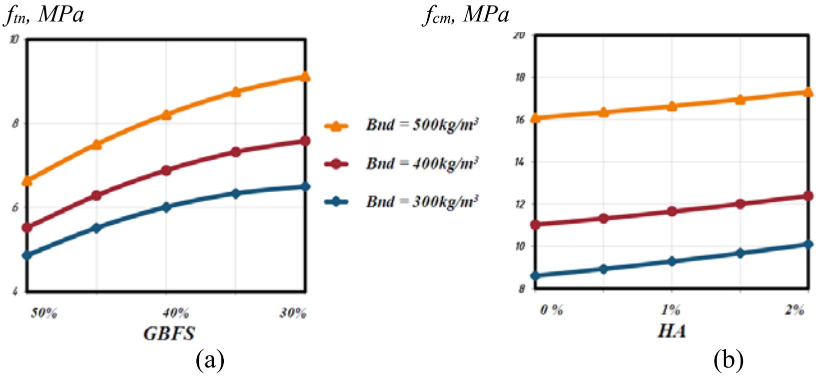


Figure 2. Graphical dependences of the compressive strength of concrete mixtures at the age of 3 days (a) and 28 days (b).

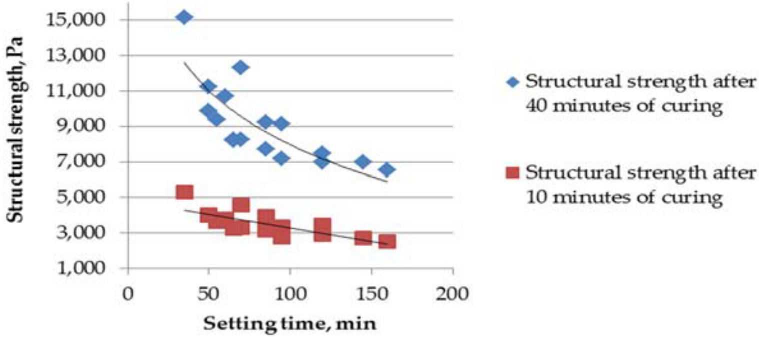


Figure 3. Relationship between setting time and structural strength of concrete.

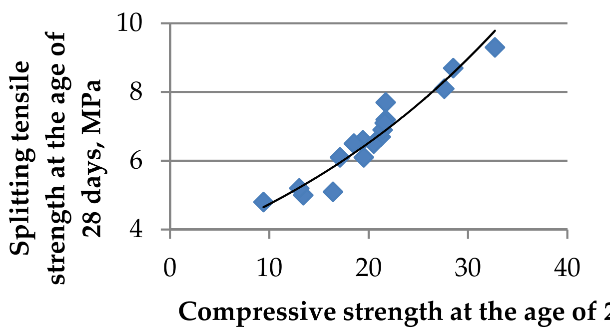


Figure 4. Relationships of tensile strength when splitting to compressive strength at the age of 28 days.

The complex of obtained models allows designing compositions of concrete mixtures intended for 3D printing, allowing obtaining the specified indicators of their properties

Conclusions.

A set of mathematical models describing the effect of composition factors on the most important for 3D printing properties of fine-grained concrete mixture and concrete on cement–slag binder in the presence of hardening accelerator additive was obtained by using mathematical planning of experiments.

As a result of the analysis of the obtained models, the nature and quantitative estimates of the mutual influence of concrete composition factors on the studied properties were established. Composition factors were ranked depending on the intensity of their influence.

The relationships between structural strength and setting time, as well as various strength indicators of concrete produced on a 3D printer, were established for different values of mixture composition factors.

The use of a binder containing 30… 40% of ground-granulated blast-furnace slag and of hardening accelerator–sodium sulfate in the amount of 1…2% by weight of the binder allows obtaining mixtures suitable for 3D printing.

An increase in the slag content of more than 40% is accompanied by a slight increase in the water consumption of the mixture to ensure the required extrusion possibility and a decrease in strength.

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