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THE EFFECT OF PLASTICIZERS ON THE PROPERTIES OF SLAG-BASED COMPOSITE BINDERS

RuslanValeryevichLesovik, Marina SergeevnaAgeeva, Larisa NikolayevnaBotsman, Galina AleksandrovnaLesovik, Galina GennadyevnaBogusevich
Belgorod State Technological University named after V.G. Shukhov,
Russia, 308012, Belgorod, Kostyukova Str., 46
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Russia, 308012, Belgorod, Kostyukova Str., 46.

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Abstract.

This paper deals with the study of the properties of composite binders based on granulated blast-furnace slag. The effect of the plasticizers Powerflow 1130, Muraplast FK 63 (MC Bauchemie), Linamix on the properties of composite binders based on granulated blast-furnace slag in amount of 20% with different specific surface area has been investigated.

The character of the dependence of the strength characteristics of composite binders on the amount of slag and the specific surface of the binders has been determined. It has been shown that an increase in strength characteristics of all binders with increasing specific surface area is due to the increased hydration activity of both clinker and slag. Continuous growth of new formations at hardening of "cement-slag-water-additive" system contributes to optimization of the processes of structure formation of composite binders due to different speed, intensity and interaction time of the slag particles with the hydration products of clinker minerals.

Keywords.Composite binders, granulated blast-furnace slag, plasticizer, structure optimization.

Introduction.

One of the most urgent problems of the XXI century is the energy saving, especially in the industry of building materials of the Russian Federation. This is because costs of production per one unit of energy in Russia are 2-3 times higher than in developed countries [1-3]. The solution to this problem lies in large-scale use of fine-grained concrete based on composite binders and man-made sand [4-6]. There has been already accumulated a huge experience in the

production of binders with active mineral additives. However, variation of compositions by introducing a variety of fillers, additives, changes in surface area and production technology opens up broad prospects for researchers and ultimately will allow to maximize the effectiveness of composite binders (CB) [7-12].

Therefore, objective of the study was to develop composite binders made of metallurgical wastes and various additives.

Methods. The studies of material composition of the raw materials included the determination of the chemical and mineral composition by differential thermal and X-ray analysis. Scanning electron microscopy (SEM) was conducted with the use of MIRA 3 LM microscope. Physical and mechanical properties of raw and synthetized materials were determined according to standard methods in accordance with state standards (GOST).

During our study we developed the formulations of composite binders based on hyper- and superplasticizers and investigated their basic properties and a microstructure.

Main part. The mechanism of action of polycarboxylates is based not on electrostatic repulsion, but on strong steric hindrance of the interaction of hydrated cement particles due to bulky side chains of the adsorbed polymer molecules; the synthesis of these products provides a unique opportunity of the directional control of properties of the modifying additives.

We also studied the possibility of using different plasticizing, additives in composite binders based on granulated blast-furnace slag. Binders CB 80 (20% ash) were prepared by co-milling all components up to the specific surface area S_{sp}= 300 m^2/kg - 600 m^2/kg. Additive consumption was 0.5% of weight of cement. Normal consistency and timing of binder setting were determined (Table 1).

Increase in the specific surface area from 300 to 600 m^2/kg results for all formulations in an increase of normal density: by 1.4 for plain cement and CB 80 KV; CB 80 P - by 2.3; CB 80 M - by 1.2; CB 80 A - by 1.5.

