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Właściwości betonów o niskim śladzie węglowym zawierających wieloskładnikowe dodatki mineralne

PERFORMANCE OF CONCRETES WITH A LOW CARBON FOOTPRINT CONTAINING MULTI-COMPONENT MINERAL ADDITIVES

Streszczenie

Zgodnie z przedstawioną przez CEMBUREAU strategią niskoemisyjnego rozwoju, konieczna jest redukcja emisji tlenku węgla na każdym etapie łańcucha technologicznego – od produkcji klinkieru, cementu i betonu po budownictwo. Znaczącą redukcję „śladu węglowego" w produkcji budowlanej uzyskuje się dzięki zastosowaniu betonów zawierających wieloskładnikowe dodatki mineralne o niskim śladzie węglowym. Projektowanie wieloskladnikowych dodatkow mineralnych uzyskuje się przez oddzielne mielenie i synergiczne łączenie nieklinkierowych składnikow różnego pochodzenia (żużel wielkopiecowy, popioły lotne, naturalny zeolit, wapień, pył krzemionkowy itp.) z optymalizacją ich składu granulometrycznego z uwzględnieniem bimodalnego rozkład wielkości cząstek według objętości i pola powierzchni. Obliczono przyrostowy współczynnik powierzchniowego rozkładu wielkości cząstek, aby ocenić udział poszczególnych frakcji w całkowitej powierzchni dodatków mineralnych. Racjonalizacja rozkładu powierzchniowego cząstek dodatku mineralnego zapewniła wzrost wytrzymałości wczesnej mieszanych cementów. Optymalizację kombinacji dodatków mineralnych przeprowadzono metodą simpleksowo-sieciową Scheffe'a według kryteriów właściwości technologicznych i wskaźnika wytrzymałościowej aktywności.

W pracy określono rodzaj i poziom dodatków mineralnych zastępujących cement portlandzki w celu uzyskania efektywności klinkieru projektowanej mieszanki betonowej oraz docelowego poziomu redukcji CO_2. Zwiększenie wczesnej wytrzymałości betonów o niskim śladzie węglowym uzyskuje się poprzez modyfikację superplastyfikatorami polikarboksylanowymi. Na bazie cementów mieszanych (współczynnik klinkieru 0,65...0,50) można znacznie obniżyć jednostkowe zużycie klinkieru na jednostkę wytrzymałości do 4,5...3,0 kg/(m^3 MPa); odpowiednio intensywność CO_2 3,9...2,6 kgCO_2/(m^3 MPa). Stwierdzono, że

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synergiczne połączenie dodatków mineralnych w mieszance betonowej z modyfikatorami zapewnia uzyskanie betonu szybkosprawnego (f_{cm2}/f_{cm28}=0,51). Dzięki racjonalnemu doborowi cementu portlandzkiego i dodatków mineralnych w produkcji betonów o niskim śladzie węglowym uzyskuje się korzyści techniczne, ekologiczne i ekonomiczne. Tym samym synergiczne połączenie dodatków mineralnych o różnej genezie i granulometrii, modyfikowanych superplastyfikatorami nowej generacji przesądza o celowości wykorzystania betonów o niskim śladzie węglowym do rozwiązywania problemów związanych z koniecznością realizacji niskoemisyjnej strategii rozwoju w budownictwie. Zoptymalizowane technologicznie mieszanki na bazie wieloskładnikowych dodatków mineralnych stają się racjonalnym rozwiązaniem problemu poprawy efektywności energetycznej oraz redukcji poziomu emisji gazów cieplarnianych do atmosfery (głównie CO_2) towarzyszącej produkcji betonów.

Abstract

According to the low-carbon development strategy presented by CEMBUREAU, it is necessary to reduce carbon dioxide emissions at every stage of the technological chain - from the production of clinker, cement and concrete to construction. A significant reduction of the “carbon footprint” in construction production is achieved by using clinker-efficient concretes based on blends obtained by mixing Portland cement with multi-component mineral additives with a low carbon footprint. The design of multi-component supplementary cementitious materials is achieved by separate grinding and by the synergistic combination of mineral additives of different origin (blast furnace slag, fly ashes, natural zeolite, limestone, silica fume, etc.) with the optimization of their granulometric composition taking into account the bimodal particle size distribution (PSD) by volume and surface area. The incremental coefficient of the surface distribution of particles size was calculated to assess the share of individual fractions in the total surface area of mineral additives. The rationalization of the surface distribution of the mineral additive particles ensured increasing of early strength of the low carbon blended cements. Optimization of the combination of mineral additives was carried out using the Scheffe simplex-network method according to the criteria of technological properties and the strenght activity index.

