

Cement stone modified with complex of polycarboxylate superplasticizer and silica fume

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Abstract. Recently, the issue of concrete durability of reinforced concrete structures and constructions, especially those used in harsh climatic conditions, has become very important. Present approaches to the formation of durable concrete involve the use of active mineral additives with modern superplasticizers based on polycarboxylate ethers. The review of literature showed that there are little data available on the effect of polycarboxylates on hydration and hardening of cement stone. It is assumed that polycarboxylate superplasticizers can be absorbed in a dense layer on the surface of cement grains and, in some cases, intercalate into neoformations. The article considers the peculiarities of how the microstructure of hydrated phases of cement stone with a complex admixture of silica fume and polycarboxylate superplasticizer is formed. It has been established that silica fume promotes the formation of predominantly low-basic hydrated phases of C-S-H (I) type in cement stone. Introduction of the complex reduces the content of calcium hydroxide in cement stone and forms a structure of amorphized low-basic calcium hydrosilicates, resistant to various environmental effects.

1. Introduction

The review of literature showed that the most dense hydrate mass with a large number of connections between particles is formed by an amorphized cement gel represented by the C-S-H (I) phase [1,2].

It is assumed [3] that rapid formation of the C-S-H (I) phase upon hydration of alit in Portland cement results from the adsorption of hydrated calcium cations to anhydrous anionic sites. Hydrated cations are used to balance the negative charge of anionic sites and significantly amorphize the cement stone, which accounts for the slightly crystalline nature of the C-S-H phase. The initially formed C-S-H phase is metastable, which proceeds to crystallize and liberate Ca(OH)_2 .

The results of calorimetric studies have shown [4] that introduction of silica fume (SF) and nanosilica leads to accelerated hydration of cement. The use of these additives promotes the formation of a stronger cement stone with reduced porosity due to pozzolanic activity [5,6].

Introduction of a silica fume additive to high-performance concretes has shown that an increase in the amount of the C-S-H phase reduces the portlandite proportion in the structure of cement stone, which has a positive effect on its strength [7,8]. The contact area of the cement stone with the aggregate has been improved due to consolidation of hydration products. A number of works point to the fact that silica fume helps to increase the hydration degree of Portland cement [9,10]. Replacing part of Portland cement with mineral additives, especially silica fume, leads to an increase in gel porosity, while the number of medium capillary pores decreases. This leads to an increase in the compressive and flexural strength [11].



To effectively apply silica fume, it is necessary to use superplasticizer (SP) admixtures, which are surfactant substances [12,13]. According to Y. Zhang and X. Kong, adsorption of naphthalene superplasticizers is single-layer, and polycarboxylate ethers have multilayer adsorption [14]. When SP is introduced, there is a directly proportional dependence of the cement paste flowability and the hydration-slowing effect on the contact area of the cement with the SP. Slowed hydration of cement with polycarboxylate SP admixture is caused by the formation of a complex of COO^- and Ca^{2+} on the surface of neoformations. The peculiarity of using polycarboxylate SPs is their adsorption on the surface of primary hydrate formations. Introduction of superplasticizers showed that polycarboxylate polymers are integrated into the surface, and may be also partially embedded in the C-S-H interlayer cavities, which increases the distance between their layers [15]. Moreover, some modifications of polycarboxylate ethers with cement aluminates have been proved ineffective [16,17].

The combined introduction of silica fume and polycarboxylate superplasticizer to mixtures with a low water-binder (W/B) ratio affects the size of silica anions and causes their polymerization. At the same time, the degree of interaction between silica fume and portlandite reduces, that is, in such mixtures the intensity of the pozzolanic reaction decreases [18]. Belite also hydrates more intensively [19].

At present, in order to evaluate resistance and durability of concrete, it is necessary to find out how the complex admixture of polycarboxylate superplasticizer + silica fume affects the structure of the hydrated phases of cement stone.

2. Materials and methods

Topkinsky Cement CEM I 42.5 B was used as a binder, its specific surface is $350 \text{ m}^2 / \text{kg}$, and normal cement paste density is 25%.

The superplasticizer was MasterGlenium ACE 430, which is an aqueous solution of polycarboxylate ether, produced by BASF, Germany.