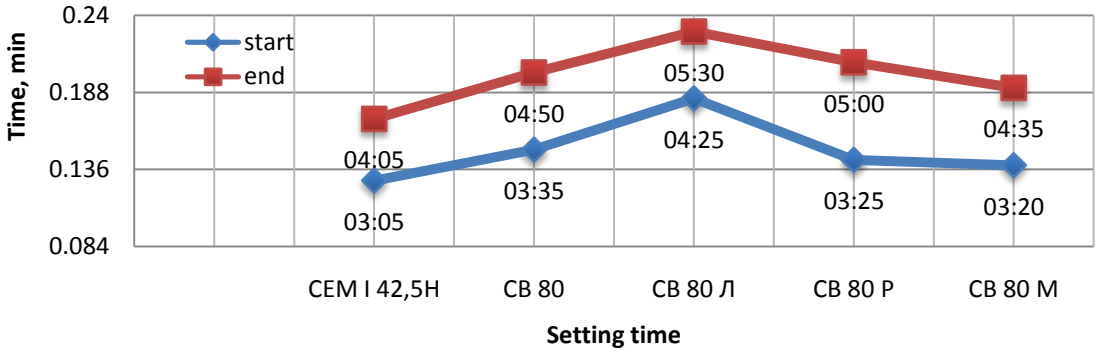
At the same time, a plain CB has higher normal consistency at any specific surface as compared with CEM I 42,5H, which is due to slag added having a developed surface with a large number of defects, chippings, cracks formed both upon grinding and upon production of slag.

Adding the superplasticizers that cover these microcracks with a thin layer and repel water provide binders CB M 80 and CB 80 P with almost the same values of normal consistency as the traditional cement does. However, this figure is much lower in CB 80 Л than that of the cement, indicating its fuller distribution over the surface of cement particles.

Table 1: Binder test results.

Type of binder	S_{sp}, m^2/kg	Cement normal consistency (CNC) %	Setting time (hour:min)	
			start	end
CEM I 42,5H	300	25.0	3:05	4:05
	400	25.4	3:10	4:15
	500	26	3:10	4:20
	600	26.4	3:15	4:10
Plain CB 80	300	26.0	3:35	4:50
	400	26.4	3:05	3:50
	500	26.8	2:00	2:30
	600	27.4	1:05	1:30
CB 80 Л Linamix	300	21.0	4:25	5:30
	400	23.7	4:18	5:30
	500	23.8	3:11	3:35
	600	22.5	2:16	2:35
CB 80 P Powerflow 1130	300	25.1	3:25	5:00
	400	25.3	2:50	4:35
	500	26.3	2:45	3:00
	600	27.4	2:15	2:35
CB 80 M Muraplast FK 63	300	25.4	3:20	4:35
	400	25.8	3:00	3:55
	500	26.3	2:45	3:05
	600	26.6	2:10	2:25

An interesting situation is observed in the analysis of changes in the setting time of binders along with an increase in specific surface. If S_{sp}=300 m^2/kg, the start and end time setting of all binders increases in comparison with conventional cement in the following sequence: 1 hour 20 minutes - start and end time of setting of CB 80 Л; 30 minutes - start time, and 24 minutes - end time of setting of CB 80; 20 minutes - start time and 55 minutes - end time of setting of CB 80 M; and 15 minutes - start time and 30 minutes - end time of setting of CB 80 P. More longer setting of the composite binders with such specific surface area compared with the cement is due to the influence of slag included in their composition.



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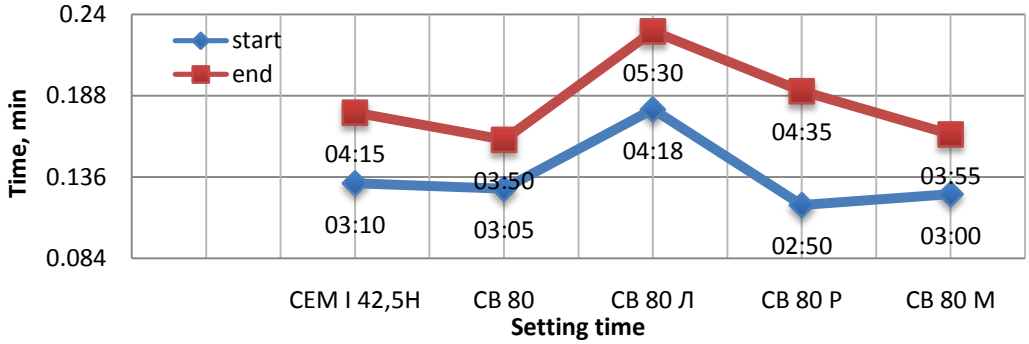

