SUBSTANTIATION OF HIGH-STRENGTH ASH-CONTAINING MORTARS EFFECTIVE COMPOSITIONS USING MATHEMATICAL MODELS

LEONID DVORKIN[1], VADIM ZHITKOVSKY[1*], VITALIY MARCHUK[1*], YURI RIBAKOV[2]
[1]National University of Water and Environmental Engineering, 11, Soborna st., Rivne 33028, Ukraine
[2]Department of Civil Engineering, Ariel University, Ariel, 40700, Israel

The research is focused on obtaining high-strength mortars from composite cements, containing up to 50% of fly ash and a polyfunctional modifying admixture. The polyfunctional modifier contains a superplasticizer and an intensifier for cement grinding. Using mathematical experiments planning, experimental-statistical models of mortars strength in bending and compression at 2 and 28 days were obtained. The models take into account the influence of the fly ash amount, superplasticizer content and type and cement grinding fineness. Analytical results based on the obtained models and the influence of the investigated factors are presented. The obtained mathematical models of mortar strength allowed optimization of the required technological solutions that provide the necessary mechanical characteristics of mortars at minimum cost.

Keywords: *mortar, fly ash, composite cements, superplasticizer, grinding, experimental-statistical models, optimization*

1. Introduction

An effective way to reduce the Portland cement clinker consumption and regulate the construction and technical properties of concretes and mortars is using active mineral additive in cement, mortars and concrete. As it was shown by numerous studies confirmed by practical experience, one of such effective mineral additives, is fly-ash [1 … 11]. Fly-ash actively affects composite building materials structure formation, consecutive transition from coagulation structure to spatial crystalline framework formation at all stages of cement systems hydration and structure formation. Due to pozzolanic activity, adding fly ash into cement-water systems increases the volume of hydrated neoplasms and also accelerates the hydrolysis process, increases the cement hydration degree [5].

Fly ash, having a high specific surface area, in addition to direct chemical interaction with cement, actively affects the physico-chemical processes near the cement paste - mineral additive distribution surface. As the cement stone condensation-crystallization structure is formed, epitaxial contacts are formed between the cement paste and mineral additives grains [12]. According to the Gibbs-Folmer doctrine, the energy of crystal nucleation is also significantly reduced in presence of crystallization centers, which are mineral additives particles [13].

An important indicator of ash quality, determining its activity, is the dispersion particles size distribution and their porosity. Ash is characterized by a significant content of particles that have small closed pores. The high content of micropores in ash causes a high value of its actual specific surface area. Measurements of the ash actual specific surface area, performed by nitrogen adsorption [14], showed that it is an order of magnitude higher than that of cement. High adsorption capacity, hygroscopicity, and hydraulic activity of ash are associated with its high specific surface. After studying the strength of cement composites obtained by mixing clinker and ash, crushed to specific surface values of 250 ... 640 and 300 ... 800 m^2/kg, respectively, the necessary correspondence between the ash particle size distribution and clinker grinding fineness was established [15]. The high increase in ash dispersion affects the mortars strength and concrete at early age. A number of researchers have shown that effectiveness of adding fly ash in cement mortars and concrete is significantly increased when conducting surfactant additives. Adding surfactants can be considered as one of the ways to activate the ash additive in mortars and concrete [12]. A necessary condition for effectiveness of surfactants is their ability to chemisorption interaction with the additives particles surface. In a general case for mineral additives of acidic nature, the most effective are surfactants of cationic type, and the base - anionic.

The expediency of activating cement with mineral additive by modifying its surface with surfactant additives follows from the Dupree-Jung equation [16], which connects the work of W_{ad} adhesion with the surface energy of a solid:

$$W_{ad} = \nu_s - \nu^*_s(m + \cos\theta) \qquad (1)$$

where ν_s is surface energy of a solid; ν^*_s is free surface energy of a solid in steam and gases environment;

*Autor corespondent/*Corresponding author*,
E-mail: v.v.zhitkovsky@nuwm.edu.ua

Table 1

Chemical composition of raw materials

Material	The content of oxides. %									
	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	$CaO_в$
Clinker	-	21.80	5.32	4.11	66.80	0.95	0.63	0.54	0.42	-
Fly Ash	5.1	84.5			2.1	2.0	2.3	1.2		2.5

Table 2

Physical and mechanical properties of Portland cement

Specific Surface, m^2/kg	Normal consistency, %	Setting time, hours-min		Strength, MPa, at 28 days	
		initial	final	flexural tensile	compressive
302	26.3	1-55	3-25	6.8	51.8

Table 3

Characteristics of sand

Indicators	Value
Fineness modulus	1.91
The total residue on the sieve 0.63, %	21.3
The content of dusty and clay particles, %	0.7
Density, kg/m^3	2690
Bulk density, kg/m^3	1380
Voidness, %	48.7

$m = \nu^*_l / \nu_l > 1$ (ν^*_l is the surface tension of liquid, oriented under the influence of the solid surface force field; ν_l is the wetting fluid surface tension); θ is the wetting edge angle.

