COMPARATIVE CHARACTERISTICS OF REACTIVE POWDER CONCRETES USING FLY ASH AND MICROSILICA

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Reactive powder concrete (RPC) is an efficient type of fine-grained concrete with extreme strength and durability characteristics. The use of RPC allows the construction of such unique objects as pedestrian and automobile bridges, thin-walled architectural forms, protective structures, hazardous waste storage facilities, etc. Obtaining RPC provides for the mandatory use of a significant amount of microsilica as an active mineral additive, which is not always available for use. The article presents the results of comparing the strength characteristics of RPC obtained on microsilica and with its complete replacement with fly ash activated by milling with sodium silicate fluoride. The studies were carried out using mathematical planning of the experiment. Experimental-statistical models of RPC water demand and compressive and flexural strength at different ages have been obtained and analyzed. It is shown that the use of activated ash in the RPC makes it possible to obtain concrete with a strength of 100...110 MPa in 28 days. A method for calculating the composition of the RPC using the obtained models is proposed.

Keywords: *reactive powder concrete, fly ash, microsilica, planning of experiments, experimental-statistical model, strength, concrete mix composition, design.*

1. Introduction

During operation, concrete and reinforced concrete structures may be subject to aggressive environments, seismic, shock and other destructive influences that cause their damage and collapse [1, 2]. Every year, the number of concrete and reinforced concrete structures collapsing increases, which leads to the need to create methods and materials for their restoration and protection.

The most effective type of fine-grained concrete for protective coatings is Reactive Powder Concrete (RPC) developed in France in the 90s of the 20th century [3]. As shown by the data of many researchers [4], in addition to high strength, RPC is also characterized by a high index of crack resistance, which is determined by the ratio of compressive strength to flexural strength. This indicator for RPC is in the range from 3.5 to 5 [2], while traditional high-strength concrete is 8...10 [3].

The extremely high mechanical characteristics of RPC can be explained by the following features [5-8]:

1. Increasing the homogeneity of RPC by eliminating large aggregates;
2. Increasing the density of concrete by optimizing the grain composition of the mixture of components;
3. By improving the properties of the cementing matrix by adding highly active pozzolanic additives, such as microsilica and by reducing the water-binding ratio by superplasticizers;
4. Formation of a dense microstructure with a high content of hydrate products by heat treatment.

The effectiveness of RPC is confirmed by data on its use in responsible buildings. RPC were used in the construction of unique automobile [9] and pedestrian bridges [7, 10-12], as well as many other projects [1, 7, 12, 13]. Due to the increased strength, durability and radiation resistance, RPC can be used as a reliable material for radioactive waste containers [14]. It is also used for thermal protection of building structures, as it provides better fire and heat resistance than ordinary high-strength concrete [14]. Researches shows that RPC allows to expand the possibilities of using concrete in the manufacture of new thin-walled structures, the production of which was previously impossible [15]. Despite the fact that the production costs of RPC are, in general, higher than for conventional concrete, there are still some economic advantages when using RPC. Due to the use of dispersed reinforcement with short steel fibers, it is possible to completely or partially eliminate the use of reinforcing bars. Due to the extremely high mechanical characteristics of RPC, the thickness of concrete elements can be reduced, which leads to savings in materials and construction costs in general [16].

The use of RPC also allows people to be protected from fragments of concrete structures formed during explosions or other dynamic impacts. Large premises with self-supporting ceilings, such as sports halls, public and industrial, buildings present high requirements for the safety of structures [17, 18, 19]. Tests have shown that layers of protection against debris made of RPC can prevent local destruction of reinforced concrete elements with a layer thickness of up to 1.5 cm. The protective layer of dispersion-reinforced RPC acts as a protective net that prevents falling debris.

The recommended compositions of RPC include a highly active mineral additive – microsilica [20], which contains up to 98% SiO_2 and has a specific surface of up to 25 m^2/g, which is almost 80 times more than Portland cement, and determines

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its high pozzolanic activity. The optimal share of microsilica is about 30% of cement. The limited volume of microsilica production, the difficulty of its transportation, storage and dosing due to the extremely high surface area complicate the production of RPC.

Along with microsilica, it is of interest to use activated fly ash from thermal power plants as an effective active mineral additive for the production of RPC. Many researchers have noted the positive effect of the dispersity of the ash additive on the strength of cement mortars [21, 22]. Many researchers have established a positive effect of the dispersion of the ash additive on the strength of cement mortars. For example, in work [23, 24], based on the results of studies of mortars with the addition of different dispersion ash (from 1000 to 4000 cm^2/g) in the amount of 25% of the mass of cement, it was established that the strength in bending and compression increase linearly with an increase in the specific surface area.

