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The influence of polyfunctional modifier additives on properties of cement-ash fine-grained concrete

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Abstract. The object of the study is the properties of cement-ash concrete with the addition of a polyfunctional modifier (PFM) intended for floors of industrial enterprises. The PFM composition includes a naphthalene-formaldehyde type superplasticizer and a vinyl acetate-vinylversatate copolymer. A prerequisite for the use of PFM additives in cement-ash concrete is the ability to actively influence the structure formation processes and, as a consequence, the properties of concrete with it. Using well-known chemical and physical methods, experimental data have been obtained on the effect of PFM additives on the degree of cement hydration, the kinetics of changes in the plastic strength of cement-ash stone during hardening. It was found that the introduction of the PFM additive allows one to reduce the open porosity and average pore sizes of cement-ash stone and also increase the pore size uniformity index. To study the properties of cement-ash concrete with PFM additive, the method of mathematical planning of experiments was applied, as a result of which a complex of mathematical models of water demand, water separation, volume of air involved, concrete strength under compression and bending was obtained. The models make it possible to quantitatively evaluate the effect on the indicated properties of concrete of water and ash-cement ratios, the content and ratio of PFM components, as well as design the compositions of cement-ash concrete with desired properties. The studies, the results of which are presented in the article, showed the possibility, with the help of PFM additives, to significantly improve the properties of cement-ash concrete, which are important when using them for floors of industrial enterprises and, in particular, reduce ultimate shrinkage deformations by 30–50 %, reduce by 1.5–3 times their abrasion and up to 20 % increase resistance to shock.

1. Introduction

To date, thanks to the studies of many authors [1–9], the foundations of the theory of cement concrete with active mineral fillers have been developed. In accordance with this theory, the properties of filled cement systems are the result of the chemical, physico-chemical and physico-mechanical effects of the fillers at various levels of their structure. Due to the vitreous aluminosilicate phase, fly ash has pozzolanic activity and chemically interacts with $Ca(OH)_2$ released during the hydrolysis of clinker minerals. The introduction of fly ash into cement-water systems not only increases the volume of hydrated compounds, but also accelerates the hydrolysis process of clinker minerals [10–13].

Having a high specific surface, in addition to direct chemical interaction with cement, ash actively affects the physicochemical processes when cement is hardened. As the condensation-crystallization structure of the cement stone is formed, epitaxial contacts are formed between the cement paste and the grains of ash [3]. In accordance with the Gibbs – Folmer theory, the energy of formation of crystal nuclei also significantly decreases in the presence of crystallization centers, which serve filler particles [14].

Ash not only increases the cohesive and adhesive strength of the cement matrix in the concrete mixture, but also reduces the voidness of the aggregate [15–17]. For fine-grained concrete (FGC), this consequence of the introduction of ash filler seems to be especially important.

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Noting the general technical and economic feasibility of introducing fly ash into FGC intended for floor coverings, problematic issues should also be pointed out.

For the floor covering material, increased tensile strength is especially important. There are indications [3] that in the period 28...180 days. the growth rate of tensile strength of ash-containing concrete is approximately the same as that of non-ash concrete. In other works, however, it is noted that for concrete with ash, as well as with other active mineral additives, a higher ratio of tensile strength to compressive strength observed [18].

Many studies contain conflicting data on the modulus of elasticity, creep, and shrinkage of ash-containing concrete [19–22].

The most negative consequence of introducing ash into a concrete mixture intended for flooring is a decrease in abrasion resistance [5].

To date, there are a number of experimental data showing the effectiveness of the joint introduction of fly ash and surfactant additives into concrete mixtures [13, 24]. In addition to reducing interfacial surface energy when creating an adsorption-active medium, which has a positive effect on the size of adhesive contacts, surfactants also have a deflocculation effect on highly dispersed ashes, prone to aggregation [20].

Superplasticizers (SP) made it possible to obtain essentially a new type of cast concrete and provide a reduction in the water demand of the concrete mix by 20...30 % and more, which is approximately two times higher than when using traditional plasticizers [25]. However, the introduction of superplasticizers additives into cement-ash concrete does not allow to significantly increase the ratio of tensile strength to compressive strength and to achieve high deformability, adhesive ability and wear resistance desired for concrete intended for flooring [26, 27]. In this direction, an additional introduction of polymer additives into concrete and, in particular, additives based on polyvinyl acetate polimers is promising [28, 29]. For superplasticizers and polyvinyl acetate polimers characteristic a different mechanism of action, which suggests that the integral modifying effect of complex additives will be stronger than the individual components.

The purpose of the work was to conduct the necessary set of studies to reveal the peculiarities of the combined effect of additives of superplasticizer and polyvinyl acetate polymer on cement-ash concrete intended for flooring industrial enterprises.

The main objectives of the research:

1. To determine the joint effect of additives of naphthalene formaldehyde superplasticizer (SP) and vinyl acetate polymer with versatate (PVAV) on the features of hydration and structure formation of cement-ash systems.

2. To obtain a set of experimental-statistical models describing the combined effect of complex additives SP + PVAV as a polifunctional modifier PFM on the properties of concrete mixtures and the strength properties of concrete, taking into account their water-cement (W/C) and ash-cement (A/C) ratios.

3. To determine the effect of PFM additives on the deformation properties and resistance of cement-ash concrete to abrasion and impact.

