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Investigations of the properties, composition, benefits of chemical additives, changes in cement properties and deformation and strength properties of heavy concrete

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Abstract

This article discusses chemical additives in modern concrete technology and their effects on concrete strength. The role of chemical additives and their importance in obtaining clear technical and economic efficiency and the strength of concrete structures are shown. Improving the efficiency and quality of concrete* and reinforced concrete is a very urgent problem and can not be fully successfully resolved without the use of chemical additives in concrete technology, among which currently in the first place are complex additives, which have a specific impact on the structure and properties of concrete.

Keywords: Concrete, structure, superplasticizer, cement, reinforced concrete polycarboxylate chemical additives, polymer, construction, slump, water retaining, macrocapillary, aggregate, dispers, capillary, monolithic construction.

Introduction

Improving the efficiency and quality of concrete and reinforced concrete is a very urgent problem and can not be fully successfully resolved without the use of chemical additives in concrete technology, among which currently in the first place are complex additives, which have a specific impact on the structure and properties of concrete.

Recently, complex additives based on polycarboxylate esters have become widespread. The use of these complex additives, the main component of which are highly effective polycarboxylate-based hyperplasticizers, allows to produce high-strength and high-quality concrete with low water-cement ratio and capillary porosity value. However the questions connected with the influence of complex polycarboxylate-based additives on the peculiarities of hydration and structure formation of cement systems and their influence on the durability of cement concrete have not been sufficiently investigated.[1]

In connection with the appearance of highly effective water-reducing additives based on polycarboxylate esters there is a tendency to obtain high-strength materials with a minimum water-cement ratio. However, in such materials there may be a deficit of liquid phase, leading to a slowdown of hydration processes and, consequently, to the appearance of stresses in the heterogeneous structure of the modified cement stone under cyclic influences.

One of the main, most affordable, technological and economical directions of improving the quality and durability of concrete and reinforced concrete is the use of various kinds of chemical additives. [16]

Classification of chemical additives abroad is based on the technological or technical effect of the additive. Thus, the international standard classifies the following types of concrete additives:

- plasticizers;

- superplasticizing;

- water retaining;

- water-retaining concrete;

- air-entraining; .

- accelerating the setting of concrete;

- accelerating hardening;

- slump retarding, plasticizing;

- slump retarding, superplasticizing;

- slump-accelerating, plasticizing;

- slump-accelerating, superplasticizing.

In domestic standards, depending on the purpose (or the main effect of the action), additives are subdivided:

- regulating properties of concrete and mortar mixtures (plasticizing, water-reducing, stabilizing);

- regulating properties of concrete and mortars (regulating hardening kinetics, increasing durability, decreasing permeability, increasing protective properties in relation to steel reinforcement, increasing cold resistance, increasing corrosion resistance, expanding);

- giving special properties to concrete (antifreeze, hydro-phobic);

- mineral additives[2].

This domestic standard provides additives that increase the frost resistance and water resistance of concrete, due to water-reduction, colmatation of pores and optimize the pore space.

Among the concrete additives that have found the widest application in the production of concrete and reinforced concrete, plasticizing additives are in the first place. This can be explained by high efficiency of this type of additives, the absence of the negative effect on the concrete and reinforcement, as well as the availability and low cost [14].

The main purpose of plasticizers - increasing mobility or reducing the stiffness of the concrete mixture, its liquefaction. The effect of liquefaction of concrete mixture is used to facilitate the formation of structures, to increase the density and strength of concrete by reducing the water content of the concrete mixture while maintaining the initial mobility, or to reduce cement consumption.

According to modern concepts plasticizers are dispersants-stabilizers that form a structured film as a result of adsorption on the interface between the solid and liquid phases. Immobilization of water bound in cement flocculi, reduction of internal friction coefficient of cement-water suspension, smoothing of microrelief of hydrating cement grains and in some cases increasing of electrostatic particle repulsion due to the significant change of their electrokinetic potential are the main factors of plasticizing effect of surface-active substances on cement-water systems, reducing their water consumption and binder consumption. [9]

All plasticizing additives according to the classification are additives that regulate the properties of concrete and mortar mixtures, and according to the value of plasticizing effect are divided into:

- superplasticizing;

- plasticizers.

