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The Properties of Slag Cement and Its Influence on the Structure of the Hardened Cement Paste

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Abstract

A ground blast-furnace granulated slag used in the production of construction materials and items differs in its chemical composition, dispersion, the quantity of amorphous phase and so on, which leads to the change of properties of the blended cement consisted of CEM I and supplemented with different amount of slag. The chemical and mineralogical composition of portland cement, the conditions of its maturing, activators and others also influence on the properties of the blended cement. The acid slag is not binding in contrast to the basic one, but due to the pozzolanic properties it interacts with the calcium hydroxide to form an additional amount of a low-basic hydrated calcium silicate in a hardened cement paste structure. The strength of the blended cement with increasing dosages of slag varies in different ways - small amount of slag in the cement even increases slightly the compressive and flexural strength in comparison with the blended cement without an additional CEM I. Increasing the dosage of slag in the blended cement, its compressive strength decreases slightly, especially at an early stage, and the flexural strength remains at the same level by increasing the dosage up to 70-80% of blended cement slag mass. Besides the CEM I dilution effect, the increase of the mixture water demand with the increased slag dosage influences the strength of mortar samples of equally and easily workable mixtures. A true water-binder ratio is increased significantly if the content of slag is over 70%.
The conducted studies have shown that the substitution of CEM I with 70% of slag is optimal both from the perspective of the impact on the technical characteristics of the resulting rock and from the economic point of view.
The rock structure obtained from the blended cement differs in terms of high concentration of amorphized low-basic hydration products and the decrease in its content of $Ca(OH)_2$. The last is proportional to the number of slag additive and affects significantly the phase composition of the rock and its properties.

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Keywords: ground blast-furnace granulated slag; portland cement; water demand; setting time; compression strength; portlandite.

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1. Introduction

When using the blast-furnace granulated slag (BFGS) as an independent binding medium or together with a portland cement it is necessary to know its phase composition and activity. The major part of BFGS, especially in the Ural region, is represented thinly by the main and acid slags, wherein the quantity of glass in these glasses fluctuates anywhere from 80 to 95% [1]. Crystalline slag phase may consist mainly of hydraulic medium and low-active minerals: melilite ($Ca_2(Al,Mg)Si_2O_7$), gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$), merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$), akermanite ($2CaO{\cdot}MgO{\cdot}2SiO_2$) and monticellite ($CaO{\cdot}MgO{\cdot}SiO_2$) of different degree of crystallinity.

Acid slags have no hydraulic activity and the glass is a pozzolanic component which reacts with the free $Ca(OH)_2$ and other alkaline components [2]. To activate slags the following components are used: fluid glass (usually sodium); alkalies Na_2O, $Na(OH)_2$; alkali salts Na_2CO_3, $NaSO_4$ and others [3-4]. The most effective is a binding medium "CEM I + BFGS", especially when it is used in the production of massive and corrosion-resistant materials, products and structures.

It is known that the hydration of portland cement (PC) in a blended cement is activated by the slag supplying $Ca(OH)_2$ in the fluid phase, which in turn is an activator for slag component [5, 6]. To apply the blast-furnace granulated slag as a binding component, it requires being ground up. According to various sources [3, 7] the slags are ground to the specific surface of 250 ... 400 m^2/kg or more. In accordance with GOST-10178-85 (All-Union State Standard) the slags should have a dispersive capacity of not less than 280 m^2/kg, but overgrinding, affecting favorably the slag activity, increases its water demand [8, 9]. Consequently, for BFGS of different enterprises, in each case, it is necessary to determine the optimum slag dispersive capability, providing the required water demand and activity.

It is believed that in construction the use of binders CEM III with 40% or 60% of slag additive to the mass of the binder is the most efficient [1, 10]. However, to clarify the influence of slags with different chemical composition on the properties of blended cement more research is needed.

Many researchers [11, 12] assert that in the process of hydration and maturing of the blended cement, compared with CEM I, the heat generation is greatly reduced, which allows using such cements in the manufacture of concretes for massive structures to prevent the occurrence of thermal cracks in the products. Hardened cement paste made of CEM III is capable of self-healing and slump reduction [13]. Besides, when the superplasticizers are used, the concretes made of CEM III are distinguished by high resistance to the action of sulfates, chlorides and other corrosive to CEM I mediums, including to the carbonization [14].