In the paper, the type and level of mineral additives replacing Portland cement were analyzed in order to obtain the clinker efficiency of the designed concrete mix and the target level of CO_2 reduction. Increasing the early strength of low-carbon concretes is achieved by modification with polycarboxylate superplasticizers. On the basis of blended cements (clinker factort 0.65...0.50), it is possible to significantly reduce the specific consumption of clinker per strength unit, to 4.5...3.0 kg/(m^3 MPa); respectively CO_2 intensity 3.9...2.6 kg CO_2/(m^3 MPa). It was found that the synergistic combination of mineral additives in the concrete mix with modifiers ensures obtaining rapid-hardening concrete (f_{cm2}/f_{cm28} = 0.51). Thanks to the rational selection of Portland cement and mineral additives in the production of low-carbon concrete, technical, ecological and economic benefits are obtained. Thus, the synergistic combination of mineral additives of various origins and granulometry as well as new generation superplasticizers determines the advisability of using low-carbon concretes to solve problems related to the need to implement the strategy of low-emission construction development. Technologically optimized blends based on combined mineral additives become a rational solution to the problem of improving the energy efficiency and reducing the level of greenhouse gas emissions to the atmosphere (mainly CO_2) associated with the production of concrete.

1. Introduction

An important problem according to the priority areas of the European Green Deal is ensuring carbon neutrality, introducing innovations, modernization and greening of industry. According to the low-carbon development strategy presented by CEMBUREAU, it is necessary to reduce carbon footprint at every stage of the production and technological chain - from the production of clinker, cement and concrete to construction. Already by 2030, it is planned to reduce CO_2 emissions during the production of cement by 30%, and at the stage of concrete production - by 40% [1, 2].

Solving the problem of energy efficiency and reducing CO_2 emissions in building production is largely determined by the search for technological and ecological ways to replace a part of Portland cement clinker with mineral additives. Due to the rational selection of mineral additives in the production of low-carbon cements, technical, ecological and economic benefits are achieved [3-5]. Another way is to add mineral additives directly to the concrete mixture instead of a part of Portland cement, which helps to reduce the cost of concrete, increase its strength in subsequent periods of hardening, and increase durability. In this case, replacing each kilogram of clinker in concrete with mineral additives allows reducing CO_2 emissions by 0.6–1.0 kg [6].

The main non-clinker constituents, which has been used in cement production for many years, are granulated blast furnace slag (GBFS) and fly ash (FA) [7, 8]. However, the availability of GBFS and FA is limited in some parts of Europe. Therefore, it is recommended to add other types of pozzolans to the composition of so-called "green" cements. At the same time, with an increased amount of pozzolans, they significantly affect the strength of concrete. So, silica fume significantly increases the strength and durability of concrete, but it has a high water demand, so it requires the use of an increased amount of water-reducing admixtures [9]. Important trend in cement production technology is the growth manufacture of Portland limestone cement CEM II/A-LL. At the same time, the addition of limestone in cement has variable effects on the properties of the blends, particularly depending on the exposure conditions. The carbon footprint for Portland cement clinker is about 850 kg CO_2/t, while for GBFS and FA it is only 2 kg CO_2/t, and for limestone - 63 kg CO_2/t [10].

Significant resources in the European region of natural pozzolans - zeolite tuffs - make it possible to solve the problem of regional application of mineral additives. Highly siliceous zeolite tuffs (the main mineral is clinoptilolite $(Na,K)_6[Al_6Si_{30}O_{72}]\cdot 24H_2O$) have unique characteristics, such as a high specific surface area and the ability to exchange cations. Currently, it is very promising to use of super fine zeolite (SFZ) [11, 12], which is a natural zeolite ground to higher fineness than cement. Being a superpozzolana, it provides an increase in the packing density of cementitious paste and significantly improve the cohesiveness at the same flowability.

The pozzolanic activity of mineral additives, which is evaluated by their reactivity, mainly depends on three parameters - the nature of the activity (hydraulic, pozzolanic), the chemical composition of CSMs and their dispersion, while mineral additives particles smaller than 10 μm are reactive [13]. The effectiveness of the increased dispersion of artificial and natural pozzolans is confirmed by the development of ultrafinely dispersed mineral additives that belong to superpozzolans and provide accelerated binding of calcium hydroxide - a product of the hydrolysis of the alite phase of Portland cement clinker [14]. Such interaction of superpozzolana with products of hydration of Portland cement clinker leads to a decrease in porosity, which helps to increase the strength, corrosion resistance of concrete and determines its durability. However, a high content of finely dispersed mineral additives causes an increase in the water consumption of concrete, which leads to a loss of early strength [15].

To overcome such a significant drawback of low-carbon cements as a decrease in their early strength, according to the concept of P.-K. Aitcin [16] both chemical and physical approaches are used. The chemical approach consists in the use of finely ground cements with an increased content of highly active minerals C_3S and C_3A in clinker. However, this approach has already practically exhausted itself, since the energy costs for their production increase significantly, in addition, the rheological properties of the mixtures deteriorate, and in the later stages of hardening, the strength does not increase significantly. Therefore, the physical approach opens significant prospects for improving the technical properties of building composites. It consists in not changing the chemical and mineralogical composition of Portland cement clinker, but reducing the water-binder ratio (W/B) of multicomponent cementitious systems and increasing the packing density of binder grains in the cement paste with the help of highly effective superplasticizers, especially of the polycarboxylate type [17].