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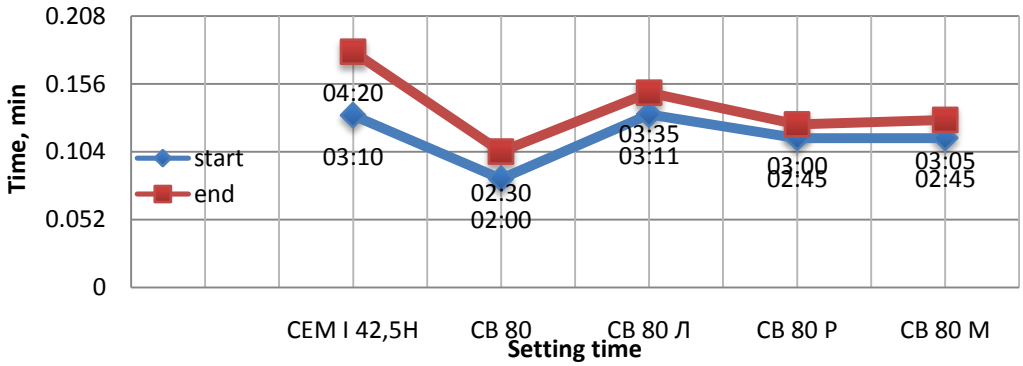

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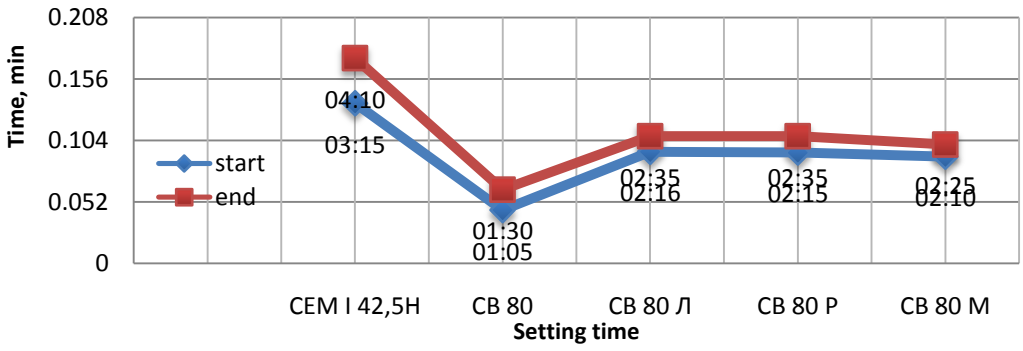


d)

Fig. 1. Setting time of multicomponent binders: a-S_{sp}=300 m^2/kg, b-S_{sp}=400 m^2/kg, c-S_{sp}=500 m^2/kg, d-S_{sp}=600 m^2/kg

It is known that the slag hydration occurs slower than in cement, and its activity increases with an increase in specific surface area. If S_{sp}=400 m^2/kg, the setting time of all binders decreases and become almost similar in values to each other, except for CB based on Linamix with almost unchanged indicators. Grinding up to a specific surface of 500 m^2/kg accelerates the setting time for CB 80 Л and makes its performance closer to that of other binders.

Grinding up to 600 m^2/kg reduced sharply the setting time of the plain CB (by 2 hours 30 minutes - start time of setting, and by 3 hours 20 minutes - end time), and virtually had no effect on the performance of a conventional cement (changes in the range of 5-10 min.). This is due to the high hydraulic activity of fine slag, which is confirmed by the setting time of this binder at a specific surface area of 300 m^2/kg: its longer than that of the cement: by 30 min - start time of setting, and by 45 minutes - end time. All binders with additives with the specific surface of 600 m^2/kg have equalized their start and end time of setting with each other. This is due to the increase in surface and, consequently, the activity of the slag particles and clinker minerals, which implies a better distribution of the additive during binder grinding, whereby the additive fully covers the binder particles. The setting period decreases along with an increase in the specific surface of CB (Figure 1).

It is known that a multimolecular layer formed on the surface of cement particles due to excessive addition of superplasticizer causes a significant slowing of the hydration process, resulting in reduced strength of the concrete. This is especially noticeable in Powerflow CB (Figure 2).

