Influence of Polycarboxylate Superplasticizer and Mineral Additives of Various Nature on the Kinetics of Early Hardening Stages of Cement Systems

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Abstract. Influence of the polycarboxylate superplasticizer and mineral additives of various natures (siliceous, aluminosilicate, and sulfoaluminate) on the kinetics of early hardening stages of cement systems, characterized by the rate of increase in the plastic strength of cement paste, have been studied with the recording of the following quantitative indicators: the initial and final setting time, time to reach the plastic strength of 5 MPa. The research results showed that the comprehensive use of organic and mineral additives allowed improving positive influence by means of synergetic effect and eliminating the negative influence of each component individually and thereby controlling the properties of cement paste and processes of early structure formation of cement stone. Introducing the carbonate filler (microcalcilte) into non-plasticized cement system (composition No. 5) decelerates the growth of plastic strength to some extent during the first 4 h of hardening as compared to non-modified composition No. 1 (Fig. 2, a). When it replaces 50% of the complex modifier SF +HAM+ESAM (see Table 1, compositions Nos. 7 and 8_1, respectively), it leads to substantial deceleration of both setting time (from 5 to 7.08 h for initial setting time and 6.08 to 8.33 h for final setting time) and the time to reach the plastic strength of 5 MPa (from 7.0 to 9.4 h).

Keywords: Cement system · Polycarboxylate superplasticizer · Mineral additive · Setting time · Plastic strength

1 Introduction

Currently, one of the high-priority trends in construction material science is the development of modified cement concretes with high performance characteristics differing in a complex multicomponent composition using individual and comprehensive additives of various natures and action mechanisms: chemical, mineral, and organic-mineral [1–4]. Using modifiers was a key to solving many process tasks, in particular, contributed to the production of high-strength cement concretes (60–100 MPa and higher) [5, 6], which is proved by the results of own studies [7–9].

An important component of modern modified cement concretes is active mineral additives enabling the control of processes of structure formation and properties of

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cement systems. For the formulation of high strength composites, finely dispersed pozzolanic additives have the highest efficiency, which contain amorphous silica, alumina and have an increased reactivity [10–12]: condensed silica fumes, metakaolin, finely dispersed ashes of thermal power plants, blast-furnace granulated slags, etc. Using these modifiers allows for a number of positive structural effects, which include two primary ones [13]: chemical effect, which consists in an opportunity to change the quality of the solid phase forming the frame of cement stone structure; physical effect related to the opportunity to change the porous space geometry by reducing the scope of capillary and process pores by filling the space between coarse cement particles with finely dispersed additive particles.

Apart from siliceous and aluminosilicate modifiers, sulfoaluminate and carbonate mineral additives have increased efficiency in the formulation of cement systems. Using expanding modifiers of sulfoaluminate type allows for controlling linear and volumetric changes when hardening cement composites by forming increased volume crystals of hydrate phases (ettringite, etc.). [14, 15]. The action of carbonate rocks (limestones, dolomites) in cement systems is based on the ability of the rock-forming mineral calcite to act as a center of crystallization for new hydrate phases [16, 17].

The authors should note a special role of using highly efficient plasticizing additives in modified compositions of cement concretes, especially IV-generation superplasticizers. These are surfactants based on polycarboxylates and acrylates ensuring a significant reduction of the water-cement ratio and water-demand of concrete mixtures (up to 35–40% or more) [18, 19]. Their liquefaction capability is significantly higher than in conventional plasticizers based on lignosulfonate, sulfo-melamine-formaldehyde, and sulfo-naphthalene-formaldehyde.

This paper was intended to study the influence of polycarboxylate superplasticizer and mineral additives of various chemical and mineralogical natures (siliceous, aluminosilicate, sulfoaluminate, and carbonate) on the kinetics of early hardening stages of cement systems characterized by the plastic strength growth and setting time of cement pastes.

2 Methods and Materials

The setting time of cement paste was measured using the standard method under GOST 310.3. When finding this characteristic using the Vicat apparatus, two conditional moments are recorded: the initial and final setting time. These indicators give no complete representation of the processes of structure formation of cement systems. The setting process can be characterized in a more comprehensive manner through study of the kinetics of the increase in the plastic strength in a developing structure. To this end, the cone plastometer method developed by the academician Rebinder was used.

This method is based on introduction the cone-shaped indentor and consists in measuring the cone immersion depth into the studied samples under the action of constant force F. The plastic strength of cement paste P_{cp} (MPa) is calculated by the formula

$$P_{cp} = K_{\alpha} \cdot \frac{F}{h_{cp}^2}, \tag{1}$$

where F is the force acting on the cone, H; h_{cp} is the cone immersion depth, mm; K_{α} is the cone constant defined as

$$K_{\alpha} = (1/\pi) \cdot \cos^2(\alpha/2) \cdot \mathrm{ctg}(\alpha/2), \tag{2}$$

where α is the cone apex angle (in its axial cross-section).

In the research, the indentor loading was 2.98 N, the cone apex angle was 70°. After the cone contacted the surface of the studied sample, the stopping devices were released and the indentor immersion depth was measured using the clock-type indicator.