It is known that superplasticizers are dispersants-stabilizers of cement suspensions, which form as a result of adsorption on the surface of the interface between the liquid and solid phases, a structured film. The main factors of superplasticizers action are immobilization of adsorbed bound water, decrease in coefficient of internal friction of cement-water suspension, smoothing of microrelief of cement grains, increase in mobility of the mixture due to electrostatic and, for some types of additives, steric repulsion [5].

The most important material properties (density, strength, water absorption, water resistance, frost resistance, etc.) depend on the value of porosity and its nature: geometry, concentration'and uniformity of distribution, over the volume of concrete, their structure - communicating pores or closed, capillary ones. According to A.E. Sheikin, the pore space of a material is all its discontinuities not occupied by the solid phase of the initial materials and new formations [17]. The pores of a cement stone, according to their size are divided as follows:

- gel or ultramicropores with a radius of less than 5 nm;

- macrocapillary or transient pores with a radius of 5-100 nm;

- capillary pores with a radius of 100-1000 nm;

- microcapillary pores with a radius of more than 1000 nm.

MATERIALS AND METHODS

From the point of view of increasing durability of heavy concrete it is more preferable to increase the number of gel pores, in which water is in a special state and does not freeze down to - 50 °C. It is known that capillary pores are the main carriers of liquid and gaseous media, so increasing the proportion of capillary pores leads to a sharp decrease in the durability of the cement stone [14].

As we already know from the example of naphthalene and melamine sulfonates, the polymer molecule is adsorbed by the surface of the cement grain due to its negative electric charge. In this case, sulfonates are rapidly and almost completely absorbed, while plasticizers can purposefully control their adsorption properties by changing the amount of carboxylate groups. In addition to dispersion due to the electrostatic repulsion of the cement grains, these grains are also kept at a distance from one another due to long side chains.

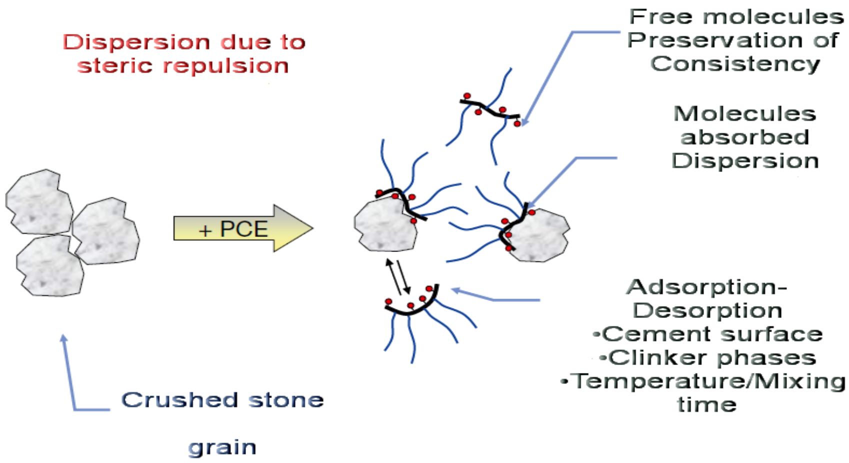

Figure 1: The principle of operation of the PCE superplasticizer:

dispersion due to steric repulsion

Foreign scientists involved in research on polycarboxylate plasticizers usually work in the laboratories of companies producing these additives or work closely with them, so they have information about the molecular structure of the polymers under study.

The determining factor in the effectiveness of a superplasticizer based on polycarboxylate esters is its adsorption properties. These properties depend primarily on the molecular structure of the polymer, the chemical conditions in the pore solution, and the physicochemical properties of the cement surface[3].

