Features of hardening and structure formation of concrete with high-dispersion mineral additives

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Abstract. The article deals with the effect of microfiller additives on the properties of high-strength concrete. The effectiveness of microcements – mixtures based on highly dispersed cement and silica fume – has been substantiated. Using the methods of thermokinetic analysis and thermoporometry, the processes of heat release and the formation of microporosity during the hardening of ordinary cement and microcements without additives and with the addition of silica fume are studied. The positive effect of silica fume on the hydration and formation of the structure of cement stone is proved. It is shown that the nature of the hydration interaction in the system of “microcement – silica fume” contributes to the compaction of the structure and reduce the development of shrinkage phenomena. It was revealed that the use of microcements allows to increase the workability of concrete mixtures and to accelerate the rate of curing of high-strength concrete. According to the results of the studies, the high efficiency of the use of components of the type “microcement – silica fume” in the technology of high-strength and durable concrete has been proved.

1. Introduction

Modern concrete science has significantly expanded the capabilities of high-strength concrete technology through the use of organomineral complexes in the form of mineral and chemical additives at the stages of production of concrete mixtures and operation of concrete [1-3]. Such additives summarize the effect of microfillers with the pozzolanic reaction of SiO$_2$-containing products and the modifying effect of superplasticizers.

These include coal fly ash with a dispersion of up to 3000 cm$^2$/g and with low pozzolanic activity [4-6]. Amorphous silica fume (SF) with a particle size of almost two orders of magnitude higher than the size of cement particles is primarily a SiO$_2$-containing product. The high efficiency of such complexes is due to the combined influence of mineral and chemical additives. The presence of active SiO$_2$ determines the possibility of alkali-silica reactions (ASR) during the hardening of concrete and, as a result, damage to the structure of neoplasms during the formation of microcracks, the sizes of which reach 0.6 μm (figure 1) [7-8]. The probability of the course of such reactions is significantly increased when using chemical additives – hardening accelerators based on Na or K [8].

The elimination of these and other shortcomings is achieved by using the so-called microcements (MC) or microconcrete – mixtures based on finely dispersed cement and fine quartz sand [9-10].
2. Materials and research methods

In this paper, we study the hardening and structure formation processes of MCs with microsilica as a filler. MCs based on Portland cement PC and slag Portland cement PCS were used (table 1).

Table 1 – Composition and properties of the MC components

| Characteristics                              | Cements                  | SF |
|----------------------------------------------|--------------------------|----|
|                                              | Ordinary cement C1 | PC | PCS |
| **Density, g/cm**                            | 3.2                      | 3.1 | 2.9 |
| **Content, %**                               |                          |    |     |
| SiO₂                                         | 21.0                     | 21.7 | 31.7 | 93.1 |
| Al₂O₃                                        | 4.6                      | 4.1 | 11.4 | 1.1 |
| Fe₂O₃                                        | 6.1                      | 1.6 | 0.6  | 0.7 |
| CaO                                          | 56.8                     | 65.8 | 44.3 | 0.4 |
| MgO                                          | 4.7                      | 0.8 | 7.0  | 0.7 |
| K₂O                                          | 0.54                     | 0.83 | 0.37 | 1.04 |
| Na₂O                                         | 0.15                     | 0.26 | 0.25 | 0.22 |
| SO₃                                          | 2.1                      | 2.4 | 0.9  | 0.0 |
| **The average particle diameter, microns**   | 13.2                     | 5.0 | 7.9  | 0.15…0.2 |
| **Specific surface area, m²/g**              | 1.0                      | 2.3 | 1.5  | 20…22 |

Figure 1. The occurrence of microcracks during alkali silica reactions

The measurements were performed in the calorimetric center of building materials science on measuring and computing calorimetric complexes [11-12].

Thermokinetic analysis, the experimental basis of which is differential microcalorimetry, was used to study the early stages of hydration by the dependences of the rate of dQ/dτ = f(τ) and the completeness of heat dissipation Q = f(τ) [11]. A Calve type microcalorimeter was used for the temperature range +5 ... + 100 °C with such characteristics: sensitivity 0.05 cal/g, mm, temperature stabilization accuracy ± 10 °C, time constant 20 s. Processing of the results includes obtaining the dependences of the speed and completeness of heat release on time with their subsequent kinetic study – an estimate of the beginning and duration of the induction period, the magnitude and time of reaching the maximum speed and completeness, and the forecast of heat release.

Thermoporometry is a method for assessing the size, volume, pore size distribution. The basis of the method is the dependence of the crystallization temperature of pore water on pore sizes. This dependence
is established from the thermodynamic equilibrium of the system "solid – water – ice", taking into account the state of the interphase surface and the well-known Laplace equation and it has the form [12]:

$$dR_p = \frac{A}{(\Delta T)} \cdot d(\Delta T).$$

(1)

where A is the methodological coefficient.

