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Eco-efficient blended cements with high volume of supplementary cementitious materials

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Abstract: The ways of reducing CO_2 emissions in the cement industry were analysed for the purposes of implementation of the low carbon development strategy. The optimal solution to this problem is the technologically optimised blended cements with high volume of supplementary cementitious materials of various genesis and fineness. The design of eco-friendly blended cements was achieved by a synergistic combination of the main constituents such as granulated blast furnace slag, superfine zeolite, fly ash and limestone, as well as by optimisation of the their granulometric composition, taking into account their bimodal particle size distribution by volume and surface area. Moreover, the article presents the technical, environmental and economic benefits of using eco-efficient blended cements.

Keywords: eco-efficient blended cements, supplementary cementitious materials, superfine zeolite, particle size distribution, synergistic combination additives

1. Introduction

Integrated solutions for the cement industry to provide low carbon development strategies are aimed at reducing energy consumption, as well as at improvement of technology and better environmental policy. The release of high-tech products in the construction industry, taking into account the reduction of the degree of environmental pollution, is largely realised by the introduction of eco-efficient (low-CO_2) cements. According to the Roadmap "The role of cement in the 2050 low carbon economy" for the Cement Sector of the EU, by 2050, the cement carbon footprint could be reduced by 32% compared with 1990 levels, using mostly conventional means. The use of SCMs in cement production has a positive effect on the economic aspect of production and, what is extremely important, is a significant factor in improving the state of the environment [1-3].

The global average clinker content in 2014 was 0.65. Reducing this indicator is technically feasible, but the availability of suitable supplementary cementitious materials in a given region may be a limiting factor. However, in the process of cement production, an important problem is the creation of suitable combinations of clinker with mineral constituents whose characteristics will increase the effectiveness of cements. Most cement plants use granulated blast furnace slag and fly ash as active mineral additives, and limestone as microfiller [4]. At the same time, blended cements based on them, as a rule, have an increased water demand, bleeding, and are characterised by low early strength. It should also be noted that in the coming years a shortage of high-quality granulated blast furnace slag is expected in the cement industry. Some countries have limited resources of these components, which is why cement plants are making efforts to find new types of blended cements with high volume of SCMs. This determines the need for new combinations of SCMs, including those containing natural and industrial pozzolans.

The high dispersity of low-calcium fly ash and the appropriate chemical composition contribute to its widespread use in the cement industry as SCMs, but fly ash-containing cements are usually characterised by low early strength. The European Region has rich resources of natural pozzolanic material – zeolite tuffs, which can be a good solution to this problem. Using zeolite tuff as a partial replacement for Portland cement clinker leads to economic benefits and an increase of durability [5]. However, zeolite tuffs need more water to obtain a paste of the same consistency as for CEM I. Therefore, such an additive can adversely affect a number of mechanical properties of concrete, since the early strength of blended cements usually decreases. Investigation of mechanical properties of concretes incorporating natural zeolite has shown that the substitution of cement by zeolite results in some reduction of strength until 90 days of hardening, but after 180 days compressive strength of such concrete exceeds the strength of concrete without zeolite [6]. It should be noted that in this study the natural zeolite was characterised by bimodal PSD curve and dominating grain in the range of 90-2000 μm, with the largest share of particles of 300 μm. At the same time, using superfine zeolite is really promising, as it can increase the packing density, improve the workability and cohesion of the cement paste [7].

Rational usage of material and energy resources with a simultaneous decrease in the negative impact on the environment in construction is largely ensured by developing an approach based on the principles of constructing multicomponent cements [8, 9]. The synergistic effect of SCMs which exhibit various types of actions has a positive impact on the properties of blended cements compared to cements containing only one type of SCMs. Insignificant development of production of multicomponent binders with high volume of SCMs is associated with insufficient practical experience in the application of these cements in concrete technology [10]. The result of these efforts, according to the cement standard EN 197-1, is the wider introduction of composite cement CEM V/A and pozzolanic cement CEM IV/B, which are characterised by a significantly reduced amount of Portland clinker. Such eco-efficient blended cements will become an alternative for traditional, commonly used cements. This paper presents the results of research into blended cements containing high volume of supplementary cementitious materials, which confirm the relevance of further development of blended cements with low-CO_2 footprint.