Therefore, an increase in the specific surface area from 300 to 600 m^2/kg results for all formulations in an increase of normal density. In comparison with the cement, the plain CB has normal consistency, and the CB with additives have either lower almost the same normal consistency. This is due to the introduction of superplasticizer, which cover with a thin layer the microcracks in the cement and slag particles formed during both grinding and manufacturing process, when repelling water.

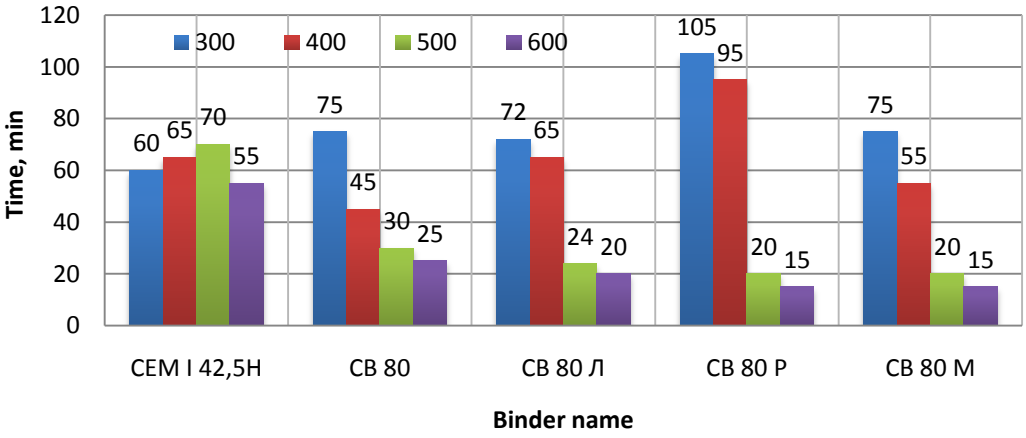
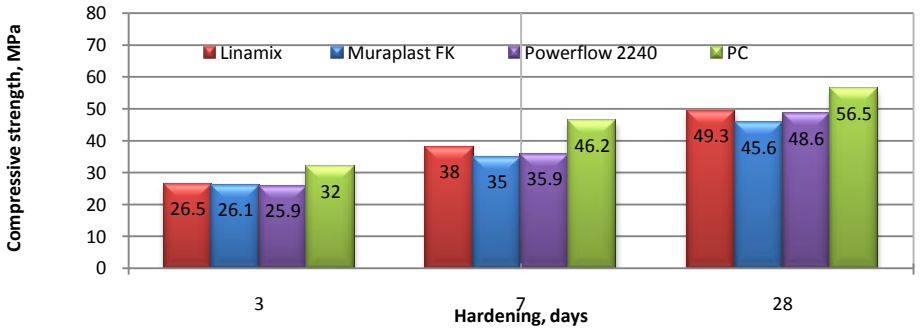


Fig. 2. Setting period of binders depending on their specific surface

All binders with additives with the specific surface of 600 m^2/kg have equalized their start and end time of setting with each other. This is due to the increase in surface and, consequently, the activity of the slag particles and clinker minerals, which implies a better distribution of the additive during binder grinding, whereby the additive fully covers the binder particles. Binding activity was determined on standard specimens - test beams 4x4x16 cm, 1:3 (binder:standard sand). Tests were carried out according to GOST 310.1÷4 B/C = 0.37 (Figure 3). The amount of additives is 0.5% of weight of cement.

In general, the following binders achieved maximum strength characteristics upon natural hardening: S_{sp}=600 m^2/kg, minimum - S_{sp}=300 m^2/kg. Increase in the values of strength characteristics of all binders along with an increasing specific surface area is due to the increased hydration activity of both clinker and slag.