2. Materials and Research Methods

The starting materials for the studies were Portland cement CEM II 42.5 N containing 20 % blast furnace granulated slag, silica sand with a fineness modulus of M_f = 2.4, and fly ash. Cement was made on the basis of clinker containing C_3S – 61.5 %, C_2S – 17.5 %, C_3A – 6.8 %, C_4AF – 14.2 %. The specific surface of the cement was 330 m^2/kg, normal consistency 27.1 %, initial setting time 1 hour 30 minutes, final – 3.5 hours, compressive strength after 28 days normal hardening – 53.4 MPa, bending strength – 6.1 MPa.

The chemical composition of the fly ash: SiO_2+Al_2O_3+Fe_2O_3 – 84.5 %, SO_3 – 2.8 %, CaO – 2.4 %, MgO – 1.8 %, Na_2+K_2O – 2.5 %; loss on ignition – 3.9 %, specific surface – 325 m^2/kg, CaO absorption activity – 43.9 mg/g.

The polyfunctional modifier included a powdery S-3 superplasticizer – a condensation product of naphthalenesulfonic acid and formaldehyde containing a mixture of oligomers and polymers (the so-called «active substance») and unreacted salt – β naphthalenesulfonic acid and sodium sulfate [29]. The content of the «active substance» in the superplasticizer was not less than 69 % and the pH of the 2.5 % aqueous solution was 7...9. The second component of the PFM was a polymer of vinyl acetate with vinyl versatate (PVAV) – a powder with a particle size of 10...40 μm and a density of 0.45 g/cm^2. Compared to polyvinyl acetate PVAV is more resistant to the action of an alkaline medium of cement.

For the implementation of algorithmic experiments, three-level, four-factor B_4 plan was selected in the work, which is close in properties to D – optimal ones [31]. A distinctive feature of this plan is the almost identical accuracy of forecasting the output parameters in the field of variation of factors.

As the criteria for the cast consistency of the FGC, the cone spread on the shaking table was selected, which, by standard determination, was 220...240 mm, and the cone immersion was 12–14 cm, respectively.

3. Results and Discussion

At the first stage of the study, we studied the effect of PFM additives on the hydration and structure formation of cement-ash stone.

The degree of cement hydration (α) was determined by a chemical method [14, 32]:

$$\alpha = h/W, \tag{1}$$

where h is the amount of hydrated i.e non-evaporating water at 105 °C, attached to 1 g of cement after a certain time from the moment of mixing;

W is the amount of non-evaporating water attached to 1 g of cement after its complete hydration.

For this purpose, samples with sizes 2×2×2 cm were made from cement and ash-cement paste with W/C = 0.5, which were crushed after the set period under normal conditions of hardening, treated with acetone to remove free water, and calcined to determine the amount of chemically bound water. The amount of non-evaporating water corresponding to the complete hydration of the cement was determined by multi-stage mixing and calcination until the termination of growth in hydrated moisture content.

The mean values of the degree of hydration of samples with PFM additives are given in Table 1. It follows from them that PFM and their components have a certain stabilizing effect on the process of hydration of cements, while the influence of SP S-3 is much weaker than PVAV. By the age of seven days of hardening, the stabilizing effect of PFM on cement hydration is significantly reduced and does not exceed 5 % by 28 days.

Table 1. The degree of cement hydration in cement and cement-ash pastes with additives PFM.

No.	PFM additive content, % by weight of cement	Fractional content of PFM components, %		Ash-cement ratio (A/C)	The degree of hydration at days		
		S-3	PVAV		1	7	28
Portland cement CEM-II (C)							
1	–	–	–	–	0.23	0.39	0.66
2	1	100	–	–	0.18	0.35	0.65
3	1	–	100	–	0.17	0.31	0.65
4	1	50	50	–	0.17	0.33	0.70
5	3	100	–	–	0.16	0.33	0.67
6	3	–	100	–	0.16	0.30	0.67
7	3	50	50	–	0.16	0.32	0.67
Portland cement CEM-II; fly ash (A)							
8	–	–	–	0.4	0.29	0.40	0.71
9	1	100	–	0.4	0.16	0.39	0.69
10	1	–	100	0.4	0.15	0.33	0.66
11	1	50	50	0.4	0.16	0.38	0.69
12	3	100	–	0.4	0.14	0.33	0.65
13	3	–	100	0.4	0.11	0.36	0.64
14	3	50	50	0.4	0.14	0.37	0.68

The structural and mechanical characteristic of the hardening dispersed systems is plastic strength [14]. The value of plastic strength in the initial period of hardening of cement and cement-ash pastes was determined using a conical plastomer. The immersion depth of the cone was fixed by an indicator with a division price of 0.01 mm. The calculations of plastic strength (P_m) were carried out according to the formula:

$$P_m = 0.096F / h^2, \tag{2}$$

where F is the load acting on the cone, N;

h is the immersion depth of the cone, mm.

The obtained plastograms (Figure 1) have characteristic two sections. The first section of the plastogram corresponds approximately to the initial of setting time, and the inflection point to the final of ash-cement pastes setting.