As it follows from the equation (1), in order to achieve high adhesive strength, it is important to ensure the necessary wettability of the additive with binders and to reduce the interfacial surface energy achieved by the treatment of the surfactant additive. The reduction of the interfacial surface energy when creating an adsorption-active medium is determined from the following equation

$$\Delta\nu_{s.l.} = KT\int_0^c n_s(c) d \cdot \ln c \qquad (2)$$

where $\Delta\nu_{s.l}$ is the difference interphase surface energy without surfactants and in presence of surfactants with a concentration of c; n_s is the amount of adsorption, determined by the number of surfactant molecules that are adsorbed per 1 cm^2 of the phase distribution surface; K is Boltzmann constant; T is the absolute temperature, K.

To date, a number of known experimental data demonstrate effectiveness of joint introduction of fly ash and superplasticizers (SP)into cement system [17, 18]. Their common feature is the ability to peptize (deflocate) the aggregated cement flocs. The water immobilized in the flocs is released and helps to thin the cement paste. Compared with traditional plasticizers lignosulfonate type SP have a longer carbon chain length and, accordingly, higher adsorption capacity [19]. Colloidal chemical phenomena at the phase boundary and the zeta potential magnitude have a significant effect on the mechanism of joint ventures action in cement and cement composites [20 ... 23]. For polycarboxylate and polyacrylate types of superplasticizers the mutual repulsion of cement particles is provided due to the so-called steric effect. This effect is due to the chains shape and the nature of the charge on the cement and hydrate grains surface [12].

As the analysis of previous studies shows, combined introduction of fly ash and superplasticizers into cement composites has a positive effect [24]. At the same time, this effect is significantly influenced by a number of additional technological factors. The purpose of the present study is to obtain quantitative dependencies that allow predicting the joint effect of fly ash content in cement and its dispersion on cement mortars strength and to propose a way to optimize the composition of high-strength mortars based on ash-containing cements.

2. Materials, research methods and results

The raw materials for the research are ordinary Portland cement CEM I 42,5, locally available fly ash and quartz sand. Naphthalene-formaldehyde and polycarboxylate superplasticizers were used as chemical modifiers. Cement grinding intensifier - propylene glycol was used.

The Portland cement is a typical medium aluminum cement. Mineralogical composition of

Table 4

Experimental planning conditions

Factors		Variation levels			Interval
Natural	Coded	–1	0	+1	
Ash content in binder, (Ash. %)	x_1	30	40	50	10 %
Specific surface (S_{sp}), m^2/kg	x_2	350	450	550	100
Content PFM_1/ PFM_2 , %	x_3	0.4/1.0	0.7/1.5	1/2.0	0.3/0.5

Table 5

Planning matrix and experimental strength characteristics values of mortars with PFM