The creation of modified concretes using multi-component mineral additives involves the optimization of their compositions due to the intensification of pozzolanic reactions in the concrete cementitious matrix. The effectiveness of such an idea lies in the maximum disclosure of the synergistic role of highly dispersed pozzolans in the composition of low-carbon cementitious systems, which will ensure a directed effect on the processes of regulating the properties of modified concretes. The assessment of the indicator of the impact of multi-component mineral additives on the environment allows to determine their suitability for the production of low-carbon concrete. In advanced EU countries, CO_2 emissions are reduced to 83.4 kg of CO_2 per 1 ton of concrete. One of the main directions of reducing the ECO_2 indicator is the replacement of a part of Portland cement CEM I type in concrete with multicomponent mineral additives, which is a relevant approach to achieve sustainability in construction industry [18].

Taking into account the need to implement the main goals of the low-carbon development strategy, research aimed at determining the impact of multi-component mineral additives on the physical and mechanical properties of low-carbon cements with a reduced clinker factor up to 0.50 and concretes based on them should be considered relevant.

2. Materials and methods

Commercially available Portland cement CEM I 42.5R produced by JSC Ivano-Frankivsk cement, Ukraine composed of C_3S: 62.42, C_2S: 13.62, C_3A: 7.06, C_4AF: 12.32, mass.%, was used as reference cement in the investigation. Ground granulated blast furnace slag (GGBFS) Kryvyi Rih, (glassy phase - 80 %), consisting of 92-96 mass.% CaO + SiO_2 + Al_2O_3 + Fe_2O_3, fine (FZ) and superfine (SFZ) zeolites with 70.5 wt.% SiO_2 provided from Sokyrnytsky quarry were utilized as mineral additive. Clinoptilolite [$(Na_4K_4)(Al_8Si_{40}O_{96})\cdot 24H_2O$] content in natural zeolite tuff was 60%. Siliceous fly ash (FA) from Burshtyn TPP with SiO_2 and CaO content 55.18 and 2.23 % respectively was used. Limestone powder with 95 mass.% $CaCO_3$ was used as microfiller. Limestone powder (LP) belongs to the LL type according to the EN 197-1 in terms of total content of organic carbon. Silica fume (SF) Elkem Microsilica Grade 940-U with 94.7 mass.% SiO_2, SSA=18 000 cm^2/g was used. Chemical composition of main components of the cement is presented in Table 1.

Table 1. The chemical composition of CEM I and mineral additives

Material	Oxide content, mass. %							
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3
CEM I 42.5 R	66.83	20.93	5.13	4.28	0.80	1.14	0.05	0.84
GGBFS	48.10	39.26	6.55	0.82	3.45	0.31	0.33	1.18
Zeolite tuff	1.63	76.92	12.95	3.95	0.18	3.68	0.53	0.16
Fly ash	2.23	55.18	24.21	12.17	2.01	2.57	0.61	1.02
Limestone powder	49.86	6.71	2.14	0.31	0.38	0.32	0	0.14

Study of fractional composition and grinding fineness of cement and mineral additives were carried out by sieve analysis and by determination of the specific surface area by Blaine.The Blaine specific surface area of CEM I, GGBFS, SFZ, FA and LP are 3500; 4000, 9700, 3300 and 8500 cm^2/g respectively. The Mastersizer 3000 uses the technique of laser diffraction to measure the particles size distribution by volume (Table 2). The particle size distribution of Portland cement CEM I is characterized by the content of fractions by volume Dv (10), Dv (50) and Dv (90), respectively, at 2.76, 18.1 and 56.5 μm, average diameters by volume D[4;3] = 24.8 μm and by specific surface area D[3;2] = 5.21 μm. The main mineral components of GGBFS, FA, natural zeolite, limestone are characterized by a volume average diameter D[4;3] within 28.6…53.7 μm and an average diameter on the specific surface D[3;2] – 5.22…8.29 μm. The amount of fine fraction up to 5.0 μm for slag and zeolite are 21.91 – 23.47 vol.%, and for fly ash and limestone – 13.11 – 16.67 vol.%. It should be noted that the super fine zeolite and limestone powder are characterized by a bimodal particles size distribution by volume.

