Modified early-strength concrete mix

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Abstract. This paper suggests new early-strength concrete mixes composed of Portland cement, coarse and fine aggregates, a complex modifying admixture containing carbon nano tubes and bishofite produced at the Volgograd deposit. The paper represents the findings of scientific and experimental research and describes the impact of the suggested admixtures on the structure formation, rheological, physical and mechanical properties of the early-strength concrete. The micro-structural analysis revealed that the concrete mix containing a complex modifier is characterized by compact cement-and -sand matrix and a more homogeneous structure at the interface with the grains of the coarse aggregate. Review of the test results proved that the suggested coposition and the complex admixture dosage contribute to decreased water-cement ratio, in-creased fluidity of concrete and a higher strength of hardened concrete at the early and final hardening stages.

1. Introduction

The cast-in-situ reinforced concrete structures made of structurally strong and compact heavy concretes are getting more and more widely used in the construction of modern industrial facilities.

During the development of concrete mixes with desired properties the technological and operational factors related to the corrosive medium impact are to be taken into account. Quantitative evaluation of physical and mechanical properties is connected with the type and composition of concrete, the time and conditions of its strengthening. While investigating various concrete properties it is necessary to conduct an integrated evaluation of parameters accounting for various properties of concrete mix and hardened concrete. It is well known that the key parameter affecting the strength is micro- and macro structure of concrete, the formation of which is determined by appropriate selection of the main components and various modifiers.

2. Relevance

At present heavy concretes having long setting and hardening time, insufficient water tightness and crack resistance are still used for construction of massive hydraulic structures, offshore oil/gas and other industrial facilities. The process of concrete pumping into forms implies the use of high fluidity concrete mixes having relatively short setting and hardening periods. In this connection the crucial task is the use of complex admixtures which improve the rheological properties of concrete mixes and accelerate setting and strengthening of concrete at the early and final hardening stages.

The existing range of plastifiers and other kind of modifiers which are currently available at the market [1-8] is not sufficient. That is why the search for and development of new materials is nowadays an urgent task.
Problem statement. In order to gain high fluidity of the concrete mix to be poured by means of pumping equipment it is necessary to increase its water requirement. However, this will lead to a higher water-cement ratio and consequentially to increased porosity of the hardened concrete, its lower strength and crack-resistance and also to its increased strengthening time. Complex modifying admixtures are used in order to ensure the desired concrete properties and control the rheological parameters of concrete mix. They reduce the water requirement of concrete mix, setting and hardening time of concrete.

The task of receiving high-strength concretes can be accomplished through strengthening of macro-, micro- and even nano-structure of the concrete matrix by means of various modifiers, including complex ones. Nanoscience and nanotechnologies were first used in construction in Russia at the beginning of the XXI century [9-11]. The first experiments implied the use of nano-additives with plastifiers for the improvement of properties including concrete for casting [12-14]. Yu. V. Pukharenko, A. A. Smolikov [15, 16] offered using fulleroid nano-structures for reinforcing cement concrete. The development of nano-modified fiber reinforced concrete is of special interest [17-19].

For development of concrete mix compositions and preparation process the major concrete components of local origin were used. For preparation of complex admixture the magnesium chloride (bishofite) solution produced at the Volgograd deposit was used as it does not require any additional processing. Its reserves amount to ca. 500 Billion Tons.

3. Theoretical part

In the course of scientific and experimental investigations the impact of various types of modifiers having different composition (including nano admixtures) was assessed.

There exists a concrete mix which is composed of Portland cement, an aggregate and a complex modifier containing calcium chloride, soap/synthetic detergent manufacturing wastes in the amount of 3 to 8 % of the cement mass odb [7]. The mentioned concrete mix has a relatively short setting time but gains little strength at the early hardening stage.

The scientific and engineering task is to develop a complex modifier to ensure higher fluidity of concrete without increasing the water-cement ratio so that better strength properties of concrete are demonstrated both at the early and the final hardening stages.

The new concrete compositions were developed based on Portland cement, fine and coarse aggregates and also on addition of concrete structure modifiers. The following basic components were used to make the samples to be tested: PC M500 D0-N Portland cement produced by ZAO ‘Oskolcement’, quartz sand (fineness modulus - 1.9) produced by ZAO Orlovsky Sandpit’ in the Volgograd Region - as a fine aggregate, crushed stone with a fraction of 5 to 20 mm - produced by Bystrorechencky Sandpit - as a coarse aggregate.

In order to accomplish the task a complex modifier was developed; it which improves the rheological properties of concrete mix, contributes to compaction and strengthening of the micro-structure of the hardened stone. The complex modifier contains the following components: sodium chloride, ACF oligomer, bishofite produced in the Volgograd Region, carbon nano tubes.

The oligomer products of acetone and formaldehyde condensation or acetone and formaldehyde resins (ACF) are viscous liquids containing up to 25 % of free water. A certain concentration of this concrete modifier affects the hydration processes of Portland cement and contributes to a considerable modification of composition and structure of the newly formed cement stone.

Addition of acetone and formaldehyde resins in the alkaline environment of the concrete leads to increased fluidity of the mix even though the water-cement ratio is somewhat decreased. The structure of matrix covered with a polymeric film contributes to increased water-resistance and, therefore, to a higher frost-resistance, water-tightness and durability under corrosive environment. During preliminary testing it was found out that with a certain dosage of ACF admixture the fluidity of concrete mix increases up to 25 %. And the water-cement ratio in that case decreased to 15 %.