Factors			W/C	Strength at the age of days, MPa					
				flexural tensile ($f_{b.tb}$)			Compressive (f_{cm})		
Ash, %	S_{sp}, m^2/kg	PFM, %		2	7	28	2	7	28
50	550	1.0/2.0	0.28/0.31	5.9/4.7	8.0/6.8	9.5/8.1	22.1/17.7	42.2/38.0	51.8/46.6
50	550	0.4/1.0	0.33/0.36	4.8/4.3	5.7/4.8	8.3/7.1	19.2/17.3	32.8/29.5	39.7/35.7
50	350	1.0/2.0	0.24/0.26	4.5/3.6	6.0/5.1	7.9/6.7	16.2/13.0	36.2/32.6	49.8/44.8
50	350	0.4/1.0	0.24/0.26	4.5/4.1	6.0/5.1	7.9/6.7	16.2/14.6	36.2/32.5	49.8/44.7
30	550	1.0/2.0	0.29/0.32	6.7/5.4	8.8/7.5	10.3/8.8	29.8/23.8	44.2/39.8	55.1/49.6
30	550	0.4/1.0	0.34/0.37	5.4/4.9	5.9/5.0	8.6/7.3	22.4/20.2	33.8/30.4	41.2/37.1
30	350	1.0/2.0	0.26/0.29	4.8/3.8	6.8/5.8	8.2/7.0	18.9/15.1	40.5/36.5	53.1/47.8
30	350	0.4/1.0	0.31/0.34	4.4/4.0	6.6/5.6	7.6/6.5	16.5/14.9	30.1/27.1	39.9/35.9
50	450	0.7/1.5	0.26/0.29	6.0/5.4	7.4/6.3	8.8/7.5	17.3/15.6	37.8/34.0	50.3/45.3
30	450	0.7/1.5	0.28/0.31	6.4/5.8	8.3/7.1	9.5/8.1	20.8/18.7	42.0/37.8	60.2/54.2
40	550	0.7/1.5	0.30/0.33	6.4/5.8	8.1/6.9	10.0/8.5	21.7/19.5	38.2/34.4	51.0/45.9
40	350	0.7/1.5	0.27/0.30	4.2/3.8	6.7/5.7	8.1/6.9	19.4/17.5	38.0/34.2	50.4/45.4
40	450	1.0/2.0	0.23/0.25	6.0/4.8	7.6/6.5	8.7/7.4	19.5/15.6	38.7/34.8	52.6/47.3
40	450	0.7/1.5	0.27/0.30	6.3/5.7	7.7/6.5	9.3/7.9	20.1/18.1	34.9/31.4	58.4/52.6
40	450	0.7/1.5	0.28/0.30	6.2/5.6	7.5/6.4	9.1/7.7	18.9/17.0	34.5/31.1	57.8/52.0
40	450	0.7/1.5	0.27/0.30	6.3/5.7	7.8/6.6	9.4/8.0	19.8/17.8	35.4/31.9	59.0/53.1

Note. Numerator - PFM_1, denominator - PFM_2.

clinker is: C_3S - 57.10%. C_2S - 21.27%, C_3A - 6.87%, C_4AF - 12.19%. The average chemical composition is given in Table 1, base physical and mechanical properties of cement are presented in Table. 2.

As it follows from the above data, the chemical composition of ash used in the frame of this study, meets the requirements to fly ash for mortars and concrete [25].

Cement with fly ash was ground in a laboratory ball mill to the desired specific surface. The specific surface area of the obtained composite cement (CC) was measured according to the Blane air permeability method [26].

As a mortars aggregate were used quartz sand. The sand properties are given in Table 3.

Chemical admixtures used in this study are powdered superplasticizers (SP) of naphthalene-formaldehyde type SP-1 and polycarboxylate type Sika ViscoCrete-225.

The binder was prepared by joint grinding of cement and fly ash with adding of one of the polyfunctional modifiers (PFM) for grinding intensification – propylene glycol. The influence of two polyfunctional modifiers PFM_1 and PFM_2, which differ by superplasticizer type, was ensured. PFM_1 modifier contained polycarboxylate SP, PFM_2 modifier contained SP naphthalene formaldehyde type. The content of the intensifier grinding in the PFM composition was 0.04% of the binder amount.

To obtain experimental-statistical models describing the influence of technological factors, the method of mathematical experiments planning was used [27… 29].

At each point of the plan, a cement-sand mortar with a modified cement-ash binder composition was prepared: at n = binder : sand – 1:3 (by mass). W/C was determined to achieve a mortar cone spread on the flow table of at least

Table 6

The coefficients of experimental-statistical models for strength of mortars based on ash containing cement with addition of PFM_1

Options	Age, days	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{12}	b_{22}	b_{32}
f_{cm}	2	19.1	-1.74	2.8	1.7	-0.99	-0.86	0.99	0.39	1.89	-1.32
	7	36.31	-0.54	1.02	3.84	-0.6	-1.43	1.18	2.68	0.88	-2.62
	28	56.14	-0.81	-0.42	4.87	-1.43	-1.88	1.6	0.97	-3.58	-6.47
$f_{b.tb}$	2	6.22	-0.2	0.68	0.3	-0.15	-0.08	0.25	0.03	-0.69	-0.27
	7	7.79	-0.33	0.44	0.6	0.5	-0.1	0.63	-0.02	-0.47	-0.57
	28	9.19	-0.18	0.7	0.4	-0.14	-0.14	0.29	0.04	-0.06	-0.66

Table 7

Coefficients of experimental-statistical models for strength of mortars based on ash containing cement with addition of PFM_2

Options	Age, days	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{12}	b_{22}	b_{32}
f_{cm}	2	17.22	-1.46	2.35	0.47	-0.83	-0.65	0.68	0.3	1.65	-2.63
	7	32.68	-0.49	0.92	3.46	-0.54	-1.28	1.06	2.41	0.79	-2.36
	28	50.53	-0.73	-0.38	4.38	-1.28	-1.69	1.44	0.88	-3.22	-5.77
$f_{b.tb}$	2	5.59	-0.17	0.58	-0.01	-0.13	-0.05	0.18	0.04	-0.77	-0.53
	7	6.63	-0.28	0.37	0.51	0.04	-0.09	0.53	-0.01	-0.4	0.48
	28	7.81	-0.15	0.6	0.34	-0.12	-0.12	0.24	0.04	-0.05	-0.56

135 mm, according to EN 1015-3 [30], the compression and flexural tensile strength of prisms (40×40×160 mm) was determined at 2, 7 and 28 days.

