

Improving the properties of composite materials for civil engineering

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Abstract. It is shown that a highly-efficient chemical activation of the cement-containing composite mixture with the help of a new generation nanostructural additive makes it possible to develop high-strength fine-grained and heavy-weight concretes with the improved strength and deformation characteristics. The recommended nanostructural additive has an increased triple effect: reactive, catalytic, and plasticizing. The use of the proposed additive many times increases the hydration activity of the hardening system, exerting a double energy effect on it, chemical and thermal, thus making it possible to develop the composite building material of a new level of physical and mechanical properties.

1 Introduction

For quick-hardening high-rise housing construction as well as for reliable and durable road surfacing, it is appropriate to use high-strength concretes having improved deformation characteristics, increased bending tensile strength, increased crack resistance, frost resistance, corrosion resistance and durability.

One of the means of developing composite materials with the mentioned set of physical-mechanical characteristics should be a chemical activation due to highly-efficient new generation chemical additives which are likely to extract internal energy reserves from Portland cement and other components of the composite mixture, involving them fully in hydration processes and synthesis reactions.

For many decades, the enterprises of prefabricated, ready-mixed and reinforced concrete have used plasticizers as chemical additives, since most researchers believed that for strength increase first of all it was necessary to reduce water-cement ratio, i.e. an efficient concrete additive had to have water-reducing properties.

Lignosulfonates (LSN) were used as first plasticizers.

In the middle of the XXth century, the extensive use of more efficient naphthalenesulfonate plasticizers started. The most common chemical additive among them was C-3.

Recently, polycarboxylate plasticizing additives have been considered and used as new generation plasticizers. These additives make it possible to reduce the water-cement ratio

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considerably and, consequently, to increase the strength and the density of the concrete, which enables to reduce cement consumption, energy and labour costs.

Table 1 presents the additives highly applied in enterprises of concrete industry.

Table 1. Modern efficient chemical additives.

Name of additive, producer	Chemical basis of additive	Efficiency	Recommended area of application
1	2	3	4
Additive for concretes and mortars of multifunctional performance «PFM NLC» «Polyplast Novomoskovsk» Ltd.	Mixture of sodium salts of polymethylnaphthalenesulphonic acids with the addition of air-entraining and hydrophobic complexes	Increase of concrete mixture flowability, increase of concrete density and concrete compression strength	For producing concretes of classes B20, B25, B30.
MasterGleniumACE 430 «BASF building systems» Ltd.	Aqueous solution based on polycarboxylic ethers	Increase of concrete mixture flowability, increase of concrete density, strength, frost resistance and water resistance	For producing high-strength concretes of classes B30, B40, B45.
Sika ViscoCrete «Sika» Ltd.	Aqueous composition of modified polycarboxylic ethers	Increase of concrete mixture flowability, increase of concrete density and strength	For producing concretes in wide range, classes B15, B20, B25, B30.
Sika Plast «Sika» Ltd.	Aqueous solution of mixture of lignosulfonates and polycarboxylates	Increase of concrete mixture flowability, increase of concrete density and strength	For producing concretes of wide range of strength, classes B7,5, B10, B15, B20, B25.
Relamix PK – «Polyplast Novomoskovsk» Ltd.	Aqueous solution based on polyoxyethylene derivatives of unsaturated carboxylic acids	Increase of concrete mixture flowability, increase of concrete density and strength	For producing concretes of classes B15, B20, B25, B30.

The analysis of the data of Table 1 shows, that the wide range of the presented additives is characterized by plasticizing effect which causes the increase of the concrete density and compression strength. Besides, durability parameters, such as frost resistance and water resistance, are supposed to be increased. It should be noted, that the use of the mentioned additives doesn't mean using new hydrated phases which would have a positive impact on deformation properties and corrosion resistance of the concrete. These challenges require new chemical additives which, besides a plasticizing effect, would be characterized by reaction activity and would have a catalytic effect on hydration processes, which would make it possible to create new complex hydration compounds of new quality.

