The use of finely ground slag in portland cement with mineral additives

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Abstract. The method of introducing of finely ground granulated blast furnace slag (GBFS) in the composition of the cement as a result of dry mixing of the material with the additive is considered. The aim of the research was to study the effect of the addition of finely ground slag on the construction, technical, physical, mechanical, and structural characteristics of cement with mineral additives. The setting time was studied, the normal density of the cement paste with the addition of finely ground slag was determined. The dependences of the strength and porosity of the cement stone on the time of hydration of samples are built. The strength of the cement was determined by the national standard GOST 30744-2001. The porosity of the cement stone was determined by saturating the samples with an inert liquid. It has been established that the introduction of 3–5% of slag 1 and 1–3% of slag 2 provides an increase in the strength of cement stone during the first days of hardening on average by 37–44%; at the grade age - by 26–30%, decrease in porosity — by 17–28%. It is shown that the introduction of finely ground slag additives compacts and strengthens the structure of the cement stone. It has been established that grinding GBFS to a size of 1 μm (slag 1) is impractical because the obtained research results are comparable with the results when slag 2 is introduced into the cement composition.

1 Introduction

In the production of metallurgical products, slags are formed in large quantities, which occupy significant land areas and pollute the natural resources of the country with toxic compounds. To improve the environmental situation, waste products are recycled and disposed. One of the methods of metallurgical slag processing is the use of it as secondary raw material in the production of building materials.

A lot of works are devoted to the use of slag in the construction industry. The pioneers in this field in Russia are N.A. Belelyubsky, N.N. Lyamin, S.I. Druzhinin, and A.A. Baikov, who conducted a series of studies of blast furnace slag and organized the production of lime-slag cement and slag Portland cement in our country at the end of the XIX century [1-3].

Despite a number of advantages (low-grade heat, increased corrosion and heat resistance, etc.), slag cements did not receive widespread use in civil engineering, which is

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associated with a slow build-up of strength in the initial periods of hardening. Already in the early 80s of the 20th century, the problem of saving energy and natural resources in the construction industry arose, which has now increased even more, leading to a reassessment and revision of attitudes towards the use of slags in the production of building materials. Scientists have conducted studies to develop ways to improve slag cements, cement and other binding compositions containing slag [4-22].

One of the ways to increase the activity of the slag is thermal activation, which consists in the combination of abrupt heating of the source material with a relatively short isothermal exposure resulting in rapid cooling of the slag [4-6].

The authors [7] found that the use of two-stage grinding of slag Portland cement (SPC) provides an increase in the strength of concrete in all periods of hardening. In paper [8], it was noted that the use of heat and moisture treatment for hardening of concrete of slag Portland cement allows increasing the strength of concrete for axial stretching and bending up to 50% and increasing the frost resistance of concrete twice. Another way to solve the problem of slow gain in strength of SPC is to use hardening accelerators, complex additives and superplasticizers [9-11]. Thus, in paper [9], electrolytes were used as accelerators for the hardening of slag Portland cement, in particular, the system of additives “Relaksol-Leader”, based on a man-made mixture of rhodanide and sodium thiosulfate, which makes it possible to increase the strength of SPC by 50 - 88%.

For the production of concrete of various functional purposes and composite materials, steel-smelting slags have recently been used. In the works [12-15], the results of studies of the properties of steel-smelting slags and their use in the production of building materials are presented. For the production of special types of cement and concrete based on them, alumina slags are used. The authors [16-19] found that the use of mineralizers, the choice of cooling mode, optimization of the dispersion of slag contribute to the management of its properties and the production of cements with enhanced performance characteristics.

In works [7, 11, 17, 18-24], the positive effect of slag fineness on the properties of the studied cements was noted, which allows us to consider it as a reinforcing component of the cement matrix. In this regard, the goals and objectives of the study were formulated, which are: to obtain finely ground slag of different dispersity and to study its effect on the properties of Portland cement with mineral additives. Studies of the effect of this slag on the properties of additive-free Portland cement and SPC were carried out earlier and are presented in [22-24].

2 Experimental

In this paper, granulated blast furnace slag subjected to grinding in a laboratory jet mill LHL-1 with restriction of the upper grinding limits to 1 and 20 μm particle sizes (slag 1 and slag 2, respectively) and Portland cement with mineral additives were used as the object of study. Portland cement was obtained by joint grinding in a laboratory ball mill of 85% of clinker, 15% of GBFS (particle size - 40-60 μm), and 5% of natural gypsum to residue on a sieve of R008 = 6%.

The characteristics of granulated blast furnace slag, including chemical and phase compositions, slag quality factor and modulus of basicity, are listed in Table 1. The particle size composition of finely ground slag (FGS) is presented in Table 2, 3, from which it follows that the prevailing sizes of slags 1 and 2 are 0.5 - 1 μm and 1 - 7 μm, respectively. The chemical and mineralogical composition of clinker is presented in Table 4.