2. Materials and methods of research

2.1. Materials

Commercially available Ordinary Portland cement (OPC) CEM I 42.5R, composed of C_3S: 62.42, C_2S: 13.62, C_3A: 7.06, C_4AF: 12.32, wt.%, was used as the reference cement in the investigation. Ground granulated blast furnace slag (GGBFS) Kryvyi Rih, (glassy phase – 80%), consisting of 92-96 wt.% 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 utilised as SCMs. 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 of 55.18% and 2.23% respectively was used. Limestone powder with 95 wt.% $CaCO_3$, 40.14 wt.% LOI was used as microfiller. Limestone powder belongs to the LL type according to the EN 197-1 in terms of total content of organic carbon. The chemical composition of the main components of the cement is presented in Tab. 1.

Table 1. The chemical composition of main constituents of cement. Source: own study

Components	Oxide content, wt.%							
	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	0.00	0.14

The Blaine specific surface area of OPC, GGBFS, FZ, SFZ, FA and LL is 3460; 4000, 6000, 12000, 4300 and 9600 cm^2/g respectively. The particle size distributions of OPC and SMCs are presented in Tab. 2. It can be seen that volume average diameter D[4;3] for OPC is 24.8 μm and for SCMs – 19.3...48.7 μm. The maximum of average diameter D[3;2] by the specific surface distribution for SFZ is 4.24 μm, for OPC – 5.21 μm and for other SCMs – 5.42...11.0 μm. It should be noted that superfine zeolite and limestone powder are characterised by a bimodal particle size distribution by volume.

Table 2. The granulometric composition of OPC and SCMs. Source: own study

Components	Ø <5 μm, %	Ø <10 μm, %	Ø <20 μm %	Ø <60 μm, %	D[3;2] μm	D[4;3] μm	Dv (10) μm	Dv (50) μm	Dv (90) μm
OPC	21.86	37.46	60.41	97.52	5.21	24.8	2.76	18.1	56.5
GGBFS	27.04	47.21	66.01	93.45	5.42	19.3	2.24	10.9	50.2
FZ	14.21	23.87	37.49	69.85	11.0	47.3	3.68	32.7	115.0
SFZ	34.58	48.86	68.79	90.67	4.24	21.2	1.53	11.2	55.6
FA	16.98	33.74	52.88	85.28	7.21	21.8	3.10	15.6	50.0
LL	25.71	35.72	45.15	65.79	7.08	48.7	2.29	28.7	128.0

Blends of OPC with GGBFS-SFZ-LL and OPC with SFZ-FA were prepared by mixing in a laboratory ball mill to produce CEM V/A and CEM IV/B cement types with high volume of SCMs according to EN 197-1.

2.2. Methods

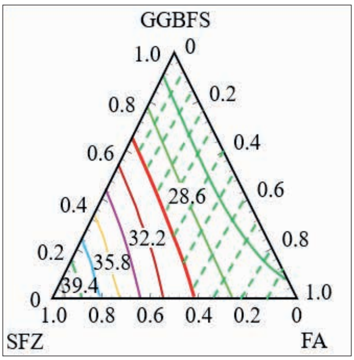
The study of fractional composition and grinding fineness of the cements was carried out by sieve analysis and by determination of the specific surface areas with the Blaine method. The Mastersizer 3000 uses the technique of laser diffraction to measure the particles size distribution by volume. At the same time, using the specially developed methodology [11], differential coefficient of particle size distribution by surface area, K_{isa}, was calculated. It is determined by the product A/V (the ratio of the surface area of the particles to their volume) for the content of each material fraction. This coefficient makes it possible to determine the degree of particles' additional active interphase surface. The phase composition of the resulting products was determined by X-ray powder diffraction. Scanning electron microscope Philips XL30 ESEM-FEG was used for studying morphology of the cement paste.

Determination of the workability of fresh cement mortars (consistence by flow table) was carried out according to EN 1015-3. Two samples of fresh mortar were investigated and the average value was determined, since the difference between them did not exceed 10%. The compressive strength data of the blended cements was determined on 40x40x160 mm mortar prisms after 2; 7; 28 and 90 days with water/cement ratio of 0.50 according to EN 196-1. Specimens were cured in moulds for 24 h in controlled temperature and humidity conditions. After extraction from moulds and labelling, the samples were placed in water for storage before testing.

The bleeding of cements was measured by the cylinder method and was determined according to the Ukrainian national standard DSTU B V. 2.7-186:2009. The evaluation of the pozzolanic activity of the SCMs was carried out by testing the ability of the mineral additive to absorb $Ca(OH)_2$ from its saturated solution. In this case, the criterion was the amount of absorbed $Ca(OH)_2$ (in mg) with 1 g of mineral additive.