The active mineral additive was granulated silica fume of Novokuznetsk. The bulk weight in the compacted state is $310\text{-}600 \text{ kg} / \text{m}^3$, the activity of calcium hydroxide is $1.4 \text{ g} / \text{g}$, the specific surface is $12\,000 \text{ cm}^2 / \text{g}$.

To study the properties and structure of cement stone, we applied derivatography on the “LuxxSTA 409 PC” device of the German company “Netzsch”, X-ray diffraction analysis with the help of DRON-3M upgraded with the PDWin adapter and electronic raster microscopy on the Jeol Interactive Corporation Japan JSM-6460LA.

3. Results

A two-factorial experiment plan was implemented to study the combined and separate effect of MasterGlenium ACE 430 and SF on the properties of cement compositions. It involved the following significant factors: X_1 - the dosage of superplasticizer, varying from 0 to 1%, and X_2 - the dosage of SF, in the range from 0 to 12%, calculated per mass of cement.

All experiments were conducted using a cement paste of normal density. As responses for the cement paste were taken the following: water-binder ratio, setting time; for the cement stone - compressive strength and phase composition of neoformations.

Since SF has pozzolanic properties and interacts with the secondary calcium hydroxide liberated during C_3S hydration, let us take it as a binder component and estimate the water demand not by water-cement (W/C), but by the water-binder (W/B) ratio. The finely dispersed SF admixture increases the water demand of the binder from 25 to 31%, and the ACE admixture, which has a water reducing effect, reduces the W/B from 0.25 to 0.21. The combined introduction of the plasticizer and SF contributes to maintaining the normal density of the cement paste at the level of the plain composition $W / B = 0.25$ or reduces it to 0.225, when introducing ACE - 1% and SF - 6%.

The beginning of the cement paste setting (Figure 1) depends largely on the amount of the ACE admixture, and the SF admixture has almost no effect.

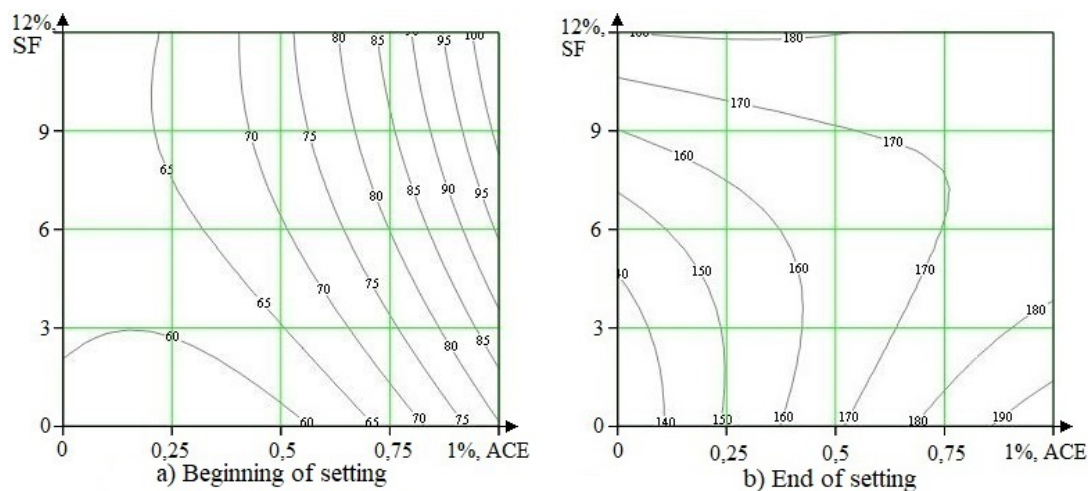


Figure 1. Dependence of the beginning and end of setting on the number of the introduced admixtures, min.

Increase in the starting time of setting is a positive factor when using a complex admixture in monolithic concrete, while the concrete mixture longer remains plastic and can be transported farther before laying. Whether the admixtures are used individually or together, they both equally slow down the setting time of the cement paste by about 30 % (from 140 to 180 minutes).

Figure 2 shows the study of strength gain by samples of cement stone cubes with an edge of 20 mm.