Table 1. Characteristics of granulated blast furnace slag.

Chemical composition of slag, %						Phase composition of slag, %		Slag quality factor Kq	Modulus of basicity Mb
CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3+ FeO	Others	Glass	Crystalline phase		
45.40	38.20	8.10	3.20	0.80	4.30	93.20	6.80	1.45	1.1

Table 2. Particle size composition of slag 1.

Particle size, μm	0-0.5	0.5-1.0	1.0-1.5	1.5-2.0	2.0-3.0	3.0-4.0	4.0-5.0
Content of fractions, wt.%	8.21	30.44	23.35	17.20	11.77	5.89	3.14

Table 3. Particle size composition of slag 2.

Particle size, μm	0-1.0	1.0-5.0	5.0-7.0	7.0-10.0	10.0-15.0	15.0-20.0	20.0-30.0
Content of fractions, wt.%	9.00	37.00	17.00	14.00	10.00	8.00	5.00

Table 4. Chemical and mineralogical composition of clinker.

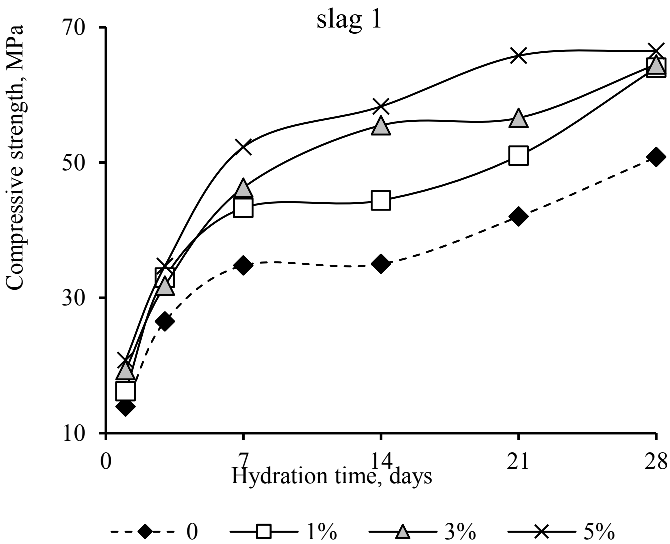
Chemical composition of clinker (%)		Mineralogical composition of clinker (%)	
CaO	62.75	Alit	60
SiO_2	20.10		
Al_2O_3	4.56	Belit	12
Fe_2O_3	8.72		
MgO	1.99	Tricalcium aluminate	3
SO_3	0.57	Calcium aluminoferrite	21
R_2O	1.58		

Finely ground slag was introduced into Portland cement with mineral additives by dry mixing the additive with cement in amounts of 1%, 3%, 5% of the cement content. The cement samples for research were prepared by mixing the resulting mixtures with water. Determination of construction, technical, physical and mechanical characteristics of the samples was carried out according to the national standard GOST 30744-2001. The porosity of the cement stone was determined by saturating the samples with an inert liquid.

3 Evaluation

To establish the effect of finely ground slag (slag 1, slag 2) on the properties of Portland cement with mineral additives, studies of the normal density and setting time of cement paste, testing of compressive strength, determination of the degree of hydration and porosity of samples were carried out. Construction and technical properties of the samples are presented in Table 5. The results of the study of the water-cement ratio of the samples showed that the introduction of slag 1 in cement did not affect the water demand of the cement paste, the introduction of slag 2 led to an increase in its water demand to 4%. An analysis of the setting time of cement paste showed that the introduction of finely ground slags into cement leads to a slower setting time. Slower setting of the specimens is observed during the initial setting period. It is also noted that the process of setting slows down with increasing dispersion and the number of additives introduced.

The effect of finely ground slag on the strength of cement stone is shown in Fig. 1.



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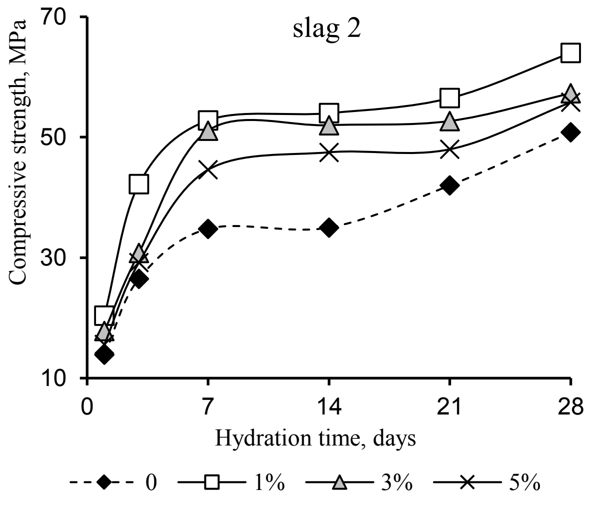