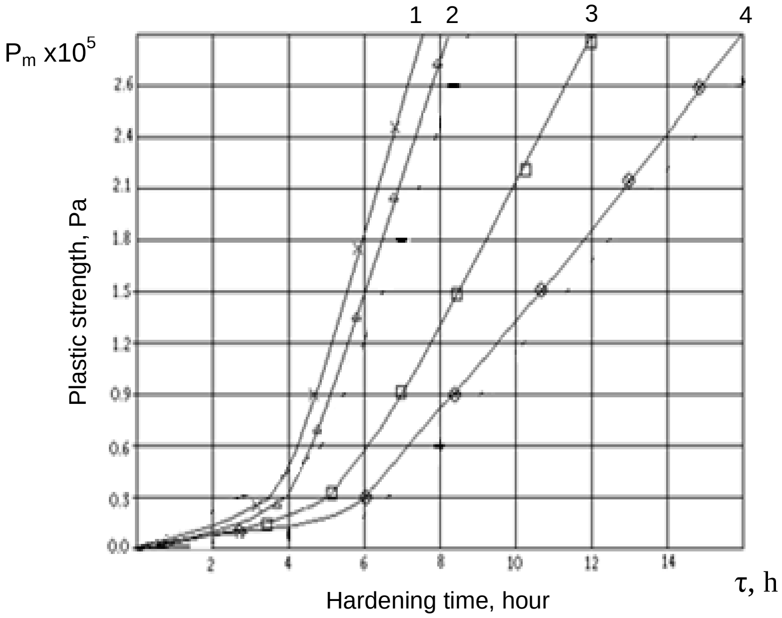

Figure 1. Kinetics of changes in the plastic strength of cement-ash pastes (A/C = 0.4): 1 – 1 % S-3; 2 – 3 % S-3; 3 – 1.5 % S-3 + 1.5 % PVAV; 4 – 3 % PVAV.

Moreover, if the first section of plastograms mainly characterizes the formation of a thixotropic coagulation structure, the second – the period of the coagulation structure strengthening and the beginning of the formation of a crystallization structure. An analysis of plastograms shows that ash and PVAV additives slightly lengthen the period of coagulation structure formation. The addition of superplasticizer, especially in ash-cement pastes, causes a more intensive increase in plastic strength in the second section of plastograms.

The nature of the modification of cement stone with PFM additives is largely determined by improvement of its pore structure. The parameters of the pore structure of cement stone were calculated according to GOST 12730.4–78 (Russian standard) by approximating the water absorption curves by an exponential function of the type [14, 32]:

$$W_\tau = W_{\max}\left[1 - e^{-\left(\bar{\lambda}\tau\right)^{\propto}}\right], \tag{3}$$

where $W_{\max}$ is the conditional value of maximum water absorption, %;

$\bar{\lambda}$ is coefficient characterizing the average size of the capillaries;

$\propto$ is coefficient characterizing the uniformity of capillary sizes;

τ is the duration of water saturation, h.

The kinetics of water absorption was determined on samples cubes with dimensions of 7x7x7 cm with continuous hydrostatic weighing according to GOST 12730.3. Three samples were made for each concrete composition.

The main results of the calculation of the parameters of the pore structure are given in Table 2. Analysis data of Table 2 shows that both with constant W/C and especially with W/C equal of cement normal consistency ($K_{n.c}$) the introduction of surfactant additives changes the parameters of the pore structure of cement and cement-ash stone. The most significant decrease in open porosity is observed when using the water reducing effect of additives, which affects the decrease in $K_{n.c}$. The value of the integral porosity for a number of compositions increases somewhat, especially with the introduction of polyvinyl acetate type additives, which can be explained by the air-entraining effect of the latters. In all cases, with the introduction of PVAV and PFM additives, including them, there is a pore redistribution towards an increase in the volume of closed pores and a decrease in open pores available for saturation with water. At the same time, there is a clear tendency towards a decrease in the average pore size and an increase in their uniformity.

The experimental planning conditions for the study properties of ash-cement concrete are given in Table 3. As can be seen from Table 3, when planning the experiment, it was supposed to study a fairly wide range of compositions of ash-cement concrete, which include both compositions without PFM and compositions that contain up to 3 % PFM.

Table 2. The main parameters of the pore structure of cement and cement-ash stone.

No.	Additive	Porosity, %		The average pore size indicator $\bar{\lambda}$	Uniformity indicator pore size α
		Integral, Pi	Open, P_o		
		Cement stone with W/C = 0.3			
1	–	23.5	19.8	1.54	0.79
2	3 % PVAV	25.1	18.7	1.25	0.82
3	15 % S-3+1.5 % PVAV	25.4	17.8	1.31	0.81
4	3 % S-3	23.9	16.9	1.30	0.83
		Cement stone with W/C = $K_{n.c}$*			
6	–	21.6	18.5	1.49	0.78
7	3 % PVAV	22.8	16.5	1.31	0.80
9	1.5 % S-3+1.5 % PVAV	20.1	15.5	1.28	0.81
10	3 % S-3	18.8	15.1	1.25	0.85
		Cement-ash stone with W/C = 0.3 and A/C = 0.4			
11	–	22.9	21.5	1.41	0.79
12	3 % PVAV	23.4	20.3	1.31	0.82
14	1.5 % S-3+1.5 % PVAV	24.1	20.8	1.32	0.85
15	3 % S-3	21.5	19.5	1.28	0.87
		Cement-ash stone with W/C= $K_{n.c}$ and A/C = 0.4			
16	–	22.5	20.1	1.40	0.80
17	3 % PVAV	22.1	18.3	1.29	0.85
19	1.5 % C-3+1.5 % PVAV	21.4	16.1	1.29	0.86
20	3 % C-3	19.5	16.0	1.25	0.88

* $K_{n.c}$ – normal consistency of cement paste.

Table 3. Experimental Planning Conditions.

No.	Factors	Coded designation	Levels of variation		
			–1	0	+1
1	PFM content, % cement mass	X_1	0	1.5	3
2	The part of S-3 in the composition of the PFM, %	X_2	0	0.5	1.0
3	Water-cement ratio (W/C)	X_3	0.4	0.5	0.6
4	Ash-cement ratio (A/C)	X_4	0.1	0.4	0.7

Tested cubes with a rib size of 70 mm hardened under normal conditions.