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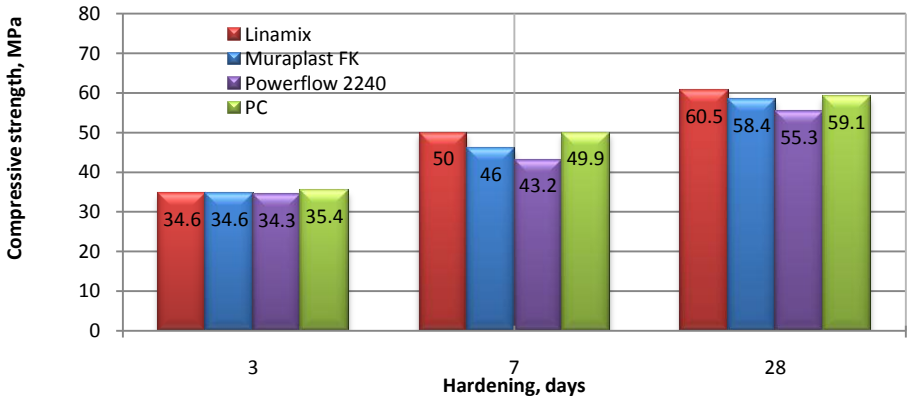

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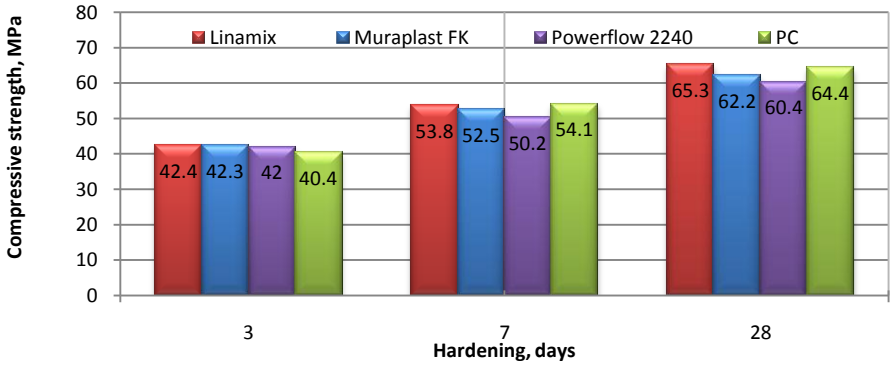

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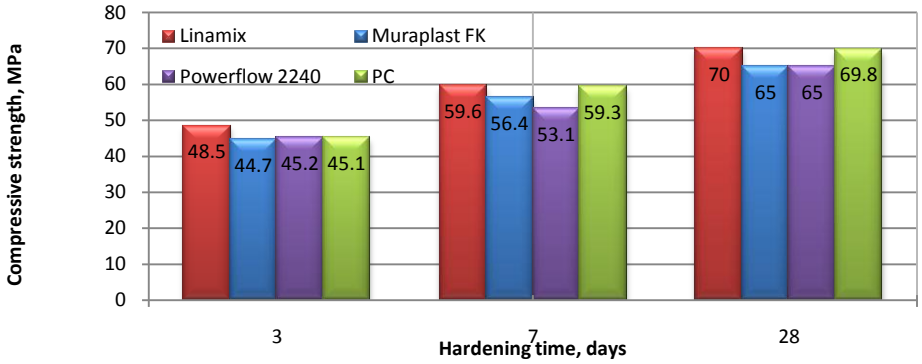

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Fig. 3. Kinetics of gain in binding strength depending on the composition and specific surface area

At the same time, 3-day-old binders are almost identical to each other in their strength indicators at S_{sp}=300-500 m^2/kg. This is due to the nature of additives and their ability to wrap the particles around. A too thick layer of molecules reduces the hydration rate, resulting in a low initial strength. If specific surface area is 300 m^2/kg, the cement strength is also high on day 3 and 7, making impossible the early demolding of products made of this type of binders. On day 3, at S_{sp}=400 m^2/kg, the activity of the cement and the obtained binders equalized, while at S_{sp}=500 m^2/kg the CB activity exceeded the cement activity. A further increase in the specific surface area leads to an increase in strength at this period of hardening in CB 80 Л under the same values of this indicator in cement and CB 80 M, and CB 80 P.