Table 2. Granulometric composition of CEM I and mineral additives

Material	D <1 μm, %	D <5 μm, %	D <10 μm, %	D <20 μm, %	D <60 μm, %	D[3;2] μm	D[4;3] μm	D_v(10) μm	D_v(50) μm	D_v(90) μm
CEM I	4.26	21.86	37.46	60.41	97.52	5.21	24.8	2.76	18.1	56.5
GGBFS	3.51	21.91	38.69	55.02	87.18	6.41	36.2	2.53	17.5	76.6
SFZ	6.65	23.47	38.75	58.76	87.92	5.22	28.6	1.93	15.6	66.6
FA	2,21	13.11	28.87	46.88	71.30	7.16	53.7	4.15	23.6	90.8
LP	1.97	16.67	33.69	50.03	77.60	8.29	46.4	3.92	23.3	125.0

The reactivity of cementitious materials is determined by the "excess surface energy", which depends more on the PSD over the surface area than on the volume. In order to quantify the PSD by surface of cementitious materials, it was calculated the coefficient of incremental surface area (K_{isa}) for each particle size according to a special methodology [18]. This coefficient is defined as the product of A/V for a particle size (the ratio of the surface area of the particle to its volume, μm^{-1}) to the content of a fraction by volume based on laser granulometry data. The value of coefficient K_{isa} characterize the surface activity of a given particle size in the grain composition of cement.

The PSD by volume of reference Portland cement CEM I and mineral additives are shown in Fig. 1a. It should be noted that the PSD curves by volume for mineral additives SFZ and LP, are constituted of two maximums. The fine particles fractions are in the range up to 10 μm and their content for SFZ and LP are 38.75 and 33.69 vol. %, respectively. In the case of CEM I and GBFS there is one maximum in the volume distribution on the PSD curves, with D_{max} at 8 μm and 30 μm, consecutively. As presented in Fig. 1b, for CEM I and GBFS there are binary variable PSD curves by surface area, whereas for SFZ and LP the impact of a fine fraction on a surface area is much higher than fraction over 10 μm. Fractions of CEM I and the mineral components, GBFS, SFZ and LP in the range up to 10 μm have the decisive contribution (70-80%) in the specific surface area of the cementitious system and determine their high reactivity in the early period of the paste microstructure formation. The increased surface areas of fine fractions and the packing density of the larger grains, make it possible to increase the early strength of multi-component Portland cements. In this case, the effect of the coarse fraction on the specific surface area of this additives is minor. Thus, fractions of mineral components CEM I, GGBFS, SFZ, LP in the range up to 10 μm make a decisive contribution (70-80%) in the specific surface area of the cementitious system and determine its high reactivity in the early period of structure formation. The increased surface activity fine fractions and powder packing density at various structural levels of cementitious system provides the opportunity to create micro-structurally designed multimodal Portland composite cements with high early strength.

a) b)

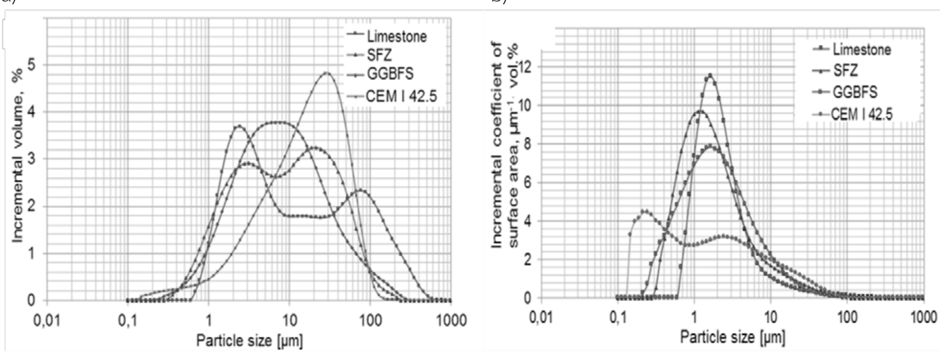

Fig. 1. Particle size distribution by volume (a) and surface area (b) of CEM I and mineral additives

The chemical composition of mineral additives was determined using an ARL 9800 XP X-ray spectrometer (Thermo Electron SA, Switzerland). Scanning electron microscope Philips XL30 ESEM-FEG was used for studying morphology of the cement paste. Determination of the strength of blends was carried out in accordance with EN 196–1:2015, bleeding in accordance with EN 196–3:2015, EN 196–6:2015. Pozzolanic activity was determined according to EN 450-1:2009, ASTM C593-06.

Sodium sulfate (Na_2SO_4) was used as an alkaline-sulfate activator of hardening concretes. Superplasticizer type polycarboxylate ethers (PCE) was used in this study.

Fine sand and aggregates of two fractions (2–5 mm and 5–20 mm) were used to design of mixture compositions. Grain composition of fine and coarse aggregates of the concrete mixture was determined by the method of dry sieving through a set of sieves according to EN 933-1:2012-03. After sieving, fractions on individual sieves were weighed and grading curve was developed. The grading curve obtained in the study (designed curve) was compared with standard curves. The method of orthogonal central compositional planning was used to study the effect of consumption of composite Portland cement and amount of PCE on concrete strength and clinker efficiency. To establish relationship between ecological and technical properties of concrete, clinker efficiency in concrete was determined by the ratio of cement consumption to compressive strength in a certain age [kg/($m^{3\cdot}$ MPa)].