Consequently, the blast-furnace granulated slags added into CEM I within precisely defined quantities allow getting effective concretes with high technical characteristics under optimal dispersive capability.

2. Research and objectives

The aim of the conducted research is the identification of the influence of blast-furnace granulated slag of the Chelyabinsk Metallurgical Plant on the properties of blended cement and the structure of received hardened cement paste.

Objectives:

- to determine the effect of different dosages of BFGS on the properties of binder;
- to identify the influence of different ratios of CEM I/BFGS on strength properties of samples made of standard mortars at different stages and depending on the conditions of maturing;
- to assess the influence of additives of different amounts of BFGS on the phase composition and the rock structural features of blended cement.

3. Research materials and methods

In order to conduct the research a blast-furnace granulated slag of the Chelyabinsk Metallurgical Plant (CMP) was used. According to its chemical composition, this slag refers to those which are acid low-active and low-maturing without activators both at room temperature in the air or in water and after thermal treatment.

According to the data of X-ray phase analysis, the slag is in amorphized condition, which is proved by the presence of up to 90% of glass phase in the slag. Besides, the slag contains gehlenite with d/n=3,06; 2,85; 2,72; 2,43; 1,92; 1,87; 1,81 Å and melilite with d/n= 3,07; 2,86; 2,45; 2,30; 2,04; 1,94; 1,82 Å. Upon availability of maturing activators or when the hydrothermal treatment is used, these minerals exert their binding properties, and the slag glass exerts its binding properties in the presence of alkaline cation, especially Ca^{+2} – puzzolanic ones. Thus, according to GOST 3476-74 the slag of CMP can be used as an additive in cement.

The specific surface of BFGS fluctuates from 342 to 414 m^2/kg, if the average value is 392 m^2/kg.

In order to obtain the blended cement the portland cement CEM I 42,5 by "IUUGPK" Novotroitsk Ltd. production which meets the requirements of GOST 31108-2003 was used.

The uniform quartz sand which meets the requirements of GOST 6139-2003 was used as a filling matter. In order to determine the influence of slag on the properties of binding mediums, the normal density (ND) and setting terms of cement-water paste were studied. The research was conducted in mortar mixtures of the standard consistence with C:P=1:3 for blended cement with different consistence of slag.

4. Experimental data and their results

The properties change of the mortar blended cement (normal density, water/binder ratio W/B) of standard consistency and mortar true W/C_{true}, with the accountancy of sand water demand of 4% and ground granulated slag of 31.6%) depending on the proportion of slag is shown in Figure 1.

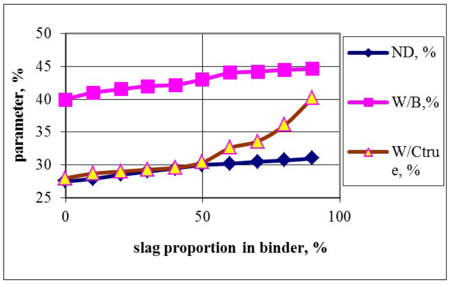

Fig. 1. Dependences of mortar parameters on the slag dosages

From Figure 1 it is clear that the increase of the proportion of BFGS in binder causes an increase in its water demand, mortar water/binder ratio and, especially, true W/C when replacing the cement with the slag for more than 70%.

The change of cement-water paste setting time is given in Figure 2 and shows that the increase of slag proportion in the binder extends the setting time not only because of the cement dilution, but also because of the increase of cement paste water demand.

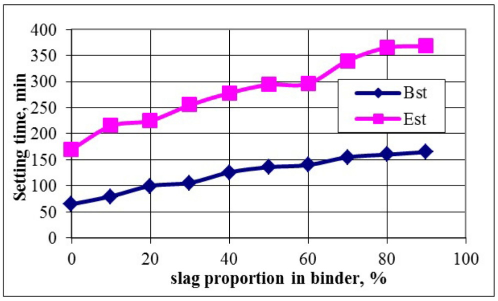

Fig. 2. The influence of BFGS in the binder on setting time – the beginning B_{st} and the end E_{st}

The change of the bending and compressive strength of samples with C:P=1:3 of the water maturing and after heat and moisture treatment according to the scheme 2 + 3 + 6 + 2 at 85˚C with different degree of substitution of slag cement and different maturing time is shown in Figure 3, where 3 HMT, 28 HMT, 180 HMT - the strength of the cement-sand samples in the age of 3, 28 and 180 days of water maturing after steaming and 3 NM 28 NM 180 NM - samples that have been stored in water for 3, 28, 180 days.