At the same time, there are studies [23] that claim that there is no sufficiently defined relationship between ash dispersion and the strength of cement and concrete. In the initial period of hardening, the presence of ash particles in the cement paste, even with increased dispersion, causes a decrease in cement strength.

With an increase in dispersion for ash, as well as for other active mineral additives, the rate of the pozzolanic reaction increases [23]. At the same time, an analysis of the literature data shows that, although the pozzolanic reaction of ash begins quite early, it begins to have a noticeable effect on the strength of cement after 28 or more days. The introduction of activators during ash milling, which include fluoride salts (sodium fluoride and sodium silicofluoride), as shown by studies [23-26] significantly affects the kinetics of structure formation reduces the level of internal stresses and significantly increases the efficiency of ash milling. According to V.B. Ratinov and T.I. Rosenberg [27] fluorides, including, sodium fluoride refer to substances that are capable of exchange reactions with a binder without the formation of screened films of poorly soluble compounds on them.

In addition to microsilica, the composition of RPC includes ground sand with the size of grains 10 μm...50 μm, the main purpose of which is to ensure the density of the mixture and improve its rheological characteristics [28, 29].

The purpose of the research, the results of which are presented in this article, was to determine the possibility of ensuring the necessary properties of RPC by introducing it as an active mineral additive of activated fly ash.

2. Materials and methods

The research was carried out using Portland cement of CEM I with a chemical and mineralogical composition given in Table 1, the main indicators of the physical and mechanical properties of cement are given in Table 2.

To analyze the comparative efficiency, the research was carried out using two active mineral additives: microsilica (Sikafume) and fly ash (Ukraine Power Station). Fly ash with an initial specific surface of 2527 cm^2/g was activated by grinding in a laboratory ball mill with the addition of sodium silicofluoride (Na_2SiF_6) in an amount of 1% by weight. The chemical composition of active mineral additives and their specific surface area is shown in the Table 3.

Table 1

Chemical and mineralogical composition of Portland cement

Chemical composition, %						Mineralogical composition, %			
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	L.O.I	C_3S	C_2S	C_3A	C_4AF
64.49	20.32	5.28	4.05	0.74	0.33	66.95	13.15	7.42	12.48

Table 2

Physical and mechanical properties of cement

Normal consistency, %	Settings time, hours-min.		Strength, MPa					
	initial	final	flexural			compressive		
			2 days	7 days	28 days	2 days	7 days	28 days
25.5	1-2	2-40	22.3	38.7	55.3	3.48	4.85	6.27

Table 3

Chemical composition of active mineral additives

Additive	Chemical composition, %							Specific surface area, cm^2/g
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	R_2O (Na_2O+K_2O)	L.O.I	
Microsilica	93.81	0.82	0.51	0.72	0.85	1.81	0.35	23158
Fly ash (activated)	56.91	22.68	9.60	3.61	1.65	1.66	3.85	3248

Quartz sand of the following grain composition was used as a aggregate: 0.16-0.315 mm – 4.5%, 0.315-0.63 mm - 36.8%, 0.63-1.25 mm – 58.7%.

The plasticizing effect in the studied mixtures was provided by the Dynamon SP3 superplasticizer based on a modified acrylic polymer.

The study of the influence of a set of factors on the properties of RPC was carried out using the methods of mathematical planning of experiments [30, 31].

3. Results and discussion

To perform the experiments, a three-level three-factor plan B_3 [31] was used, which provides for the possibility of obtaining a quadratic polynomial model of the form (1):

The consumption of water at each point of the plan was determined from the condition of ensuring concrete mixture spread by 250-300 mm on the Suttard viscometer. The matrix of the experimental plan and the composition of the concrete mixture are given in Table 5, and the results of the experimental data in Table 6 and 7.

Coefficients mathematical models obtained as a result of statistical processing of experimental results are given in Table 8.

Graphical dependences that illustrate the influence of technological factors on the water-cement ratio and the compressive and flexural strength of concrete at the age of 1 and 28 days of normal hardening are shown in Fig. 1...5.

$$y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (1)$$

The conditions for planning the experiments are given in Table 4.

Table 4

Conditions for planning the experiment

No.	Factors		Levels of variation			Interval
	Coded	Natural view	-1	0	+1	
1	X_1	Consumption of cement (C), kg/m^3	720	840	960	120
2	X_2	Mineral additive to cement ratio by weight (A/C)	0.2	0.3	0.4	0.1
3	X_3	Consumption of superplasticizer (SP) Dynamon SP-3, %	1	1.5	2	0.5

The consumption of water at each point of the plan was determined from the condition of ensuring concrete mixture spread by 250-300 mm on the Suttard viscometer. The matrix of the experimental plan and the composition of the concrete mixture are given in Table 5, and the results of the experimental data in Table 6 and 7.