Further hardening of all grinding variants led to increased strength of formulations based on Linamix with similar strength values of cement. This indicates both thefuller distribution of the additives on the particle surface of the binder and its properly selected concentration.

In general, the difference in strength between the CB based on Muraplast FK 63 and on Powerflow 1130 was 3.6%, and about 9.8% between the CB based on Linamix and Powerflow 1130. This indicates that Powerflow 1130 additive is difficult to distribute evenly in the mixture with an increasing specific surface area. And the Linamix molecules during grinding (CB manufacture) are not simply "mechanically" fixed on cement particles, but are chemisorptively "drawn" in their surface layer.

Comparison of the activity of the resulting binders with the cement activity shows that at S_{sp}=300 m^2/kg cement has greater strength. However, an increase in specific surface makes the developed binders more active as compared with portland cement (Figure 4). Their strength performance becomes 17-33% higher than of conventional cement at S_{sp}=300 m^2/kg and nearly by 5-10% at S_{sp}=600 m^2/kg.

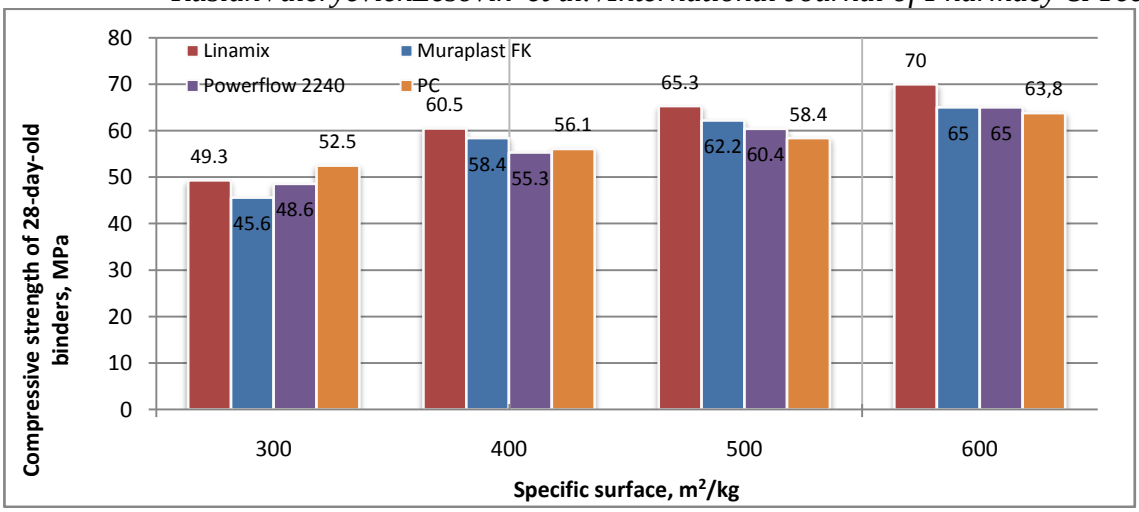
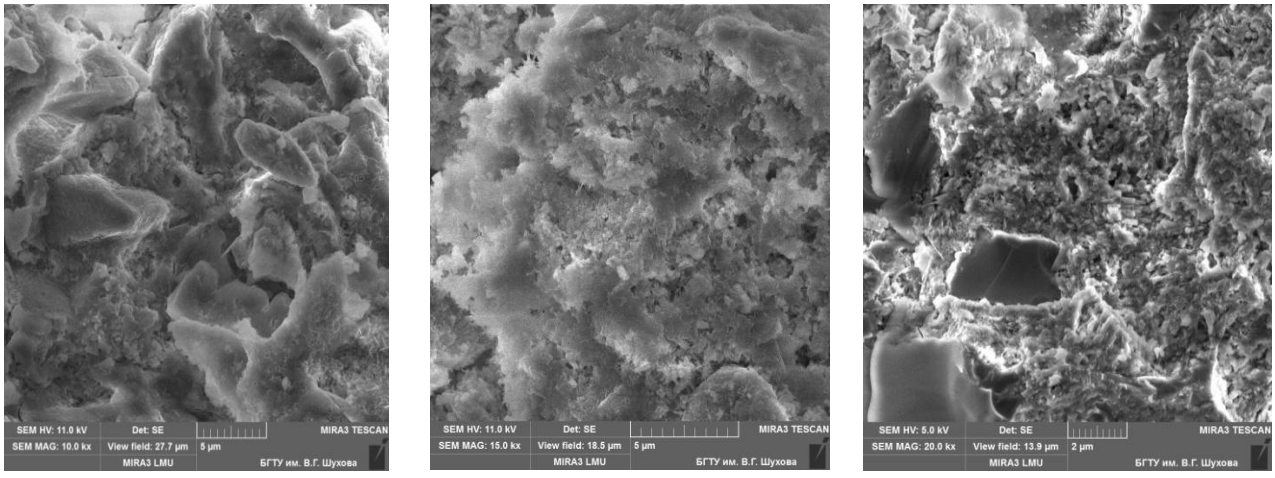