On the magnitude and nature of the porosity of concrete affects the degree of hydration of cement, the amount of mixing water, curing regimes, the phase composition of the cement stone. Increase in water-cement ratio affects the morphology of hydrate formations, while the proportion of capillary pores increases and increases their average size, which ultimately affects the strength properties and durability of the cement stone [16].

Steaming of the items leads to an increase in the capillary pores due to evaporation of water from the concrete. The formation of a coarser and more crystallized structure is observed. Curing of concrete for a long time leads to colmatation of pores by hydrate formations, thus capillary porosity decreases. The total porosity decreases with increasing degree of cement hydration[4].

Obtaining high strength and high quality cement concrete is possible with the purposeful formation of cement stone structure, characterized by a low proportion of capillary pores, hydrate formations of reduced basicity, and evenly distributed in the structure of the cement stone calcium hydroxide. Modifying the cement concrete with complex additives is the most affordable and easiest way to significantly increase the efficiency of cement concrete.

Application of hyperplasticizers in concrete technology allows to increase durability and decrease porosity of cement stone with decrease of water-cement ratio up to 40 % and the same workability. To densify the structure of cement, increasing the number of hydration products, especially low-base calcium hydrosilicates and increase the strength of the crystal structure should be applied hardening gas pedal additives. To significantly increase the durability of concrete it is necessary to use hydrophobic additives. Hydrophobization of internal surface of pores and cement stone capillaries in concrete, which is achieved by chemisorptional interaction of organic compounds with hydrate new formations of cement, helps to decrease the probability of salt crystal nucleation and growth, which, combined with the effect of plasticizing and reducing the water consumption of concrete mixture, significantly increases the durability and service life of concrete [10,11].

Thus, the modification of cement concrete complex additives that combine a hyperplasticizer, gas pedal hardening and hydrophobic, will significantly increase the strength, durability in hostile environments and durability of heavy concrete.

Superplasticizer additives have significant water-reducing effect. These modifiers allow reducing water-cement ratio up to 25 % depending on mineralogical composition of cement, amount of introduced additive and their basis.

To densify the structure of cement stone, increasing the number of hydration products, especially low-base calcium hydrosilicates and increase the strength of the crystal structure should be applied additives - hardening gas pedals. The use of hydrophobizers in combination with the effect of plasticizing and reducing the water consumption of concrete mix will significantly increase the corrosion resistance and durability of heavy concrete.

Thus, the use of hyperplasticizers in combination with high-performance gas pedals of hardening and hydrophobizers will accelerate the set strength, increase the degree of hydration of clinker minerals, will contribute to the formation of a dense, homogeneous structure of stable hydrate phases, which will increase the strength, density and durability of concrete, as well as increase the economic effect of complex additives in precast and monolithic construction, due to the reducing[6].

Table 1 - Classification of superplasticizers

Type of superplasticizer	**Polymer basis**	**Mechanism of action**		**Water reducing effect,%**	**Relative cost of dry polymer, %**
		electrostatics	**sterical**		
NF	**Sulfated naphthalene formaldehyde**	**+ + +**	**4-**	**15-25**	**30**

MF	**Sulfated melamine formaldehyde**	+ + +	+	**15-25**	**70**
LSTM	**Modified lignosulfonate**	+ + +	+	**10-20**	**25**
P	**Polyoxide polycarboxylate (acrylate)**	+ +	+ +	**20-30**	**80**
EP	**Polyoxide polycarboxylate (acrylate) with grafted ester**	+ +	+ + +	**25-40**	**100**

As can be seen from Table 1.1, the greatest efficiency at the moment.

