Problems and prospects of self-compacting concrete mixes for high-strength concrete

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Abstract. The prospects and problems of multilevel optimization of the dispersed composition of self-compacting concrete are considered with the aim of significantly increasing its construction and technical properties, with a minimum content of binder. Theoretical and practical principles have been developed for designing the rational composition of concrete with an increased concentration of solid phase per unit volume and operational properties with a complex organomineral additive based on the optimal ratio of finely dispersed mineral and chemical components that optimize its dispersed composition and structure. It is shown that it is advisable to use particles of the clinker phase of several geometric sizes. To study the properties and structure of concrete, we used two fractions of fine aggregate, granite-gab rubble FR. 5-10 mm, Portland cement of class CEM I 42.5N, finely dispersed granulated blast furnace slag, metakaolin, silica fume, highly dispersed cement fraction, Glenium 430 superplasticizer and highly valent hardening accelerator. Research methods: the shape and size of the dispersed particles of the components were determined by a laser analyzer, the mobility of the concrete mix in accordance with GOST 10181-2014, the compressive strength of concrete in accordance with GOST 10180-2012. The structure of the cement stone was studied using scanning electron microscopy, thermographic and X-ray phase analysis methods. The strength of concrete with an optimized dispersed composition, superplasticizer and a highly valent hardening accelerator prepared using self-compacting concrete mixtures, aged 1 day after hardening under normal conditions (NU) was 58; 67; 77, and in 28 days - 150; 186; 219 MPa with cement consumption of 650, 710, 770 kg/m³, respectively. Multilevel dispersion-granulometric analysis in combination with chemical modification of the composition of self-compacting concrete mixtures ensures the synthesis of high-strength concrete with a minimum consumption of Portland cement and high physical and mechanical properties. It is advisable to use several structural levels of particles of the clinker component.

1. Introduction

Significant disadvantages of currently used high-strength concrete is a high absolute consumption of a binder, as well as its low specific consumption per unit of strength.

Multi-component with the goal of multi-level dispersed modification of the composition is the main method for producing highly efficient concrete with a minimum binder content and high construction and technical properties called Reactive Powder Concrete (RPC). The main principle of obtaining RPC is to ensure the creation of a dense highly filled solid phase of the initial components of a homogeneous structure by optimizing the particle size distribution at various structural levels and low water content of the concrete mixture [1-3]. A promising direction for the production of RPC is the use of self-compacting concrete mixtures (SCC) [4, 5]. In the production of self-compacting concrete, it may be...
necessary to meet the requirements of a number of conflicting factors that contribute to the non-separability of the mixture and its quality compaction. In particular, the concrete mixture should be characterized by high values of the viscosity index and its fluidity, water separation and delamination should not be observed, and the strength of concrete should have a maximum value. A high level of these characteristics is ensured by the use of modern polycarboxylate type superplasticizers, finely dispersed mineral materials, as well as various highly effective chemical additives in the form of viscosity modifiers, setting retarders, and hardening accelerators as a part of self-compacting concrete [4].

In addition, to ensure high-quality self-compaction of the concrete mixture, such technological methods are used as increasing the proportion (up to 0.5 and above) of sand in the aggregate mixture, reducing the consumption of coarse aggregate and maximum grain size (most preferred size is 5(3)-10 mm), low water-binding ratio [6]. The effect of maximum fluidity and self-sealing of the concrete mixture is achieved by reducing contact interactions between aggregate grains, as well as a high content of cement paste. The indicated types of concrete with a high cement content are characterized by increased heat generation, significantly increasing the kinetic energy in the initial period of the cement system. For this reason, the fixation of the formed particles of hydrated phases during structure formation due to molecular selection can occur mainly in the position of long-range coagulation, thereby determining a significant increase in defectiveness and an increase in its microporosity, as well as a decrease in the construction and technical properties of concrete [2, 7, 8]. Obtaining concrete mixtures with a high content of cement paste at a lower consumption of clinker cement is possible when it is partially replaced by highly dispersed mineral materials - finely ground granulated blast furnace slag, fly ash, silica fume, etc. [5, 9-13]. Replacing part of the cement with dispersed mineral additives will make it possible to obtain a cement paste with a high level of fluidity without sedimentation, water separation and delamination, and a concrete mixture with a higher viscosity. The most important factors in terms of significance in this case are the choice of the type, dispersion, pozzolanic activity and energy state of mineral modifiers [2, 14], which provide a high concentration of the solid phase in a unit volume and a high binding energy between particles.