This scientific research is on the development of the new generation additive.

2 Methods of research

To develop a new generation additive, we suggest using highly-efficient modern surfactants represented by polycarboxylate polymers. As efficient modifiers we used nanostructural elements represented by nanodispersions $\text{SiO}_2 \cdot n\text{H}_2\text{O}$.

Nanodispersions, thanks to increased surface energy, are supposed to possess increased mobility and reaction capacity.

The modifiers, which are included in the composition of the developed additive, due to the alleged reaction activity, are supposed to react with $\text{Ca}(\text{OH})_2$ or with tobermorite-like hydrosilicates like CSH(I) which are formed in hydration of calcium silicates included in Portland cement. In this, new phases may be formed represented by low-basic hydrosilicates having fibrous structure which has a reinforcing effect on a forming structure of a hardening material, which increases bending tensile strength [1, 2] and, as a result, crack resistance of the material. Scientific studies [3, 4] confirm a good compatibility of silica sol, consisting of nanodispersions $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, and polycarboxylate polymers [5-21].

To increase the density and deformation characteristics of the material, it is efficient to put high-molecular compounds into the additive which are characterized by branched structure. In combination with polycarboxylate polymers they will create branched and elongated polymer chains which will contribute to the reduce of the material porosity and the formation of compact structure with the increased number of low-soluble hydrated compounds. With the developed nanostructural additive, the hardening system is supposed to be subjected to a double energy effect, chemical and thermal, because the heat from the increased number of hydration reactions and as a result of the increased density of the concrete is supposed to be accumulated inside the hardening material with positive impacts on further hardening processes. Consequently, with the additive, through the double energy effect, the Portland cement phases of lower activity, such as dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$, will join hydration processes at an earlier age. And also, with the mentioned additive blast furnace metallurgical slag is supposed to show its hydration activity effectively. Blast furnace metallurgical slag is composed of high-grade phases, such as akermanite, $2\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$, in hydration of which bending tensile strength is supposed to increase additionally due to the special structure of magnesium-containing hydrated compounds.

Blast furnace slags are low-recyclable technogenic products of metallurgical enterprises. Using slag in concrete production in combination with super-efficient chemical activation would make it possible to produce modern concretes with a new level of properties.

The use of the proposed additive is supposed to have a positive impact on increase of water resistance, frost resistance and corrosion resistance of the concrete as well as the durability and reliability of the whole concrete and the structures constructed on its base.

The assessment of each component's performance and the additive as a whole was made by the mortar flowability change as well as by change of compression strength, bending tensile strength and the value of water absorption of concretes B25, B30 as the most common concretes in construction. The efficiency of the additive as a whole was additionally assessed when replacing the part of Portland cement with blast furnace metallurgical slag.

3 Results of the study and discussion

To do the research the following materials were used:

1. Portland cement PC500 D0 to GOST 10178-85, GOST 30515-2013 «Pikalevo Cement» JSC, N.G. – 25.7%, initial setting– 2¹⁵ (hour-min), final setting– 4²⁵ (hour-min);

2. construction sand to GOST 8735-88, in accordance with tests the sand has the following physical-mechanical characteristics:

- fineness modulus, M_f – 2.28;
- content of dust and clay particles– 0.98%;
- lumps of clay – no;
- bulk density in the state of natural moisture – 1460 kg/m³;

3. crushed granite of fraction 5-10 mm.

In accordance with the tests complying with GOST 8969.0-97 «Crushed stone and gravel made of dense rocks and industrial wastes for construction works. Methods of

physical-mechanical tests». Crushed stone had the following physical-mechanical characteristics:

- by grain composition it complies with fraction (5-10) mm;
- content of dust and clay particles– 0.76%;
- lumps of clay – no;
- bulk density– 1310 kg/M³;
- crushability complies with F300;

4. granulated fine blast furnace slag (complies with TU 38.32.22.150-004-00186217-2018 was tested in compliance with GOST 5578-94 «Crushed stone and sand made of slag of ferrous and non-ferrous metallurgies for concretes» and has the following physical-mechanical characteristics:

- bulk density– 1079 kg/M³;
- fineness of grinding:

1. average value of the rest on a sieve №008 – 6.7%;

2. average value of specific surface, $S_{spc.}=317$ m²/kg;

- average value of pH of aqueous extract of daily preparing by the value pH=10,9 (alkaline environment).