Using the specific properties of superplasticizers, their influence on the rheological properties of the mobile concrete mixture, preservation of its cohesiveness and non-scratchability, in foreign practice these additives are widely used in manufacturing monolithic structures from cast concrete mixtures with a slump of the cone of 20 cm. According to the data of some authors, application of such mixtures is economically reasonable, since labor costs for its processing are decreasing, labor productivity by 50-90 % increases. Cast concrete mix, obtained through the introduction of superplasticizer, allows combining good workability with high compressive, tensile and flexural strength of concrete. Cast concrete mixtures, as shown in, have high water-holding capacity and reduced water separation. Especially appropriate is the use of cast concrete mixtures in monolithic densely reinforced structures. In this case, as noted in labor intensity of placement of such concrete is reduced by 3-4 times. In our country, as well as abroad, mobile concrete mixtures with superplasticizers additives are also used in precast structures. The use of mobile mixtures reduces labor costs for the preparation, transportation of concrete mixture and shaping structures, significantly improves working conditions of workers, improves the quality of products and their appearance. A distinctive feature of superplasticizers compared with conventional powders is their property not to slow down the hardening and hydration of binders and the lack of air entrainment, so that concrete with such additives have high strength properties. The introduction of super-plasticizers into equal-plastic concrete mixtures reduces their water consumption by 25-30% compared to compositions without additives, while the density and durability of concrete increase significantly and its strength increases by 50-70%.[18],

Most researchers prefer to classify superplasticizers by chemical composition and mechanism of action.

RESULTS

The mechanism of plasticizing action of superplasticizers, according to the data [is the chemical interaction of sulfonate groups of polymer molecules with calcium ions on the surface of cement particles with the formation of calcium salts of polymer preventing particle sticking and improving their sliding relative to each other. The works [23, 53, 120] indicate that significant water reduction of cement systems in the presence of NF, MF, LSTM is achieved mainly due to adsorption on cement grains and hydrate phases and providing them with homogenous electrostatic charge, which causes repulsion and dispersion of cement flocculi. At the same time, it is known that the use of these additives leads to retardation of cement hydration in the early stages of hardening, can lead to delamination of cement suspensions, which is an obstacle to obtain modern cast, self-strengthening and high quality cement concrete.

All cements are ordinary industrially produced. Specific surface area of the given cements was in the range of 3000-3500 cm2/g. The physical and mechanical properties of cement stone, cement-sand mortar with the studied additives were determined on the given cements. Physical-mechanical characteristics of the above cement compounds, defined according to GOST 310.1.2.3-76 and GOST 310.4-81 are given in Table 2.

Table 2 Physical and mechanical properties of cements

Physical and mechanical properties	Type of cement		
	1	2	3
True density, g/cm^3	3.1	3,1	3,1
Bulk density, kg/m^3	1,3	1,3	1,3
1 . Normal thickness, %	26.0	27,0	25,0
2. Timing of setting, hours-min.			
- Beginning	2-30	2-15	4-00
- end of	4-40	4-45	6-04
3. Grind fineness, %	7,2	7.7	6,2
4. Ultimate strength at the age of 28 days, MPa:			
- under compression	43.0	41,3	51,0
- at bending	7.1	7,4	8,5
Uniformity of volume change	Endured	Endured	Endured

Cements meet the requirements of GOST 10178-85.

Fine aggregate

As the fine aggregate for mortars used sand Chinazfield, which meets the requirements of GOST 8736-93 and GOST 8735-88, with a true density - 2.6 g / cm3, bulk density - 1.53 g / cm3, the vacancy rate P = (1 - 1.653/2,6) * 100 = 36.42%.

The fine aggregate was tested in accordance with GOST 8735-88 requirements.

The particle size distribution is presented in Table 3

Name of residuals	Sieve sizes, mm.							Passed
	10	5	2,5	1,25	0,63	0,315	0,14	0,14
Private, g	-	26	107	115	133	423	166	6,9
Private, %	-	2,6	10,7	11,5	13,3	42,3	16,6	0,7

Full, %	-	2,6	13,3	24,5	38,1	80,4	97	97,7

Coarseness modulus:

Mcr= (13.3 + 24.8 + 38.1 + 80.4 + 97.7) : 100 = 2,54

The content of organic particles - the color of the liquid over the sand is lighter than the reference.

