

Improving the strength and resistance of cement composites to the external environment by utilizing complex additives

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Abstract. The article discusses the influence of complex additives on the strength and resistance of cement composites to environmental impacts. One of the additives - PFM-NLK (concrete modifier)- a factory fabricated mixture of a superplasticizer with the addition of air-retaining and water proofing substances. Another one is a complex additive containing a superplasticizer, sodium tetraborate and boric acid. Common denominator is the content of the superplasticizer. It allows reducing the W / C ratio of the mixture thereby increasing the density and strength of the composite, and, accordingly, its frost and corrosion resistance. PFM-NLK water-proofing and air-retaining substances additionally work toward the formation of a material structure with increased frost resistance. The components of the other additive, boric acid and sodium tetraborate, form a borate buffer system, which leads to the softening of the "chemical impact" and thus further increases the corrosion resistance. The research findings revealed the effectiveness of complex additives and substantiated the regularity that if each factor is separately facilitative for property improvement, then, when they are combined, the effect is multiplied. The PFM-NLK components, when combined, contribute to obtaining a material structure with high frost resistance. An additive containing a hyperplasticizer, boric acid and sodium tetraborate leads to an increase in strength and acid resistance.

1 Introduction

Today's creation of effective cement composites is firmly linked with the introduction of additives into their compositions. Their use ensures the appearance of high-strength, frost-resistant and corrosion-resistant cement concretes [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Additives are widely used to produce special concretes [14, 15, 16, 17, 18]. Today, cement concretes requirements may be revised in such a way that, in most cases, they are difficult to achieve without admixing additives. They allow to save materials and energy resources utilized in concrete technology [19, 20].

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The additive may have one or more physical and chemical mechanisms of interaction with the internal and external media of the material. An additive that has several interaction mechanisms usually contains several substances (a complex additive), each of which is aimed at providing a specific property of the concrete mixture and or concrete. It is obvious that the effect of a complex additive may be aimed at delivering on a select property or properties of the material. At the same time, it is taken into account that if each factor separately contributes to the improvement of the property, then when they act together, the effect multiplies [12].

A slight amount of substances admixed into the material, with targeted mechanisms of physical and chemical interaction, are known as active additives. According to [12], an active additive should be called a substance that is admixed into the system and actively interacts with the elements of internal and external environment, or only with the elements of one of them, modifying the composition, structure, and, accordingly, the properties of the system, depending on the action direction. Active mineral additives containing amorphous silica and, in some cases, other compounds (active alumina and aluminosilicates, etc.), which bind the most reactive component of the cement paste (matrix) – calcium hydroxide, preventing its washing out and thereby protecting the paste matrix from decomposition, find wide application [18, 21, 22].

Another type of active additives is the substances admixed into cement systems in order to interact with aggressive media and to reduce their impact on the material [12, 13, 23, 24]. Some of them are poorly soluble and remain still in the material, while others are water-soluble and able to come up to the surface of the composites and react with penetrating media. The additives of a second type can effectively protect the boundaries of the active material, such as cement composites when exposed to water-containing media and anticipatory water penetration, if the following conditions are met [13]:

- the structure of the material should contain a soluble additive and a solvent (water);
- the nature of the admixture, the composition and structure of the material should ensure its fast dissolution and filling of the surface layers;
- the amount of the admixture active substance transferred per unit of time through the protected surface in an equivalent proportion should not be less than the amount of the medium's aggressive component transferred at the same time, i.e.:

$$D_{E.S} k_e \frac{\partial c}{\partial x} ds dt \geq D_{E.A} \frac{\partial c_A}{\partial x_A} ds_A dt \quad (1)$$

where $D_{E.S} k_e \frac{\partial c}{\partial x} ds dt$ – is the amount of active substance transferred per time dt through sample's unit of surface ds , non-corroded and x lateral; $D_{E.A} \frac{\partial c_A}{\partial x_A} ds_A dt$ – is the same as to aggressive media through unit of internal surface of ds_A layer, corroded; c and c_A – are concentration of active substance and aggressive medium in points x and x_A at the moment of time t respectively, $D_{E.S}$ and $D_{E.A}$ – are the effective diffusion coefficients of the additive's active substance and the aggressive medium, respectively; k_e – is a coefficient of equivalence.

