Influence of Superplasticizer-Microsilica Complex on Cement Hydration, Structure and Properties of Cement Stone

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Abstract. According to the study results, the influence of complex additives based on microsilica and superplasticizers on the processes of the heat release, hydration, hardening, formation of the structure and properties of cement stone was determined. Calorimetry, derivatography, X-ray phase analysis, electronic microscopy and physical-mechanical methods for analyzing the properties of cement stone were used for the studies. It was established that plasticizing additives, in addition to the main water-reducing and rheological functions, regulate cement solidification and hardening while polycarboxylate superplasticizers even contribute to the formation of a special, amorphized microstructure of cement stone. In a complex containing microsilica and a polycarboxylate superplasticizer the strength increases sharply with a sharp drop in the capillary porosity responsible for the density, permeability, durability, and hence, the longevity of concrete. All this is a weighty argument in favor of the use of microsilica jointly with a polycarboxylate superplasticizer in road concretes operated under aggressive conditions.

1. Introduction

Development and introduction of high-performance and durable concretes into production is one of the main trends of scientific and technical progress in the field of construction [1-3]. This is primarily about road concrete, used in the construction of highways, high-speed railways, bridges, overpasses, road junction, tunnels, etc. Such concrete must match high requirements for strength, frost resistance, water tightness, sulfate resistance and durability [1]. Modern trends in the development of the technology for binders and concretes based on them are characterized by the complication of compositions of the materials and additives used with a view to produce articles with high performance characteristics [3-7]. In this regard, the development of high-performance concretes requires the deepest understanding of the mechanisms of cement hydration which can be significantly supplemented by calorimetry [8-11].

The goal of the work is to study and supplement the features of hydration and hardening of the cement systems of high performance concrete with the help of calorimetry.

Objectives of the paper:

- Determination of the influence of microsilica and complexes of microsilica (MS) + superplasticizer (SP) on the heat release, cement hydration, hardening, formation of the structure and properties of cement stone;
• Interpretation and comparison of the observed heat release with other process characteristics involving complex methods for analyzing phase and structural transformations as well as using basic principles and laws of thermodynamics and chemical kinetics.

2. Research materials and methods
The following raw materials were used for the study:
• cement PC 500 D-0, medium aluminate, LLC Dyckerhoff Korkino Cement CEM I 42.5 N in accordance with GOST 31108-2016 [12], 27.9% normal density;
• superplasticizer polycarboxylate Glenium ACE 430, BASF concern (Germany);
• superplasticizer naphthalene formaldehyde SP-1, LLC Polyplast UralSib, Pervouralsk;
• microsilica of MS-85, Novokuznetsk, in accordance with TU 5743-048-02495332-96 "Condensed Microsilica. Technical Conditions", with pozzolanic activity of 1575 mg/g.

The study of the effect of additives on heat release processes was studied using an 8-channel isothermal calorimeter "TAM Air" at a constant temperature inside the isothermal channel (20 ± 1 °C).

To determine the growth in the compressive strength of cement stone during hardening, sample cubes with a face size of 2 cm were made, the tests were carried out in accordance with the Paragraphs 7.1 and 7.2 of GOST 10180-2012 [13]. The cement stone samples were made at W/C = 0.3 without additives with the addition of MS (8% of cement mass) and MS with superplasticizers (1% of cement mass). Samples were hardened for 28 days at a temperature of 20 ± 5 °C and a relative humidity of 95 ± 5%.

To study the effect of additives on the phase composition of cement stone, derivatographic analysis (DTA) was used, which was performed on the derivatograph of the Luxx STA 409 system made by Netsch. The cement stone samples taken for testing were pre-treated with ethanol, then dried at 50°C and stored at the same temperature until the tests administration. This contributed to the almost complete exclusion of further hydration and carbonization of cement stone [14].

X-ray diffraction (XRD) was used to study the phase composition of cement stone and determine the degree of its hydration. The survey was conducted on a DRON-3 diffractometer upgraded with a PDW in attachment, in the angular interval of 6-70°, under 30 kW voltage, 20 mA current strength, and 1 mm output slit width. The degree of cement stone hydration was determined according to the methodology of Yu. S. Malinin’s internal standard [14,15] on the change in the intensity of the analytical lines of the clinker minerals C3S – 1.77 Å and β-C2S – 2.86 Å, fluorite reflection (CaF2) – 1.64 Å was used as the internal standards, the accuracy of determination of 5 %.