To study the influence of these factors on strength characteristics, cement-ash mortars and corresponding quantitative estimates, a three-level three-factor plan B_3 [29] was implemented. The factors planning conditions are given in Table. 4 and the experimental results are presented in Table. 5.

After the experimental data processing and statistical analysis [29], mathematical models of the mortars compression and flexural tensile strengths were obtained in a form of polynomial regression equations. The mathematical models have the following form:

$$y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ij} x_i x_j + \sum_{i=1}^{k} b_{ii} x_1^2 \qquad (3)$$

where y is the output parameter; b_0, b_i, b_{ij}, b_{ii} are regression coefficients; x_i, x_{ij}, x_{ii} are the investigated factors and k is the number of factors.

The coefficients of experimental-statistical models for the ash-containing mortars strength are given in Tables 6 and 7. Statistical processing [28] showed that the obtained models can be considered adequate with a 95% confidence level.

Graphic dependencies illustrating the influence of technological factors on compression and bending strength of ash-containing CC are shown in Figures 1 ... 4.

3. Results and discussion

Analysis of the graphs shown in Figure 1 shows that the specific surface (S_{sp}) has a significant effect on the early strength of mortars

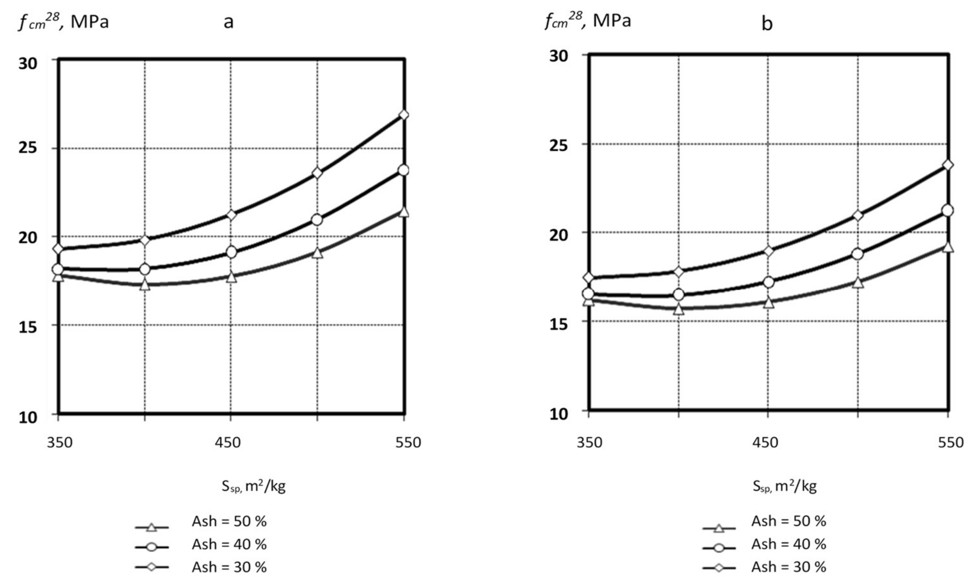

Fig. 1 - The influence of technological factors on mortars compression strength at 2 days: (a) with PFM_1, (b) with PFM_2