Melflux 1641 F polycarboxylate superplasticizer (SP) was used as modifier for cement systems along with the following types of mineral additives (MAs):

1) siliceous MA – condensed non-compacted silica fume MK-85 manufactured by Kuznetsk Ferroalloys JSC (SF);
2) aluminosilicate MA – highly active metakaolin MKZhL-2 manufactured by Plast-Rifey LLC (HAM);
3) sulfoaluminate MA – expanding sulfoaluminate modifier manufactured by Parad-Rus LLC (ESAM);
4) carbonate MA – microcalcite manufactured by Polypark LLC (MC).

The studies used non-plasticized and plasticized cement systems, the mixed binder of which included 90% of Portland cement 500-D0-N (PC) manufactured by Mordovcement PJSC and 10% of a mineral additive. In plasticized compositions, the superplasticizer dosage was 0.1 and 0.25% of the binder weight (PC + MAs). Cement mineral pastes were prepared with the constant water-binder ratio of W/(PC + MAs) = 0.27 corresponding to the normal density of cement paste of no-additive composition. The studied compositions of cement systems are given in Table 1.

Table 1. The studied compositions of cement systems (W/(PC+MAs) = 0.27)

Composition numbers	Portland cement	Type of mineral additives				SP Melflux 1641 F
		SF	HAM	ESAM	MC	
	% by weight of binder (Portland cement+mineral additives)					
1	100	0	0	0	0	0
2	90	10	0	0	0	0
3	90	0	10	0	0	0
4	90	0	0	10	0	0
5	90	0	0	0	10	0
6_1	100	0	0	0	0	0.25
6_2	100	0	0	0	0	0.1
7	90	3.333	3.333	3.333	0	0.25
8_1	90	1.667	1.667	1.667	5	0.25
8_2	90	1.667	1.667	1.667	5	0.1

3 Results and Discussions

In the experimental study controlled indicators quantitatively characterizing the growth kinetics of plastic strength of cement systems were the initial and final setting time, as well as the time to reach the plastic strength of 5 MPa. The initial and final setting time for cement pastes of the compositions under study are given in Fig. 1, the curves of plastic strength growth of cement systems are given in Fig. 2.

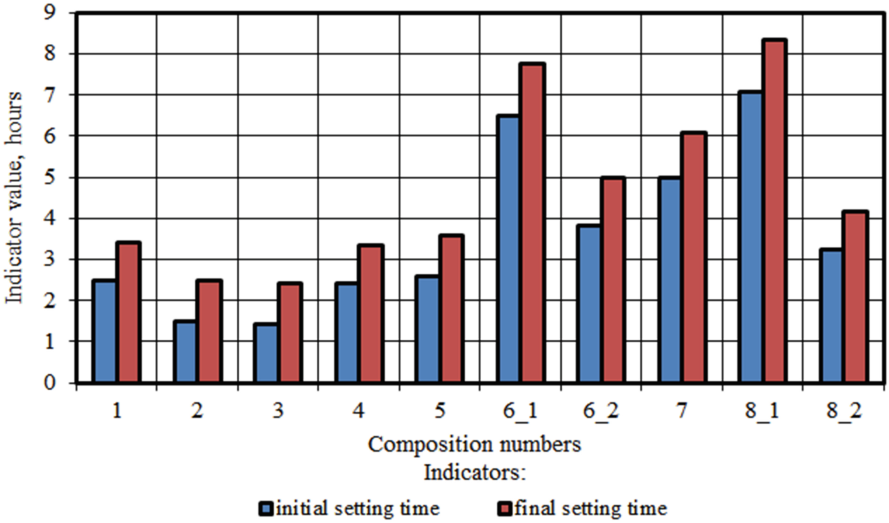

Fig. 1. Initial and final setting time of the studied cement pastes with constant water content.

The studies found that introducing silica fume and metakaolin (compositions Nos. 2 and 3) into the formulation of the control no-additive composition No. 1 instead of 10% Portland cement allowed reducing the initial and final setting time by 40–43 and 27–29%, respectively (Fig. 1). Increased setting rate of the no-plasticized cement pastes of compositions Nos. 2 and 3 is caused by high dispersion of SF and HAM particles being the source of excessive surface energy at the interface and the presence of reactive compounds in modifiers composition (amorphous silica SiO_2 and aluminum silicate $Al_2O_3{\cdot}2SiO_2$) promoting intensified hydration at early stages of cement systems hardening.

Using expanding sulfoaluminate modifier and microcalcite (compositions Nos. 4 and 5) in non-plasticized compositions has almost no effect on changes in the setting time of cement pastes.

