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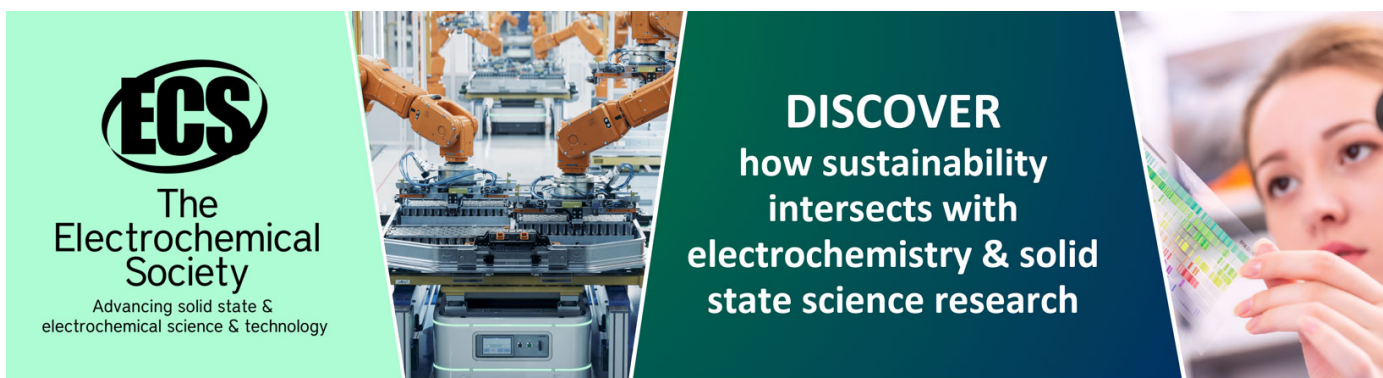
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Reactive powder concrete incorporating metakaolin and fly ash for monumental architectural objects

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Abstract. The paper gives coverage on the properties of reactive powder concrete, incorporating metakaolin and fly ash and polyacrylate superplasticizer. There are given results of comparative research of reactive powder concrete (RPC) containing silica fume. There are also considered the impact of curing conditions on the strength of RPC specimens. The combination of fly ash and metakaolin is the effective composite mineral additive that allows to obtain RPC without silica fume. The optimal dosage of metakaolin in composite admixture from the point of maximum flexural and compressive strength was about 10% by cement weight. The curing of the RPC specimens in the hot water at $t=80^{\circ}\text{C}$ increases compressive strength of concrete at 20-25%. Adding the combination of metakaolin and fly ash with permits to achieve RPC high values of mechanical properties compatible to RPC containing silica fume. High fluidity of fresh concrete along with high performance of hardened concrete allows to apply RPC for manufacturing architectural elements of non-linear geometry, thin structures, and other.

1. Introduction

Reactive powder concrete (RPC) is the most effective type of fine-grained concrete, which has increased homogeneity, strength and deformability is developed in France in the 1990s [1]. For such concrete, the typical compressive strength is within the range from 150 to 200 MPa [1, 2]. According to the data of researches [3, 4], such concrete can achieve strength up to 800 MPa under special conditions. As it is shown by the many researches [1-3], RPC is also characterized by a high crack resistance, which is characterized by the higher ratio of flexural strength to compressive strength.

Significant progress in RPC technology at the present stage has become possible mostly due to the development of production and use of chemical and mineral admixtures, in particular superplasticizers and silica fume [1, 5]. Fine powders such as ground quartz and silica fume with a particle size 0.1-600 μm are applied for RPC manufacturing [6-8]. The grain distribution of different powders is optimized to achieve the increased density of the concrete matrix [7, 9, 10]. High-range water reducers permit to reduce the water-cement ratio (W/C) from 0.4... 0.5 to 0.2 [9].



The effectiveness of the RPC is confirmed by data on its use for different types of specific structures. RPC is applied in construction of roads [11, 12] and bridges [6, 7, 8, 9], as well as fortification structures and many other projects [4, 9, 13]. Due to its increased strength, durability and radiation resistance, it can be used as a reliable material for containers of radioactive wastes from nuclear power plants [14]. It is also used for thermal protection of building structures, as it provides better fire and heat resistance than ordinary high-strength concrete. High energy absorption provides greater structural reliability of RPC in earthquakes [15].

