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MULTIMODAL COMPOSITE PORTLAND CEMENTS, MODIFIED WITH ULTRAFINE MINERAL ADDITIVES

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The principles of creating of multimodal composite Portland cements with optimized void filling, that based on synergistic combination of ultrafine active mineral additives with superplasticizer were established. The optimization of multimodal multicomposite Portland cements was carried out and the relationship between the phase composition, microstructure and strength of the cement matrix were investigated.

Key words: multicomodal composite cement, ultrafine mineral additives, modifier, strength, microstructure.

Показано принципи створення мультимодальних композиційних портландцементів з оптимальним заповненням пустот, що полягають у синергічному поєднанні ультрадисперсних мінеральних добавок та суперпластифікаторів. Здійснено оптимізацію складу мультимодальних композиційних портландцементів та визначено взаємозв'язок між фазовим складом, мікроструктурою та міцністю цементної матриці.

Ключові слова: мультимодальні композиційні портландцементи, ультрадисперсні мінеральні добавки, модифікатор, міцність, мікроструктура.

Introduction

In the conditions of growing requirements for protection of the environment, production of cements with a high content of mineral additives is gradually increased every year, in the same time and clinker cements should be considered as cements for special purposes. Replacement of the most energy intensive component of Portland cement – clinker by active mineral additives and fillers makes a positive contribution to the conservation of natural resources and reduces emissions of harmful substances into the atmosphere. However, reducing the clinker content into the cement composition may have an influence on the rheological properties of mixtures and reduction in kinetics of early strength development of concrete on their base [1].

So the problem of the impact of the secondary components in composite Portland cements on their properties is very urgent. It is necessary to consider the optimization of the secondary components and optimize the particles size distribution of cement with voids filling. Significant potential for optimization is discontinuous grain size, which is arranged according to the designing multimodal composite cements [2]. At the same time, classes with different maximum grain size should be separated from each other, what creates an opportunity to use different materials for individual fractions of grains. As a result, a classical optimization problem in terms of the potential of early and final strength development, available grain size, impact of the components on the rheology, cost of the components, including their preparation, is required. According to that, considerable practical interest consists in the development of multimodal composite cements obtained by modifying of Portland cements by different kinds of ultrafine mineral additives [3-6].

Identification of new features of the multimodal composition systems "cement - ultrafine mineral additive - superplasticizer" on the level of microparticles energy state and their effects on coagulation phenomena allows to provide hardening of binders considering the possibility of their modification in the direction of improving of the composite properties. Therefore, the study of the effect of dispersion mineral additives in combination with superplasticizers on hydration processes and structure of composite cements,

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achieving high strength in all terms and providing High Performance concretes and mortars on their base, is extremely important.

The purpose of the work is to investigate the impact of ultrafine mineral additives of various types on the physical and mechanical properties of Portland cement composition, phase composition and microstructure of cement paste.

Materials and methods

Ordinary Portland cement (OPC) CEMI - 42,5 R and CEMII/A-SJSC "Ivano-Frankivsk cement" based on Portland cement clinker with normal mineralogical composition (mass.%: C_3S – 57.44; C_2S – 17.65; C_3A – 6.0; C_4AF – 11.89; alkali oxide contents in terms of Na_2O_e is 0.78 mass.%) was used in the investigations. The limestome of Dubivetsky quarry with content of $CaCO_3$ 95 mass.% (SSA=910 m^2/kg) and ultrafine quartzs and with content of SiO_2 98 mass.% (SSA=1300 m^2/kg) were used as microfillers. Ultrafine fly ash from Burshtyn powerplant (SSA=1200 m^2/kg) blast granulated furnace slag from Kryvyi Rigp lant (in the amount of CaO, SiO_2, Al_2O_3, Fe_2O_3 constitute 92-96 mass.%, absorption of $CaSO_4$ from saturated solution – 231,4 mg/g), and zeolite of Sokyrnytsky quarry were used as active mineral additives. Silica fume and metakaoline were used for comparison.

Physical and mechanical tests of cements and concretes were carried out according to usual procedures. The evaluation of the properties of plasticized multimodal cementations systems was carried out through a flowing and compressive strength tests. The physical and chemical analysis (methods of X-ray diffractometry, electron microscopy, differential calorimetry) were used for investigation of multi-modal cementations systems hydration processes. The particle size distribution of fine ground mineral additives was determined by a laser granulometer Mastersizer 2000.