In permeable composites, the fulfillment of condition (1) cannot retain, since there is a rapid decrease in the additive's concentration gradient owing to its consumption at the boundary of the contact fronts due to a chemical reaction with the components of the aggressive medium and the subsequent washing of the interaction products. Obviously, increasing the density of the cement composite will increase its strength and corrosion resistance. One of the main means to increase the density of the cement material, while ensuring the necessary fluidity of the mixture, is the admixing of plasticizing additives, including superplasticizers, into its composition.

The paper [25] presents studies into the use of complex active additives to protect cement composites from the effects of low-concentration sulfuric acid solutions. The additive composition included: barium carbonate (BaCO_3), at the interaction of which with sulfuric acid solutions, an insoluble, thickening surface layers barium sulfate (BaSO_4) is formed without changing the volume, as well as mixtures consisting of a weak acid and its salt, forming buffer systems that can soften the "chemical impact" on the material. At the same time, the components of the buffer systems are highly soluble, may rise to the surface of the material and, if condition (1) is met, may be able to slow down its destruction.

The admixing of active complex additives in the cement compositions led to the increase in their corrosion resistance. Thus, the resistance coefficients (indexes) of composites with these additives are 1,5-2 times higher compared to additive-free material. Moreover, according to [25], this trend holds true for both compressive strength and bending resistance.

2 Method

Cement materials with and without additives were exposed to testing. To fabricate paste matrix, Portland cement M500 D0 manufactured by Alekseevsky Cement Plant located in the Republic of Mordovia was utilized, containing tricalcium aluminate in the range of 6-8%. Such a content of this mineral in the composition of cement meets the requirements set for the binder in the production of cement concrete with increased frost resistance.

The PFM-NLK additive was used in the manufacture of paste matrix and cement concretes. It is a mixture of a superplasticizer (sodium salts of polymethylenephthalene sulfonic acids of various molecular weights) with the addition of air-retaining and water proofing agents. Paste matrix was obtained from cement paste with $W/C = 0,25$. By dispensing the PFM-NLK into the compositions we sought to increase the fluidity and water repellence of the mixture, to ensure the necessary air entrainment and by this to produce dense (air-free), owing to low W/C , strong and frost-resistant concretes in the future. The fluidity of the cement paste was estimated by Southard viscometer.

Paste matrix strength was evaluated by testing $20 \times 20 \times 20$ mm samples, hardened under normal conditions ($t = 20^\circ\text{C}$, $W = 95-100\%$), and the strength and frost resistance of concrete by testing $100 \times 100 \times 100$ mm samples, hardened by steaming and under normal conditions. At the same time, frost resistance was determined by a short-time method according to GOST 10060-2012 Concretes. Methods for determining frost resistance.

Another complex additive contained (Table. 1) boric acid (H_3BO_3), sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and superplasticizer – modified sodium polymethylene naphthalene sulfonate (CemPlast, Russia). It is obvious that the paste matrix obtained from a mixture with a large W/C ratio will be characterized by greater porosity.

To pursue the research, three types of paste matrix samples of $20 \times 20 \times 20$ mm in size with a complex additive with its select components and additive-free were fabricated according to Table 1. The paste matrix was hardened under normal conditions. Then the samples were immersed in a 2% solution of sulfuric acid, which was changed every two weeks of exposure, and after a certain time of exposure to an aggressive environment, they were tested to determine the compressive strength and the resistance coefficient. The values of paste matrix acid resistance with a complex additive were compared with those of additive-free sample containing only one of the components of the additive. The latter two were hardened and tested in the same way.

Table 1. Cement mixture compositions

com-	Cement	W/Cration	Amount of additive, % of the cement weight
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position no.	content, %		Boricacid	Sodiumtetra borate	Superplasticizer
1	100	0.34	0.1%	0.1%	0.7%
2	100	0.34	0	0	0.7%
3	100	0.42	0	0	0
4	100	0.42	0.1%	0.1%	0

3 Results and discussion

The results of the study into the complex additive PFM-NLK effect on the mixture fluidity, the paste matrix strength and the technical characteristics of concretes, including frost resistance, are shown in Fig. 1, Fig. 2 and Table 3. And Fig.3 and Fig.4 show the effect of another complex additive on the initial strength and paste matrix acid resistance coefficient at the exposure to 2% of H₂SO₄.