To shorten the setting and strengthening time of concrete electrolyte admixtures were added: sodium chloride and bishofite containing up to 96 % of magnesium chloride water solution (MgCl₂·6H₂O). The use of bishofite which is produced in the Low Volga Region and requires no further processing as well
as of sodium chloride as components of the complex admixture contributes to accelerated hydration of the cement-water paste with formation of compacted and strong crystallization centres due to increased ion activity of the mix. 

As their efficiency has been proved by many experimental investigations [17-20], the carbon nano modifiers were used to control the micro- and nano-structure of concrete with the view to increase the strength of hardened concrete. For this investigation the carbon nano modifier (model name - Taunit) invented by the State Technical University of Tambov was used. The multilayer carbon tubes are cylinder-shaped cavities with a 8 to 40 nm diameter and a 2 to 50 µm length.

Thus, addition of the complex modifier containing sodium chloride, bishofite, ACF polymer and certain quantities of nano tubes helps to receive the fluid concrete mix having a low water-cement ratio.

As a result the hardening process is accelerated and the homogeneous compact and strong structure of concrete is formed.

4. Results of experimental studies
The experimental investigation was intended to identify the impact of different dosages of complex admixture on the fluidity of concrete mix and on the strength of hardened concrete.

The early strength modifying mix is to be prepared as follows. The complex modifier containing the ACF polymer, sodium chloride, bishofite and carbon nano admixture should be first dissolved together with the mixing water in the ultrasonic disperser under a frequency of up to 25 kHz unless the homogenized solution is received. As a result of the high speed ultrasonic intermixing the almost homogeneous mix demonstrates the long lasting stability and high capability of reaction.

Simultaneously the Portland cement and aggregates are batched and subsequently mixed inside the standard concrete mixer. The mixing water and the complex modifier are added to the prepared dry mix and all of the components are jointly intermixed within 3 to 5 minutes.

As soon as the intermixing was over the fluidity of concrete mix was measured by means of standard cone and after that the standard cube-shaped forms sized 100x100x100 mm were filled to be then compacted at the laboratory vibroplatform. After that the samples hardened under natural conditions at a temperature 18-25 °C and humidity of 80 – 95 % during 28 days.

A number of mix compositions with different contents of components were prepared. The received concrete compositions were tested after 24 hours and 28 days of hardening by destructive method (with the use of press) and non-destructive ultrasonic method.

The developed compositions of the complex modifier for the early strength concrete mix are presented in table 1.

| Complex admixture ratio | Proportion of components, mass % |
|-------------------------|---------------------------------|
|                         | 1  | 2  | 3  | 4  |
| Sodium Chloride         | 1.5| 2.25| 3.0| 3.25|
| Bishofite               | 1.5| 2.25| 3.0| 3.25|
| Oligomer ACF            | 0.1| 0.2 | 0.3| 0.4 |
| Nano Admixture Taunit   | 0.05| 0.05| 0.05| 0.05|
| Water                   | 96.85| 95.25| 93.65| 93.05|

Fluidity of concrete mix and strength properties of concrete at various hardening stages are shown in table 2.

The micro-structural analysis of the concrete mix samples was conducted by means of CAMEBAX scanning electron microscope. The micro-pictures of various zoom rate as shown in figures 1 to 4 prove that the early-strength concrete with a complex modifier has a more compact matrix and a better adhesion at the interface with the concrete aggregates.
Table 2. Properties of the developed early-strength concrete mixes.

| Concrete mix properties | Existing mix [7] | Raw mix compositions 1 | Raw mix compositions 2 | Raw mix compositions 3 | Raw mix compositions 4 |
|-------------------------|------------------|------------------------|------------------------|------------------------|------------------------|
| Slump of standard concrete cone, cm | 3-12 | 13 | 15 | 15 | 15 |
| Start of setting, min | 16-35 | 31 | 33 | 35 | 38 |
| Compression strength at the age of 24 hours, MPa | 4.5 | 3.9 | 4.83 | 6.7 | 5.8 |
| Compression strength at the age of 28 days, MPa | 19.5-32.1 | 38.6 | 39.3 | 40.4 | 39.6 |

Newly formed cement stones of a larger size such as calcium hydrosilicates and others were revealed in the concrete containing the complex admixture.

As a result strength and density of the early strength heavy concrete by far exceed similar parameters of concrete containing no such complex admixture.

Figure 1. Micro-structure of heavy concrete with a complex admixture. CAMEBAX, × 300.

Figure 2. Micro-structure of standard heavy concrete without admixture. CAMEBAX, × 300.
5. Conclusions
Review of the findings of the experimental investigations proved that all of the developed compositions of the early-strength heavy concrete containing the complex modifier have better values of fluidity and strength properties of the concrete mix and hardened concrete at the early and final hardening stages. Further increase of the complex admixture content will not lead to increased concrete fluidity, and strength parameters are somewhat reduced (see table 2, composition 4). Any further increase of the quantity of the complex admixture may also entail salt corrosion of reinforcement or concrete of the concrete structure.

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