3. Results and discussion

3.1. Properties of low-carbon blended cements

For the development of low carbon blended cements, a complex assessment of mineral components dispersion and water demand has been carried out. Ultrafine mineral additives are characterized by a highly developed specific surface area that causes an increase of water demand. Particularly the high water demand is for mineral additives of sedimentary origin (zeolite). For GGBFS and FA the water demand is 22 and 27 % respectively; SFZ is characterized by the highest water demand – 55 %. For limestone powder water demand is 24 %. Combinations of various genesis and fineness mineral additives can provide water demand acceptable level (WD ≤ 30%). At the same time superfine zeolite, due to the features of the crystalline structure of clinoptilolite and high surface area to volume ratio, can noticeably decrease liquidity and cause difficulties in achieving a desired blend of workability (Fig. 2a, b).

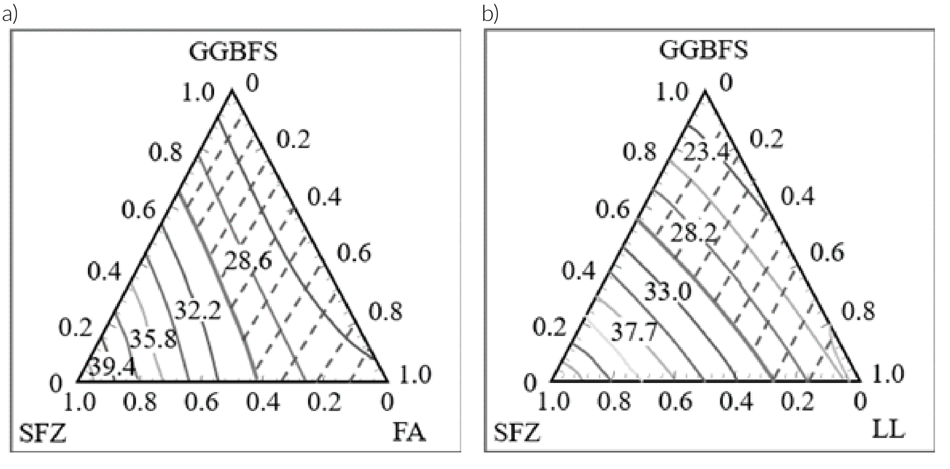

Fig. 2. The impact of additives on the water demand of blends in the systems GGBFS-SFZ-FA (a) and GGBFS-SFZ-LL (b)

The GGBFS and FA are characterized by high bleeding – after 120 min bleeding coefficients (K_{vol}) are 27.1 and 39.7 % respectively (Fig. 3). At the same time, FZ and SFZ are characterized by the lowest bleeding coefficient (K_{vol} = 2.0-3.3 %). For limestone powder bleeding coefficient is 24.1% after 120 min. The suspension with the addition of SFZ is the most stable – after 2 h, the level of bleeding does not change. The combined use of mineral addirives such as GGBFS, SFZ, FA and LP with different genesis and properties provides to stabilization of the blends from bleeding.

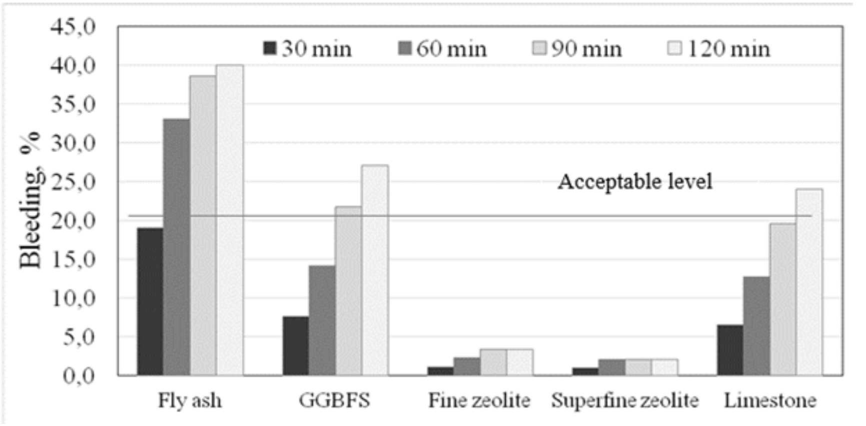

Fig. 3. The bleeding of mineral additives

The reactivity mineral additives was determined by the method of absorption lime by the additive from a lime solution. SFZ is characterized by highest pozzolanic activity (after 30 and 38 days – 192 and 230 mg CaO/g accordingly). At the same time for fly ash pozzolanic activity is lowest and is equal to 30 and 42 mg CaO/g respectively after 30 and 38 days. GGBFS after 30 days has the reactivity such as SFZ after 10 days, that is 3 times lower.