Despite the fact that the production cost of RPC is generally higher than that for ordinary concrete, there are some economic advantages in its application. Ultra-high mechanical characteristics of RPC provide reduction in thickness of concrete elements, which leads to materials savings and the cost of manufacturing [16]. RPC has advantages as an architectural concrete, especially at the construction of monumental structures and elements of non-linear geometry with high requirements for physical and mechanical properties. Due to the high workability, RPC improves shaping properties, which allows to make both thin-walled structures and to create a variety of complex architectural forms with high surface quality. Dispersed reinforcement of short steel fibers can replace completely or partially traditional reinforcing elements. Technology of RPC involves the introduction of high-range water reducers and highly active dispersed mineral admixtures, mainly silica fume [5]. Under modern circumstances, silica fume is a scarce component and its application makes some difficulties with its transportation and dosing. There are known the research results of influence of alternative mineral admixtures on properties of special types of concrete: UHPC incorporating very fine fly ash or metakaolin in replacement of silica fume [17], RPC containing fly ash as mineral admixture [18], fly ash and slag as alternative silica containing mineral admixtures for RPC [19, 20]. The research data on determination the curing conditions on RPC with alternative mineral admixtures are given in [21, 22, 23]. However, there is a limited data on the application of fly ash in combination with metakaolin in RPC and the impact of terms of curing on mechanical properties of such concrete.

There are research results describing the application of alccofine – a new generation micro fine supplementary cementitious material for HSC and RPC. According to the data its effectiveness of alccofine on workability and compressive strength of RPC is higher than silica fume [24], as well as split tensile strength [25]. However, this admixture is rather expensive and currently unavailable in Ukraine.

2. Aim and scope of the research

The aim of the research was to estimate the possibility of partial or complete replacement of silica fume as part of the RPC with more available mineral admixtures. The influence of fly ash and metakaolin as local mineral admixtures, on mechanical properties of RPC under different terms of hardening was under investigation.

As fly ash has low pozzolanic activity and low water demand, whereas metakaolin has high pozzolanic activity and high water demand, it was suggested that the combination of these admixtures will have a synergetic effect on properties of RPC. There had been determined the terms of thermal treatment of RPC (type of thermal treatment and temperature of isothermal heating). The comparative study of influence of silica fume on compressive and flexural strength of RPC was considered.

3. Materials and methods

Portlan Cement CEM I 42,5R, fine quartz sand with grain size 0.16-1.25 mm were used. Polyacrylate superplasticizer Mapei Dynamon SP3 was added in all the batches of the experiment. As mineral admixtures metakaolin, fly ash and silica fume were applied (see table. 1).

W/C ratio of fresh concrete was determined by the required fluidity at Suttard viscometer equal to diameter of flow spread 25...30cm. For each batch cube specimens with 10 cm edge and prisms 4×4×16 cm in size were prepared.

Table 1. Mineral admixtures used in the research.

Mineral admixture	Specific surface area (SSA), cm ² /g	Manufacturer
Metakaolin (MK)	10,125	LLC "Western Kaolin Company" (Ukraine)
Fly ash (FA)	2,527	Burshtyn coal-fired power plant (Ukraine)
SikaFume-HR/TU	23,158	Sika

The compressive and flexural strength at the age of 1, 7, 28 days of hardening under normal conditions and under steam curing and hot water saturation was determined. For the selection of effective compositions of reactive powder concrete, C_f coefficient was calculated. It characterizes the specific consumption of cement per compressive strength unit. Y. Bazhenov and V. Kalashnikov used this coefficient [26] to determine the effectiveness of the compositions of reactive powder concrete

$$C_f = \frac{C}{f_{cm}}, \text{ kg/MPa} \quad (1)$$

where C is the cement content per 1 m³ of concrete, kg; f_c - compressive strength of concrete, MPa.

4. Results and Discussion

4.1. Determination the impact of type and dosage of mineral admixtures on strength and C_f coefficient

At the first stage of the research there was considered the influence of the type of mineral admixtures at equal dosages on compressive and flexural strength and effectiveness coefficient of reactive powder concrete.

Concrete compositions and results of the experiment are given in table 2 and figure 1. As can be seen from the figure 1b and table 2, specimens of RPC made of high-flowable mixture with a maximum content of Sika Fume-HR/TU 360 kg/m³ have compressive strength 162.4 MPa at the age of 28 days of normal hardening. The results meet the known data [4, 30]. Partial or complete replacement of silica fume with other investigated admixtures makes it possible to obtain concrete with strength values in the range of 102-133 MPa. Such values of strength, while ensuring high fluidity of fresh concrete, indicate that the RPC can be characterized as material with high workability and high performance under conditions of various loads occurring at performance of the building structures.