3. Research results

For the development of blended cements, a complex assessment of the dispersion of mineral components and water demand was carried out. Ultrafine SCMs are characterised by a highly developed specific surface area that causes an increase of water demand. Water demand is particularly high for mineral additives of sedimentary origin (zeolite). For GGBFS and FA, water demand is 22 and 27% respectively; SFZ is characterised by the highest water demand – 55%. For limestone powder, water demand is 24%. As can be seen from Fig. 1, combinations of SCMs of various genesis and fineness, namely those that exhibit hydraulic action (blast furnace granulated slag), pozzolanic action (fly ash, superfine zeolite), and micro-filler (limestone powder), can ensure an acceptable level of water demand (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.



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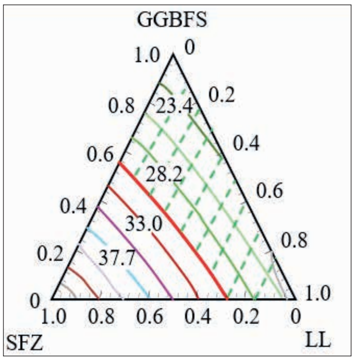


B

Fig. 1. The impact of additives on the water demand of SCMs blends in the GGBFS-SFZ-FA (a) and GGBFS-SFZ-LL (b) systems. Source: own study

The GGBFS and FA are characterised by high bleeding – after 120 minutes, bleeding coefficients (K_{vol}) are 27.1 and 39.7% respectively (Fig. 2). At the same time, FZ and SFZ are characterised 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 SCMs such as GGBFS, SFZ, FA and LL with different genesis and properties reduces bleeding of the blends (acceptable level of less than 18%).