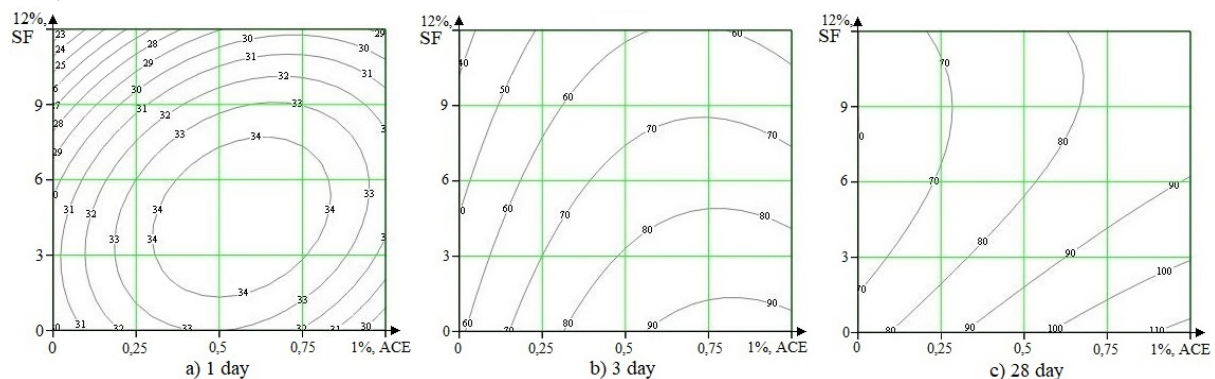


Figure 2. Compressive strength, MPa at the age of 1, 3, 28 days.

The presented dependences suggest that on the first day of hardening, the admixtures used in the amount of 0.4-0.8 % ACE and 6-8 % SF of the cement mass contribute to the formation of cement stone with the greatest strength of 34 MPa. The cement stone gains in strength most intensively during the period up to 3 days, reaching 70-80 MPa with the optimum ratio of admixtures.

A combined use of ACE 0.8-1 % and SF 8-12 % in the grade-age cement stone provides the strength of 80-90 MPa, which later increases to 100 MPa. Introduction of 0.5-1 % plasticizer makes cement stone gain in strength up to more than 100 MPa, which is due to a lower $W/B = 0.21$, compared to $W/B = 0.22 \dots 0.25$ when ACE 1 % and SF 6-12 % are introduced.

According to DTA (Fig. 3), each of the admixtures, ACE and SF, at the age of 28 days, helps to reduce free $Ca(OH)_2$ in the cement stone.

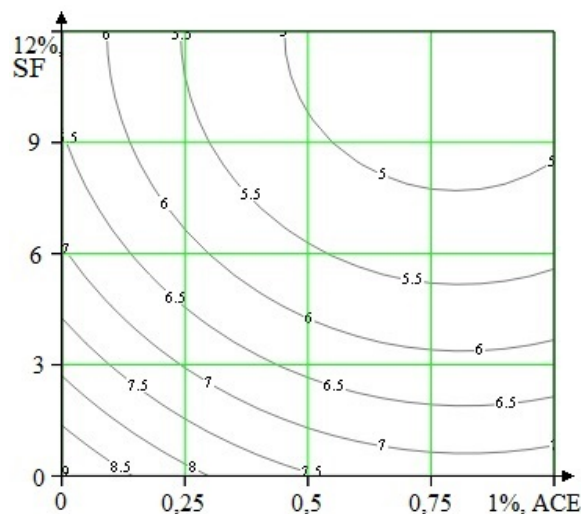


Figure 3. Content of Ca(OH)_2 in cement stone, according to the dosage of admixtures.