In the first stage of this study, we assessed the efficiency of polycarboxylate polymers. For this purpose we prepared 20% aqueous solution of density $\rho=1.031$ g/cm³, pH=6.5±0,1.

Table 2 presents the results of the study.

Table 2. Evaluation of effectiveness of 20% aqueous solution of polycarboxylate polymer.

No	Class of concrete , B	Material consumption for 1m ³ concrete mixture, kg					W/C ratio	Flowability mark, P, flowability of concrete mix by cone slump, cm	Strength, MPa, 7 days old		Water absorption, W, %
		Portland cement	Sand	Crushed stone	additive 20% solution of polycarboxylate polymers, % of cement mass	Water			Compression	Bending tensile	
1	2	3	4	5	6	7	8	9	10	11	12
1	B25	400	760	1012	-	208	0.52	P4 (16-20)	22.7	2.6	4.8
2		400	760	1012	0.6% (2.4 kg)	191	0.48	P4 (16-20)	25.0	2.9	4.4
3		400	760	1012	0.8% (3.2 kg)	183	0.46	P4 (16-20)	25.7	3.0	4.2
4		400	760	1012	1.0% (4.0 kg)	177	0.44	P4 (16-20)	26.3	3.1	4.1
5		400	760	1012	1.2% (4.8 kg)	172	0.43	P4 (16-20)	26.0	2.9	4.1
6	B30	440	710	1020	-	220	0.5	P4 (16-20)	27.6	3.3	4.6
7		440	710	1020	0.6% (2.64 kg)	198	0.45	P4 (16-20)	30.6	3.6	4.2
8		440	710	1020	0.8% (3.52 kg)	189	0.43	P4 (16-20)	31.2	3.7	4.1
9		440	710	1020	1.0% (4.4 kg)	182	0.41	P4 (16-20)	32.3	3.8	3.8
10		440	710	1020	1.2% (5.2 kg)	180	0.41	P4 (16-20)	31.8	3.7	3.9

The analysis of the data presented in Table 2 shows that for concrete B25 and B30 the performance of the additive, represented by 20% aqueous solution of polycarboxylate polymers, is expressed mainly by reduce of water-cement ratio by 0,08 – 0,09, which corresponds to reduce of water consumption by 15 – 17% to provide the same flowability of the concrete mixture. The highest reduce of water consumption without strength reduce is observed using 1% wt aqueous solution of polycarboxylate polymer of 20% concentration, in so doing, the concrete is characterized by the same increase of compression and bending tensile strength, which means that new phases appear not to be formed in the hardening system and the concrete strength increase is due to the concrete structure density increase. It has been found that on average the concrete density increases by 15.4 – 17.5%, which is confirmed by the concrete water absorption decrease from 4.8 – 4.6% value to 4.1 – 3.8% value.

It has been established experimentally that the rational number of 20% aqueous solution of polycarboxylate polymer, used as a concrete additive, is 1,0 % wt of cement mass. In further studies this percent of the additive was used.

The next stage of the study is about the effectiveness evaluation of the combined performance of polycarboxylate polymer and nanostructural elements $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, put additionally into the polymer solution in the form of 10% silica sol $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ c pH=3.5±0.5. For this purpose B25 concrete was used as the most common in construction. Table 3 presents the results of the studies.

Table 3. Evaluation of effectiveness of complex additive consisting of polycarboxylate polymer and nanostructural element $\text{SiO}_2 \cdot n\text{H}_2\text{O}$.