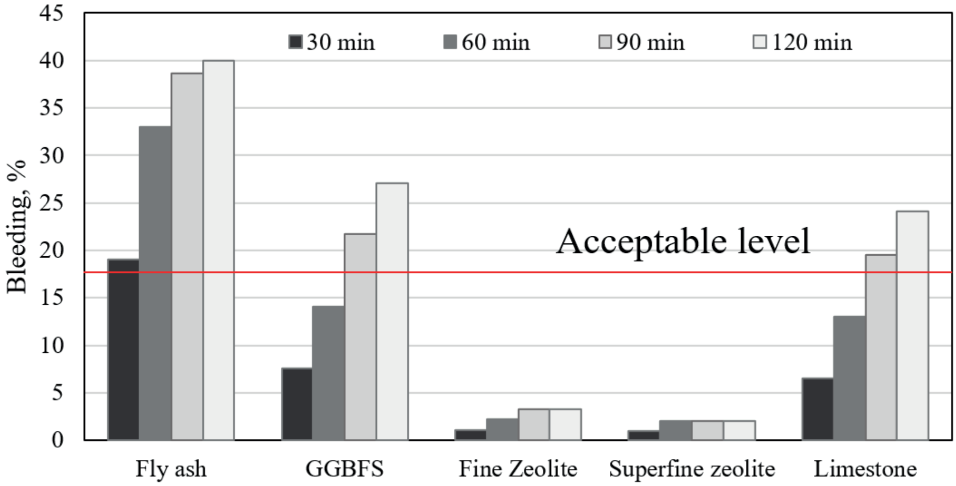


Fig. 2. The bleeding of SCMs. Source: own study

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

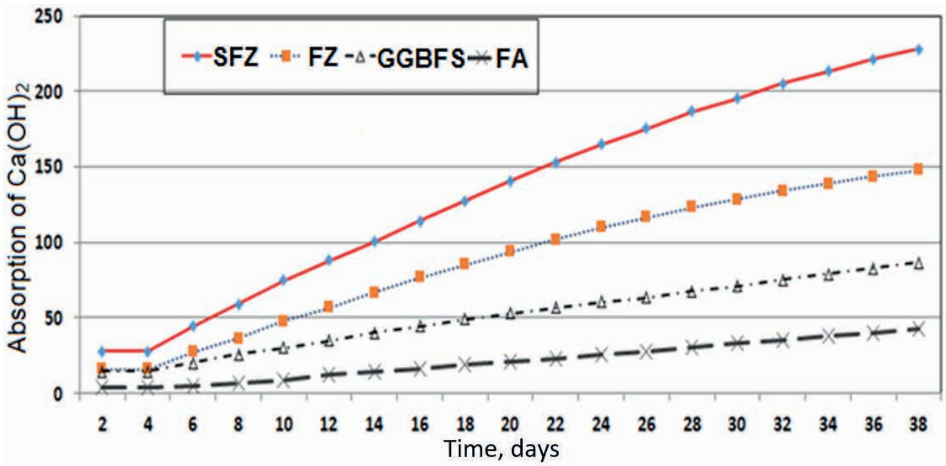


Fig. 3. The absorption kinetics of $Ca(OH)_2$ by SCMs. Source: own study

The impact of high volume of GGBFS, SFZ and LL additives on the physical and mechanical properties of blended cements was investigated. Results of the study into the consistency of fresh mortars determined by the flow table according to EN 1015-3 demonstrate (Fig. 4a) that an addition of SFZ significantly reduces the workability of blended cements, but limestone powder contributes to an increase in their workability. Compressive strength test results have shown (Fig. 4b) that the use of high volume of SCMs leads to a significant decrease in the strength of blended cements, especially at an early age.

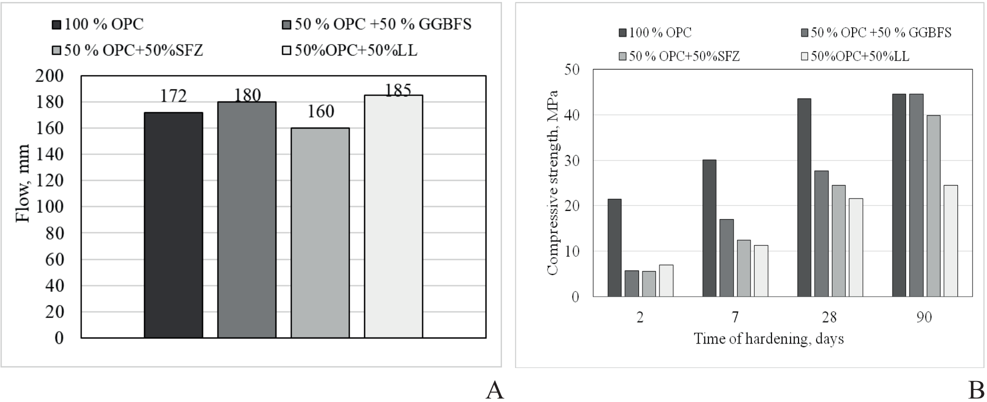
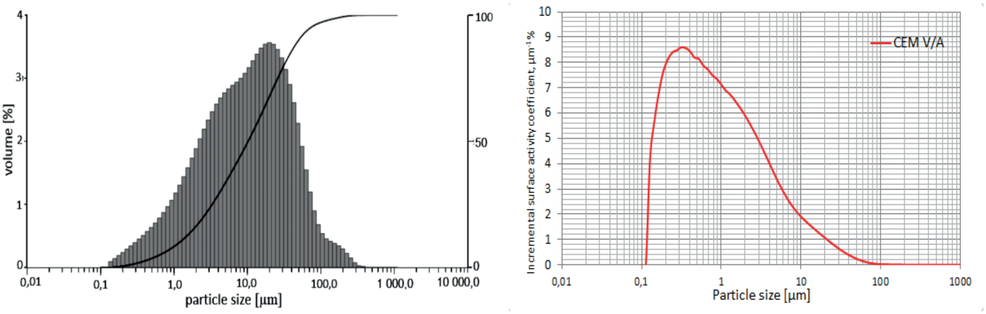


Fig. 4. The consistency of fresh mortars (a) and the compressive strength (b) of blended cements. Source: own study

The study of the influence of the ratio of the main components (GGBFS, SFZ and LL) on the properties of blended cements obtained by mixing 50 wt.% SCMs and 50 wt.% CEM I was carried out by the method of mathematical planning in accordance with the plan of a two-factor three-level experiment. Based on the isoparametric lines of SCMs' influence on the strength of multi-composite CEM V/A-type cements at 2 and 28 days, it was established that the optimal balance between non-clinker constituents is 25 wt.% GGBFS, 18 wt.% SFZ and 7 wt.% LL, with the compressive strength at 2 and 28 days amounting to 11.4 MPa and 38.5 MPa respectively. According to EN 197-1, this composition complies with CEM V/A 32.5.