Results and discussion

The content 10.0; 50.0 and 90.0 vol.% of CEM I-42.5 particles is equal to 5.8; 19.4 and 56.3μm correspondingly. The data of particle size distribution such as D_{10}, D_{50}, D_{90} of mineral additives are given in Table 1.

Table1

Particle size distributionof mineral additives

Material	D_{10}, μm	D_{50}, μm	D_{90}, μm
CEM I-42.5	5.8	19.4	56.3
Limestone microfiller	3.2	9.7	11.2
Ultrafine quartz sand	0.5	1.96	11.69
Ultrafine fly ash	0.39	1.62	7.78
Zeolite	2.3	12.2	42.3
Silica fume	0.07	0.15	0.3
Metakaoline	2.2	10.3	13.7

It was established that the maximum value of the differential coefficient of surface activity (K_d), which is defined as the product of the surface activity of the contents of each fraction material for ultrafine fly ash, quartz sand is 15.82 μm^{-1}•vol % and 15.21 μm^{-1}•vol % respectively, while the CEM I-42.5 – 3.81 μm^{-1}•vol %, with the main contribution to the specific surface area of make the particles up to 1 μm, what characterize their high surface energy. With ultrafine grinding the interface increases, which has defined a supply of free surface energy that can accelerate chemical reactions that detect catalytic action.

To determine the degree of incremental active phase interface, the coefficient of surface activity K_{isa}, which is evaluated by the ratioof surface area of the particles to their volume, was introduced. With ultrafine grinding, surface energy approaches the inside and surface atoms can significantly influence on the properties of ultrafine additives. It was shown that the differential coefficient of the surface activity (K_{isa}), for ultrafine fly ash and quartz sand is 3.8...4.0 times higher than the value of the same parameter for CEM I-42.5 containing up to 5 mass. % additives of finely dispersed limestone, what indicates high surface

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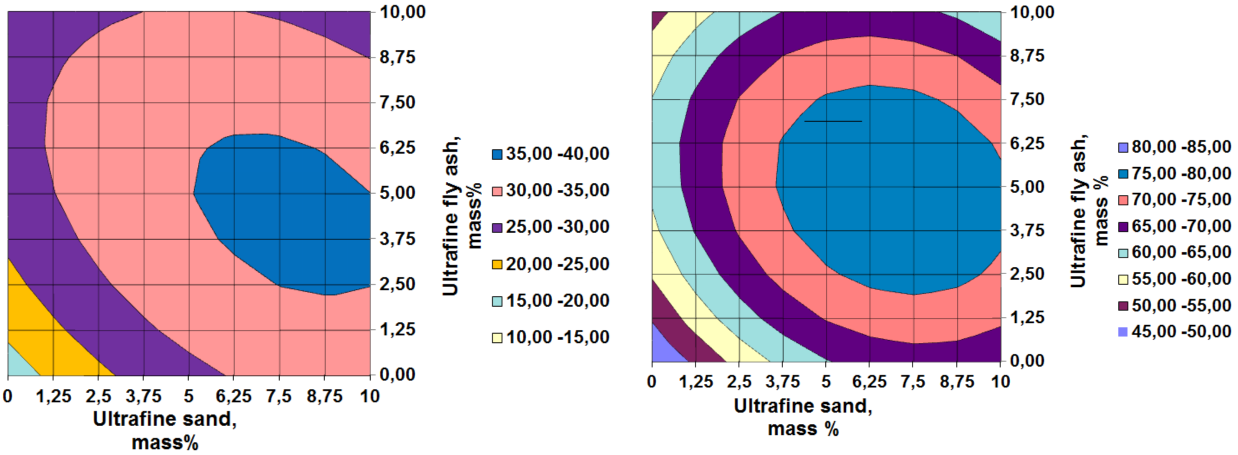
energy of ultrafine particles of mineral additives. With ultrafine grinding the interface increases, which has defined a supply of free surface energy of particles less than 2-3 µm that can accelerate chemical reactions and detect catalytic activity.