Obviously, a structure with a high concentration of the solid phase can be achieved by obtaining the densest packing of particles and grains of a multicomponent cement system only by using them with optimal parameters (dispersion, content) for each hierarchical level, at which each subsequent finer fraction is distributed mainly in interparticle or intergranular voids are less dispersed with their maximum filling [2]. The mazically distributed oppositely charged minerals on the surface of clinker particles and mineral modifiers and the electrostatic interaction between them will contribute to their spontaneous spatial orientation and to be fixed in the interparticle voids of the multicomponent system at their dispersed structural levels. At such a level of self-organization of the structure, a decrease in the degree of disorder of the multicomponent system, an increase in its potential energy and viscosity, which ensures higher uniformity and unrefillability of the self-compacting concrete mixture, will be observed.

Of particular importance in self-compacting concrete mixtures for the production of high-strength concrete is the use of finely dispersed nanometer-level components (carbon fibers, fullerenes, conventionally silica fume, etc.). Obviously, their content due to the high dispersion and energy state, for example, the presence of a large amount of Gibbs free energy, as well as molecular selection during structure formation should be insignificant, providing high rheological properties of cement paste, density and strength of concrete. The stated theoretical position is confirmed by the results obtained by most researchers of this problem [15, 16]. For example, a study of the microstructure of the cement matrix of fine-grained concrete containing carbon nanofibers in an amount of only 25 g/m³ showed its very high density (figure 1).
Obtaining high strength classes of RPC from self-compacting concrete mixtures can be achieved by creating a discrete - continuous dispersion-granulometric composition of particles and grains of a solid phase. In this case, each subsequent, finer-dispersed fraction should be distributed in optimal amounts with maximum filling of interparticle or intergranular voids between particles or grains less dispersed. The volume of remaining voids in such a system will be minimal [2]. In real systems of a conglomerate or composite type of structure, there is a possibility that two or more dispersed particles can combine and constitute a separate aggregate [19]. In such microvolumes of cement systems, the pozzolanic reaction practically does not proceed, and they are pseudo-pores 5-7 microns in size (case of three particles) and 0.5-1.5 microns (two particles). The indicated structural defects make a significant contribution to the decrease in strength, frost resistance, and deformation characteristics of cement stone.

The choice of materials for a uniform distribution of particles at different levels of the structure in terms of dispersion and content in order to form a more ordered structure should ensure either a uniform course of their hydration or a pozzolanic reaction in each microvolume of a multicomponent cement system. In addition, in order to obtain high strength of such systems, dispersed particles of all levels must have high elastic moduli and most expediently coincide in value, providing a more uniform stress state, including when approaching a system of energy or substance [2]. The level of allowed input energy to the material in this case increases.

An increase in strength indicators, in addition to increasing the density of the initial particle packing, is also provided by limiting the degree of hydration of clinker minerals while maintaining the maximum volume of the unhydrated part — relics of particles with a strength of 310 MPa (average strength of hydrated phases is 135 MPa).

Thus, the synthesis of a multicomponent cement system with a multilevel dispersion-granulometric modification of the structure is most expedient to be carried out using the following fundamental principles.

Coarse aggregate is taken in fractions of 5 (3)-10 mm, and its content in concrete does not exceed sand consumption in order to ensure a low level of ultimate shear stress (yield strength) of the concrete mixture [20, 21]. Fine aggregate is taken in the form of two or three fractions, for example, a coarse fraction on average 0.3 mm in the amount of 80% and fine - 0.12 mm - 20%, providing a significant reduction in its intergranular voidage and air entrainment in the concrete mixture during its preparation [1]. The volume of a multicomponent binder is determined by the absolute volume method, and dispersed structural levels can be synthesized as follows. For example, the first level is in the form of Portland cement with a dispersion of 270 - 350 m² / kg or less in order to ensure long-term preservation of clinker particles, durable with a high elastic modulus, in a cement stone. To fill the first level of interparticle voids of Portland cement, finely dispersed blast furnace granular slag is used in an amount of 20-25% of the cement mass with an optimum dispersion of 450-500 m²/kg [2]. Due to optimal dispersion and the presence of mazically distributed oppositely charged minerals on the surface and electrostatic interaction with clinker particles, its particles are spontaneously volume oriented and are fixed with high energy binding to them in its interparticle voids. For the second level, finely dispersed Portland cement is used in an amount of 4-12% - 900-1100 m²/kg [1, 2], which ensures a uniform pozzolanic reaction in all microvolumes containing a mineral modifier and prevents the formation of their aggregates, for the third metakaolin - 2-15% - 1450-1500 m²/kg, and the fourth - silica fume - 2-
6% - 18000-21000 m²/kg, which contributes due to the presence of a small number of particles at the nanometer level of stabilization of the structure of cement stone and fixation due to molecular selection of particles of hydrated fa coagulation in the proximal position, significantly increasing its density [7, 8, 20] and also due to the formation of strong secondary pozzolanic reaction low-basic hydrosilicate phases. This is due to the fact that highly dispersed amorphous silica, interacting with calcium hydroxide, forms nanometer-level fibrous calcium hydrosilicates during the preparation of the concrete mixture, which create structural agglomerations that contribute to the clustering of hydrated phase particles in high-density packaging. The optimal content of silica fume and metakaolin in this case will be insignificant and determined experimentally.