To calculate the basic compositions of concrete, the absolute volume condition was used:

$$C/\rho_c + A/\rho_a + W/\rho_w + S/\rho_s = 1000, \tag{4}$$

where C, A, W, S are the consumptions of cement, ash, water and sand;

$\rho_c, \rho_a, \rho_w, \rho_s$ are the densities of these materials.

From the formula (4) it is possible to find the consumption of cement, then the remaining components at the given values of A/C, W/C and $n = S/C$:

$$C = \left(\frac{1000}{1/\rho_c + (A/C)/\rho_A + W/C + n/\rho_s} \right) \rho_c, \tag{5}$$

$$A = C \cdot (A/C);\; S = C \cdot (S/C);\; W = C \cdot (W/C)..$$

The calculated water consumption for a given W/C was corrected taking into account the achievement of the necessary spreading or immersion of the cone to achieve a cast consistency of the mixture, and also the influence of additives included in the PMF. With the corrected consumption of water, the consumptions of cement and ash were adjusted at the given values of W/C and A/C. Sand consumption was specified from condition (4).

The main concrete compositions used when obtaining of models (6)–(9) are given in Table 4.

Table 4. Examples of concrete compositions used in the models (6)–(9).

PFM content, % cement weight	The share of S-3 in the PFM	Water-cement ratio	Ash-cement ratio	The composition of the concrete mixture, kg/m³			
				W	C	A	S
1	0.75	0.5	0.4	238	477	191	1416
1.5	0.5	0.5	0.4	235	471	188	1432
2.6	0.75	0.45	0.4	212	472	189	1491
1.5	0.5	0.6	0.7	245	409	286	1358
3	0.5	0.5	0.4	208	415	166	1575
3	0.5	0.6	0.4	204	340	136	1680
3	1	0.45	0.4	204	454	181	1536

The planning matrix and the results of the experiments are given in Table 5. In each row of the matrix, the samples were duplicated and the average values of the output parameters were found. The regression equations adequate for the experimental data obtained for the water demand, volume of the entrained air compressive and bending strength are shown in Table 6.

Table 5. Planning matrix and the results of experiments to determine the properties of ash-cement concrete.

No.	Coded Factor Values				Water demand, l/m³	Volume of air entrained, %	28-days strength, MPa	
	X_1	X_2	X_3	X_4			compressive	bending
1	+1	+1	+1	+1	255	1.1	25.8	4.3
2	+1	+1	+1	–1	220	1.5	24.2	3.8
3	+1	+1	–1	+1	250	0.6	45.3	5.7
4	+1	+1	–1	–1	195	0.7	43.5	5.1
5	+1	–1	+1	+1	335	1.5	22.2	4.8
6	+1	–1	+1	–1	310	2.9	27.4	4.1
7	+1	–1	–1	+1	283	1.7	42.1	6.1
8	+1	–1	–1	–1	225	2.1	44.2	5.9
9	–1	+1	+1	+1	275	1.1	24.3	3.8
10	–1	+1	+1	–1	240	1.5	25.7	3.2
11	–1	+1	–1	+1	390	1.1	44.1	5.8
12	–1	+1	–1	–1	351	1.6	46.2	5.3
13	–1	–1	+1	+1	375	1.9	24.9	3.7
14	–1	–1	+1	–1	343	2.1	21.5	3.4
15	–1	–1	–1	+1	385	1.1	40.5	5.7
16	–1	–1	–1	–1	347	1.3	43.1	5.4
17	+1	0	0	0	230	1.5	33.6	4.7
18	–1	0	0	0	260	1.7	37.5	5.0
19	0	+1	0	0	228	0.9	38.5	5.1
20	0	–1	0	0	265	1.4	36.6	5.6
21	0	0	+1	0	220	1.7	29.5	4.0
22	0	0	–1	0	295	1.3	48.9	6.5
23	0	0	0	+1	275	1.1	31.1	4.7
24	0	0	0	–1	235	1.5	32.0	4.1

Table 6. Regression equations for properties of cast ash-cement FGC with PFM additives.

No.	Property	Regression equation	
1	Water demand, l/m³	$y_1 = 235.3 - 37.13X_1 - 25.98X_2 - 29X_3 + 19.99X_4 + 9.48X_1^2 + 10.69X_2^2 + 19.19X_4^2 + 25.44X_1X_3 - 19.94X_2X_3$	(6)
2	Volume of air entrained, %	$y_2 = 1.355 - 0.33X_1 + 0.213X_2 - 44X_3 + 0.242X_4 + 0.242X_1^2 - 0.208X_2^2 + 0.142X_3^2 - 0.058X_4^2 - 0.2X_1X_2$	(7)
3	Compressive strength, MPa (R_c)	$y_4 = 36.7 - 1.07X_2 - 9.88X_3 - 1.21X_1^2 + 0.79X_2^2 + 2.44X_3^2 - 5.21X_4^2 - 0.21X_1X_2 + 0.46X_3X_4$	(8)
4	Bending strength, MPa ($R_{t.b}$)	$y_5 = 5.03 + 0.18X_1 - 0.15X_2 + 0.92X_3 + 0.24X_4 + 0.19X_1^2 + 0.31X_2^2 + 0.21X_3^2 - 0.64X_4^2 - 0.12X_1X_2 + 14X_1X_3$	(9)

In accordance with the well-known recommendations [34], when using ash, a possible (up to 20...30 %) reduction in compressive strength at the age of 28 days should be taken into account. As follows from the data obtained (Table 5), the decrease in the strength of cement-ash concrete is completely leveled with the introduction of the proposed additives.