The flexural strength for all the specimens varied within the range from 18.3 to 32.2 MPa (figure 1a).

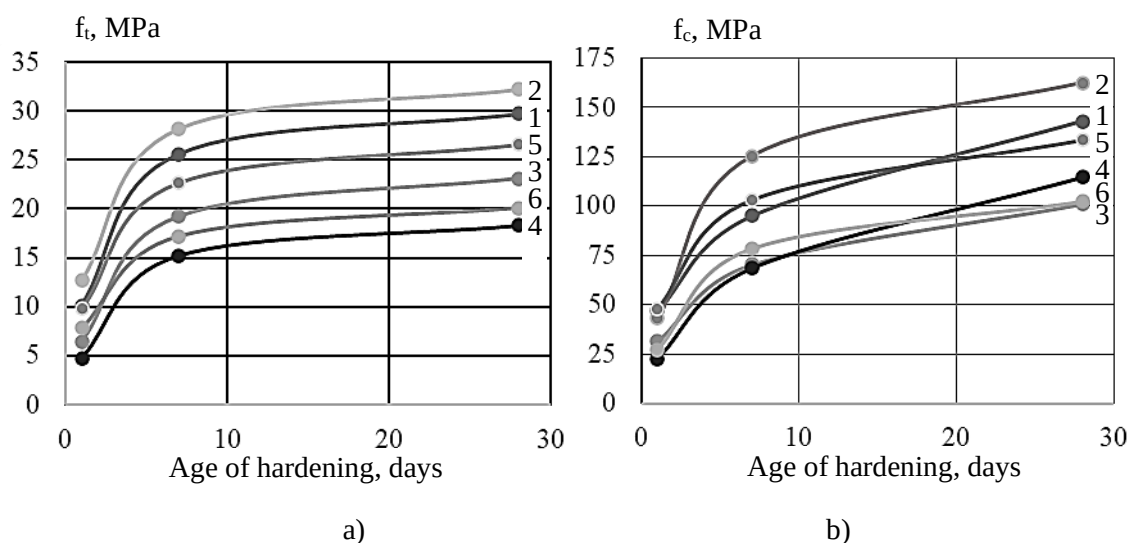
As is known [28], the ratio of flexural strength to compressive strength characterizes the resistance of concrete to the formation of cracks and its deformability. For ordinary concretes, the ratio f_t to f_c is usually within the range of 0.12 - 0.15 and for reactive powder concrete it is equal to 0.16 - 0.2. Therefore, the increased crack resistance and deformability of RPC is a determining property that allows to recommend this concrete for structures operating under conditions of high dynamic loads.

In the case of the fly ash use, the maximum strength was achieved by increasing the content of mineral additives up to 360 kg/m³ at a later age. As is known [29], due to the high consumption of cement, a significant amount of calcium hydroxide is released in hardened cement matrix of RPC. Mineral admixtures interact actively with it to form water insoluble compounds. Fly ash, in its turn, exhibits some plasticizing effect due to the peculiar shape of the grains [30]. It allows to keep low value of W/C ratio and dense structure of cement stone even at high cement consumption.

The use of highly active admixtures of silica fume and metakaolin proved to be the most effective from the point of compressive strength values. The addition of metakaolin leads to maximum compressive strength value 133.4 MPa and showed slightly less efficiency than silica fume (162.4 MPa). The kinetics of the strength of the RPC (figure 1) corresponds to the known data [27].

Table 2. Impact of mineral admixtures on the flexural and compressive strength of reactive concrete.