The impact of high volume of GGBFS, SFZ and LP additives on the physical and mechanical properties of blended cements was investigated. Results of a consistency of fresh mortars determined by flow table according to EN 1015-3 testify that is an addition of SFZ significantly reduces the workability of blended cement but limestone powder provide to an increase in their workability. Compressive strength test results have shown that application of mineral additives high volume leads to a significant decrease in strength of blended cements especially at an early age.

Highly dispersed mineral additives such as super fine zeolite and silica fume are characterized by increased water demand – 42.5 and 55.0%, while having low bleeding (3.0 and 1.0%, respectively). Fly ash has a lower dispersion compared to other pozzolanic materials. Fly ash is characterized by particles of the correct spherical shape, which provide a plasticizing effect due to the "roller bearing effect". Therefore, its water demand is reduced (27.0%), but it is characterized by significant bleeding (34%). According to EN 450-1:2009, the strenght activity index (SAI) after 28 days should be more than 75%, and after 90 days - more than 85%. As can be seen from Fig. 4, super fine zeolite (SFZ) and silica fume (SF) reach the corresponding indicator of $P_{SAI} \geq 75\%$ already after 2 days of hardening. The SAI of fly ash meets the requirements of EN 450-1:2009, but is significantly lower compared to super fine zeolite and silica fume.

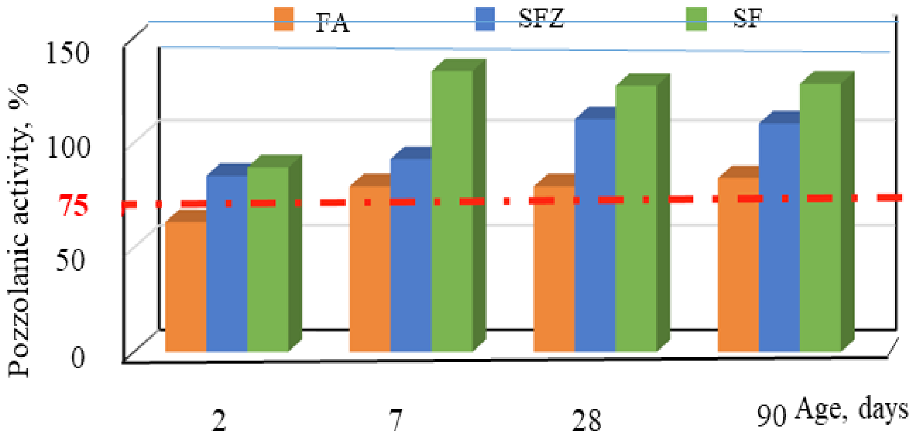

Fig. 4. Pozzolanic activity of mineral additives according to EN 450-1:2009

Thus, an in-depth interpretation of the role of multicomponent mineral additives, as well as taking into account their synergistic interaction, contributes to the most effective implementation of the potential binding properties of low-carbon cements. The advantages of such cementitious systems are a high level of energy saving and low CO_2 emissions during the production of cements, combined with a higher durability of concretes based on them. However, the degree of replacement by mineral additives is limited due to the delayed set of early strength of low-carbon cements and concretes due to the low reactivity of such components compared to clinker phases.

3.2. Properties of low-carbon concretes

The potential for reducing CO_2 emissions in concrete is achieved by optimizing the use of binders with the use of modern technologies that combine a high content of fillers and a significant reduction in water consumption. According to the concept [19], which takes into account the technical characteristics of building materials, the efficiency indicators of the binder or clinker in concrete (clinker intensity) in [kg/(m^3·MPa)] and CO_2 emission intensity (CO_2 intensity) should be calculated in [kgCO_2/(m^3·MPa)] when producing 1 m^3 of concrete of the given strength. It is noteworthy that with the increase in concrete strength, these indicators decrease, since clinker is used more efficiently. At the same time, the strength class of the designed concrete, as well as construction standards and norms, are decisive.

The potential contribution of emissions to global warming GWP according to Environmental Product Declarations (EPD) for non-reinforced and reinforced concrete in terms of CO_2 is 250 and 312 kg CO_2eq/m^3 of concrete, respectively. For traditional concretes with a compressive strength of 30 MPa, the minimum value of clinker intensity is about 8 kg/m^3·MPa, but the average value is, as a rule, 12 kg/m^3·MPa. The minimum CO_2 intensity is about 2 kg CO_2/(m^3·MPa) for concretes above 40–50 MPa and increases exponentially for lower strengths. In the complex, the parameters of clinker and CO_2 intensities characterize the clinker efficiency of concrete, which can be increased by replacing part of the clinker with active mineral additives with a low carbon footprint (granulated blast furnace slag, zeolite tuff, fly ash, etc.) [20].