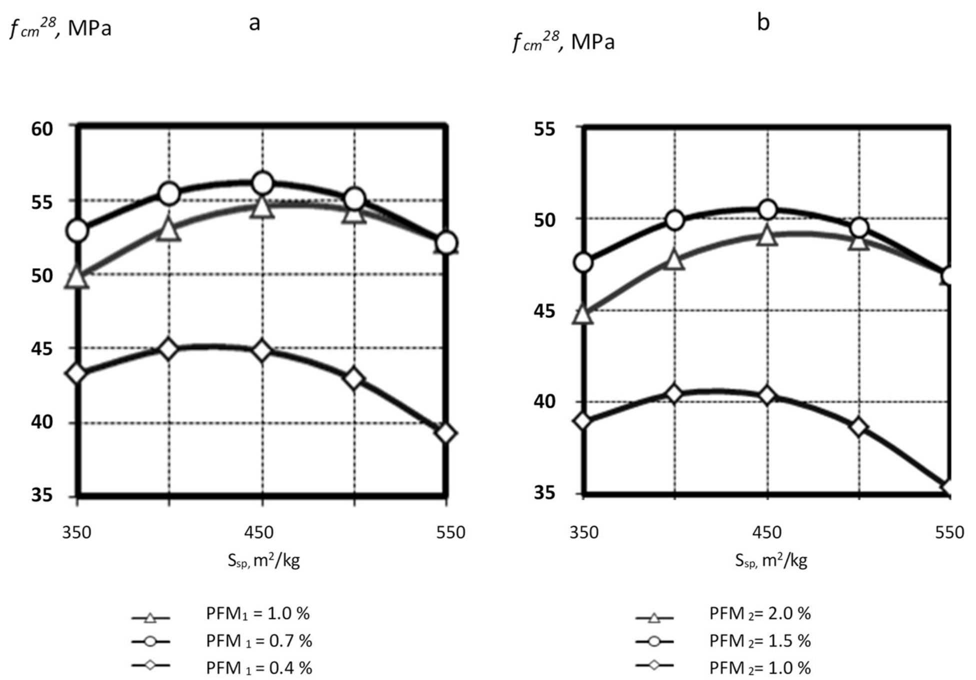

Fig. 2 - The influence of technological factors on mortars compression strength at 28 days: (a) with PFM_1, (b) with PFM_2

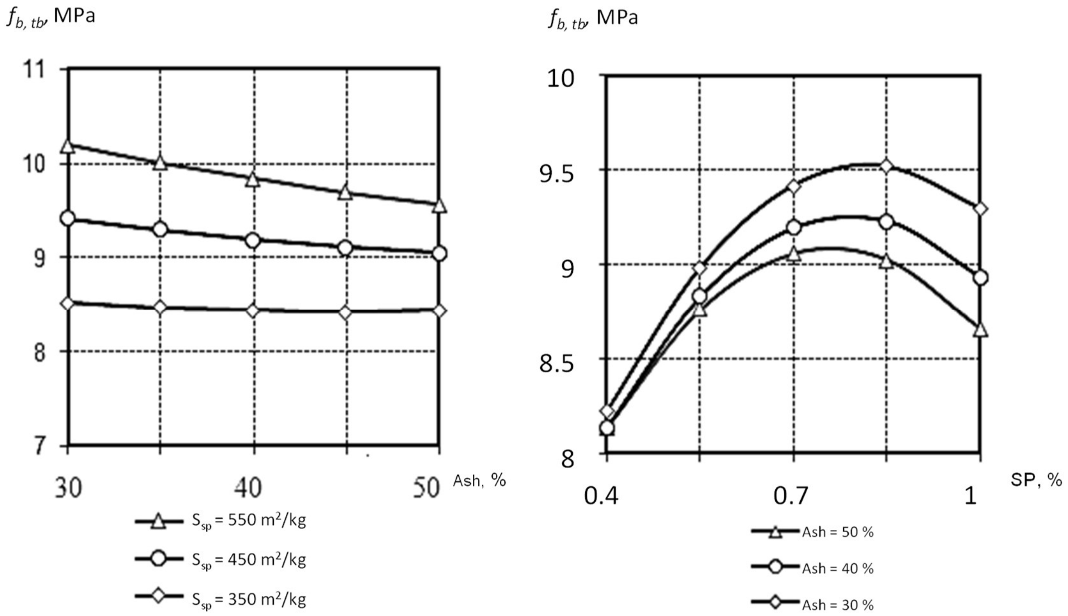

Fig. 3 - The influence of technological factors on mortars bending strength at 28 days when using PFM_1

based on finely ground cement-ash binders. With an increase in S_{sp} from 350 to 450 m²/kg, the mortars compressive strength at 2 days increases by 30 ... 45%. The increased cement dispersion is better manifested at fly ash consumption of 30%, compared to 50%. The optimal consumption of Sika VC 225 superplasticizer in the modifier is 0.7 ... 1%, and for SP-1 it is 1.5%, which leads to an increase in early strength by 25 ... 35%. A further increase in the amount polycarboxylate type superplasticizer is impractical, since the strength practically does not increase, and, as known, SP-1 superplasticizer at increased dosage inhibits hardening.

Following Fig. 2, the fly ash content in the binder has the highest effect on mortar strength at 28 days. As the ash content in binder increase the composite cement strength decreases. Under such conditions, to increase the mortar strength, it is advisable to add a superplasticizer, which reduces the mixture water demand. With an increase in superplasticizer consumption W/C decreases and the mortar strength increases accordingly.