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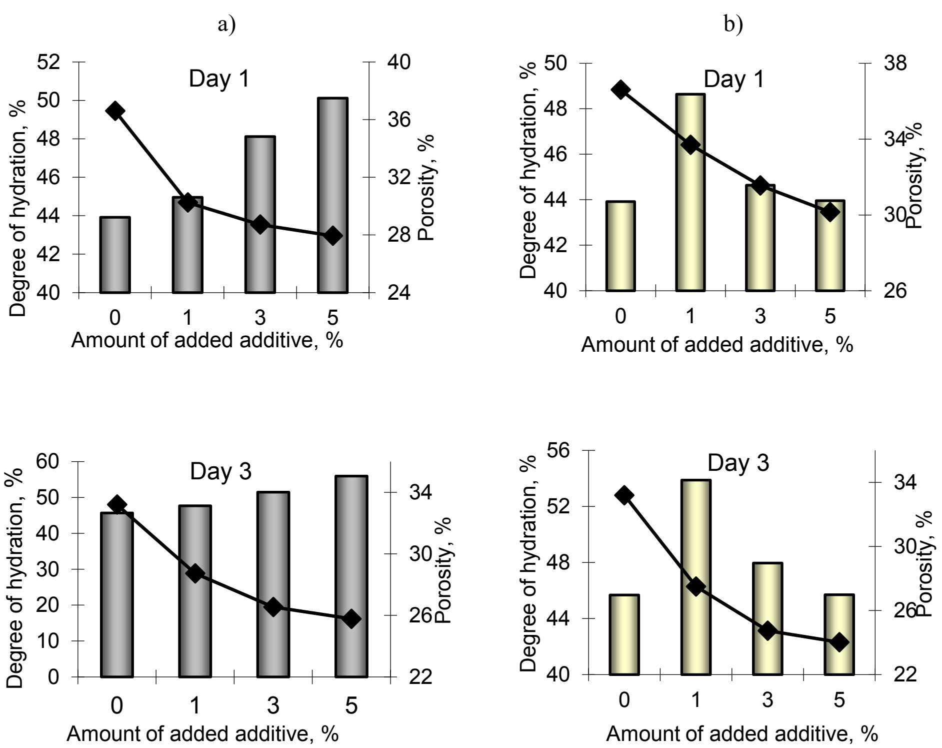
Fig. 1. The effect of finely ground slag on the strength of samples based on Portland cement with mineral additives: a) slag 1; b) slag 2.

It is established that the introduction of finely ground slag increases the strength of samples during all periods of hardening. The greatest increase in samples is provided by the introduction of 3–5% of slag 1 and 1–3% of slag 2. For the first day of hardening, the strength of samples containing 3–5% of slag 1 increased on average by 44%; 1 - 3% of slag 2 - by 37%. At the grade age, there is an increase in the strength of samples in the above limits by 30 and 26%, respectively.

Table 5. Construction and technical properties of cement paste.

Type of additive	Additive content, %	Normal density, %	Setting time of cement paste, h-min		Slowing down the cement paste setting process, %	
			Beginning	End	Beginning	End
without additive	-	25.00	2-40	4-20	-	-
slag 1	1	25.00	3-05	4-35	16	6
	3	25.00	3-15	4-45	22	10
	5	25.00	3-35	4-55	34	13
slag 2	1	25.50	3-10	4-40	19	8
	3	25.50	3-20	4-55	25	13
	5	26.00	3-40	5-25	38	25

The positive role of ground slag was noted in the formation of the structure of cement stone, as evidenced by the decrease in the porosity of samples with an increase in the degree of hydration of the cement stone (Fig. 2).