Table 5

Experiment planning matrix and concrete composition

No.	Planning Matrix			Concrete Composition			
	X_1	X_2	X_3	C, kg/m^3	Mineral additive, kg/m^3	Sand, kg/m^3	SP, kg/m^3
1	+1	+1	+1	960	384	899	26.8
2	+1	+1	-1	960	384	913	13.4
3	+1	-1	+1	960	192	1095	23.0
4	+1	-1	-1	960	192	1106	11.5
5	-1	+1	+1	720	288	1242	20.1
6	-1	+1	-1	720	288	1252	10.0
7	-1	-1	1	720	144	1389	17.2
8	-1	-1	-1	720	144	1397	8.6
9	+1	0	0	960	288	1003	18.7
10	-1	0	0	720	216	1320	14.0
11	0	+1	0	840	336	1076	17.6
12	0	-1	0	840	168	1247	15.1
13	0	0	+1	840	252	1156	21.8
14	0	0	-1	840	252	1167	10.9
15	0	0	0	840	252	1162	16.4
16	0	0	0	840	252	1162	16.4
17	0	0	0	840	252	1162	16.4

Table 6

Results of experimental studies of the concrete composition effect on its strength
(mineral additive - activated fly ash)

No.	W, l/m^3	W/B**	W/C	$f_{c.tf}^1$, MPa	f_{cm}^1, MPa	$f_{c.tf}^7$, MPa	f_{cm}^7, MPa	$f_{c.tf}^{28}$, MPa	f_{cm}^{28}, MPa
1	250	0.19	0.26	8.2	32.9	13.7	72.3	23.6	111.8
2	278	0.21	0.29	7.7	29.7	12.4	57.6	22.5	99.3
3	230	0.20	0.24	8.9	35.6	14.9	73.1	23.3	112.1
4	250	0.22	0.26	7.8	32.2	13.8	62.1	23.8	101.3
5	209	0.21	0.29	7.0	25.4	12.8	56.6	22.5	104.6
6	223	0.22	0.31	6.0	21.9	11.5	55.8	21.4	93.6
7	187	0.22	0.26	7.6	28.1	14.1	57.3	22.2	105.5
8	209	0.24	0.29	6.2	24.4	12.9	60.4	22.8	96.2
9	259	0.21	0.27	8.7	36.8	15.1	70.4	24.1	115.2
10	209	0.22	0.29	7.2	29.2	14.2	61.7	23.0	108.4
11	244	0.21	0.29	7.4	30.9	12.6	61.1	22.3	106.7
12	227	0,23	0.27	7.7	33.5	13.9	63.8	22.8	108.2
13	218	0.20	0.26	8.2	35.7	14.6	65,5	23.2	114.7
14	235	0.22	0.28	7.2	32.3	13.4	59.6	22.8	103.8
15	235	0.22	0.28	7.9	35.2	14.3	64.6	23.1	112.6
16	235	0.22	0.28	7.9	35.2	14.3	64.5	23.2	112.6
17	235	0.22	0.28	7.9	35.2	14.4	64.6	23.2	112.6

* - concrete composition is given in Table 5.
** -W/B – water-binder ratio

Table 7

Results of experimental studies of the concrete composition effect on its strength
(mineral additive - microsilica)

No.	W, l/m^3	W/B**	W/C	$f_{c.tf}^1$, MPa	f_{cm}^1, MPa	$f_{c.tf}^7$, MPa	f_{cm}^7, MPa	$f_{c.tf}^{28}$, MPa	f_{cm}^{28}, MPa
1	248	0,18	0,26	12.4	49.0	29.1	119.1	33.6	165.3
2	304	0,23	0,32	11.3	44.8	26.6	108.9	30.7	151.2
3	255	0,22	0,27	11.0	43.4	25.8	105.5	29.7	146.5
4	249	0,22	0,26	10.0	39.7	23.6	96.5	27.2	134.0
5	202	0,20	0,28	11.3	44.7	26.6	108.7	30.6	150.9
6	250	0,25	0,35	10.6	41.9	24.9	102.0	28.7	141.6
7	215	0,25	0,30	10.5	41.5	24.7	100.9	28.4	140.1
8	201	0,23	0,28	9.9	39.2	23.3	95.4	26.9	132.4
9	270	0,22	0,28	11.6	46.0	27.3	111.8	31.5	155.2
10	224	0,24	0,31	11.0	43.6	25.9	106.0	29.9	147.2
11	259	0,22	0,31	11.8	46.5	27.6	113.1	31.9	157.0
12	238	0,24	0,28	10.7	42.3	25.2	103.0	29.0	143.0
13	227	0,21	0,27	11.5	45.6	27.1	111.0	31.3	154.1
14	248	0,23	0,30	10.7	42.4	25.2	103.2	29.1	143.2
15	246	0,23	0,29	11.4	45.1	26.8	109.8	30.9	152.3
16	235	0,22	0,28	11.4	45.2	26.9	110.0	31.2	153.0
17	235	0,22	0,28	11.5	45.0	26.6	109.9	31.0	152.5