No.	Cement (kg/m ³)	Quartz sand 0.16... 1.25 mm (kg/m ³)	Mineral admixture, (kg/m ³)	Water, (l/m ³)	W/C	Flow spread dia- meter, cm	Concrete strength (MPa)					
							Effectiveness parameter (kg/MPa)					
							f _{c.tf} ¹	f _{cm} ¹	f _{c.tf} ⁷	f _{cm} ⁷	f _{c.tf} ²⁸	f _{cm} ²⁸
							C _{f1}		C _{f7}		C _{f28}	
SikaFume-HR/TU (SF) (SSA=23,158cm ² /g)												
1	1080	1200	120	240	0.22	30	10.1	$\frac{47}{22.9}$	25.6	$\frac{95}{11.4}$	29.7	$\frac{143}{7.6}$
2	840	1200	360	240	0,29	12	12.7	$\frac{43.3}{19.4}$	28.2	$\frac{125.5}{6.7}$	32.2	$\frac{162.4}{5.2}$
Fly Ash (FA) (SSA=2,527 cm ² /g)												
3	1080	1200	120	240	0,22	30	6.46	$\frac{31.5}{34.2}$	19.22	$\frac{70.3}{13.7}$	23.1	$\frac{100.9}{9,5}$
4	840	1200	360	240	0,29	30	4.76	$\frac{22.8}{36.8}$	15.22	$\frac{68.5}{12.2}$	18.3	$\frac{114.5}{7.34}$
Metakaolin (MK) (SSA=10,125 cm ² /g)												
5	1080	1200	120	240	0,22	30	9.8	$\frac{48.1}{22.5}$	22.7	$\frac{103.1}{10.5}$	26.6	$\frac{133.4}{8.1}$
6	840	1200	360	270	0,33	10	7.8	$\frac{27.2}{30.9}$	17.2	$\frac{78.5}{10.7}$	20.1	$\frac{102.4}{8.2}$

**Figure 1.** Flexural (a) and compressive strength (b) kinetics of RPC depending on the type and dosage of mineral admixture (# of batches according to table 2)

Specimens containing silica fume (360 kg/m³) and metakaolin (120 kg/m³) had maximum rate of hardening. It should be mentioned that the specimens reached values of compressive strength after 1

day of hardening from 23 to 48 MPa. This strength can be considered sufficient for high-speed construction.

The nature of the effect of different types of mineral admixtures on the flexural strength of RPC (table 2) is the same as for the compressive strength. Composites containing silica fume, have the maximum flexural strength from 29 to 32 MPa, composites containing metakaolin and fly ash has slightly lower values (26 - 27 MPa for metakaolin).

The maximum efficiency of the metakaolin is observed at its consumption of about 10% by binder weight, this result confirms the data obtained by us earlier in the study of high-strength concrete [28]. A further increase in the amount of metakaolin leads to the increase in water consumption of the concrete mixture and an increase in W/C, while the strength of concrete decreases (figure 1).

The compositions containing the raised amount of Sika Fume-HR/TU (table 1) are considered the most effective from the position of the 28-day strength per kilogram of cement. RPC with the admixtures of fly ash and metakaolin in higher quantities in terms of efficiency of cement are equal to RPC with lower content of silica fume (120 kg/m³). Thus, considering the established effectiveness of fly ash and metakaolin for RPC, as well as the difference in mechanism of their action on the properties of fresh and hardened concrete, we can expect their mutual effect on the properties of RPC.

4.2. Determination the impact of metakaolin dosage in composite fly-ash -metakaolin admixture

At the second stage there was determined the effect of combination of fly ash and metakaolin on RPC strength properties. When performing a series of studies, the composition of RPC was as follows: cement - 840 kg/m³, mineral admixture - 360 kg/m³, quartz sand 0.16-1.25 mm - 1,200 kg/m³, the consumption of superplasticizer polyacrylate type Dynamon SP-3 - 2% by the weight of the binder (cement + mineral admixture). Water consumption was determined to provide flow-spread diameter 25... 30 cm at the Suttard viscometer. As a mineral admixture, fly ash was used; in addition, metakaolin additives in the amount of 5, 10 and 15% by weight of cement were added to the concrete.

The obtained results (table 3, figure 2) indicate that additional introduction of metakaolin leads to increasing RPC strength: compressive strength of concrete increases up to 122... 126 MPa. However, increasing in metakaolin content by more than 10% by weight of cement is inefficient due to a significant increase in the viscosity of the mixture and subsequent increase in water consumption. The positive effect of fly ash on the flowability of fresh concrete compensates to some extent with the increase in viscosity inherent in metakaolin [27].

The effectiveness of the compositions of mineral admixtures from the standpoint of flexural strength was similar. The maximum values of f_t (23-25 MPa) are achieved when combining 10% of metakaolin by weight of cement with fly ash.

Table 3. Research results of metakaolin and other mineral admixtures on strength properties of reactive powder concrete.