The content of dusty and clayey particles determined by the method of weaning was 0.96%.

The tested sand meets the requirements for the preparation of the concrete mixture used in concreting.

Coarse aggregate

Gravel crushed stone was used as coarse aggregate, the particle size distribution of which is given in Table 2.5.

The coarse aggregate was tested in accordance with the requirements of GOST 8269.0-97.

The particle size distribution is presented in Table 4.

Name of residuals	Sieve sizes, mm.									Passed
	40	25	20	15	12,5	10	7,5	5	2,5	0,14
Private, g	-	-	0,4	0,2	0,1	0,1	5,74	2,84	0,4	0,2
Private, %	-	-	4,0	2,0	1,0	1,0	57,4	28,4	3,5	2,0
Full, %	-	-	4,0	6,0	7,0	8,0	65,4	93,8	97,3	99,3

The density of crushed gravel - 2.72 g/cm3;

The average density (the definition was carried out according to GOST 8269.0-97) - 2.62 g/cm3;

Bulk density - 1,400 g/cm3;

Porosity - 1,3%;

Voidiness - 44,54%.

Presence of lamellar and needle grains Table 5.

Type aggregate	Sample weight, g	Number of lamellar and needle grains	
		g	%
Crushed stone	5000	1310	26,2

In accordance with Section 4.3.2 crushed stone belongs to the fourth group with grains of plastic (flaky) and needle-shaped up to 35%.

Thus, the presented crushed stone in terms of granulometry, the content of silt and clay particles, organic impurities and flaky grains meets the requirements of GOST for concrete.

Average density of cement stone was determined on samples-cubes of 2x2x2 cm, cement-sand mortar - on bars of 4x4x16 cm in size and concrete - on cubes with 10 cm rib, dried to a constant mass at a temperature of 105 ° C.

Compressive and flexural strength of cement-sand mortar was determined on samples of bars 4x4x16 cm in size according to GOST 310.4-81.

Compressive strength of cement stone was determined on the samples - cubes of 2x2x2 cm. Tests of compressive strength of concrete samples were made on samples 100x100x100 mm according to the method of GOST 10180-90 "Concretes. Methods for Determining Strength on Control1 Samples", and at bending and prism strength on the prisms of size 10x10x40 cm.

Determination of mobility, average density of mortar mixtures was carried out according to GOST 5802-86 "mortars construction. Test Methods". Determination of the average density of concrete was carried out according to GOST 12730.1-78 "Concretes. Methods of determination of density.

The corrosion resistance of 1:3 cement mortar of equal plastic mixtures of normal consistence was studied on beam specimens of 4x4x16 cm by complex method, which included determination of coefficient of resistance Kc combined with changes in linear size and mass of control specimens exposed to aggressive medium for 180 days with respect to control specimens exposed to fresh water for 180 days.

Frost resistance of heavy concrete with additives was studied by the known method according to GOST 10060.3-91 "Concretes. Dilatometric method of the ascending determination of frost resistance". Researches were carried out on cube samples of 10x10x10 cm which were kept in a chamber of normal storage for 28 days. Samples of heavy concrete with optimum content of additives were tested for frost-resistance.

Waterproofing capacity of concrete with optimum content of additives was determined according to GOST 12730.5-84 "Concretes. Waterproofing test methods", as well as according to appendix 4 of GOST 12730.5-84 "Accelerated method of determination of water impermeability of concrete as per its air permeability" on 150 mm diameter and height cylinder samples with the help of "Agama-2RM" device. The degree of water tightness of concrete is characterized by the highest water pressure at which it is not yet observed, seepage through the samples during the test.