In order to increase the effectiveness of quaternary composite cements CEM V/A, mechanical activation was performed in a vibration mill. According to the particle size distribution by volume of such mechanically activated composite cement (SSA=7210 cm^2/g) fractions Ø1; Ø5; Ø10 and Ø20 µm constitute respectively 8.05; 29.77; 43.73 and 63.24%, and the grain size d10; d50 and d90 corresponds to 2.05; 18.2 and 61.7 µm (Fig. 5a). To assess the contribution of individual particles to total specific surface area, particle size distributions by surface area were calculated and an incremental coefficient of surface area (K_{isa}) was suggested. The maximum value of K_{isa} (8.72 $\mu m^{-1}\cdot$vol.%) for composite cement was achieved for the fraction of 0.35 µm, and for the fraction of 5.0 µm this coefficient decreases by 2.9 times; with a further increase in particle size, it is significantly reduced (Fig. 5b).

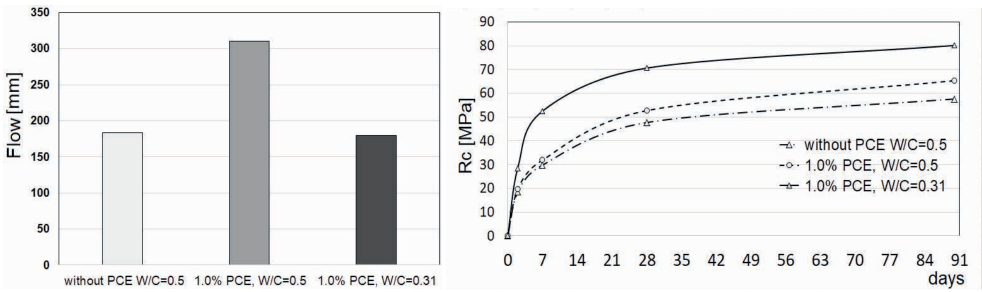
It is demonstrated that the superfine fraction of up to Ø =1.0 µm, despite its small content (V = 8.05%), makes a significant contribution (up to 50%) to the specific surface area of mechanically activated composite cement. Such quaternary composite cement is characterised by a significant reserve of excess surface energy, primarily due to ultrafine particles of superfine zeolite and limestone powder. The high level of excess surface energy of CEM V/A cement leads to an increase of its hydration rate at an early age of hardening.



A B

Fig. 5. The particle size distribution by volume (a) and surface area (b) of mechanically activated composite cement CEM V/A. Source: own study

As can be seen from Fig. 6, the flow of fresh mortar based on mechanically activated CEM V/A is 183 mm and the compressive strength of tested mortars after 2, 28 and 90 days of hardening is 17.5, 46.2 and 57.4 MPa respectively. Such composite cement corresponds to the class 42.5 of CEM V/A according to EN 197-1. Polycarboxylate ether superplasticizer PCE (1.0%) was added to obtain composite cements CEM V/A with improved properties. In this case, due to the addition of PCE, the flow of fresh mortar increased by 68% (technological effect). On the other hand, due to the reduction of water-cement ratio (ΔW/C = 38%), the strength after 2, 7, 28 and 90 days increased by 53, 76, 46 and 36%, respectively (technical effect). Thus, such a composite cement CEM V/A is characterised by high early strength and a significant increase in strength (over 70 MPa) after 28 days of hardening.



A B

Fig. 6. The influence of PCE on workability (a) and compressive strength (b) of CEM V/A. Source: own study

The phase composition of hydration products of the CEM V/A paste (W/C = 0.50) after 28 days of hardening is represented by ettringite (4.39 wt.%) and a small amount of portlandite (3.64 wt.%). Amorphous C-S-H phase content is 53.9 wt.%. According to the SEM data, the crystalline structures of ettringite, calcium hydroaluminates, portlandite and calcium hydrosilicates form a dense structure of cement paste (Fig. 7). The use of pozzolanic additives with high pozzolanic activity promotes fuller binding of calcium hydroxide in calcium hydrosilicates and significantly affects the ultimate compressive strength, permeability and chemical durability of composite cements. Using superfine zeolite is needed to enhance the hydrolysing ability of the zeolite mineral – clinoptilolite. The increased pH value and the transition to the liquid phase of Na^+ ions create the necessary conditions for the alkaline activation of blast furnace granulated slag as part of modified composite cement, which allows for achieving the required early and standard strength.