No	Content of MTK (%) by cement mass	W/C	Flow spread diameter (cm)	Concrete strength (MPa) depending on the age of hardening					
				$f_{c.tf}^1$	f_{cm}^1	$f_{c.tf}^7$	f_{cm}^7	$f_{c.tf}^{28}$	f_{cm}^{28}
1	5	0.29	30	7.21	21.0	17.09	75.8	22.77	115.6
2	10	0.29	30	7.65	29.2	18.87	79.9	25.28	126.2
3	15	0.29	30	7.12	20.1	16.91	73.1	21.81	111.0

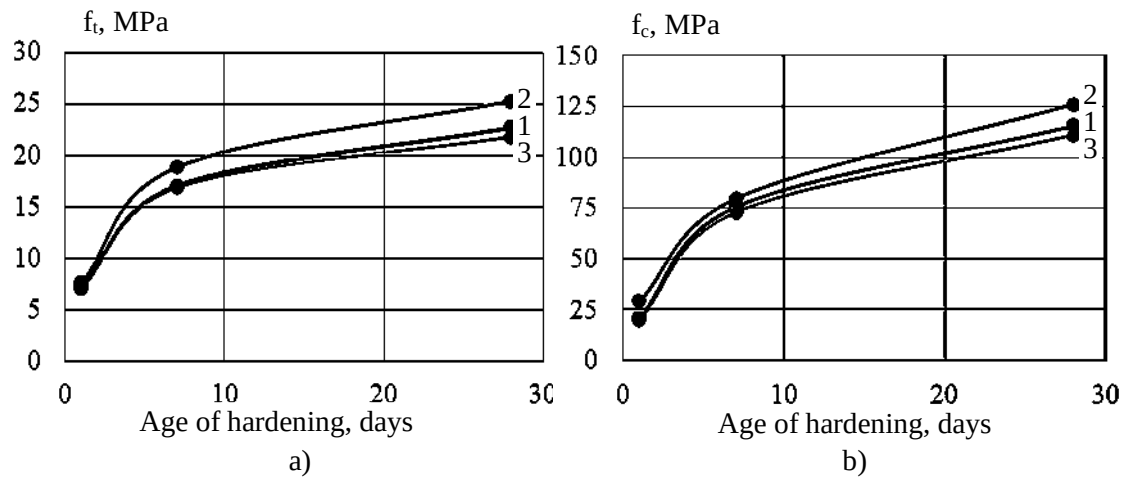


Figure 2. Flexural (a) and compressive strength (b) kinetics of RPC depending on the metakaolin content (# of batches according to table 3)

Influence of curing mode on the mechanical properties of RPC

In order to determine the effect of heat treatment on the curing process and the strength of RPC containing fly ash and metakaolin, the third stage of experiments was conducted. The content of metakaolin was 10% by weight of binder. Steam curing was carried out in the laboratory steaming chamber according to the following mode: preliminary aging - 2 hours; temperature rise at a rate of 25°C/h; isothermal heating - 8 hours, cooling under normal conditions. Compressive strength of the samples was determined after 2 h of steam curing and at the age of 7 and 28 days. Along with steam curing there are research results, where maximum hydration and pozzolanic reactivity in RPC was obtained at hardening the specimens in the hot water [31]. To determine the curing efficiency of the RPC compositions, the specimens were cured in water at a temperature of 50°C and 80°C. The results of determination the strength are given in table 4 and figure 3.