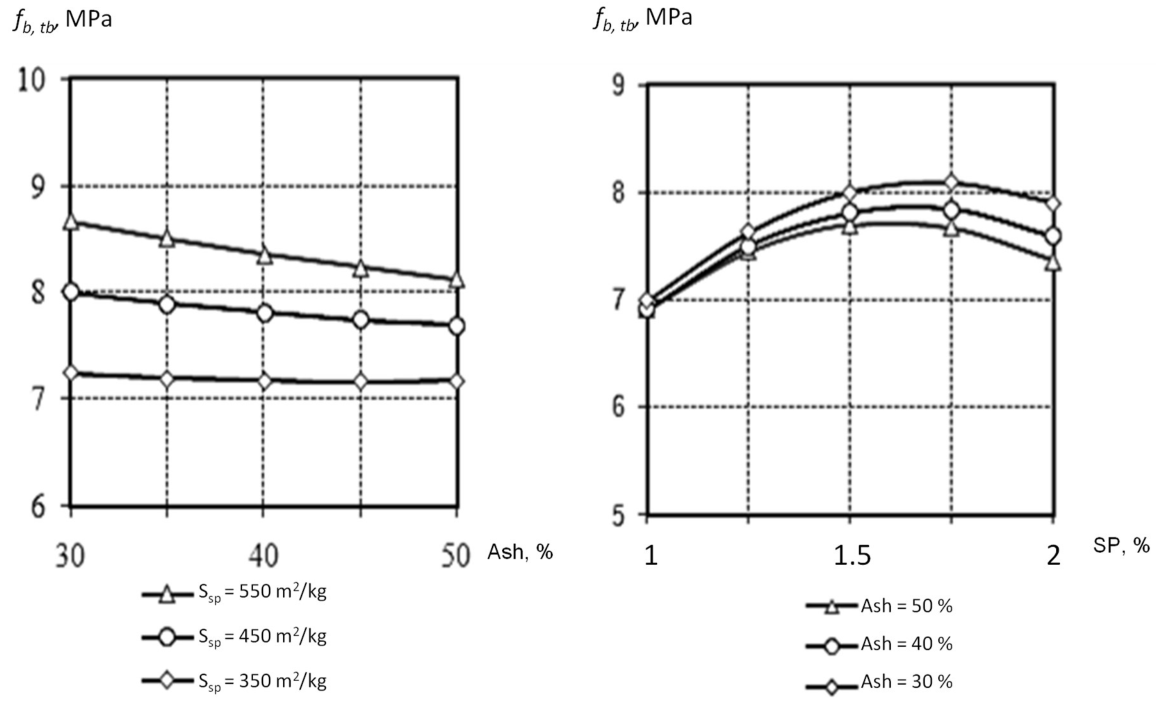

Fig. 4 - Influence of technological factors on mortars bending strength at the 28 days when using PFM_2

The optimal superplasticizer consumption in binder when using PFM_1 is 0.7%, which leads to an increase in strength by 20 ... 25%, compared to PFM_1consumption of 0.4%. In case of PFM_2dosing, it is optimal to use an SP in an amount of 1.5%, which leads to an increase in strength by 15 ... 20% compared with a consumption of 1%. However, a further increase in the SP amount is impractical and the mortars strength practically does not increase. An increase in the specific surface to 450 m^2/kg leads to an increase in strength by 25 … 35% compared to 350 m^2/kg, but with a specific surface of about 550 m^2/kg, a significant increase in strength is not observed.

The main factor that significantly affects the binder strength during bending is the specific surface. An increase from 350 m^2/kg to 550 m^2/kg increases the bending strength by 15 ... 25%. Increase in fly ash content in the binder mass from 30% to 50% leads to a slight decrease in strength to 10% (Figures 3, 4).

The obtained mathematical models enable to carry out multi-parametric mathematical optimization of technological factors in order to achieve the required strength at 2 and 28 days at the minimum cost of mortars.

Example. To solve the optimization problem described above, the add-in MS Excel "Solver" was used. It allows solving the problem of choosing the values of factors satisfying the established constraint. For economic calculations, the following values were taken: the cost of clinker - 90 euros per 1 ton, fly ash - 27 euros per 1 ton; naphthalene-formaldehyde type superplasticizer - 1.05 EUR per kg; polycarboxylate type superplasticizer - 2.85 euros per kg.

Mathematical optimization was carried out limiting the maximum cement specific surface area of less than 400 m^2/kg, as well as without this restriction. The cost of CC grinding to a specific surface of 400 m^2/kg was assumed to be equal to 720 EUR per 1 tone, for a specific surface of 550 m^2/kg – 1760 EUR per 1 tone. The optimization results are given in Table 8.