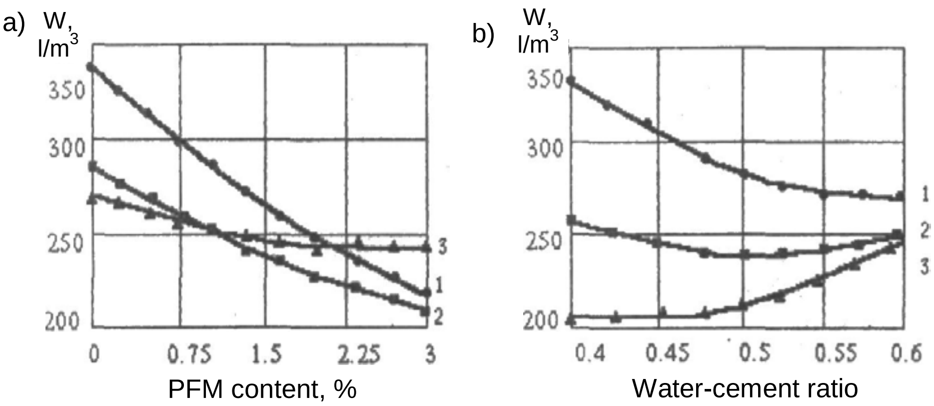

Figure 2. Estimated dependencies of water demand of ash-cement concrete mixes with additives (PFM): a) W/C: 1 – 0.4; 2 – 0.5; 3 – 0.6; (X_2 = 0; X_4 = 0); b) the content of the PFM: 1 – 0; 2 – 1.5; 3 – 0.3 %; (X_2 = 0; X_4 = 0).

When analyzing the mathematical model of the water demand of the mixture, attracts attention that the influence of factors which characterize the amount (X_1) and composition (X_2) of PFM in ash-cement cast mixtures and mixtures without the addition of ash is quite close. The significant effect of the interaction between X_1 and X_2 shows that the greatest plasticizing effect, both at large and low doses of PFM, occurs when the S-3 superplasticizer prevails in the latter. Opposite but close in magnitude linear and quadratic effects at X_3 show that, its increased values, leads to an insignificant increase in water demand, while at the same time at low W/C (X_3 < 0), water demand significantly increases. This pattern is well known in concrete technology as a rule of constancy of water demand [14].

Graphical dependences of water demand, volume of air entrained, compressive and bending strength, depending on water-cement ratio, PFM content and composition obtained by analyzing the regression equations are shown in Figures 2, 3, 4. It follows from them that for certain values of ash-cement and water-cement ratios, it is possible to change the main properties of concrete mixtures and concrete in a significant range, choosing of the PFM consumption and the ratio of its constituent components.

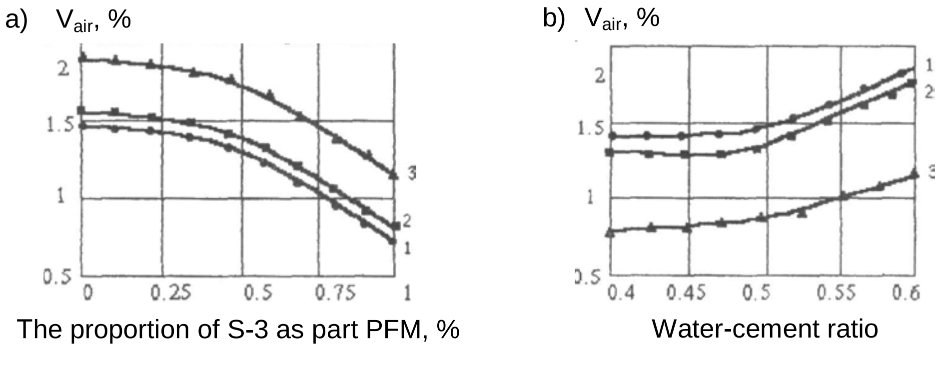

Figure 3. Air entrainment of ash-cement concrete mixtures with PFM additives: a) W/C: 1 – 0.4; 2 – 0.5; 3 – 0.6; (X_1 = 0; X_4 = 0); b) the part of S-3 in the PFM: 1 – 0.4; 2 – 0.5; 3 – 0.6; (X_1 = 0; X_4 = 0).

The criteria of the deformability of concrete and its crack resistance are the ratios of the splitting tensile strength or bending strength to a static or dynamic elastic modulus [14]. These parameters are quite close. As shown in [11], for fine-grained concrete, the formulas for calculating the tensile strength at splitting ($R_{t.sp}$) and tensile strength at bending ($R_{t.b}$) differ only in the coefficients:

$$R_{t.sp} = 0.57R_c^{2/3}, \quad R_{t.b} = 0.99R_c^{2/3}, \tag{10}$$

where R_c is compressive strength at 28 days.