2. Materials and methods
The study of the properties and structure of concrete was carried out using two fractions of fine aggregate with a size of 0.315 and 0.16 mm, respectively, in the amount of 80 and 20%, granite-hornbeam crushed stone with a size of 5-10 mm, Portland cement of class CEM I 42.5N with a specific surface area of 296 m²/kg, finely divided blast furnace granulated slag – 453 m²/kg, metakaolin, silica fume, highly dispersed cement fraction. Cement consumption, incl. multi-component, depending on the research task, varied in the range of 450-800 kg/m³ of concrete. Glenium 430 (LLC BASF-Stroitelnye Sistemy) in the amount of 0.45-0.56% of the cement mass and a highly valent accelerator hardening accelerator in the amount of 0.007% in accordance with the Schulze-Hardy rule were used as superplasticizer [22, 23].

The following research methods were used: the shape and size of the dispersed particles of the components were determined by a laser analyzer, the mobility of the concrete mixture in accordance with GOST (Russian Standard) 10181-2014, the compressive strength of concrete in accordance with GOST (Russian Standard) 10180-2012. The structure of cement stone was studied using thermographic and X-ray phase analysis methods.

3. Results and discussion
The study of the structure of cement stone using scanning electron microscopy with microanalysis showed that finely ground granulated blast furnace slag with optimal parameters (dispersion and quantity) is characterized by a uniform distribution (coefficient of variation 0.5%) of its particles in the matrix of a multicomponent cement stone. Such parameters of the components of the first hierarchical level of the microstructure provide a significant decrease in its porosity, a high level of solid phase filling, a uniform course of the pozzolanic reaction in all microvolumes, and also the presence of relics of the coarse fraction of clinker particles.

The finely dispersed fraction of the clinker component for multicomponent cement was used with a fineness of 890-900 m²/kg and was characterized by a content of particles of 5-8 microns or less in an amount of up to 11.3-12.5%, and particles -5-30 microns - up to 60%, almost more than 2 times higher than their content in Portland cement for industrial production. The functional need for its application is as follows. Firstly, the filling of the second hierarchical level in order to increase the concentration of the solid phase in a unit volume. Secondly, ensuring a homogeneous reaction between portlandite and silicon dioxide in all microvolumes of cement paste and stone. Such a mechanism of action provides a more uniform distribution structure of hydrosilicate phases in each microvolume of cement stone, its lower imperfection and high concrete strength. Thirdly, a decrease in the degree of hydration of particles of the coarse fraction of the clinker component, large durable relics of which will make a significant contribution to increasing the strength of cement stone and concrete.

In the initial period, finely dispersed clinker particles of mainly the second hierarchical level of the structure of multicomponent cement are almost completely hydrated and, as a result of molecular selection, are distributed in the form of hydration products around the neighboring larger particles in terms of their composition and structure of hydrated phases. In the same period, activation of the processes of hydration of slag minerals will be observed. The hydrosilicate gel layer thickens outward from the unhydrated surface of the clinker particle, absorbing ettringite crystals and thus synthesizing a conglomerate type of cement stone microstructure. Calcium hydrosulfoaluminates. being impurity
inclusions, in the microstructure of the potassium-silicate hydrate phase they contribute, owing to their needle-shaped and/or more isometric hexagonal-prismatic, in the presence of plasticizing modifiers in the composition of the concrete structure and nanometer size, increasing its density and strength. Obviously, at the same time, their inclusion as an impurity phase reduces the strength of the hydrosilicate neoplasms of cement stone. Thus, the contribution of calcium hydrosulfoaluminates to the strength of the structure of cement stone is twofold. Therefore, for the production of high-strength concrete, it is advisable to use cements with a low content of mineral C3A.

Calcium hydroxide released as a result of hydration of calcium-silicate clinker minerals interacts with silica of silica fume and other silicon-containing additives, which are mainly in an amorphous state, forming strong low-base, so-called, secondary calcium hydrosilicates. Obviously, in this case, acceleration of the hydration processes of clinker minerals C3S and C2S is observed. The product formed as a result of the pozzolanic reaction at a lower kinetic energy of the particles of the hydrated phases, and called the hydraulics by V. Michaelis, is characterized by a higher density and strength, due to the fixation of these particles mainly in the position of near coagulation, and less by 1.5-2 times the content of chemically bound water in them [19]. With a sufficient volume of hydration products of the calcium-silicate phases of clinker, slag, and the pozzolanic reaction, they merge into a strong dense, less defective, relatively homogeneous, finely dispersed conglomerate type structure with a high concentration of the solid phase and containing mainly pores of helium size. A significant contribution to the strength of such a structure will be made by calcium-silicate hydrate phases, relicts of clinker and slag particles, as well as particles of strong mineral additives, if any.