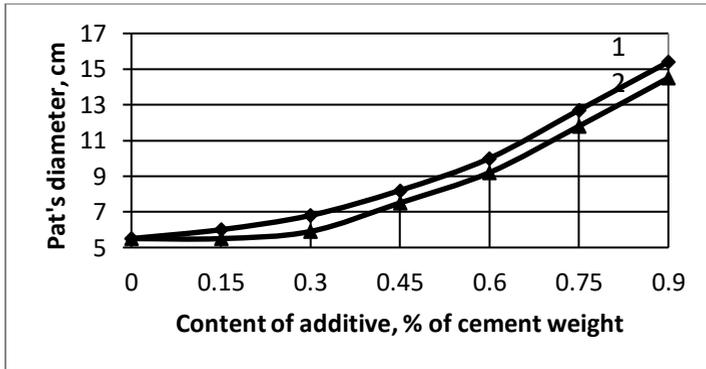


Fig. 1. The effect of complex additive PFM-NLK on viscosity of cement paste as opposed to hyperplasticizer effect S-3: 1 – paste matrix with PFM-NLK, 2 – the same with S-3

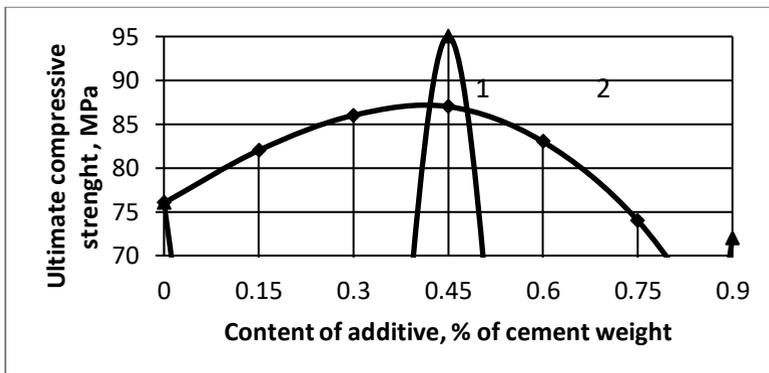


Fig. 2. The effect of complex additive PFM-NLK on paste matrix ultimate compressive strength as opposed to hyperplasticizer effect S-3: 1 – paste matrix with PFM-NLK, 2 – the same with S-3

It is clear that the increased content of the PFM-NLK additive increases the fluidity of the cement mixture. However, when the content of the additive is more than 0,8% of the cement weight, significant losses of initial strength are observed. In this regard, it was concluded that the most preferred additive content in the concrete mix should be 0,8% of

the cement weight. With such an amount, the concrete mixture acquires the necessary fluidity and a sufficient volume of air-entraining pores (3-4% of the total concrete volume), which allows, according to the scientific literature [26], to significantly increase the frost resistance of concrete. The resultant small evenly distributed closed spheroid pores in the structure of the material play the role of buffers that mitigate the negative effect of the internal pressure that develops in the concrete during the formation of ice in the pores. And the spheroid pores, which partially connected with capillaries, are spare capacities into which water is squeezed out when it expands during the transition to ice.

Table 2 shows the compositions of the mixtures, and Table 3 shows their fluidity and technical characteristics of concretes hardened under normal conditions ($t=20\pm 2^\circ\text{C}$, $W=95-100\%$) and through steaming.

Table 2. Cement concrete mixture compositions to obtain concretes with high strength and frost resistance

no.	Materials consumption per 1 m ³ of mixture, kg					
	Portland cement	Crushed stone	Glass sand	Water	PFM-NLK additive	W/Cratio
1	515	1250	521	185	3.6	0.36
2	515	1211	547	175	4.12	0.34
3	515	1211	560	170	4.12	0.33
4	515	1190	567	175	4.12	0.34
5	515	1211	495	195	3.6	0.38

Table 3. Fluidity of mixtures, hardening conditions and concretes' technical characteristics

no.	Mixture fluidity, cm	Hardening conditions	Concrete technical characteristics		
			Medium density (γ), kg/m ³	Ultimate compressive strength (σ_0), MPa	Frost resistance (F_0), cycles
1	14-16	normal conditions	2500	60.7	—
2	12-15	steaming	2467	58.4	550
3	10-12	steaming	2475	51.9	500
4	11-14	normal conditions	2480	50.8	-
5	25-28	normal conditions	2420	52.9	-

It is obvious that the use of a complex additive in concretes containing plasticizing, air-entraining and water repellent substances makes it possible to obtain materials of high strength and frost resistance. Reducing the mixture fluidity beyond the limit leads to a decreased air entrainment, and, accordingly, frost resistance. It is also obvious that in this case, the components of the complex additive enable the formation of a material structure that physically prevents its destruction when saturated with water, at freezing and thawing.