Comparison of the experimental values of the static (E_c) and dynamic elastic moduli (E_{dyn}) shows that the ratio E_c/E_{dyn} for concrete is in the range 0.87...0.95. The lower values are typical for concrete with a compressive strength of less than 25 MPa. The ratio $R_{t.sp}/E_{dyn}$ is close to the value of ultimate extensibility and is called the conditional extensibility (ε_c) [11]. It is easy to show that:

$$\varepsilon_{\text{c}} = \frac{R_{t.sp}}{E_{dyn}} \approx \frac{0.57 \times R_{t.b}}{0.99 \times 1.1 E_c} \approx 0.52 \frac{R_{t.b}}{E_c}. \quad (11)$$

Table 7 shows the calculated values of the studied parameters depending on various parameters of concrete compositions. Values $R_{t,b}$ are calculated using model (8). Values are E_c calculated using the formula [14]:

$$E_c = \frac{5.2 \times 10^4 R_c}{23 + R_c}, \quad (12)$$

where R_c is concrete compressive strength calculated according to model (8).

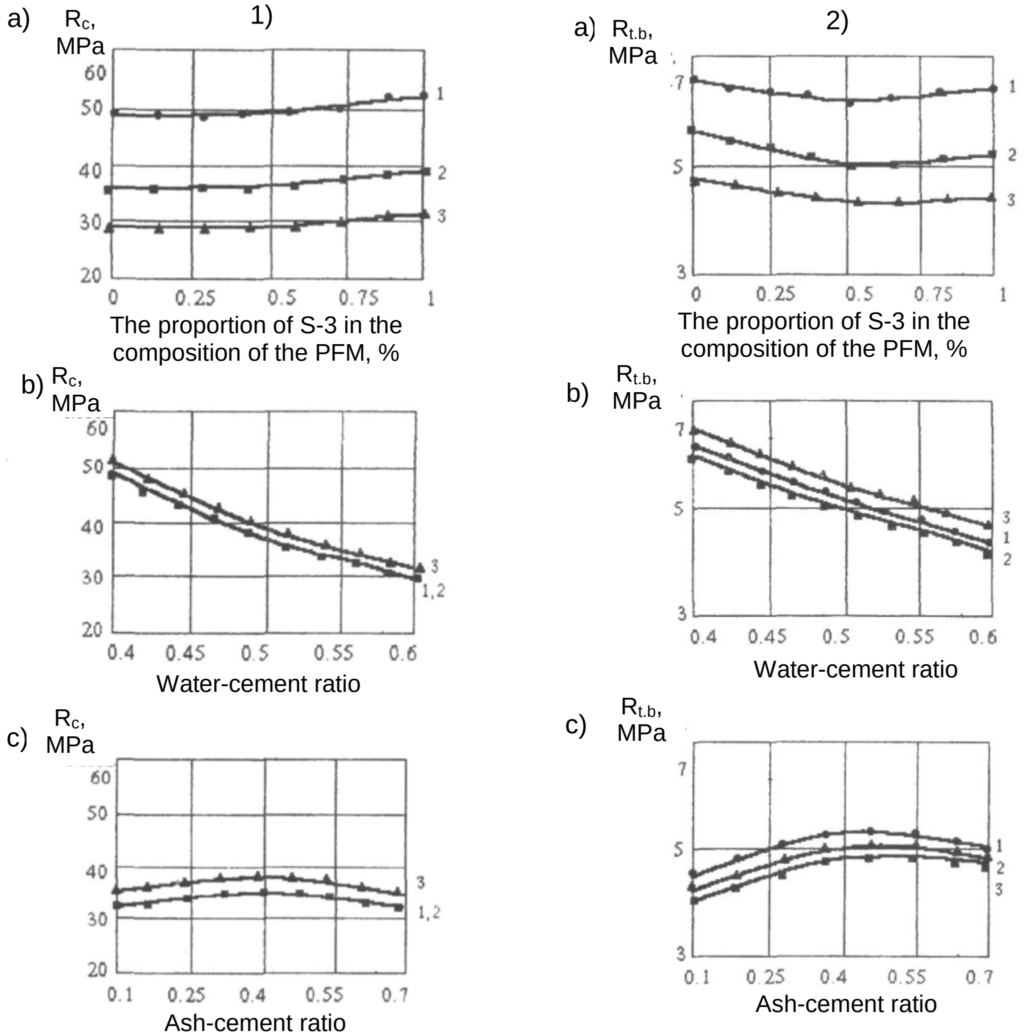

Figure 4. The effect of the composition of ash-cement FGC with PFM additives on the compressive strength (1) and bending (2) (X_1 = 0): a) W/C: 1 – 0.4; 2 – 0.5; 3 – 0.6; (X_1 = 0; X_4 = 0); b) the proportion of S-3 in the PFM: 1 – 0.4; 2 – 0.5; 3 – 0.6; (X_1 = 0; X_4 = 0); c) the proportion of S-3 in the composition of the PFM: 1 – 0.4; 2 – 0.5; 3 – 0.6; (X_1 = 0; X_3 = 0).

Shrinkage curves of investigated concrete determination in accordance with Russian State Standard GOST 24544–81 on prisms with dimensions 70×70×280 mm are shown in Figure 5. Their analysis shows that for all the studied compositions, shrinkage deformations stabilize by 100 days. Concretes without PFM additives have the highest shrinkage values. Their ultimate shrinkage, depending on the W/C, fluctuates in the range 0.2...0.7 mm/m typical for fine-grained concrete. In the first stages of hardening, the addition of fly ash increases shrinkage deformations, which are then aligned with deformations of concrete without ash. PFM additives consisting of S-3 and PVAV reduce ultimate shrinkage deformations by 30...50 %. Moreover, the degree of reduction of shrinkage deformations increases with the increase in the plasticizing effect of PFM.

Table 7. Estimated values of the deformability of cast FGC with additives PFM.