The degree of hydration $\alpha$ was calculated using the formula:

$$\alpha = \frac{\beta - \gamma}{\beta} \times 100\%$$

where $\beta$ is the area of analytical peak for the initial cement, pulse deg / sec; $\gamma$ is the area of the analytical peak of the treated cement system, pulse deg / sec.

To study the cement stone samples of 28-day normal-hardening in an electron microscope, polished samples were made. The polished samples allowed for more reliable assessment of the structure of cement stone, since it provides for taking into account both weak and strong sections of cement stone.

3. Research results
This paper studies the processes of hydration and hardening of cement systems with microsilica, both in the presence of superplasticizers and without them.

3.1. Heat Release Analysis
The processes of wetting, adsorption and hydrolysis of cement minerals, and then the induction period of cement hydration with various superplasticizers at W/C 0.5 and 0.3 are studied in detail in the paper.
[16]. In the present research, the stages of cement hydration and cement systems with microsilica are of a similar nature, and the period of accelerated hydration deserves special attention.

The heat flow in Figure 1, released at the cement hydration during the induction and accelerated period as a function of time and additives, reveals the following.

Using MS both with SP and without them significantly increases the heat release (Figure 1) and accelerates hydration processes. It is known that microsilica enters into a pozzolanic reaction with Ca(OH)₂ and forms low-basic calcium hydrosilicates (CSHs) [17-19]. As a result, the concentration of calcium ions and the environment pH decreases, and the hydrolytic decomposition of C₃S, according to the Le Chatelier principle, proceeds further – towards the external impact compensation. This increases the degree of hydration in the early periods and also promotes the formation of the predominantly low-basic hydrated phases such as CSH-I.

After the active hydration stage, the compositions with microsilica are distinguished from others by the lower heat release (Figure 1, after 40 hours). This is due to the lack of metastable hydrate phases prone to recrystallization during this period.

The heat energy of hydration obtained by the time of heat flow integration (Figure 1) is shown in Figure 2. The dependences obtained clearly demonstrate that MS in the first two days increases the heat release which indicates the cement hydration acceleration.

The heat energy of hydration and hardening fixed after 180 hours shows the minimum values for the compositions with MS (Figure 2). This owes to the fact that MS promotes the formation of low-basic hydrate phases since it is known [20,21] that they are formed with reduced heat energy.

3.2. Physical Indicators Analysis
Figure 3 depicts the compressive strength of cement stone with various additives at the age of 1, 2, 3, 7 and 28-day hardening.

On the first day of hardening the MS-containing compositions show increased strength (Figure 3) due to the acceleration of hydration processes which is confirmed by the increased heat release (Figures 1 and 2) during this period. Compared with the non-additive composition, the cement stone with complex additive MS + SP demonstrates an increased strength (Figure 3), especially with the use of a polycarboxylate superplasticizer.
To determine the porosity of cement stone, the samples for water absorption were tested on days 1, 2, 3, 7 and 28. Water absorption by mass as well as open porosity are shown in Figure 4.

On the very first day, water absorption by mass in the compositions with MS has lowered indices against a no-additive composition. This confirms the assumption that, in the presence of MS, the hydration processes are accelerated.

The MS-containing compositions show low water absorption (Figure 4), especially with the use of a polycarboxylate superplasticizer. This confirms earlier findings [7] that polycarboxylate SP (Glenium ACE 430), in comparison with naphthalene formaldehyde SP (SP-1), forms a denser cement stone structure consisting of poorly crystallized hydrate phases.

It is important to note that the composition without additives shows an increase in water absorption within two days while in the compositions of C + MS and C + MS + SP-1 - within three days. This may be due to the contraction/shrinkage of cement stone in the early periods of hardening and, as a result, its increased open porosity. The cement stone with MS + ACE differs from others in that its hydration and hardening take place without increasing the water absorption in the early periods of hardening. This is probably due to the fact that polycarboxylate superplasticizers contribute to contraction/shrinkage reduction, and this can positively affect the strength, water resistance and frost resistance of concrete.