* - concrete composition is given in table 5.
** -W/B – water-binder ratio (binder: cement + mineral additive)

Coefficients mathematical models obtained as a result of statistical processing of experimental results are given in Table 8.

Graphical dependences that illustrate the influence of technological factors on the water-cement ratio and the compressive and flexural strength of concrete at the age of 1 and 28 days of normal hardening are shown in Fig. 1...5.

Table 8

Coefficients of experimental-statistical models (Eq. (1) type) of RPC properties

Type of mineral additive: activated fly ash										
Properties	Coefficients									
	b_0	b_1	b_2	b_3	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Water consumption of concrete mixture, l/m^3	234,7	23	10,1	-10,1	0,2	1,7	-7,3	1,5	-1.5	-
Flexural strength at 1 day, MPa	7,9	0,72	-0,2	0,5	0,07	-0,3	-0,21	-0,1	-	-0,1
Compressive strength at 1 day, MPa	35.3	3.82	-1.3	1.7	-2.2	-3.0	-0.21	-	-0.1	-0.05
Flexural strength at 7 days, MPa	14.4	0.5	-0.7	0.6	0.3	-1.1	-1.2	0,01	-	0.05
Compressive strength at 7 days, MPa	64.6	4.4	-1.3	2.9	1.5	-2.12	-2,0	-3.5	-	0,95
Flexural strength at 28 days, MPa	23.2	0,6	-0.25	0.14	0.4	-0,6	-0,13	-	-	0,4
Compressive strength at 28 days, MPa	112.9	3.1	-0.7	5,5	-1,0	-5.3	-3,5	0.2	0.4	0,4
Type of mineral additive: microsilica										
Properties	Coefficients									
	b_0	b_1	b_2	b_3	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Water consumption of concrete mixture, l/m^3	246,3	23,3	10,4	-10,5	0,6	2,1	-8,4	1,5	-2	-0,8
Flexural strength at 1 day, MPa	11,4	0,3	0,52	0,41	-0,08	-0,17	-0,27	0,15	0,1	0,03
Compressive strength at 1 day, MPa	45,1	1,2	2,07	1,61	-0,32	-0,69	-1,08	0,59	0,4	0,13
Flexural strength at 7 days, MPa	26,8	0,7	1,23	0,96	-0,19	-0,41	-0,64	0,35	0,2	0,07
Compressive strength at 7 days, MPa	109,7	2,9	5,04	3,92	-0,79	-1,67	-2,63	1,44	0,8	0,31
Flexural strength at 28 days, MPa	30,9	0,8	1,42	1,11	-0,22	-0,47	-0,74	0,41	0,2	0,09
Compressive strength at 28 days, MPa	152,3	4,	7,00	5,45	-1,10	-2,32	-3,65	2,00	1,2	0,43

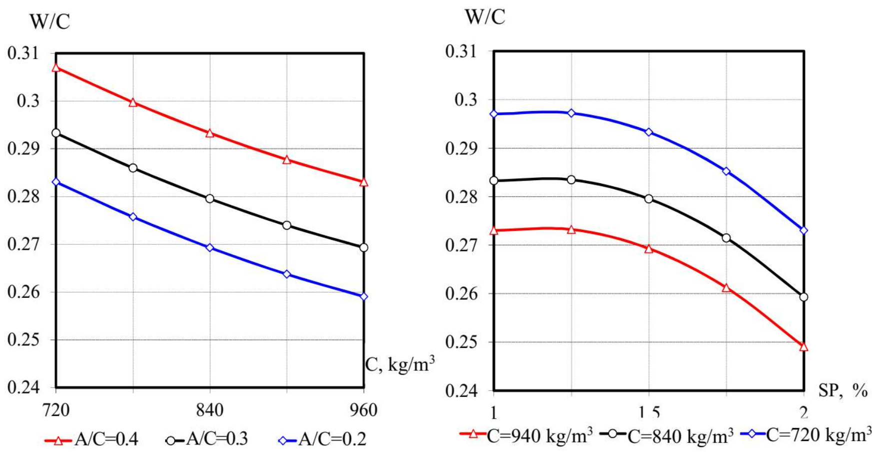

Fig. 1 - Effect of technological factors on water-cement ratio of RPC produced using fly ash