No.	PFM additive, % cement mass	Mass fraction of S-3 in the PFM	Water cement ratio	R_c, MPa	$R_{t.b}$, MPa	E_c, x10^{-5} MPa	ε_c, x10^{-5} mm
1	0	–	0.5	35.49	4.66	25.24	9.6
2	1	0	0.4	48.57	6.51	28.23	12.0
3	1	0.5	0.4	48.91	6.09	28.29	11.2
4	1	1	0.4	50.83	6.28	28.64	11.4
5	3	0	0.4	47.74	6.59	28.07	12.2
6	3	0.5	0.4	47.81	6.31	28.09	11.7
7	3	1	0.4	49.46	6.35	28.39	11.6
8	1	0	0.6	28.80	4.63	23.13	10.4
9	1	0.5	0.6	29.15	4.43	23.25	9.9
10	1	1	0.6	31.07	4.63	23.90	10.1
11	3	0	0.6	27.98	5.03	22.83	11.5
12	3	0.5	0.6	28.05	4.61	22.86	10.5
13	3	1	0.6	29.70	4.65	23.44	10.3

Note: In the calculations, the ash-cement ratio of 0.4 is adopted.

To determine the abrasion of the investigated concrete, we used cubic samples with an edge size of 7 cm in an air-dry state, hardening for 28 days. The tests were carried out on a device whose working body is a rotating disk using an abrasive material obtained by mixing corundum up to quartz (GOST 13087–81). The test results are shown in Figure 6.

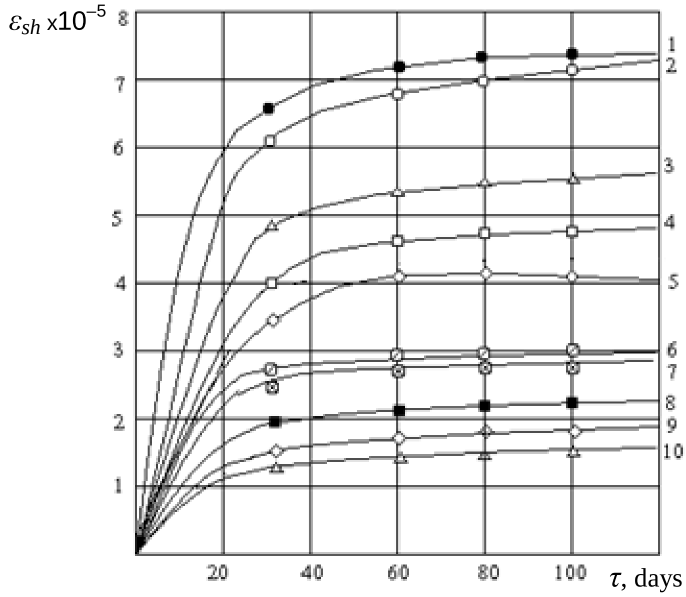

Figure 5. Shrinkage deformation (ε_{sh}) of ash-cement concrete with additives PFM: 1–5 – W/C = 0.6: 1 – concrete without additives A/C = 0.4; 2 – concrete without additives A/C = 0; 3 – concrete with the addition of 3 % PVAV; A/C = 0.4; W/C = 0.6; 4 – concrete with the addition of 3 % PFM (50 % S-3; 50 % PVAV); A/C = 0.4; 5 – concrete with the addition of 3 % S-3; A/C = 0.4; 6–10 – W/C = 0.4; 6 – concrete without additives A/C = 0.4; 7 – concrete without additives A/C = 0; 8 – concrete with PVAV additive 3 %; 9 – concrete with the addition of 3 % PFM, (50 % S-3; 50 % PVAV); 10 – concrete with the addition of 3 % S-3.

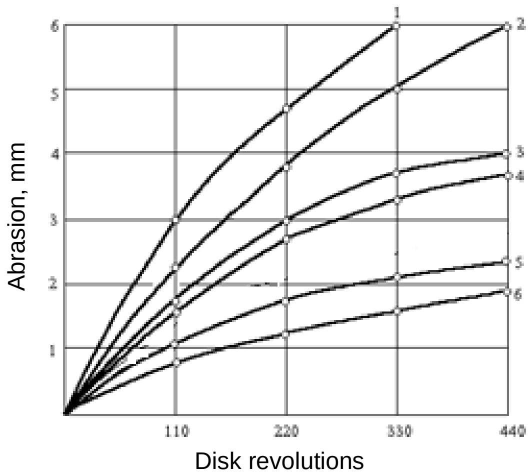

Figure 6. Abrasion of ash-cement concrete with PFM additives (W/C = 0.5; A/C = 0.4): 1 – without PFM; 2 – A/C = 0 without PFM; 3 – 1 % PFM (0.5 % S-3 + 0.5 % PVAV); 4 – 1 % PVAV; 5 – 3 % PFM (1.5 % S-3 + 1.5 % PVAV); 6 – 3 % PVAV.

The nature of the curves in Figure 6 confirms the well-known conclusion [33] on the power dependence of concrete abrasion depth on the number of disk revolutions (N).

$$U = KN^m. \tag{13}$$

The coefficients K and m depend on the composition of concrete and the type of additives. Already 1 % of PFM reduced abrasion by more than 1.5, and 3 % by more than 3 times. At the same time, an increase in the proportion of PVAV in the composition of PFM increases the abrasion resistance.

Comparative impact tests of concrete were carried out using a pendulum driver on samples 4x4x16 cm in size [32]. When determining the impact work, for convenience of comparison, the found values of the fracture load of the samples were recalculated to the specific work of the impact per 1 cm^2 of their cross section. The results of determining the impact resistance of concrete are shown in Table 8.