A synergetic combination of superfine zeolite as a highly reactive natural pozzolan and limestone powder as a microfiller in composite cement CEM V/A 42.5 ensures the formation of dense microstructure of paste and increases its strength. In addition to the environmental benefits generated by the use of high content of SCMs as a substitute for cement, the obtained results reveal a significant long-term improvement in strength properties and durability performance of composite cements. Superfine zeolite, which is characterised by high surface area, contributes to the intensification of the processes of structure formation in the early period of hydration.

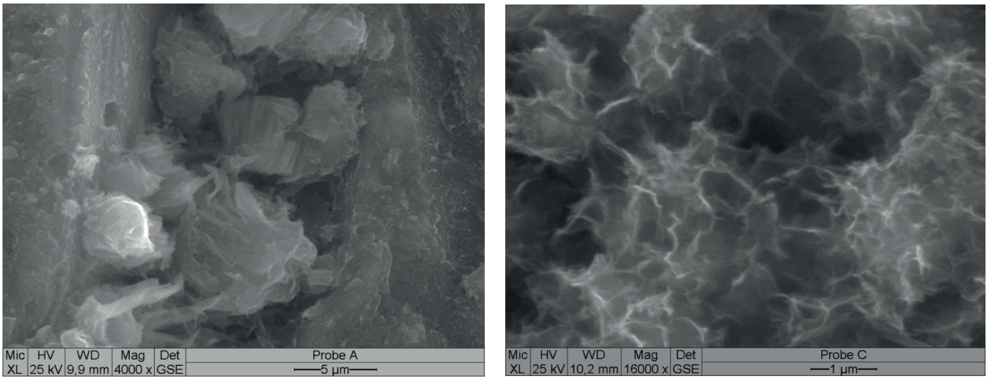


Fig. 7. SEM images of paste based on composite cement CEM V/A 42.5 after 28 days of hardening. Source: own study

High value of SFZ pozzolanic activity in the form of absorption of CaO and $CaSO_4$ results in the intensive binding of $Ca(OH)_2$ into calcium hydrosilicates and hydrosulfoaluminates. The surface of limestone particles provides excellent conditions for the nucleation and growth of nanodispersed C-S-H(I) gel, which causes a higher total volume of hydrates and lower porosity whereby higher compressive strength is reached. The clinker factor decreased to 0.50 in CEM V/A reduces the CO_2 emission in the cement production process by 50% per 1 tonne of cement.

Note that for regions deficient in GGBFS, an effective solution to reducing the clinker factor of blended cement is the production of pozzolanic cement CEM IV/B, containing blends of different types of pozzolans such as superfine zeolite and siliceous fly ash. In this case, SFZ has the decisive influence on bleeding and reactivity, while FA decreases water demand due to its spherical particles, as this increases the mobility of the mixture ("roller bearing effect"). On the other hand, a combination of natural (SFZ) and industrial (FA) pozzolans with opposite properties regarding water demand and bleeding makes it possible to improve the workability of the mixtures based on pozzolanic cement CEM IV/B [12, 13].

It is noteworthy that the compressive strength of the ternary pozzolanic cement CEM IV/B (50 wt.% CEM I 42.5 R; 27 wt.% SZ, 23 wt.% FA) exceeded the strength of slag cement

CEM III/A. At the age of hardening, the difference in strength between CEM IV/B and ordinary Portland cement CEM I decreased and the strength activity index of CEM IV/B became higher after 90 days. Power consumption for grinding CEM IV/B is reduced to 31 kWh. The carbon footprint of the products of CEM IV/B is 458 kg of CO_2 per 1 tonne of cement, which is 47% less than in the case of ordinary Portland cement CEM I 42.5 [3, 14].

4. Conclusions

Eco-efficient blended cements with high volume of SCMs are an optimal solution to the problem of improving the energy saving of cement production. The strategy of such development involves combining highly reactive SCMs of different fineness and genesis and with hydraulic and pozzolanic properties with micro-fillers. This helps to reduce the clinker factor. This approach also involves technological optimisation of cement properties (workability, standard and early strength, durability, cost, environmental impact).

Innovative binders (clinker factor – 0.50) which have a combination of the above-mentioned properties are quaternary composite cements CEM V/A, containing granulated blast furnace slag, superfine zeolite and limestone powder, and ternary pozzolanic cement CEM IV/B, containing superfine zeolite and fly ash. The production of eco-efficient blended cements with high volume of SCMs of different genesis and fineness meets the principles of the strategy of sustainable development and is a practical solution to the problem of reducing costs, power consumption and CO_2 emissions in the construction industry.

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