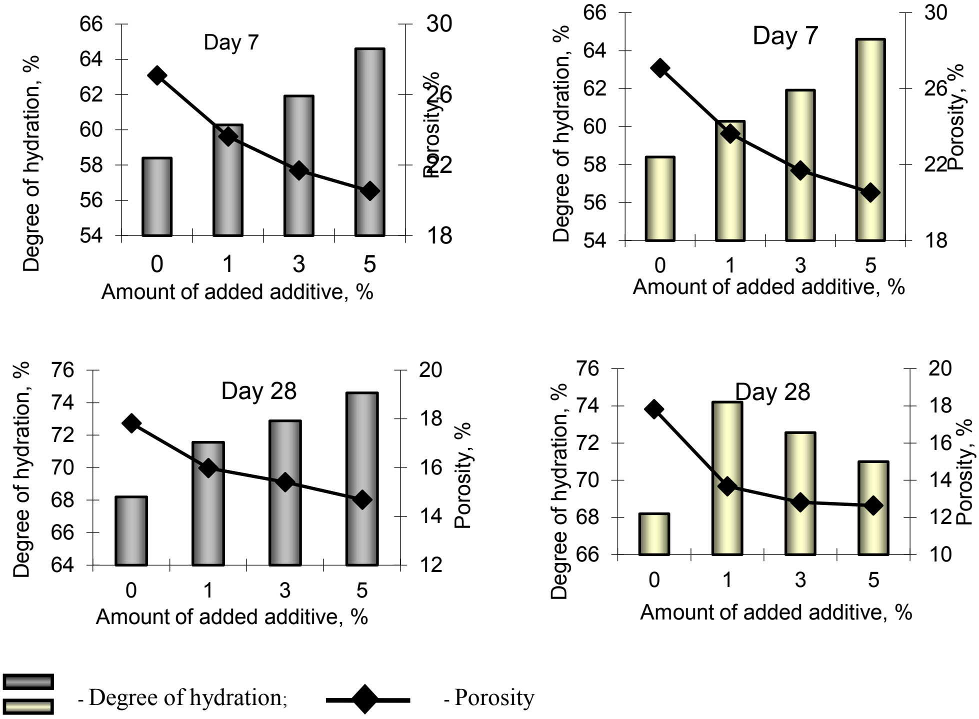


Fig. 2. Degree of hydration and porosity of samples at the 1, 3, 7, and 28 days of hardening: a) slag 1; b) slag 2.

An increase in the degree of hydration and a decrease in porosity in the structure of cement stone are noted in the samples from the very first day of hardening. For samples containing slag 1 in amount of 3–5%, the degree of hydration during the first days of hardening increased on average by 9–14%; for samples containing slag 2 in amount of 1–3%, by 2–9%. At the same time, the porosity decreased by 17 - 24 and 8 - 18%, respectively. The hydration process is most intense in samples with slag 1. In samples containing 3–5% of slag 2, the hydration process proceeds less intensively. This is due to the lack of calcium hydroxide formation necessary for the activation of slag grains. Thus, slag 2 within these limits dilutes the original cement system.

In the subsequent periods of hardening, an increase in the degree of hydration and a decrease in porosity in the structure of the cement stone are also noted. At 28 days of hardening, the degree of hydration in samples with slags 1 and 2 is 6–9%; cement stone porosity decreased by 10–18% and 23–29%, respectively.

The research results allowed concluding that finely ground slag is distributed in the cement matrix as centers of directional crystallization, contributing to the reinforcement of the hardening system. New crystalline hydrate formations are formed, ensuring the consolidation of the cement frame and the strengthening of the hardening system as a whole. It is noted that slag 2 contributes to the formation of a more dense structure of cement stone.

The composition of slag 2 is polyfractional (Table 3). Thus, thinner fractions ensure the formation of a large number of crystallization centers; “larger” fractions, filling the space between hydrating cement particles, provide good adhesion between them and compaction of the cement stone structure, which is consistent with the results of work [26]. It was also found that for the other characteristics, samples with slag 2 are slightly inferior to samples with slag 1. This eliminates the use of slag 1 as a part of Portland cement with mineral additives, thereby excluding additional energy costs for its ultrafine grinding.

4 Conclusions

1. When grinding GBFS in a laboratory jet mill, finely ground slags are obtained (slag1 and slag 2). The study of the granulometric composition of slags showed that particles with sizes of 0.5 - 1 μm dominate in slag 1; in slag 2 - particles with sizes of 1 - 7 μm.
2. In determining the construction and technical properties of cements with finely ground slags, it was established that the introduction of slags into the cement composition leads to a slower setting time, especially in the initial period, while the setting process slows down with an increase in the dispersion and the amount of the added additive. It was also found that the introduction of slag 1 does not affect the water demand of the cement paste, the introduction of slag 2 increases its water demand by up to 4%.
3. In the study of the physical and mechanical properties of cements with finely ground slags, it was established that the introduction of slags increases the strength of the samples during all periods of hardening. The greatest increase in the strength of the samples is provided by the introduction of 3–5% slag 1 and 1–3% of slag 2. During the first days of hardening, the strength of the samples increased by an average of 37–44%, at the grade age by 26–30%.
4. In the study of the structural characteristics of cement stone with the addition of finely ground slag, a decrease in the porosity of the samples during all periods of hardening is noted. At the grade age, the average porosity decreased by 17–28%.
5. Studies of the characteristics of samples with slags showed that finely ground slag is distributed in the cement matrix as centers of directional crystallization, forming new growths contributing to the formation of a more dense and durable structure of the cement stone.
6. It has been established that the results of studies of samples with slag 1 and 2 additives are comparable, which makes it possible to abandon the use of slag 1 as a part of Portland cement with mineral additives, thereby eliminating additional energy costs for its ultrafine grinding. The recommended amount of slag additive 2 in the composition of Portland cement with mineral additives is 1 - 3% of the cement content.

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