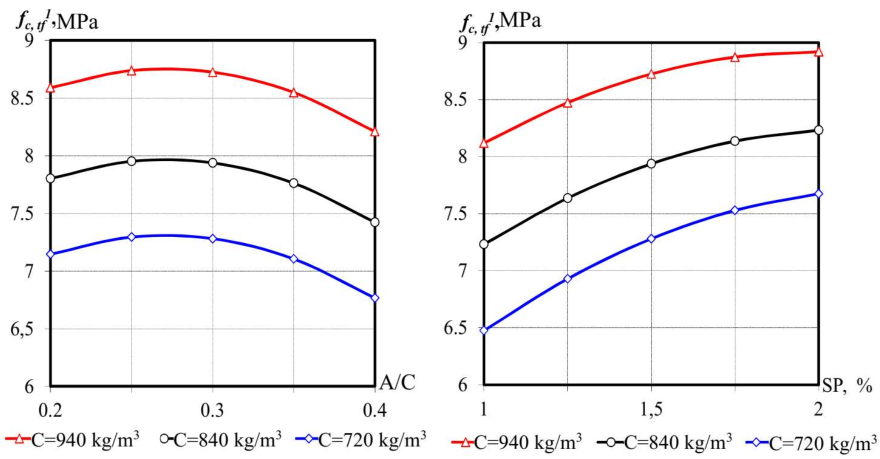

Fig. 2 - Effect of technological factors on flexural strength of RPC at 1 day

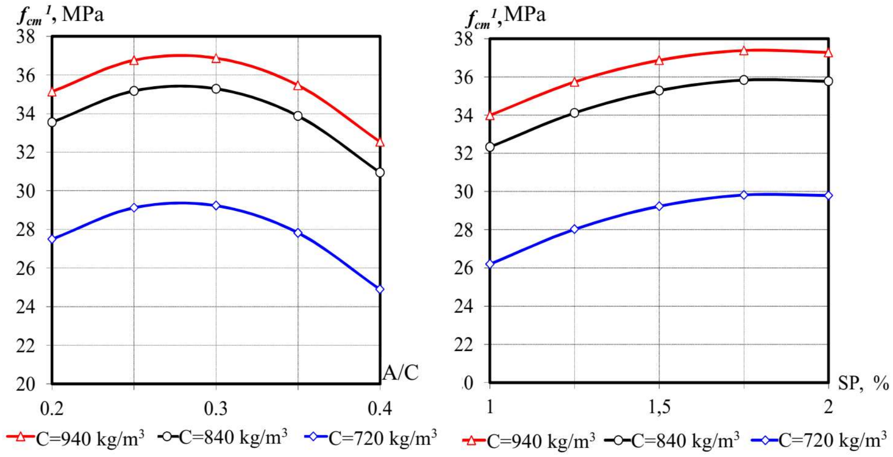

Fig. 3 - Effect of technological factors on compressive strength of RPC using fly ash at 1 day

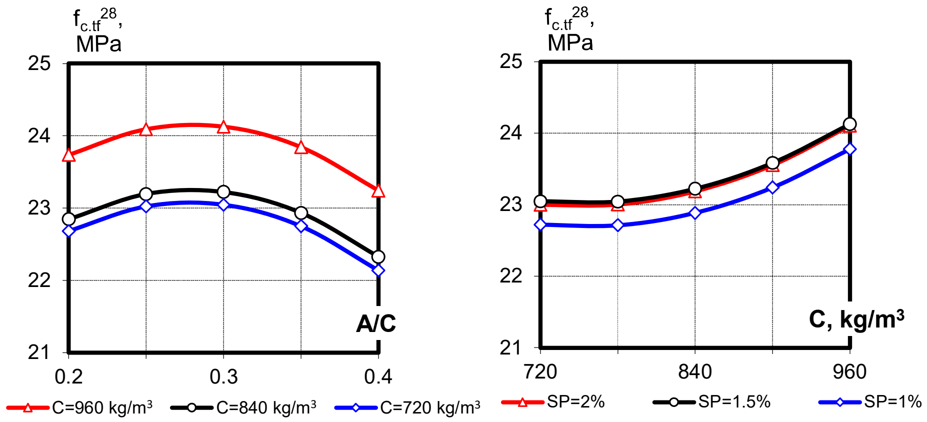

Fig. 4 - Effect of technological factors on flexural strength of RPC produced using fly ash at 28 days