Table 8. Concrete impact test results (W/C = 0.5) for impact.

No.	Ash-cement ratio	Additive PFM, % mass of cement	The composition of the PFM in parts by weight		Work Impact, J	Specific work impact, J/cm^2
			C-3	PVAV		
1	–	–	–	–	154	9.6
2	–	1	1	–	161	10.1
3	–	1	0.5	0.5	160	10.0
4	–	1	–	1	165	10.3
5	–	3	1	–	165	10.3
6	–	3	0.5	0.5	163	10.2
7	–	3	–	1	170	10.6
8	0.4	–	–	–	165	10.3
9	0.4	1	1	–	170	10.6
10	0.4	1	0.5	0.5	172	10.7
11	0.4	1	–	1	175	10.9
12	0.4	3	1	–	175	10.9
13	0.4	3	0.5	0.5	180	11.2
14	0.4	3	–	1	182	11.4

Ash-cement concrete with PFM additives showed a higher impact resistance, which is consistent with known data [14]. The increase in impact work in ash-cement concrete with PFM additives compared to non-additive amounted to 20 %. The increase in impact strength with S-3 and PVAV additives can be explained by the adsorption modification of the structure of cement stone which becomes more dispersed as a result of an increase in the supersaturation due to surface-active substances during the hardening of cement paste [14]. The change in the mass ratio of S-3 and PVAV in the composition of PFM did not lead to a significant change in their effect on impact strength. An analysis of the results suggests that the introduction of the proposed PFM additive into the composition of cement-ash concrete makes it possible to remove the known limitations on their use in the conditions of abrasion and impact [3, 34].

The practical technology of cast FGC with PFM additives can be based on the direct introduction of additives in the manufacture of finished mixtures or on the preliminary receipt of dry mixtures that are mixed with water per object. It is possible to use the combined method, when only one component of PFM is introduced into the dry mixture, the second one is used in the form of an aqueous solution or emulsion in preparing the concrete mixture ready for use.

4. Conclusions

1. Additives of polyfunctional modifiers, including the superplasticizer of the naphthalene-formaldehyde type (S-3) and the polymer of vinyl acetate and vinyl versatate (PVAV) actively influence the hydration process of cement and cement-ash pastes, having a certain stabilizing effect in the first stages of hardening. It affects a decrease in the degree of hydration and a slowdown in the growth of plastic strength, especially at the stage of coagulation structure formation. By the age of 28 days, the stabilizing effect of PFM additives on the degree of hydration of cement and cement-ash pastes becomes almost imperceptible.

2. The introduction of PFM additives significantly affects the parameters of the pore structure of cement-ash stone, reducing open porosity, average pore size and increasing the uniformity of their distribution.

3. The analysis of experimental data and mathematical models obtained by their statistical processing shows that the properties of ash-cement concrete mixtures and the properties of concrete significantly depend on the composition of the PFM and their dosage. The introduction of PFM additives allows to adjust the water demand and air content of concrete mixtures, as well as to increase the ultimate extensibility of concrete.

4. The introduction of PFM additive including naphthalene formaldehyde superplasticizer S-3 and a polimer of vinyl acetate with vinyl versatate PVAV in an amount of 1.5...3 % with a 1:1 ratio of water-cement and ash-cement ratio in the range of 0.4–0.5 allows to obtain fine-grained concrete of classes B25...B35. The introduction of the PFM additive allows, when optimal values of its consumption and composition, by 30–50 % to reduce shrinkage deformations, increase the abrasion resistance by 1.5–3 times and increase the resistance of cement-ash concrete to impact by up to 20 %.

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Влияние добавок полифункционального модификатора на свойства цементно-зольного мелкозернистого бетона

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Ключевые слова: Зола-унос, прочность, усадка, истираемость, добавки, суперпластификатор, структура

Аннотация. Объектом исследования являются свойства цементно-зольных бетонов с добавкой полифункционального модификатора (ПФМ), предназначенных для полов промышленных предприятий. В состав ПФМ входит суперпластификатор нафталин-формальдегидного типа и сополимер винилацетата с винилверсататом. Предпосылкой к использованию добавки ПФМ в составе цементно-зольных бетонов является возможность с его помощью активно влиять на процессы структурообразования и, как следствие, на свойства бетона. С применением известных химических и физических методов получены экспериментальные данные о влиянии добавки ПФМ на степень гидратации цемента, кинетику изменения пластической прочности цементно-зольного камня в процессе твердения. Установлено, что введение добавки ПФМ позволяет уменьшить открытую пористость и средние размеры пор цементно-зольного камня а также увеличить показатель однородности пор по размерам. Для изучения свойств цементно-зольных бетонов с добавкой ПФМ применен метод математического планирования экспериментов, в результате реализации которых получен комплекс математических моделей водопотребности, водоотделения, объема вовлеченного воздуха, прочности бетона при сжатии и изгибе. Модели позволяют количественно оценить влияние на указанные свойства бетона водо- и золоцементного отношений, содержания и соотношения компонентов ПФМ, а также проектировать составы цементно-зольных бетонов с заданными свойствами. Исследования, результаты которых приведены в статье, показали возможность с помощью добавки ПФМ существенно улучшить свойства цементно-зольных бетонов, важные при использовании их для полов промышленных предприятий и, в частности, на 30–50 % уменьшить предельные усадочные деформации, снизить в 1.5–3 раза их истираемость и до 20 % повысить сопротивление ударным воздействиям.

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