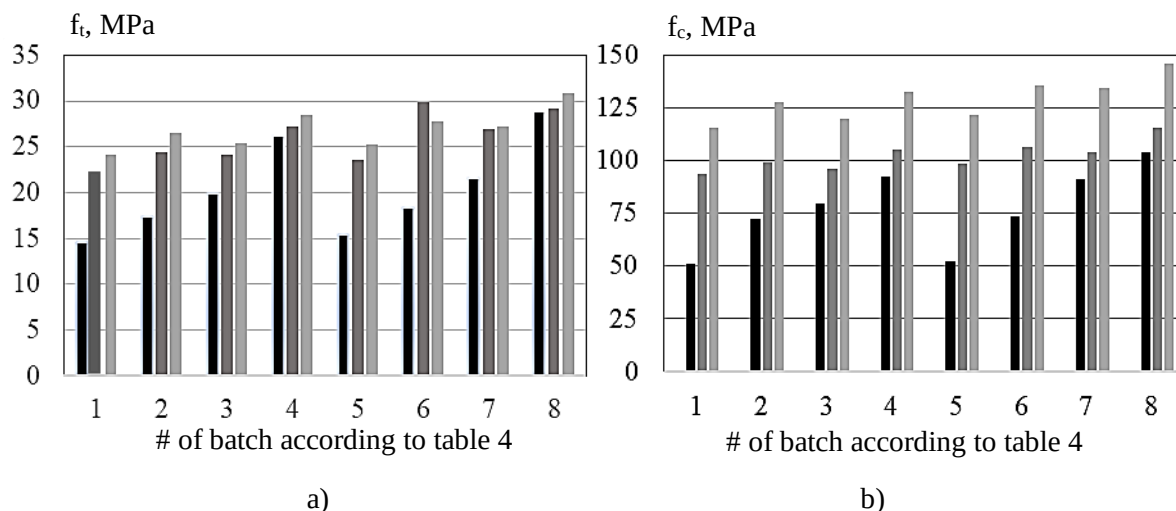


Figure 3. Flexural (a) and compressive strength (b) of RPC depending on the curing conditions and composition of mineral admixture (# of batches according to table 4)

■ after steam curing ■ at 7 days of normal hardening
 ■ at 28 days of normal hardening

Table 4. Impact of steam curing on properties of RPC.

No.	Type of mineral admixture (kg/m ³)	W/C	Flow spread diameter (cm)	Concrete strength (MPa) depending on the age of hardening					
				f _{c,tf} ^{SC}	f _{c,tm} ^{SC}	f _{c,tf} ⁷	f _{c,tm} ⁷	f _{c,tf} ²⁸	f _{c,tm} ²⁸
Steam curing									
Isothermal heating, t=50 ⁰ C									
1	Fly ash (FA)	0.29	30	14.6	51.2	22.5	93.7	24.1	115.6
2	Fly ash (FA)+ metakaolin (MTK)	0.29	30	17.4	72.4	24.40	99.2	26.5	127.6
Isothermal heating, t=80 ⁰ C									
3	Fly ash (FA)	0.29	30	19.9	79.7	24.1	96.1	25.4	120.0
4	Fly ash (FA)+ metakaolin (MTK)	0.29	30	26.2	92.6	27.2	105.3	28.5	132.6
Water curing									
Isothermal curing, t=50 ⁰ C									
5	Fly ash (FA)	0.29	30	15,4	52,2	23,5	98,4	25.2	121.7
6	Fly ash (FA)+ metakaolin (MTK)	0.29	30	18,4	73,6	29,9	106,2	27.7	135.8
Isothermal curing, t=80 ⁰ C									
7	Fly ash (FA)	0.29	30	21.6	91.0	26.9	103.9	27.2	134.4
8	Fly ash (FA)+ metakaolin (MTK)	0.29	30	28.9	103.9	29.1	115.7	30.8	145.9

Steam curing of RPC at a temperature of 50°C causes an increase in compressive strength for 1 day on average by 2.5... 3 times, for 28 days - by 1.5... 2% comparing to normal hardening. Increasing the temperature of isothermal heating clearly causes an increase in the strength of the RPC. Compared to the specimens hardened under normal conditions, steam curing at 80 °C causes an increase in strength for 1 day in 3.5... 4 times, for 28 days - by 4... 5%. As is known [32], heat and moisture treatment significantly activate pozzolanic activity of various mineral admixtures. The obtained results show that the use of heat steaming significantly increases the strength caused by the addition of fly ash (figure 3). At 50-80 °C temperature range, heat treatment accelerates the interaction of calcium hydroxide with amorphous silica of fly ash. The positive effect of steaming is also reflected in the flexural strength (figure 3a). The maximum values of the strength for RPC specimens were obtained after curing in water with a temperature of 80° C (table 4). RPC containing composite mineral admixture containing metakaolin 10% and fly ash (10%) reached a compressive strength of 145 MPa at the age of 28 days of hardening, flexural strength - 30.8 MPa, which is 15... 17% higher than the strength of concrete of the same composition hardened under normal conditions.

Conclusions

The results of determination the influence of different types of mineral admixtures (highly reactive silica fume and metakaolin and low-reactive fly ash) and their compositions on the compressive and flexural strength of RPC and kinetics of strength growth prove the possibility to obtain concrete with compressive strength values in the range of 100 - 133 MPa.

It is established that the combination of metakaolin with fly ash is an effective composite mineral admixture that allows to replace silica fume in RPC. The compressive strength of such a composition

under normal curing conditions is – 124 - 126 MPa, and after keeping in water at a temperature of 80 °C it reaches 145 MPa. The synergistic effect of this composite admixture is explained by the positive effect of spherical ash-removal particles on the workability of concrete mixtures, that to some extent compensates for the increase in viscosity caused by adding metakaolin. High flowability of fresh concrete along with high mechanical properties permit to apply RPC as architectural concrete, in particular for large-scale objects.

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