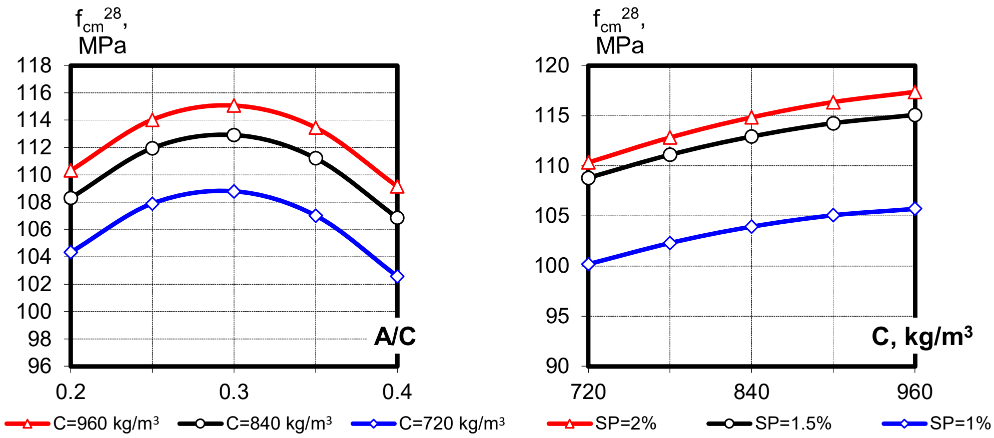

Fig. 5 - Effect of technological factors on compressive strength of RPC produced using fly ash at 28 days

Studies have shown that the reduction of the water-cement ratio of RPC made with the use of fly ash leads to an increase in the consumption of cement and the consumption of plasticizing additives. With an increase in the content of these substances in the composition of RPC, the decrease in W/C is on average 10...12%. An increase in the content of mineral additives leads to a certain increase in W/C, which is associated with a decrease in the total amount of cement in the binder. It is also worth noting that when fly ash is used as an active mineral additive of RPC at all points of the plan, there is an average decrease of W/C by 5-7%. This is explained by the spherical shape of the ash particles, as well as their reduced porosity, which, accordingly, leads to an additional plasticizing effect.

The nature of the influence of various factors on the strength characteristics of RPC, as it follows from the analysis of the set of obtained experimental-statistical models and graphical dependencies built on their basis, does not change significantly when the duration of concrete hardening is increased. An increase in the strength of concrete both in compression and bending leads to an increase in the consumption of cement and the addition of Dynamon SP-3 superplasticizer, which is associated with a sharp decrease in the water-cement ratio and a corresponding increase in the density of the samples. Also, an increase in the amount of active mineral additive in the range from 20 to 30% of the mass of the binder leads to some increase in strength. A further increase in its amount leads to a sharp decrease in strength, which is caused by a decrease in the amount of the active clinker component in the total mass of the binder.

The influence of this factor on the strength characteristics of RPC is extreme.

The maximum compressive strength of 115.2 MPa and flexural strength 24.1 MPa of the RPC is observed with the following ratio of varied factors: cement consumption at the maximum level – 960 kg/m³, the ratio between the amount of ash and the amount of cement at the average level – 0.3; consumption of Dynamon SP-3 superplasticizer at the maximum level – 2% of the mass of the binder. It should be noted that close values of compressive strength (112...113 MPa) can also be obtained at a cement consumption of 840 kg/m³ with a maximum superplasticizer content.

An analysis of the obtained models (Fig.6,7) shows that when varying the components of the RPC with microsilica, the strength indicators of concrete exceed similar indicators by an average of 20...25% with the same consumption of cement (Table 8).