Fig. 4. The dependence of the activity on the specific surface of binders on day 28.

Thus, we have conducted the studies of the effect of various additives on properties of composite binders based on granulated blast-furnace slag in amount of 20% with different specific surfaces. It was found that the binders with S_{sp}=600 m^2/kg have the maximum strength values, which 17-33% higher than those of the conventional cement at S_{sp}=300 m^2/kg.

The study of the microstructure of the developed binders on day 28 found the following (Figure 5). All samples form homogeneous, dense matrix with micropores. The hardened stone in all binders consists of individual grains of slag with different particle sizes and shows distinct chemical interaction with new formations.

Moreover, these slag particles are almost completely covered with hydration products, because they are centers of crystallization and the forming substrates for new formations, which causes an abundance of globules fused to their surface.



1 2 3

Fig. 5. Photomicrograph of cement stone surface:

1 - Powerflow 1130-based composite binder; 2 - Muraplast FK 6-based composite binder; 3 -

However, the Linamix-based composite binder has a homogeneous structure as compared with other CBs. Lime is released upon hydration, which reacts with the slag mass. After complete binding of free CaO, the CSH(B) hydrosilicates start forming, which also compacts the composite.

Both compaction and hardening of the structure is caused by the growth of the crystalline phase and the replacement of water contacts between new individual crystals formations – crystal contacts. This specifics of the microstructure determines the higher strength of a binder.

Conclusion. Thus, in general, the strength properties of the slag-based binders grow along with an increase in the specific surface area of the particles of both man-made component and the cement particles, thus increasing the amount of the finest particles, as well as an increase in the percentage of surface defects of larger particles, growing hydraulic activity of the slag due to its finer grinding, creating thereby a high-density packing of binder particles. At the same time, slag particles themselves are the centers of crystallization and the substrates during cement hardening. The additives thinly cover microcracks in the binder particles, repel water, and reduce the number of micro-defects and pores in the hardened composite.

Summary. Thus, we have conducted the studies of the effect of various additives on properties of composite binders based on granulated blast-furnace slag in amount of 20% with different specific surfaces.

Grinding up to 600 m^2/kg reduced sharply the setting time of the plain CB, and virtually had no effect on the performance of a conventional cement (changes in the range of 5-10 min.). This is due to the high hydraulic activity of fine slag. All binders with additives with the specific surface of 600 m^2/kg have equalized with each other their start and end time of setting, which also decreased significantly as compared with a plain formulation. This is due to the increase in surface and, consequently, the activity of the slag particles and clinker minerals, which implies a better distribution of the additive during binder grinding, whereby the additive fully covers the binder particles.

We have investigated the effect of plasticizers Powerflow 1130, Muraplast FK 63 (MC Bauchemie), and Linamix on properties of composite binders based on granulated blast-furnace slag in amount of 20% with different specific surfaces. It was found that the binders with S_{sp}=600 m^2/kg have the maximum strength values, which 17-33% higher than those of the conventional cement. Thus, a continuous growth of new formations at hardening of "cement-slag-water-additive" system contributes to optimization of the processes of structure formation of composite binders due to different speed, intensity and interaction time of the slag particles with the hydration products of clinker minerals.

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