As it can be seen from the obtained data, limiting the specific surface area to less than 400 m^2/kg the finest mortar with a compressive strength at 28 days can be obtained using cement with an ash content of 50%, naphthalene formaldehyde superplasticizer - 0.92% or polycarboxylate - 0.34 %. The strength requirement at 2 days will be provided at a level of at least 10 MPa. To increase the early strength to 20 MPa, it is necessary to reduce the ash content to 30%, abandon naphthalene formaldehyde superplasticizer and increase the specific surface area of cement to 374 m^2/kg. It is impossible to provide early strength of 30 MPa at the given restriction on fineness of grinding. To obtain mortar with a strength of minimum 50 MPa at 28 days and minimum 10 MPa at 2 days, it is economically advantageous to increase the specific surface area of cement to 365 m^2/kg with an ash content of 50% and superplasticizer polycarboxylate type content of 0.63%.

Removing the restriction on the maximum specific surface area (within the variable range) makes it possible to further ensure the early concrete strength at a level of minimum 30 MPa. It is necessary to increase the grinding cement fineness to a maximum of 550 m^2/kg, as well as

Table 8

Technological factors obtained using the MS Excel "Solver" add-on optimization results

Compressive strength, MPa		Technological factors		
		Fly ash content, %	Superplasticizer content, %	Specific surface area, m^2/kg
28 days	2 days			
Maximum specific surface area of ash containing cement is 400 m^2/kg				
30	10	50* 50**	0.57* 0.34**	350* 350**
	20	-* 30**	-* 0.76**	-* 374**
40	10	50 50**	0.92 0.34**	350 350**
	20	-* 30**	-* 0.76**	-* 374**
50	10	-* 50**	-* 0.63**	-* 365**
	20	-* 30**	-* 0.76**	-* 374**
Maximum specific surface area of ash containing cement is 550 m^2/kg				
30	10	50* 50**	0.57* 0.34**	350* 350**
	20	-* 30**	-* 0.76**	-* 374**
40	10	50* 50**	0.92* 0.34**	350* 350**
	20	-* 30**	-* 0.76**	-* 374**
	30	-* 30**	-* 0.93**	-* 550**
50	10	-* 50**	-* 0.63**	-* 365**
	20	-* 30**	-* 0.76**	-* 374**
	30	-* 30**	-* 0.93**	-* 550**

*polycarboxylate superplasticizer;
*naphthalene formaldehyde superplasticizer

significantly increase the superplasticizer polycarboxylate type content (up to 0.93%).

4. Conclusions

1. The obtained mathematical models allow proper evaluation of the combined effect of fly ash content in cement, its specific surface area and the consumption of polycarboxylate and naphthalene-formaldehyde superplasticizers on the compressive and flexural strength of mortars.
2. Using the obtained mathematical models and the MS Excel "Solver" software, the possibility of optimizing the mortars composition while ensuring the specified strength indicators and minimizing their cost is shown.

REFERENCES

[1] V. G. Papadakis, Effect of fly ash on Portland cement systems. Part I. Low-calcium fly ash, Cement and Concrete Research, 1999**, 29** (11), 1727-1736.

[2] L. Dvorkin, V. Zhitkovsky, N. Lushnikova and M. Fursovych, Reactive powder concrete incorporating metakaolin and fly ash for monumental architectural objects. IOP Conference Series: Materials Science and Engineering, 907, Innovative Technology in Architecture and Design (ITAD 2020) 21-22 May 2020, Kharkiv, Ukraine. Available at: https://iopscience.iop.org/article/10.1088/1757-899X/907/1/012024/pdf.

[3] J. Bapat, Mineral Admixtures in Cement and Concrete, Boca Raton, 2013, CRC Press, 310 p. doi.org/10.1201/b12673.

[4] S. Thilagavathi, G. Dhinakaran and J. Venkata Ramana, Effects of Mineral Admixtures, Water Binder Ratio and Curing on Compressive Strength of Concrete, Journal of Civil Engineering Research and Practice, 2007, **4** (2), 31-42.

[5] M. Kokubu, Fly Ash and Fly Ash Cement. Fifth International Symposium on the Chemistry of Cement, 1969, p. 75.

[6] T. R. Danya, N. Sakthieswaran, Effect of Fly Ash and Metakaolin on the Strength and Stability Characteristics of Self Compacting Concrete, Romanian Journal of Materials, 2020, **50**(4), 531 - 536

[7] V. Dinh Dau and P. Stroeven, Strength improvement efficiency of mineral admixtures in concrete, Proceedings of the International Conference on Advances in Concrete and Structures. RILEM Publications SARL, 2003, 785 – 792.