Data analysis represented in Fig. 1 shows substantial increase in setting time for plasticized systems. Introducing polycarboxylate superplasticizer Melflux 1641 F into the cement pastes in the amount of 0.1 and 0.25% of the binder weight (PC+MAs) (compositions Nos. 6_2 and 6_1) leads to decelerated setting time as compared to non-

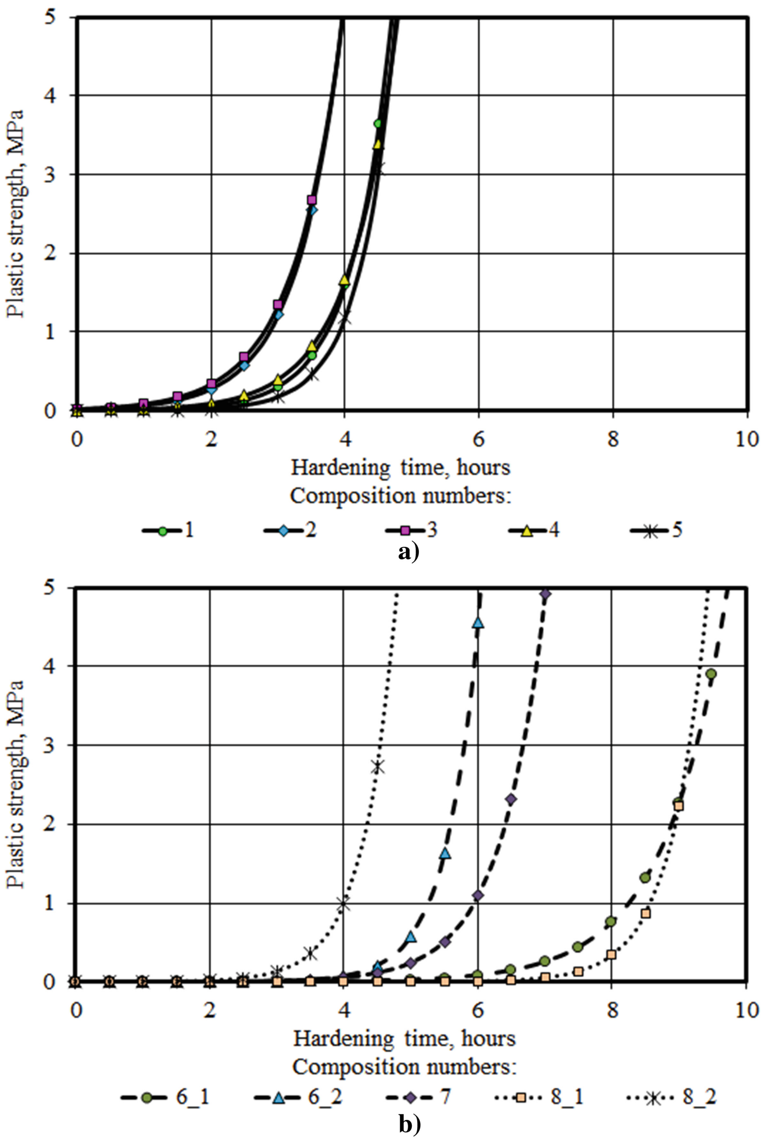

Fig. 2. Curves of plastic strength growth of the studied non-plasticized (a) and plasticized (b) cement systems with constant water content (W/(PC+MAs)) = 0.27).

plasticized additive-free composition No. 1 by 1.5 to 2.6 times for the initial setting time and 1.5 to 2.3 times for the final setting time, respectively.

Comparison of plasticized cement systems without mineral additives Nos. 6_1 and 6_2 with compositions Nos. 8_1 and 8_2 containing complexes of MAs introduced in the amount of 10% of the Portland cement weight (5% (SF+HAM+ESAM) and 5%

MC, respectively) showed setting time decelerated by 15–16% with the Melflux 1641 F content of 0.1% and acceleration by 7–9% with the plasticizer share of 0.25% of the binder weight (PC+MAs).

The analysis of plastic strength growth curves (Fig. 2) generally proves the above conclusions on the effects of plasticizing and mineral additives and their complexes on the kinetics of early hardening stages of cement systems. In particular, introducing 10% SF or HAM (compositions Nos. 2 and 3) into the cement paste formulation allows reducing the time to reach the plastic strength of 5 MPa by 15–16%, at that using the plasticizer in quantity of 0.1 or 0.25% of the binder weight (PC+MAs) (compositions Nos. 6_2 and 6_1) increases this indicator by 1.3 and 2.1 times, respectively. Introducing the carbonate filler (microcalcilte) into non-plasticized cement system (composition No. 5) decelerates the growth of plastic strength to some extent during the first 4 h of hardening as compared to non-modified composition No. 1 (Fig. 2, a). When it replaces 50% of the complex modifier SF+HAM+ESAM (see Table 1, compositions Nos. 7 and 8_1, respectively), it leads to substantial deceleration of both setting time (from 5 to 7.08 h for initial setting time and 6.08 to 8.33 h for final setting time) and the time to reach the plastic strength of 5 MPa (from 7.0 to 9.4 h).

4 Conclusion

To sum up the above, it should be noted that the comprehensive use of polycarboxylate superplasticizer and mineral additives of various natures (siliceous, aluminosilicate, and sulfoaluminate) allows improving positive influence by means of synergetic effect and eliminating the negative influence of each component individually and thereby purposeful management of the cement paste properties and processes of early structure formation of cement stone.

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