No	Class of concrete	Material consumption for 1m ³ concrete mixture, kg							W/C ratio	Flowability mark, P, (cone slump) cm	Strength, MPa, 7 days old		Water absorption, %
		Portland cement	Sand	Crushed stone	Complex additive			Water			Compression	Bending tensile	
					Quantity, % of cement mass	Additive's composition							
						20% polycarboxylate polymer	10% silica sol						
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	B25	400	760	1012	-	-	-	208	0.52	P4 (16-20)	22.7	2.6	4.8
2		400	760	1012	1.0	100	-	177	0.44	P4 (16-20)	26.3	3.1	4.1
3		400	760	1012	1.0	99.5	0.5	174	0.43	P4 (16-20)	27.5	3.3	4.0
4		400	760	1012	1.0	99.3	0.7	168	0.42	P4 (16-20)	28.8	3.6	3.8
5		400	760	1012	1.0	99.1	0.9	172	0.43	P4 (16-20)	28.4	3.5	3.8
6		400	760	1012	1.0	99.0	1.1	173	0.43	P4 (16-20)	27.9	3.4	3.9

It has been established experimentally that nanostructural elements, put as 10% aqueous solution of silica sol, have a low plasticizing effect, reducing additionally water consumption by not more than 5.0%. In so doing, it has been found that the nanostructural elements of 0.7% of the mass of 20% aqueous solution of polycarboxylate polymer have an effective influence on compression strength increase which is 27% of the benchmark

composition; and also there is bending tensile strength increase, which is 38% at the age of 7 days; the density of the hardening concrete increases by 21.0% with water absorption $W=3.8\%$.

It has been found that the ratio of the components is:

- 20% aqueous solution of polycarboxylate polymer – 99.3%
- 10% silica sol with $\text{pH}=3.5\pm 0.5 - 0,7\%$.

The obtained complex additive is put into concrete mix 1.0% wt of cement mass.

The obtained positive results confirm the assumptions that nanostructural elements possess a reaction activity and provide an additional formation of hydrated compounds, including new phases, which have a positive impact on the increase of bending tensile strength (see Table 3).

Further studies deal with the evaluation of the effectiveness of the complex additive consisting of an efficient ratio of 20% polycarboxylate polymer aqueous solution, 10% silica sol solution and the additional use of aqueous solution of 10% concentration of high-molecular compounds. For this purpose, as in the previous case, concrete B25 was used. The results of the studies are presented in Table 4.

Table 4. Evaluation of effectiveness of complex additive consisting of polycarboxylate polymer, nanostructural element $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ and high-molecular compound.

No	Class of concrete	Material consumption for 1m ³ concrete mixture, kg								W/C ratio	Flowability mark, P, (cone slump) cm	Strength, MPa, 7 days old		
		Portland cement	Sand	Crushed stone	Complex additive				Water			Compression	Bending tensile	Water absorption, %
					Quantity, % of cement mass	20% polycarboxylate polymer	10% silica sol solution	10% aqueous solution of high molecular compounds						
1	B25	400	760	1012	-	-	-	-	208	0.52	P4 (16-20)	22.7	2.6	4.2
2		400	760	1012	1.0	100	-	-	177	0.44	P4 (16-20)	26.3	3.1	4.1
3		400	760	1012	1.0	99.3	0.7	-	168	0.42	P4 (16-20)	28.8	3.6	3.8
4		400	760	1012	1.0	98.8	0.7	0.5	164	0.41	P4 (16-20)	31.3	3.7	3.5
5		400	760	1012	1.0	98.3	0.7	1.0	160	0.40	P4 (16-20)	33.7	4.1	3.3
6		400	760	1012	1.0	97.8	0.7	1.5	156	0.39	P4 (16-20)	35.8	4.5	3.0
7		400	760	1012	1.0	97.3	0.7	2.0	152	0.38	P4 (16-20)	36.9	4.7	2.7
8		400	760	1012	1.0	96.8	0.7	2.5	148	0.37	P4 (16-20)	38.6	5.2	2.3
9		400	760	1012	1.0	96.3	0.7	3.0	152	0.38	P4 (16-20)	38.0	4.7	2.5
10		400	760	1012	1.0	95.8	0.7	3.5	156	0.39	P4 (16-20)	37.6	4.6	2.7