3.3. Cement Stone Phase Composition Analysis

The content of calcium hydroxide in cement stone with various additives at the age of 7 and 28 days is shown in Figure 5. From the results obtained it follows that the compositions of cement stone with MS have a reduced content of calcium hydroxide (Figure 5). This indicates a rather high pozzolanic activity of the additive.

The content of chemically bound water (Figure 6) can indirectly reflect the degree of cement hydration. To check the robustness of results, the hydration degree was analyzed by means of a comparative quantitative X-ray phase analysis of the initial cement and the examined hydrated samples by using Yu.S. Malinin’s method. The calculation results are shown in Figure 7. In this example, the cement hydration degree (Figure 7) fairly correlates with the content of chemically bound water (Figure 6).

According to the hydration degree (Figures 6 and 7), it is clearly seen that microsilica increases the degree of cement hydration by 7th and 28th days of hardening, and increases it even more with the use of a polycarboxylate superplasticizer.
3.4. Electron Microscopy

Electron microscope photos of the main compositions (3 and 10 thousand-times magnification) are shown in Figure 8. The Table 1 describes the structure of cement stone observed using the electron microscope.

Figure 5. Calcium Hydroxide Content in Cement Stone (7 and 28 Days).

Figure 6. Chemically Bound Water Content in Cement Stone (7 and 28 Days).

Figure 7. Cement Hydration Degree (7 and 28 Days).

Figure 8. Electron Microscope Photos of Main Compositions with 3 and 10 Thousand-Times Magnification.
Table 1. Comparative Characteristics of Electron Microscope Images of Cement Stone.

| Composition       | Structure Characteristic                                                                 |
|-------------------|-----------------------------------------------------------------------------------------|
| C (no additives)  | There are both amorphous and loose, well crystallized areas.                            |
| C + 1%SP-1        | There are somewhat more amorphous phases there, compared with the non-additive composition, but calcium hydroxide, microcrystals, or crystallization centers of the CSH phase are present everywhere. |
| C + 1%ACE         | The structure is represented mainly by amorphous high-basic CSHs. Large-grained local accumulations of calcium hydroxide are found. |
| C + 8%MS          | Hydrate phases are mainly represented by amorphous neoplasms, which include nuclei of crystalline phases and local accumulations of calcium hydroxide. |
| C + 8%MS + 1%SP-1 | Amorphized, but contains a significant amount of crystalline micro-formations comparing to the composition based on MS and polycarboxylate superplasticizer. |
| C + 8%MS + 1%ACE  | The structure is almost completely represented by amorphous low-basic CSHs.              |

4. Conclusion

According to the results of the study of the influence of complex additives based on microsilica and superplasticizers on heat release processes, cement hydration and hardening, the following main aspects can be inferred.

The introduction of microsilica either with superplasticizers or without them leads to:
- acceleration of hydration processes;
- increase of cement hydration degree;
- reduction of hydration and hardening heat energy due to the formation of low-basic CSHs;
- reduction of water absorption of cement stone;
- cement stone formation mainly from low-basic CSHs and reduction of recrystallization activity after the accelerated hydration period.

Polycarboxylate superplasticizer, in combination with microsilica, promotes:
- high plasticity;
- reduction of water absorption and shrinkage of cement stone;
- increase of hydration degree at the optimal dosages;
- cement stone formation mainly from poorly crystallized (amorphized) low-basic CSHs.

By virtue of calorimetric studies it was established that plasticizing additives, in addition to the basic water-reducing and rheological functions, exhibit the functions of setting and hardening regulators. Polycarboxylate superplasticizers additionally contribute to the formation of an amorphized, crystallization-resistant microstructure of cement stone. Complex polycarboxylate SP + MS increases strength and provides a sharp decrease in capillary porosity responsible for density, permeability, and hence, the longevity of concrete. This complex additive enables to obtain cement stone mainly from poorly crystallized (amorphous) low-basic CSHs which are more resistant to various cyclic influences such as freezing and thawing, moistening and drying, as well as cyclic mechanical loads. All this is a weighty argument in favor of using microsilica jointly with a polycarboxylate superplasticizer in road concretes operated under aggressive conditions.

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