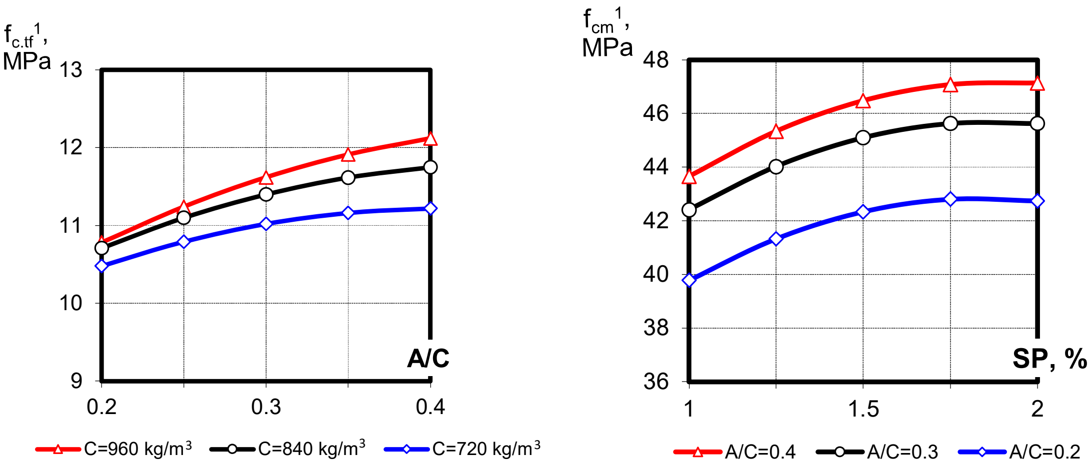

Fig. 6 - The influence of the studied factors on the flexural strength ($f_{c.tf}$, MPa) and compressive strength (f_{cm}, MPa) of RPC with microsilica at the 1 day.

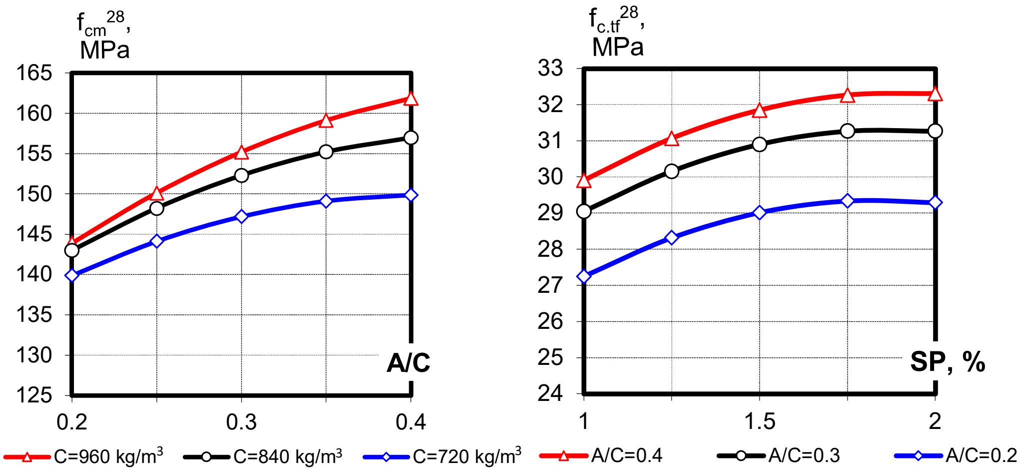

Fig. 7 - The influence of the studied factors on the flexural strength ($f_{c.tf}$, MPa) and compressive strength (f_{cm}, MPa) of RPC with microsilica at the 28 days.

At the same time, with the design concrete compressive strength up to 100...115 MPa, the economic preference of RPC using activated fly ash is obvious.

The obtained experimental-statistical models (Table 8) can be used to design RPC compositions with a given strength and workability. The calculation method is the following:

1. According to the models of compressive strength after 28 days and, if necessary, other strength characteristics, the coefficients of which are given in Table. 8, we determine the consumption of the superplasticizer Dynamon SP-3, the consumption of cement and the content of the mineral additive, which will provide the specified strength of the RCC. To determine the required values of these factors, various methods of mathematical optimization can be used or found graphically using the nomogram construction method (Fig. 8).
2. With the help of the water demand model of the concrete mixture, at given costs of the superplasticizer, cement and additive, we establish the water demand, which will provide the concrete mixture with a fluidity of 25 - 30 cm (according to the Suttard viscometer).
3. The aggregate consumption can be calculated knowing the cement paste volume ($V_{c.p}$) in the concrete mix. The cement paste volume, *l*/m^3 is:

$$V_{c.p} = \frac{C}{\rho_c} + \frac{A}{\rho_A} + W \qquad (2)$$

The volume of sand, *l*/m^3 is:

$$V_S = 1000 - V_{c.p.} \qquad (3)$$

The sand weight *S,* kg/m^3 is:

$$S = \rho_s V_s \qquad (4)$$

In the above equations ρ_c, ρ_A, ρ_s are the densities of cement, mineral additive and sand, respectively.

3.1.Calculation example

Calculate the composition of RPC produced using activated fly ash as an active mineral additive, with a 28-day compressive strength of 115 MPa and fluidity of 25...30 cm according to the Suttard viscometer. Dynamon SP-3 superplasticizer is used as a plasticizing additive. The actual density of cement ρ_c=3,1 g /cm^3, fly ash ρ_A=2.8 g/cm^3, sand ρ_s=2.65 g/cm^3.