For the production of low-carbon concretes, the optimization of the granulometric composition of the components is decisive for the density of grain packing. Polyfractional aggregates (sand fractions 0.125–2.0 mm, crushed stone fractions 2–4; 4-8; 8-16 mm) were used to design the curve of the required granulometric composition of the commercial concrete mixture, the grain composition of which was determined by the method of dry sieving through a set of sieves according to EN 933-1:2012-03. At the same time, the designed granulometric curve of aggregates is in the region of satisfactory compositions, which guarantees the appropriate ease of placement and consistency of the concrete mixture with the smallest possible amount of water and cement. The correct selection of various components of the mixture of aggregates and microfillers, as well as the introduction of superplasticizers based on polycarboxylate ether (PCE) allows to obtain a dense packing of the components of the construction composite, as well as to reduce the distance between cement particles in the initial period of the hydration process. At the same time, the fine-dispersed fractions of mineral additives improve the pore structure, which leads to an increase in the waterproofing and durability of concrete, and the ECO_2 emission index can be reduced by 70% for the same concrete strength class.

The impact of recipe and technological factors on the properties of concrete was evaluated using the method of experimental and statistical modeling [21]. The consumption of CEM II/B-M(S-P-L) 32.5R (X_1=320; 370; 420 kg/m^3) and the amount of superplasticizer PCE (X_2=0; 0.8; 1.6 mass.%) were selected as variable factors. In order to accelerate the acquisition of early strength, an alkaline hardening activator (2.0 mass.% Na_2SO_4) was also introduced into the composition of concrete. The analysis of the obtained concrete strength models established that with the consumption of composite Portland cement in the range of 320...420 kg/m^3 in a concrete mixture without additives (OK=16–18 cm), the W/C index varied from 0.62 to 0.48; at the same time, such concrete was characterized by reduced strength at an early age (after 1 day f_{cm1} = 3.1 ... 5.8 MPa). With the introduction of 1.0–1.6 mass.% PCE due to the significant water-reducing effect (27-34%), the strength of modified concrete increased 3.5-4.6 times after 1 day. The highest values of strength at the age of 2 and 28 days (f_{cm2}=47.0 MPa; f_{cm28}=80.0 MPa) are achieved for modified concrete with cement consumption 420 kg/m^3 and superplasticizer 1.6 mass.% PCE (Fig. 5a). For modified concrete, the specific consumption of clinker per unit of strength after 28 days decreases to 4.5...3.0 kg/(m^3·MPa) (Fig. 5b), and the CO_2 intensity is 3.9...2.6 kgCO_2/(m^3 ·MPa).

To obtain modified rapid-hardening carbon concretes, it is necessary to ensure the formation of a dense contact zone between the coarse aggregate and the cementing matrix. Using the method of raster electron microscopy, it was established that the cementing matrix of concrete without additives is characterized by a porous microstructure with weak adhesion between hydrated phases. Ultradisperse mineral additives improve the effectiveness of cementitious materials due to high pozzolanic activity and the ability to fill capillary pores. The results obtained using the SEM and EDX methods show that the addition of microsilica improves the microstructure of concrete due to the formation of additional clusters of dense gel C-S-H(I), which contribute to the crosslinking of particles in the cementitious matrix (Fig. 6a, b).

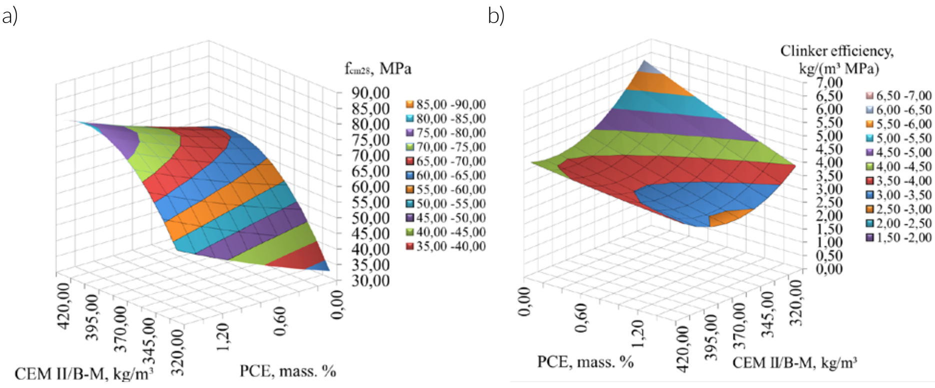

Fig. 5. Isoparametric diagrams of compressive strength (a) and clinker intensity (b) of concrete after 28 days