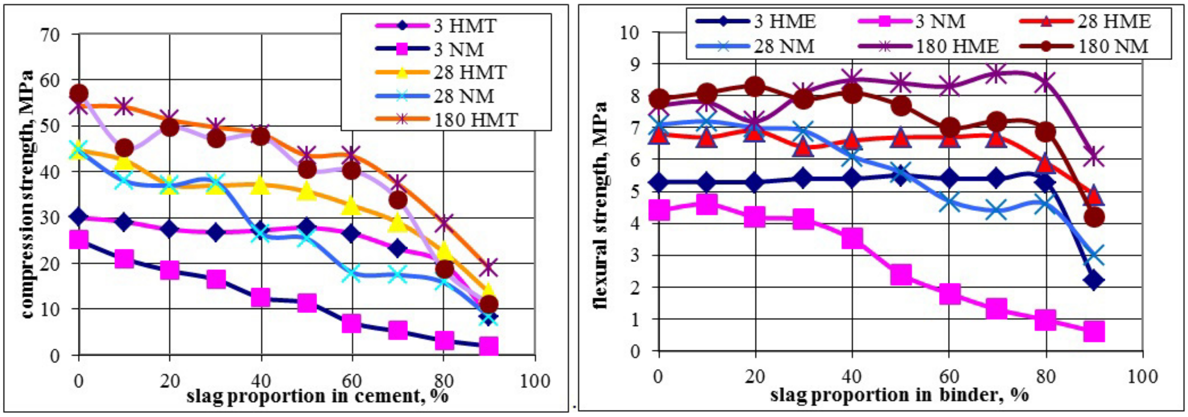

Fig. 3. The influence of slag proportion in binder on a) R_{comp} b) R_{flex}

The research have shown that the strength of the samples during compression (R_{comp}) and flexion (R_{flex}) stabilizes after longtime maturing without heat treatment and early after heat treatment, when the content of the slag is from 0 to 80% for R_{flex} and from 0 to 50 % for R_{comp}, which indicates the increase in the slag activation with time and the growth of its proportion in the composition of the blended cement. This suggests that the slag content of up to 70% is optimal in the mixed cement. Practically constant R_{flex} with the increase of slag dosage from 0 to 80% of the total mass of the mixture suggests an increase in the volume of gelled phase from hydrosilicate combination in the hardened cement paste.

The decrease of R_{comp} of mortar samples, with the increase of BFGS dosage is connected not only with the cement dilution by less active component, but also by the increase of water demand of equally and easily workable mixtures in case when the substitution level of cement by slag is increased. When the maturing time is increased, the strength of samples of mixed cements leads up to the strength of samples made of CEM I. Consequently, the portland cement is a good activator of slag maturing.

The results of determination of the free calcium hydroxide ($Ca(OH)_2$) and chemically bounded water ($W_{c.bw}$) in hydrated phases by the method of DTA are given in Table 1.

The content of calcium hydroxide ($Ca(OH)_2$) and chemically bounded water ($W_{c.bw}$) in hardened cement paste decreases with the increase of the slag proportion in the binder, wherein the content of $Ca(OH)_2$ in hardened cement paste made of the binder with the slag dosage of up to 70% is over 4% and is enough for providing the preservation of reinforcement in the concrete.

The decrease of the chemically bounded water content with the increase of the slag proportion in the binder highlights the presence of hydrated calcium silicate with the low-basic capacity in the hardened cement paste, which is favorable for the increase of mortar frost and water resistance, and the resistance to chemical agents in the blended cement.

X-ray diffraction analysis of the hardened cement paste has confirmed the presence of a significant amount of $Ca(OH)_2$ in it with d/n = 4.91; 3.11; 2.65; 1.95; 1.97 Å when adding the slag up to 70%. Consequently, the slag in the composition of the blended cement contributes to the hydration activation of clinker minerals, including the minerals β-C_2S, which hydration proceeds much slower in PC. When 30% of the slag is injected into the cement by 28 days of maturing the main reflections β-C_2S almost disappear, which proves what was mentioned before. XRD analysis also proves the increase of low-basic hydrated calcium silicate in the rock of the binder. Thus, with the increase in the amount of slag in the binder in X-ray patterns the intensity of reflections increases in the field of narrow angles with d/n = from 16.54 to 9.0 Å, as well as with 3.07 and 2.6 Å. The low peak intensity in the X-ray patterns points at the amorphization of the binding rock structure with the increase of slag additives and its positive effect on the resistance to the aggressive impact and water resistance.