The analysis of the data presented in Table 4 shows that input of the additional component in the form high-molecular compounds contributes significantly to the increase of density of the forming concrete structure because water absorption reduces by 52%, which contributes to an efficient conservation of heat generated at the initial period of hydration reactions. And consequently, the heat inside the system increases the reaction activity of all the components of the hardening system, including nanostructural elements, providing not only the formation of the increased amount of hydrated phases, increasing compression strength within 70%, but it also provides formation of new phases of a special structure, increasing bending tensile strength twice, and it increases crack resistance of the material by more than 25%.

The results confirm that the complex nanostructural additive is the additive of a new generation which is characterized by a highly-effective reactive and plasticizing effect. The efficient ratio between the components of the developed additive has been determined. The following sustainable composition has been determined:

- 20% aqueous solution of polycarboxylate polymer –96.8%;
- 10% aqueous solution of silica sol – 0.7%;
- 10% aqueous solution of high-molecular compound –2.5%.

Table 5. Test results.

No	Class of concrete, B	Material consumption for 1m ³ concrete mixture, kg						W/binder	Flowability mark, P, (cone slump) cm	Kinetics of strength range, MPa		
		Binder		Sand with M _r =2.78	Crushed stone fr. (5-20) mm	Nanostructural complex additive	Water			Age, days		
		PC500 D0H	Fine granulated furnace slag (FGFS)							3	7	28
1	2	3	4	5	6	7	8	9	10	11	12	13
1	B30	380	-	800	1050	-	187	0.49	10.0	15.8	32.3	40.2
2		380	-	800	1050	3.8	144	0.38	10.0	33.0	53.0	58.0
3		304	76	800	1050	-	184	0.48	10.0	13.0	25.5	30.5
4		304	76	800	1050	3.8	141	0.37	10.0	24.3	39.8	50.6
5		228	152	800	1050	3.8	137	0.36	10.0	23.2	40.4	50.4
6		190	190	800	1050	3.8	133	0.35	10.0	22.9	39.6	50.8
7		152	228	800	1050	3.8	133	0.35	10.0	17.2	36.2	39.1

During the research we replaced part of the cement with fine granulated furnace slag (FGFS), starting from 20% and up to 60% inclusive.

It has been established experimentally, that replacing the part of Portland cement with FGFS (comparison of research results Tables №1 and №3) without the additive causes the decrease of concrete mixture water demand, but the concrete strength does not increase, it even decreases by approximately 25%. At the project age of concrete (28 days) the actual strength is lower than the needed one for concrete B30, also bending tensile strength and crack resistance indicators are improved.

Strength indicator decrease is probably caused by FGFS which is characterized by low hydration activity under natural conditions, and to increase the hydration activity it is necessary to have an additional impact of energy.

The developed complex nanostructural chemical additive put into the concrete mixture causes a considerable increase of hydration activity of the concrete mixture. Replacement of 50% of Portland cement with 50% of FGFS gives the actual concrete strength which is more than 20% higher of the needed strength for concrete B30.

4 Results

The nature of the components and their efficient ratio has been found to develop a highly-efficient complex nanostructural chemical additive of a new generation.

It has been found that the developed nanostructural additive is characterized by the high reaction activity and superplasticizing properties.

It has been established experimentally that the recommended nanostructural chemical additive due to its high reaction activity is capable to involve low-reaction low-soluble phases at an early age, e.g. calcium-magnesium silicates, having a positive impact on the improvement of concrete deformation characteristics.

It has been found that with the nanostructural chemical additive it is efficient to use fine granulated blast furnace metallurgical slag instead of Portland cement, which is supposed to provide the improvement of crack resistance, strength, corrosion resistance and durability of the concrete, i.e. the development of high-strength concrete with the improved physical-mechanical characteristics.

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