In contrast to PFM-NLK, another type of complex additive contains a component that is chemically active to an aggressive environment. The effect of the aggressive medium on the material is weakened due to the decrease in permeability caused in its turn by the increase in the density of the structure and the interaction of the medium with the active water-soluble additive. The effectiveness of the additive increases, since there is a combination of two factors aimed at increasing the material's corrosion resistance (see Fig. 3 and Fig. 4).

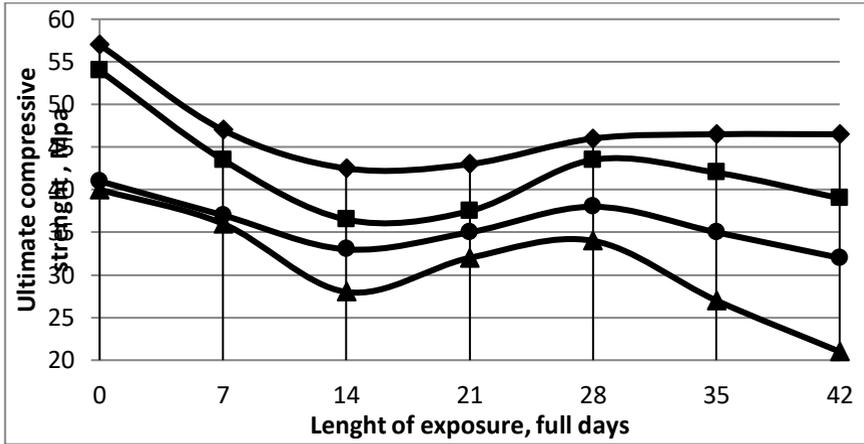


Fig. 3. Effect of additives on paste matrix strength at the exposure to 2% sulfuric acid (compositions no.no. 1-4 as per table 1)

Fig.3 shows that the paste matrix with a complex additive containing boric acid, sodium tetraborate and superplasticizer (see Table.) has a higher strength during the exposure to 2% sulfuric acid. In addition, the paste matrix of this composition during the last two weeks of exposure does not lose strength in an aggressive environment.

Paste matrix composition no.2, containing only a superplasticizer as an additive and the same fluidity as in other compositions, has an initial strength close to that of the material with a complex additive. However, like the additive-free samples, it is characterized by a rapid loss of strength in the first two weeks of exposure to an aggressive environment. These losses are greater than at the end of the exposure. Unlike paste matrix with a complex additive, the strength stabilization at the end of exposure is not observed, which points to a positive effect on the acid resistance produced by additives forming the borate buffer system.

The effect of boric acid and sodium tetraborate retains even in the absence of a hyperplasticizer in the composition (Fig. 4, Composition 4). However, the paste matrix composition no.4 initially differs significantly in strength from compositions no.1 and 2 (Fig. 3). It can also be assumed that owing to a higher W/C ratio, and consequently high porosity compared with the paste matrix composition no.1, there is a rapid consumption of borate buffer system additives, which leads to a recurring loss of strength at the end of exposure (see Fig. 3 and Fig. 4).

Therefore, the effect of a complex additive containing a borax buffer system and a hyperplasticizer on paste matrix increased strength and corrosion resistance is obvious. Let us present the prerequisites for the application and the physical and chemical specificity of the complex additive components' action. If a part of the aggressive medium completely binds to the introduced additives, then its amount in contact with the structure-forming components of the composite will be decreasing to varying degrees, which is equivalent to the decrease in permeability. In relation to a composite with active additives, we can put down [13]:

$$V_x + V_p \leq V_b \tag{2}$$

where V_x – is the rate of chemical interaction, V_p – is the medium penetration rate, V_b – is the rate at which penetrant is bound by additives.

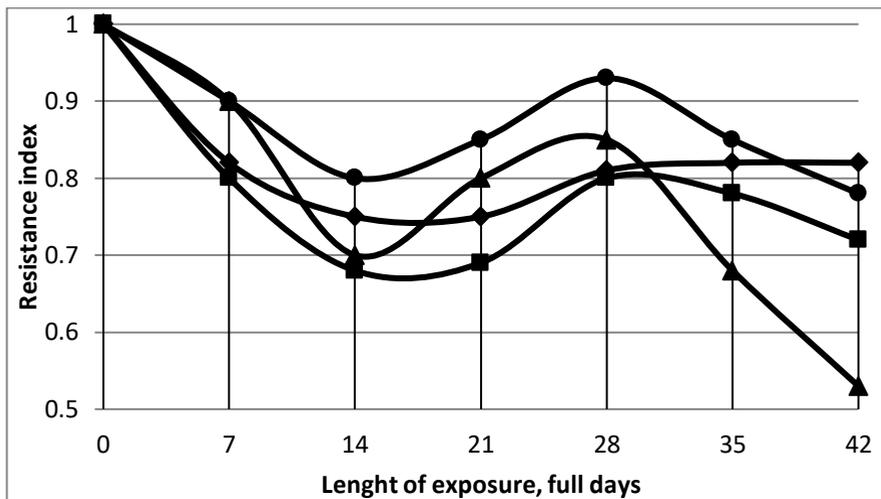
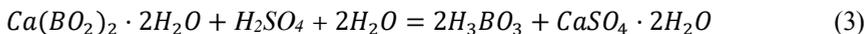