The content of portlandite in samples without admixtures is relatively small (9.3 %), this was confirmed by H. Taylor, who showed that if W / C decreases, the amount of free lime in the cement stone significantly decreases [20]. Introduction of SF up to 12 % reduces the content of calcium hydroxide to 6.5 %. The use of the ACE superplasticizer up to 1 % has less effect. Thus, the amount of Ca(OH)_2 decreases to 7.5 %, while the complex effect of admixtures on cement minerals maintains its content at the level of not more than 5 %. Consequently, both admixtures interact quite actively in the cement paste and stone with secondary calcium hydroxide, which is required to ensure the protective properties of concrete with respect to steel reinforcement. SF is known to react with Ca(OH)_2 to form low-basic hydrated phases C-S-H (I), i.e. cement gel. ACE may probably contribute to the formation of complex compounds with calcium ions and the preservation of high-basic amorphized calcium hydrosilicates of enhanced basicity. It was shown that the use of a complex of polycarboxylate superplasticizer and silica fume produced a synergistic effect of reducing the amount of free lime in the cement stone.

A significant increase in the strength of cement stone samples with admixtures is associated with an increase in the degree of cement hydration. Table 1 presents the comparative results of the alit hydration degree in the 28-day cement stone.

Table 1. Evaluation of the hydration degree by the change in the intensity of the analytical alit peak in the cement stone.

Used admixtures	Alit hydration degree in the cement stone (analytic line $d/n=1,77$)
Without admixtures	67 %
ACE 1 %	63 %
SF 12 %	92 %
ACE 1 % + SF 12 %	84 %
ACE 1 % + SF 6 %	80 %

According to the data obtained, the maximum hydration degree is provided by the introduction of SF additive and it reaches 92 %, compared to 67 % without admixtures. SF, which binds Ca(OH)_2 , is a kind of accelerator of cement hydration and hardening. The surfacetant admixture - superplasticizer ACE - somewhat slows the alit hydration to 63 %, and the introduction of a complex admixture provides a C_3S hydration degree in the range of 80-84 %.

The rate of strength gain and the strength properties of cement stone upon hardening depend to a large extent on the phase composition of neoformations.

Cement stone without admixtures mainly consists of $\text{Ca}(\text{OH})_2$ ($d/n = 0.493, 0.263, 0.193, 0.179, 0.169, 0.1485 \text{ nm}$); of gel-like hydrosilicates of the C-S-H (I) type ($d/n = 1.25, 0.28, 0.183 \text{ nm}$) and C-S-H (II) phases ($d/n = 0.307, 0.285, 0.28 \text{ nm}$); of C_3S alit relicts ($d/n = 0.3034, 0.2776, 0.2608 \text{ nm}$) and $\beta\text{-C}_2\text{S}$ belit ($d/n = 0.277, 0.2609, 0.2184 \text{ nm}$). Figure 4 shows the X-ray diffraction pattern of normally hardened 28-day cement stone samples with a complex admixture of 12 % SF + 1 % ACE.