[8] Anon. 2002, ACI PRC-232.2-18: Report on the Use of Fly Ash in Concrete. American Concrete Institute, USA.

[9] V.G. Papadakis and S. Tsimas, Supplementary cementing materials in concrete Part I: efficiency and design, Cement and Concrete Research, 2002, **32**, 1525-1532.

[10] A. Boudchicha, M. C. Zouaoui, J. L. Gallias and B. Mezghiche, Analysis of the effects of mineral admixtures on the strength of mortars: Application of the predictive model of Feret, Journal of Civil Engineering and Management, 2007, **13** (2), 87-96.

[11] J. Halbiniak and B. Langier, The Characterization of Porosity and Frost Resistance of Concrete with Fly Ashes Modified, Advanced Materials Research, 2014, **1020**, 193–98. doi.org/10.4028/www.scientific.net/amr.1020.193.

[12] L. I. Dvorkin, V. I. Solomatov, V. N. Vyrovoj, and S. M. Chudnovskij, Czementnye betony s mineralnymi napolnitelyami [Cement-based concrete with mineral fillers]. Kyiv: Budivelnyk, 1991,136 p. (In Russian).

[13] A. F. Polak, Tverdenie monomineral'nykh vyazhushchikh veshchestv [Hardening monomineral binders]. Moscow: Stroyizdat, 1966, 280 p (in Russian)
[14] P. C.Hewlett, Lea's Chemistry of cement and concrete, 4th edition, Butterworth-Heinemann, Oxford, 2004, 1092 p.
[15] M. Venua, Tsement i beton v stroitel'stve (Cement and concrete in construction), Moscow, Stroyizdat, 1980, 415 p. (In Russian)
[16] K. Eriksen and P. Nepper – Christensensen, Experiences in the Use of Superplasticirers in some special fly-ash concretes, Amer. Concr. Inst., SP –68, 1981,1 –20.
[17] V. S. Ramachandran, Concrete admixtures handbook: properties, science and technology, 2nd ed., Noyes Publications, New Jersey, 1995, 1183 p.
[18] Kishore Kaushal, Concrete Mix Design With Fly Ash & Superplasticizer, ICI Bulletin, April – June 1997, 29-30.
[19] V. S. Ramachandran, Adsorption and hydration behavior of tricalcium aluminate-water and tricalcium aluminate – qypsum-water systems in the presence of superplasticirers, J.Am Concr. Inst., 1983, 80, 235 – 241.
[20] D. Lowke and C. Gehlen, The zeta potential of cement and additions in cementitious suspensions with high solid fraction, Cement and Concrete Research, 2017, **95**, 195 - 204.
[21] V.B. Ratynov and T. Y. Rozenberh, Dobavky v beton [Concrete admixtures]. Moscow: Strojizdat, 1989, 188 p. (In Russian).
[22] D. Roy, Effect of Admixtures upon Electrokinetie phenomena durinq hydration of C3S.C3A and port - land cement, 7th intern Congr. Chem. Cements, Paris, vol II, 1980, 242 – 246.
[23] D. Sathyan, K. B. Anand, K. M. Mini and S. Aparna, Optimization of superplasticizer in portland pozzolana cement mortar and concrete, International Conference on Advances in Materials and Manufacturing Applications, 17–19 August, 2017, 310, Bengaluru, India.
[24] A. Borsoi, S. Collepardi, L. Coppola, R. Troli and M. Collepardi, Effect of superplasticizer type on performance of high-volume fly ash concrete, ACI Spec. Publ., 2000, **195**, 17–28.
[25] EN 450-1:2012, Fly ash for concrete. Definition, specifications and conformity criteria.
[26] ASTM C204-18e1, Standard Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus, ASTM International, West Conshohocken, PA, 2018, www.astm.org
[27] D. C. Montgomery, Design and analysis of experiments, 5th ed. New Jersey: Wiley, 2000, 688 p.
[28] G. E. P. Box, J. S. Hunter and W. G. Hunter, Statistics for experimenters: design, discovery, and innovation, 2nd ed. Wiley: New Jersey, 2005, 672 p.
[29] L. Dvorkin, O. Dvorkin and Y. Ribakov, Mathematical experiments planning in concrete technology, New York, Nova Science Publishers Inc., 2012, 173 p.
[30] EN 1015-3: 1999, Methods of test for mortar for masonry - Part 3: Determination of consistence of fresh mortar (by flow table), 10 p.

****