1. Using the compressive strength nomogram shown in Fig. 8, we establish that to ensure the specified compressive strength of 110 MPa, the minimum possible consumption of cement will be – 840 kg/m^3, the content of mineral additives – 27.5% of the mass of cement, the consumption of Dynamon superplasticizer SP-3 – 2% of the mass of the binder.

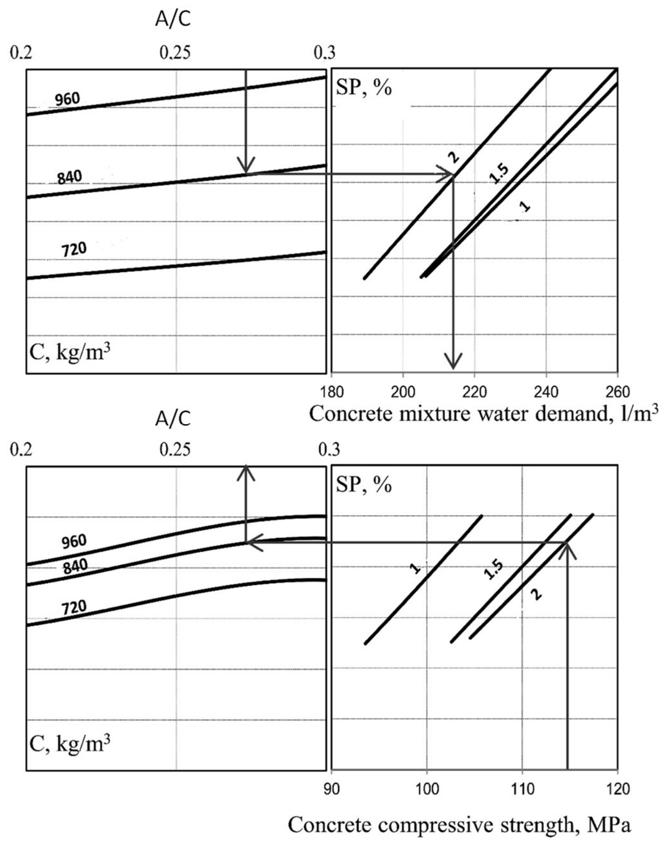

Fig. 8 - Nomograms of water demand and compressive strength of RPC made using activated fly ash

2. Using the nomogram of water consumption shown in fig. 8, we establish that with the calculated component composition of concrete, the minimum possible amount of water, which ensures the specified fluidity of concrete mix 25...30 cm according to the Suttard viscometer, will be 215 l/m^3.
3. We calculate the consumption of aggregates, knowing the volume of cement paste ($V_{c.p}$) in the concrete mixture.

Volume of cement paste:

$$V_{c.p} = \frac{C}{\rho_c} + \frac{A}{\rho_A} + W = \frac{840}{3.1} + \frac{231}{2.8} + 215 = 568.5 \text{ l/m}^3$$

Volume of sand:

$$V_s = 1000 - V_{c.p} = 1000 - 568.5 = 431.5 \text{ l/m}^3$$

Mass of sand S:

$$S = \rho_s V_s = 2.65 \cdot 431.5 = 1143 \text{ kg/m}^3$$

The calculated concrete has the following composition: cement – 840 kg/m^3, fly ash – 231 kg/m^3, water – 215 l/m^3, sand (fraction 0.16...1.25) – 1143 kg/m^3. The consumption of Dynamon SP-3 superplasticizer is 2% of the binder mass.

4. Conclusions

1. A method is proposed for ash activation as an active mineral additive for reaction-powder concretes with additional grinding and with sodium silicofluoride as an activator.
2. Experimental studies have been carried out that have made it possible to obtain mathematical models of the strength characteristics of reactive-powder concretes containing activated fly ash and microsilica. Analysis of the models showed that the replacement of microsilica in the RPC with activated ash makes it possible to achieve a compressive strength of 115 ... 118 MPa in 28 days, and more than 24 MPa in bending. This is 34...37% lower than the strength of RPC with microsilica.
3. Obtaining reactive powder concrete of high fluidity and with a compressive strength of 100...110 MPa in 28 days is possible with a cement consumption of 750...850 kg/m^3 and when activated fly ash is used as an active mineral additive in an amount of about 30% of masses of cement
4. The obtained experimental-statistical models of water demand and strength characteristics of RPC made it possible to develop a method for designing the RPC composition using activated fly ash.

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