Table 1. The change of phase composition of the hardened cement paste at the age of 28 days depending on the slag dosage and maturing conditions.

Slag and cement proportion	$Ca(OH)_2$ content, %	$W_{c.bw}$ content, %	$Ca(OH)_2$ content, %	$W_{c.bw}$ content, %
	Normal maturing		HME	
0/100	14,4	14,2	15,6	15,4
10/90	14,0	14,9	14,4	15,4
20/80	13,2	14,1	12,5	14,8
30/70	11,3	13,8	10,2	14,4
40/60	9,2	12,3	9,3	13,5
50/50	8,2	11,9	8,2	13,3
60/40	6,2	11,1	4,6	12,6
70/30	5,5	10,6	4,0	11,9
80/20	2,8	9,2	1,9	8,9
90/10	1,3	7,3	1,2	6,7

The microphotographs obtained from the raster electron microscope of spalls of hardened cement paste are presented in Figures 4-6 and prove the data of DTA and X-ray diffraction analysis.

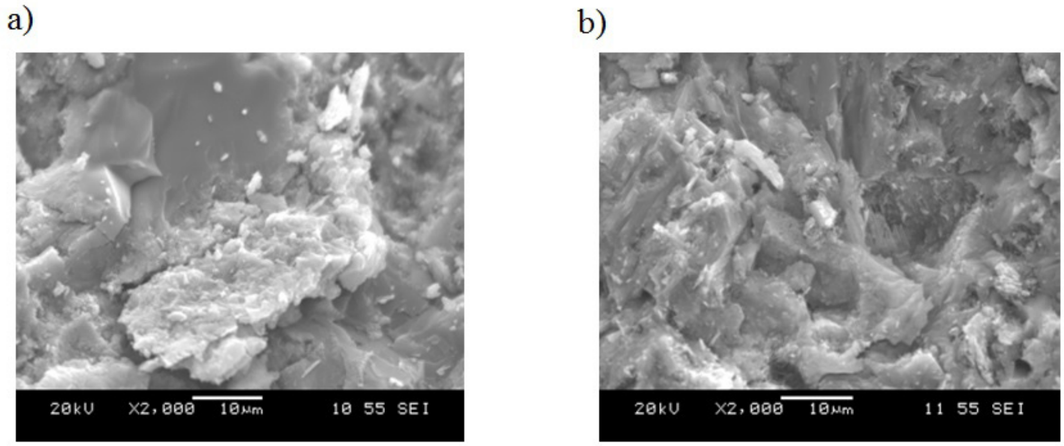

Fig. 4. The hardened cement paste structure on the basis of binding medium with 0/100 slag and cement proportion at the age of 28 days
a) normal maturing; b) HMT

Well-crystallized products of hydration of the binder and calcium hydroxide can be marked out at the spall of hardened cement paste without adding the slag (Figure 4), which corresponds to the rock structure composed of highly basic hydrated calcium silicate.

When the amount of slag in the binder increases (Figure 5), the rock structure is amorphized and transforms into the block one for blinders with the slag and cement proportion 70:30 and is presented by alternated sections in relation to the crystallized and amorphous components.

For the hardened cement paste with maximum content of slag (Figure 6), the structure presented by the particles of slag that are weakly bound between each other in the surface by some quantity of hydration products is characteristic. The areas of gel are visible in the separate areas on the rock samples.