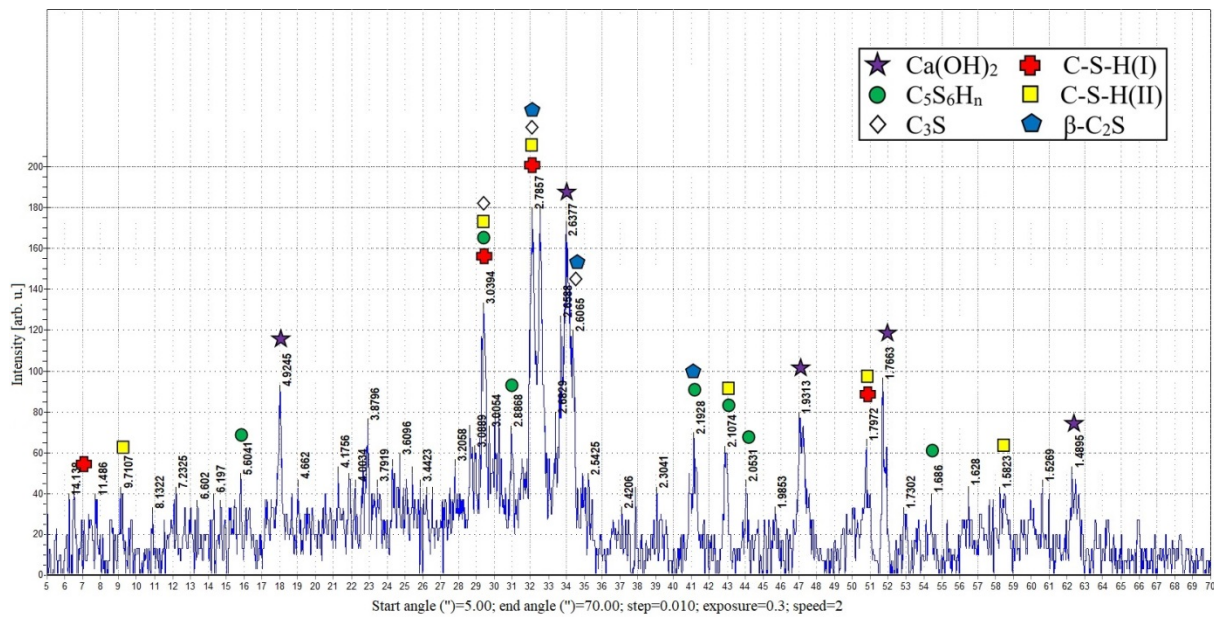


Figure 4. Cement stone with 12 % SF and 1 % ACE.

Figure 5a shows a micrograph of a cement stone without admixtures. The spall surface has well-formed $\text{Ca}(\text{OH})_2$ crystals, weakly crystallized masses of C-S-H (II) hydrosilicates and areas of calcium oxide-saturated silica gel. Pores and voids are visible.

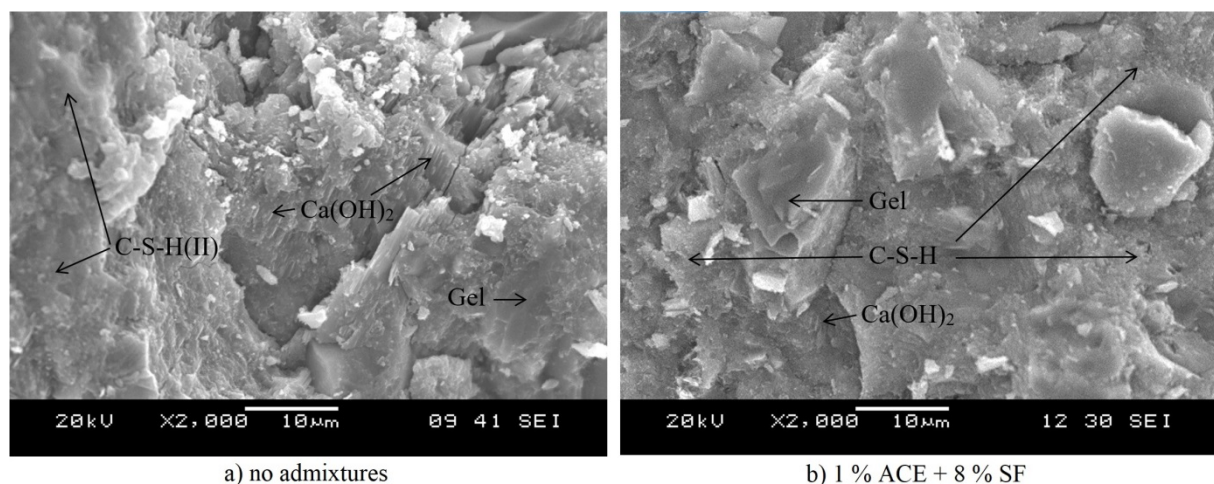


Figure 5. Characteristic images of the cement stone surface.

On the spall surface (Figure 5b) of the cement stone, modified with the ACE and SF admixtures, the areas of silica gel and gel-like C-S-H phase are visible and separate inclusions of calcium hydroxide can be observed.

4. Conclusions

Cement stone without admixtures has low strength, high porosity, maximum content of Ca(OH)_2 - 9.13 %, and the shortest setting time. It forms hydrosilicates represented by C-S-H (I) and C-S-H (II) phases.

When a complex admixture (MasterGlenium ACE 430+ silica fume) is introduced, the structure of grade-age cement stone is represented by a predominately low-basic amorphized C-S-H(I) phase with a minimum content of Ca(OH)_2 ~ 5 %, which increases the stability of the formed hydrate phases and positively affects the durability of concrete.

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Acknowledgments

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