Fig. 4. Effect of additives on paste matrix resistance index at the exposure to 2% sulfuric acid (compositions no. 1-4 as per Table 1)

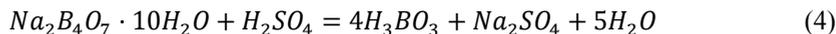
When $V_b=V_p$, the rate of chemical interaction of the aggressive medium with the structure-forming components of the material is zero, that is, $V_x=0$. It is obvious that the active additives will be effective at low permeability of the material, that is, at its high density. In this case, the consumption time of the active substance of the additive increases, and, accordingly, the condition (1) sustains, when the amount of the transferred active substance of the additive in an equivalent ratio is not less than the transferred component of the aggressive medium. Otherwise, i.e., with a porous structure of the material, the additives are quickly consumed when interacting with aggressive media.

In our case, boric acid (H_3BO_3) and sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) (borax) are water-soluble and, according to [27, 28], when combined, form buffer systems that aid to preserve the pH of the medium, and, accordingly, the material exposed to aggressive media. When dispensed into cement mixtures, these substances interact with the components of the cement binder. Thus, according to [27], boric acid reacts to form calcium borates with the general formula $Ca (BO_2)_2 \cdot nH_2O$. Sodium tetraborate, depending on the conditions of hardening and operation conditions of cement composites, their age, can be in a free, bound or partially bound state with the formation of calcium borates, and in particular tetraborates.

When paste matrix is exposed to 2% H_2SO_4 , on its surface there occurs an interaction with the formation of both components of the buffer system [13]. For example, when $Ca(BO_2)_2 \cdot 2H_2O$ interacts with a solution of H_2SO_4 , boric acid is formed according to the equation:



Sodium tetraborate can be supplied directly by the components of the material, if it is contained in them in free form, or formed by the interaction of the reaction product (3) - boric acid with paste matrix caustic alkalis. In its turn, sodium tetraborate interacts with the sulfuric acid solution, weakening its effect, according to the equation



In this case, as per [24], the change in the internal medium's pH slows down than if the reaction took place in the absence of the borax buffer system's components. In this regard, the corrosion of paste matrix will also slow down. The necessary components of the buffer system forming in the surface layers are the result of interaction and in a dissolved state.

The dissolution is explained by the fact that the sulfuric acid solution is formed from two substances, one of which, acid, is consumed on the surface, and the second, water, penetrates earlier into the surface layers of the material and dissolves the components of the buffer system at the inner boundary of the interaction zone.

Therefore, at the interface of the interaction between the material and the aggressive medium, there occur processes determined by the presence of active substances of the additive, which weaken the medium aggressiveness and conduce to the increase of its corrosion resistance.

4 Conclusion

1. The research discusses the potential of complex additives to effectively ensure the technical properties of cement composites. This potential consists in the fact that if each factor separately, including the additive with a targeted action, contributes to the improvement of the property, then when they act together, the effect multiplies.
2. The research paper provides theoretical prerequisites for increasing the paste matrix corrosion resistance by admixing a complex additive consisting of a superplasticizer and substances that are active to the aggressive environment and form a borax buffer system.
3. The experimental findings confirm the effectiveness of the complex additive PFM-NLK. It helps to form a material's structure which physically prevents its destruction when saturated with water, at freezing and thawing, and allows you to obtain cement composites of high strength and frost resistance.
4. Complex additive containing a hyper-plasticizer and a borax buffer system not only works toward the formation of the dense structure, but also further weakens the aggressive environment through active interaction with it. The additive facilitated, with equal fluidity of cement mixtures, to increase the ultimate compressive strength of the hardened paste matrix by 40 %, its resistance index by 1,5 times compared to samples without the additive.

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