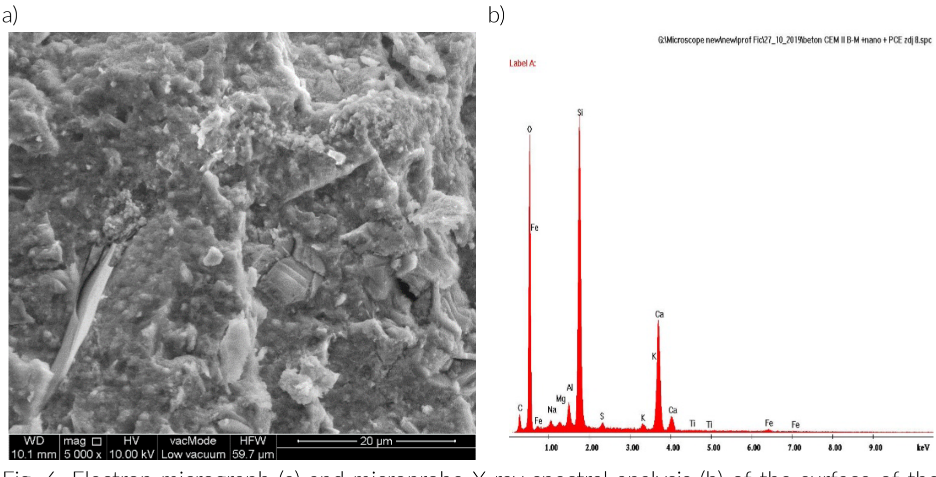

Fig. 6. Electron micrograph (a) and microprobe X-ray spectral analysis (b) of the surface of the cementing matrix of modified low-carbon concrete after 28 days

The accelerating effect of microsilica in combination with PCE and alkaline activator (Na_2SO_4) makes it possible to compensate for the slowing down of the hardening kinetics of composite Portland cement CEM II/B-M compared to CEM I in the composition of low-carbon concrete. At the same time, the modification of the cementitious matrix helps to increase the contacts between the particles of the low-basic phases C-S-H(I) with the formation of a compositionally cross-linked microstructure, which provides a significant acceleration of hardening and high strength of low-carbon concretes.

Carbon dioxide emissions of concrete are significantly reduced when using mineral additives based on a mixture of FA, SFZ and SF. For blended pozzolanic binders (clinker factor - 0.50), CO_2 emissions are reduced to 456 kg/t, which is 45% less compared to Portland cement CEM I 42.5 R.

Technological optimization due to the combination of mineral additives of different genesis and surface energy ensures the production of low carbon Portland cement of the

CEM II/C-M type. The combination of 28% GBFS + 12% LP additives in CEM II/C-M (S-LL) reduces water consumption to 27% and increases flow by 210 mm, which makes it possible to use such binders for ready-mix concrete. The compressive and bending strength after 28 days of hardening of such binders reaches CEM I values. For Portland composite cement CEM II/C-M (S-LL) 42.5N-LH (clinker factor – 52%), CO_2 emission is 450 kg per Mg of cement. The clinker capacity indicator is 11.61 kg of clinker/t of cement/MPa, the strength is 28 days, the environmental ranking of cement is 12.6 kg of CO_2/t of cement / MPa in 28 days. The blends based on CEM I and multicomponent mineral additives (GBFS, limestone powder, super fine zeolite) makes it possible to obtain homogeneous concrete mixtures with low segregation parameters. The practical implementation of large-scale production of low-carbon cements and concretes significantly contributes to solving the urgent problem of further development of resource- and energy-saving technologies in construction [22].

The procedure for the development of low-carbon concretes with efficient use of reactive materials involves the selection of cement of a high strength class and eco-friendly mineral additives. The multi-component additives containing slag, fly ash, zeolite and limestone, which were optimized by changing of the particle size distribution, allow the components to compensate for possible mutual disadvantages due to a synergistic effect. By changing the type, the amount and particle size distribution of additives the possibility of obtaining the micro-structurally designed cementitious materials. The correct selection of multicomponent mineral additives and microfillers on the one hand, as well as the introduction of superplasticizers based on polycarboxylate ether on the other hand makes it possible to obtain dense packing of the mixture and reduce the distance between cement particles at the initial stage of the hydration process, which contributes to increasing strength and durability. Finely dispersed fractions of mineral additives improve the porous structure, as a result of which the water resistance and durability of concrete increases.

4. Conclusions

The principles of obtaining low-carbon concretes with multi-component mineral additives have been developed. It was shown that optimization of particle size distribution of concrete mix components at different structural levels is of paramount importance for achieving high grain packing density. The influence of the consumption of blended cements and polycarboxylate superplasticizer on the strength of concrete, was investigated by the method of experimental-statistical modeling. To evaluate the relationship between technical and environmental performance of concrete, was determined the effectiveness of clinker in concrete. It is shown that with the increasing of strength of modified concrete it is possible to significantly reduce the specific consumption of clinker per unit strength up to 4.5…3.0 kg/($m^3 \cdot$ MPa); accordingly, the CO_2-intensity is 3.9...2.6 kgCO_2/($m^3 \cdot$ MPa). Significant intensification of the processes of early structure formation of low carbon concretes are ensured by the complex using of polycarboxylate superplasticizers, sulfate-alkaline activation and the use of multicomponent mineral additives. Modified concretes with a low carbon footprint enables a rapid pace of construction and addresses the challenges associated with the need for a low-carbon development strategy.

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