The indices of porosity of cement stone were determined by the procedure of GOST 12730.478 "Concretes. Methods for determination of porosity indexes". Total pore volume, the volume of open capillary pores of concrete, the volume of open non-capillary pores of concrete and microporosity index were determined. Average pore size and homogeneity of pores in concrete were determined according to kinetics of water absorption on samples cube size 7.07x7.07x7.07 cm in accordance with Annex GOST 12730.478.

Water absorption of cement mortar at capillary leakage with additives was being determined according to the GOST 31356-2007 "Dry mortars on cement binder. Test methods" on ball specimens of 40x40x160 mm in size. Samples were pre-dried to a constant weight, then the side edges of the samples were covered with melted paraffin.

Shrinkage and swelling of cement mortar with additives were determined by the method of hydrocement [36], according to which samples of bars with the size 4x4x16 cm, made from dough of normal density or mortar mixture of normal consistence in a day from the time of manufacture ¬ saturate with water for 5 days, After that they are placed in a desiccator over supersaturated potash solution and after 7, 14, 28, 90, 180 days to determine on a special device change in linear dimensions with the help of indicator hour type with a division price of 0. 01 mm. Shrinkage (swelling) has been determined as a difference between the length of sample and reference (steel) rod of length 160 mm and expressed in mm per m of length of sample.

CONCLUSION:

Modulus of elasticity and indicators of prismatic strength; determined according to the method of GOST 24452-80 "Concretes. Methods of determination of prism strength, modulus of elasticity and Poisson's coefficient".

1.On the basis of analysis of domestic and foreign literature and. following experimental testing the most effective components of the complex additive have been selected and its composition has been optimized. It has been shown that new complex additive for heavy concrete based on polycarboxylate ethers, sodium sulfate and polyphenylethoxysiloxane can significantly increase physical-mechanical properties and durability of heavy concrete.

2.The introduction of a complex additive in the composition of concrete reduces the water consumption of concrete mixture by 27-30% and increases the compressive strength: after a day of normal hardening by 79-123%, after 28 days - by 32-66%.

3.Complex additive allows you to increase the frost resistance and water tightness of heavy concrete in 4-5 times (from F150 to F800, from W4 to W20).

4.The regularities of the effect of the new complex additive on the physical-mechanical properties and durability of heavy concrete have been established for the first time. It has been found that the increase of durability, frost resistance and water impermeability of heavy concrete with the introduction of this complex additive provides due to the formation of dense and homogeneous concrete structure (total porosity decreases from 15.3% to 5.0%, the average pore size (X) decreases from 50.8 to 26.3), characterized by the capillary porosity decrease from 9.8 to 2.2% while increasing the share of closed pores and capillaries.

5.The modification of heavy concrete with complex additive leads to

Increase of concrete sulfate resistance (sulfate resistance coefficient increases from 0.54 up to 0.96). It is provided due to increase of cement stone density, increase of cement hydration rate, decrease of free calcium hydroxide portion due to its binding to low basic calcium hydrosilicates crystallizing predominantly in the fine disperse form. '

6.Influence of conditions of hardening of modified concrete (natural hardening, steaming, autoclave processing) on formation of micro- and macrostructure and physical and mechanical properties of concrete has been established. It is shown that the greatest strength gain is achieved during autoclave curing, which is associated with a 29 % increase in the degree of cement hydration, formation of a microcrystalline structure of the cement stone with an increased content of low-base calcium hydrosilicates, which have a higher specific surface area (from 344 to 421 m2/g).

7.Mathematical dependences of influence of composition and dosage of complex additive and its components on strength, frost resistance and water-permeability of heavy concrete have been obtained.

8.Rational fields of application of heavy concrete modified by complex additive have been established. The most effective application of concretes with complex admixture in precast concrete production in order to reduce cement consumption (up to 30%) and to decrease the duration of concrete testing from 12 hours to 8 hours, and in some cases even to complete rejection of concrete testing when 80% of final strength is obtained after 24 hours of normal hardening. Economic effect of the use of a complex additive to reduce the consumption of Portland cement in concrete, which have high requirements for frost resistance and water resistance.

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