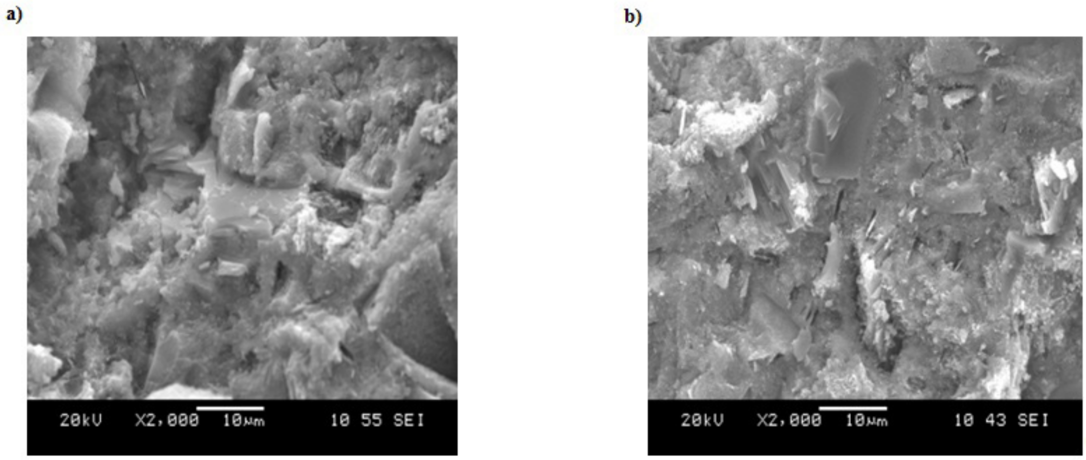

Fig. 5. The hardened cement paste structure on the basis of binding medium with 50/50 slag and cement proportion at the age of 28 days a) normal maturing; b) HMT

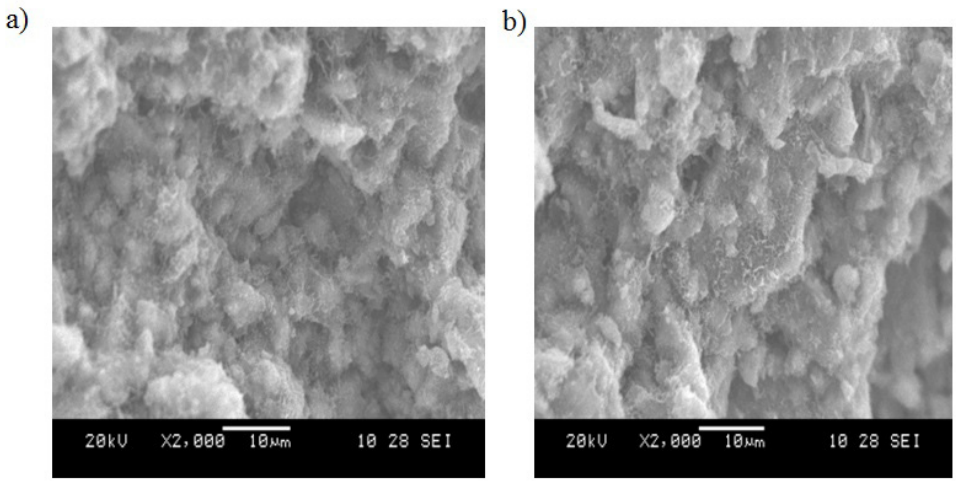

Fig. 6. The hardened cement paste structure on the basis of binding medium with 90/10 slag and cement proportion at the age of 28 days a) normal maturing; b) HMT

5. Conclusions

- The studied slag meets the requirements of GOST 3476-74 “Blast-furnace and electrical thermal phosphoric granulated slags for cement production” and can be used as an additive to cement. It does not possess the hydraulic activity, but is a highly effective pozzolan in the mixture with portland cement.
- The increase of the slag dosage in the blended cement (CEM 1+BFGS) awakes the paste and mortar water demand growth, slows down the concrete setting and maturing process.

- The decrease of the concrete strength consisted of the equally and easily workable mixtures with the increase of the slag dosage in the binder in the early stages of maturing occurs as by increasing the proportion of low active ingredient, as well as due to the increase of water-binder ratio. The slag dosage of up to 70% in the binder contributes the active set of concrete compressive and flexural strength, especially in the later stages of maturing.
- According to physical and chemical research, the portlandite content decreases actively in the binder with the growth of the slag proportion. When the slag content in the binder is up to 70%, the quantity of $Ca(OH)_2$ in the hardened cement paste is 4% or more, which guarantees the safety of reinforcement in the reinforced concrete in the blended cement. In addition, the slag which is in the composition of the blended cement activates the hydration of clinker minerals.
- The increase of quantity of the slag additive leads to the preferable formation of the structure of the hardened cement paste made of low basic hydrated calcium silicate.

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