Thus, to significantly increase the strength of concrete, multilevel dense hierarchical packing of a multicomponent system with a high degree of dispersion-particle size distribution is required, which ensures a uniform hydration of the clinker minerals or pozzolanic reaction in all microvolumes, as well as a low water-cement ratio. Obviously, to ensure the high strength of such a structure, complete hydration of the minerals of clinker particles in this case is not required. Self-compacting concrete mixture with a cone spread (RK) of 87 cm, prepared taking into account the above provisions, is characterized by high rheological properties, the absence of mortar and water separation and separation. On the surface of the concrete mixture, uniformly distributed grains of coarse aggregate are observed, confirming the properties described above figure 2.

Figure 2. Self-compacting concrete mixture with CS = 87 cm

Experimental studies have shown that the optimal amount of highly dispersed cement is 6%, metakaolin - 3%, silica fume - 3%, used to replace the equivalent amount of cement, as well as a complex chemical modifier consisting of Glenium ACE 430 - 0.45-0.56 % of the mass of cement and hardening accelerator "AC" - 0.07%. The use of the hardening accelerator provided a synergistic effect of the use of Glenium 430 and made it possible to further reduce the water content of the concrete mixture to 20%.

It was also established that the dispersed multicomponent composition, which is optimized and ordered at 4 levels and self-organized due to optimal geometric and quantitative parameters, as well as the practical mosaic energy state of the surface of the initial powder components, ensures a decrease in
interparticle voids by 12-14% and an increase in concrete strength by more than 2 times (up to 200 MPa and higher). In particular, the compressive strength of concrete at the age of 1 day after hardening in NU was 58; 67; 77, and in 28 days - 150; 185; 219 MPa, with cement consumption of 650, 710 and 770 kg/m³, respectively.

To assess the quality of the structure of concrete, thermographic and X-ray phase studies of its samples were carried out at the age of 28 days after hardening under normal conditions and TVO (Table 1).

Table 1. The composition and test results of concrete

| №  | Type of mineral modifier - content | Mass loss, %, at t°, °C | Ca(OH)₂ | The degree of hydration, % |
|----|----------------------------------|--------------------------|---------|----------------------------|
|    | At the age of 28 days after hardening under normal conditions | 136-147 | 519-531 | 822-832 |                              |
| 1  | Control composition              | 19.1                     | 23.8    | 32.1                       | 24.8 | 55                           |
| 2  | Fine Slag - 20                   | 13.6                     | 22.1    | 24.6                       | 18.2 | 73                           |
| 3  | Fine Slag - 20                   | 13.6                     | 13.7    | 19.8                       | 14.3 | 86                           |
|    | Silica fume - 3                  |                          |         |                            |      |                              |
|    | Metakaolin - 3                   |                          |         |                            |      |                              |
|    | Fine fraction of cement - 6      |                          |         |                            |      |                              |
| 4  | Control composition              | 14.1                     | 15.9    | 23.7                       | 29.2 | 51                           |
| 5  | Fine Slag - 20                   | 12.9                     | 17.6    | 19.8                       | 19.6 | 66                           |
| 6  | Fine Slag - 20                   | 10.8                     | 11.9    | 18.3                       | 6.4  | 81                           |
|    | Silica fume - 3                  |                          |         |                            |      |                              |
|    | Metakaolin - 3                   |                          |         |                            |      |                              |
|    | Fine fraction of cement - 6      |                          |         |                            |      |                              |

The structure of concrete with mineral-chemical modifiers having optimal parameters is characterized by a significantly lower content of portlandite and the degree of hydration of Portland cement is 81-86%, exceeding that of the control composition by 29-30%, confirming its higher strength.

4. Conclusion
Multilevel dispersion-particle size distribution in combination with a chemical modification of the composition of self-compacting concrete mixtures is one of the effective directions for producing high-strength concrete with a minimum absolute and specific per unit strength flow rate of Portland cement and high physical and mechanical properties.

SCC in this case are characterized by high viscosity at a low level of ultimate shear stress, and the combined use of superplasticizers and hardening accelerators is characterized by a synergistic effect in the aspect of plasticization of concrete mix. It is advisable to use a differently dispersed clinker component, which ensures an increase in the concentration of the solid phase in a unit volume, a uniform course of hydration reactions of clinker minerals and a pozzolanic reaction in all microvolumes of a multicomponent cement system, as well as the presence of strong large sizes of clinker particle relics that make a significant contribution to the integral strength of high-strength concrete additive).

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