The volume dV of pores is found from the ratio:

$$dV = \frac{\Delta H}{W_v} \cdot d(\Delta T).$$

(2)

From (2) we obtain the values and distribution of pore volume depending on temperature. Pore size distribution is represented as $dV/dR = f(R)$. A feature of thermoporometry is the determination of parameters only of those pores that are filled with water and are in the range of 1.5 ... 100 nm, which is due to the fulfillment of the Kelvin equation.

The pore volume obtained by thermoporometry corresponds to the volume of free water in the material.

The amount of adsorbed water was determined by calculation, based on the polymolecular theory of adsorption and the volume and radius of the pores.

Chemically bound water corresponds to the difference between the initial content and the sum of free and adsorbed water.

We studied cement samples without (C1) and with the addition of silica fume (C2). For thermokinetic analysis, the sample weight was 1 g. The duration of the experiment was 1 day. In the method of thermoporometry, samples of 3, 6, 12, and 24 h of curing were tested. Their weight averaged 25 mg. W/T in all experiments was 0.5.

3. Discussion of the results

The kinetics of heat release of cement C1 characterizes it as quite active. Hydration of C2 proceeds less intensively, probably due to the reduced energetics of the formation of low-basic CSH (I) hydrosilicates during the interaction of SiO₂ and Ca(OH)₂ (figure 2, a). Already within 24 h, the heat release completeness is lower by 15 cal/g (figure 2, b). A distinctive feature of the hydration of cement C2 is the presence of a doublet of the main maximum heat. The bifurcation, apparently, is due to the interaction of SiO₂ and Ca (OH)₂ at the stage of formation of the cement stone structure at the age of 12 h. The value of the first heat release maximum for C2 samples is almost 2.5 times lower than for C1. This circumstance is probably associated with a high specific surface of silica fume. Water molecules are adsorbed on the surface of silica fume grains, which leads to a decrease in the number of molecules involved in cement hydration.

The study of formation of microporosity of cement stone was carried out using the method of thermoporometry. The research results are presented in figure 3.

A characteristic feature is the reduction in the size and volume of micropores with the addition of silica fume, which is due to the filling of a part of the pore space of cement stone with its particles.

An increase in the specific surface of cements also contributes to a decrease in the size of micropores and a decrease in their total volume (figure 3). The number of capillary pores decreases with a simultaneous increase in the number of gel micropores.
The positive effect of silica fume on the formation of the structure of cement stone is, in our opinion, also due to the fact that even before the concrete mixture begins to harden, the bulk of the alkali of cement compounds will be bound by silica. The decrease in alkali content in the liquid phase caused by this process, in turn, inhibits the development of processes of internal corrosion of concrete [13], which contributes to an increase in durability.

The nature of the pore structure of samples of the obtained MC-SF systems was also investigated by the method of mercury porosimetry. It was noted that microcements contribute to a decrease in the number of capillary (diameter 0.01 ... 100 μm) and the growth of gel pores (diameter less than 0.01 μm), which is in good agreement with the data of thermoporometry. The conclusion about the formation of a denser and less defective structure of the hardened cement stone along with the high homogeneity of the neoplasms determines the high durability of concrete based on them. In [14], activation of the formation of hydrosilicates of the CSH (I) type in this case is noted, which affects the hardening kinetics and structural strength.

Figure 2. Heat release during hydration of cement C1
a) heat release rate; b) heat of hydration
1 – control; 2 – with the addition of SF
The nature of the hydration interaction in the system “microcement – silica fume” “MC-SF” contributes to the compaction of the structure (figure 3). This circumstance affects shrinkage phenomena. For the control composition at the PC, shrinkage at a relative humidity of 90-95% reaches 1.6 mm/m after 2 days. The introduction of silica fume causes a slower development of shrinkage. In 14 days, its value is 2.35 mm/m. Microcement RS in combination with silica fume determines the shrinkage value of 0.9 mm/m in only 2 days.

Concretes for comparative tests contained 430 kg/m³ of “MT-SF” mixture, W/T = 0.37, the consumption of superplasticizer was 0.9% of the weight of cement.

When evaluating workability, it was found that the features of wetting and adsorption of the liquid phase by dispersed components caused a sharp decrease in this important technological characteristic with the introduction of SF and, on the contrary, its improvement in the case of MC, especially on a slag Portland cement basis.

The conclusion about the effect of the micro-fillers type on the strength of concrete is quite unambiguous - cements somewhat reduce it compared to silica fume. However, the rate of curing to a level of 80-90 MPa, i.e. for high-strength concrete, at microcements is much higher. At the age of 7 days, concrete at the MC-RS reaches 95% of brand strength. The increase in the content of micro-fillers ambiguously affects the kinetics of the strength, which, of course, is associated with the composition and properties of cement.
Thus, the studies have shown the high efficiency of using the type “MC-SF” components in the technology of high-strength and durable concrete.

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