The optimal ratio between ultrafine mineral additives (fly ash and quartz sand) was determined to obtain high flowability and strength of multimodal Portland cements with superplasticizer content (1,0 mass. %) of fine grained concrete (C:S=1:2; W/C=0.36) due to plan of two-factor three-level experiment. According to test results, the regression equation were obtained and constructed isoparameter diagram was built (Fig. 1), which shows the optimal balance between additives that ensure Portland Cements with high rheological properties (flowability 250 mm) and high early and standard strength, respectively R_2=39,8 MPa and R_{28}=81,6 MPa.



a *b*

Fig. 1. Izoparametrical diagrams of compressive strength of fine grained concrete after 2(a) and 28 (b)days of hardening

The method of differential calorimetry revealed that heat of 24 hours hydration of CEM I-42,5 is 268.3 J/g, and Portland cement modified by ultrafine ash and PC – 216.52 J/g. This cement is characterized by decrease in the maximum of first and second exoeffect on 31.8% and 36.2 % respectively, when comparing to the CEM I-42.5 and PC. Moderate heat evolution of Modified Portland cements at high early strength has a positive effect on stress reducing in concrete,which arises from exothermal processes during hydration.

Tests implemented according to DSTU B V.2.7-187-2009 on multimodal composite Portland cement, modified by ultrafine mineral additives and polycarboxylates were done. It was shown that modified Portland cement is characterized by high flowability 160 mm, which provides technological effect. At this, early strength increases up to 7% and standard - up to 4,5% compared to CEM I-42,5. High water reducing effect (ΔW/C = 35.9 %, flowability 110 mm) provides high value of early (R_2=43,5 MPa) and standard (R_{28}=73.2 MPa) strength (technical effect). The results of testing of Portland cements according to EN 196 (W/C=0.50) revealed that ensuring plasticizing effect (ΔF=62,5 %) results in early strength increases in 1,8 times, and the standard strength is 54.7 MPa. Water reducing effect provides increasing of standard strength of modified Portland cementR_{28}=82.3 MPa.

It was observed that using of 5-15 mass.% of limestone in cement CEM II/A-S (C:S=1:3; flowability 113-115 mm) can reduce water demand of composite Portland cements to 7,7-15,4 %. The addition of limestone in an amount of 5 and 10 mass.% provides accelerating of the early structure formation, and the compressive strength after 2 days of curing increases, respectively, by 10,1 and 24,0 % compared with Portland cement CEM II/A-S. Increasing amount of limestone up to 15 mass.% leads to some retarding in processes of strength development of composite Portland cement in all terms of hardening. The highest strength after 28 days of hardening (41 MPa) is achieved for composite Portland cement, which contained 10 mass.% of limestone. Structure formation of ultrafine limestone microfiller with high surface energy in the composition of multimodal Portland cements is determined by chemical interaction of calcium

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carbonate with the products of hydration of three calcium aluminates with formation of hexagonal crystals of hydrocarboaluminates $C_3A \cdot CaCO_3 \cdot 12H_2O$.

Ultrafine fly ash and quartz sand as additives in multimodal Portland cements influence the processes of structure formation, phase composition, causes pores colmatation and increasing cement strength. The process of hardening of multimodal Portland cements, modified with ultrafine additives of various types, followed by hydration of clinker minerals and pozzolanic reaction of ultrafine additives with $Ca(OH)_2$, which is the weakest part of the cement structure in unclinker part.

According to X-ray diffraction analysis, the degree of hydration of multimodal Portland cement modified with ultrafine mineral additives of fly ash and quartz sand after 2 days of hardening is 50.1%, which is 7% higher than CEM I-42.5. The main role of ultrafine fly ash is to improve the properties of cement stone by reducing the quantity and size of hydrates (calcium hydroxide and hidrosulfoaluminate) with increasing of low alkali calcium hydrosilicates. Thermogravimetric analysis showed the reduction of calcium hydroxide in the cement stone modified by ultrafine ash by 5.1% compared to the stone based on CEM I-42.5, which is 11.3 %.

Electron microscopic analysis of the microstructure of cement without additives (W/C=0.5;flowability 230 mm) shows that the main hydration phases after 7 days of hardening are needle crystals of ettringite and hexagonal crystals of portlandite with size from 5-10 microns, but because of cleavage by planes (0001), they limit increasing of compressive strength. Using of ultrafine fly ash and quartz sand in cement provides binding portlandite into low alkali calcium hydrosilicates with pores colmatation during hardening. Cement stone microstructure with the addition of ultrafine particles of size less than 1 μm is very dense, which provides increasing of compressive strength and durability.

Conclusion

Physical and chemical peculiarities of hydration of multimodal composite Portland cements are determined by the processes of early formation of cement matrix microstructure of High Performance Concretes. Multimodal composite Portland cements based on the Portland cement CEM I-42.5 modified by ultra fine fly ash and quartz sand additives provides the possibility of obtaining building constructions with high building-technical properties and durability.

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