

Tetiana KROPYVNYTSKA¹
Myroslav SANYTSKY²
Iryna GEVIUK³

PROPERTIES OF PORTLAND-COMPOSITE CEMENTS WITH ZEOLITE TUFF

Growing requirements for protection of the environment every year gradually increase production of cements with a high content of mineral additives and clinker cements should be considered as cements for special purposes. The strong development of a quaternary Portland cement composite system containing blast-furnace slag, zeolite tuff and limestone powder is presented. The composition and particle size distribution of the constituents are optimized by the incremental coefficient of the surface activity of the zeolite-containing Portland composite cements. Zeolite tuff and limestone powder of high specific surface area lead to the increase of the surface activity of the entire system and a corresponding improvement in the performance of the cement. It was shown that low-energy Portland-composite cements “green cements” obtained by separate grinding are characterized by higher early compressive strength. The optimization of Portland-composite cements was carried out and the relationship between the phase composition, microstructure and strength of the cement matrix were investigated. The main role of zeolite is to improve the properties of cement stone by reducing the quantity and size of hydrate calcium hydroxide with increasing of low alkali calcium hydrosilicates. It is shown that a synergistic combination of mineral additives of different groups with substantial reduction of high energy-consumption clinker component in the Portland-composite cements allows to improve rheological properties and provides of strength increase of binder.

Keywords: Portland-composite cement, zeolite tuff, particle size distribution, compressive strength, properties

1. Introduction

The basic principles of the sustainable development strategy in the cement industry, providing optimum using of non-renewable natural raw materials, application of energy saving technologies, utilization of industrial wastes as well

¹ Corresponding author: Tetiana Kropyvnytska, Lviv Polytechnic National University, 12 S. Bandera str., 79013 Lviv, Ukraine, e-mail: tkropyvnytska@ukr.net

² Myroslav Sanytsky, Lviv Polytechnic National University, 12 S. Bandera str., 79013 Lviv, Ukraine, e-mail: msanytsky@ukr.net

³ Iryna Geviuk, JSC “Ivano-Frankivsk Cement”, e-mail: irynageviuk@ukr.net

as comprehensive environmental protection and reduction of CO₂ emissions. Large-scale production of efficient composite eco cements ensures the implementation of the cement industry of progressive models of rational use of natural raw materials, fuel, electricity with minimal greenhouse gas emissions, but also allows to implement cleaner production practices [1, 2].

The main problem for process engineering of composite cements is to prepare and mix suitable combinations of clinker and interground additives so that the performance lies in the same range as comparable Portland cements. Most cement plants use granulated blast furnace slag and fly ash as a mineral additives and limestone as microfiller. These various blended cements, especially the ternary and quaternary, were optimized with a synergistic effect, allowing component ingredients to compensate for any mutual shortcomings [3]. At the same time an excellent supplementary cementitious material is a type of natural pozzolanic material – zeolite tuff. They have unique characteristics such as high specific surface area and cation exchange capacity. Like other pozzolanic materials, the replacement of cement by natural zeolite tuff can improve the mechanical properties of cement and concrete composites. The exploitation of natural zeolite tuff, when used as a partial replacement for cement, can lead to a considerable economic benefit and durability [4, 5]. Principles governing the properties of such multi-component quaternary composite cements are examined and some results are discussed in this article.

The purpose of 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.

2. Materials and methods

Ordinary Portland cement CEM I 42,5R JSC "Ivano-Frankivsk Cement" composed of C₃S: 62.42, C₂S: 13.62, C₃A: 7.06, C₄AF: 12.32, mass. %, was used in the investigation. Limestone powder with 95 mass. % CaCO₃ was used as micro-filler. Grain granulated blast furnace slag (GGBFS) consisting of 92-96 mass. % CaO + SiO₂ + Al₂O₃ + Fe₂O₃ and zeolitic tuff with 70-73 mass.% SiO₂ provided from Sokyrnytsky quarry were utilized as mineral additives. Portland-composite cements were obtained by mixing of CEM I 42,5R, GGBFS, zeolite tuff and limestone powder. The chemical analysis of materials are presented in Figure 1.

Grain size of particles was measured by laser granulometr Mastersizer 3000. The coefficient of incremental surface activity K_{isa} , which shows the influence of particle content in total volume was calculated by the product of surface activity coefficient and incremental volume of each fraction [6].

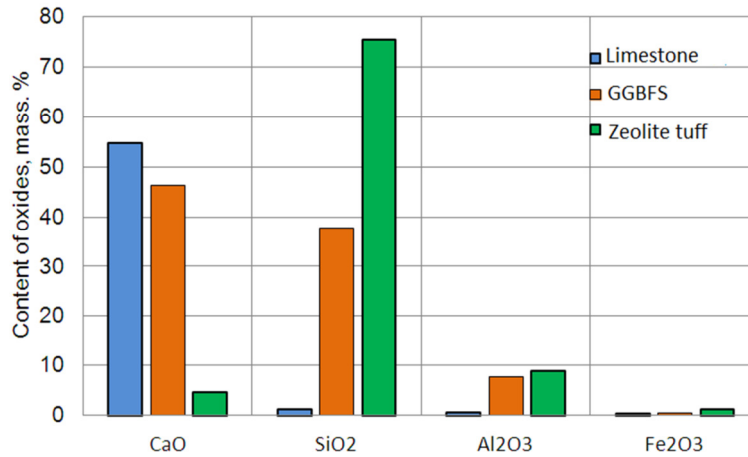


Fig. 1. Chemical analysis of additives

The phase composition of the resulting products was determined by X-ray powder diffraction: patterns were recorded at room temperature with Co K α radiation on a PANalytical X'pert Pro diffractometer equipped with the X'celerator detector in the 2θ range from 5° to 70° (step 0.033° , time/step 50s). Scanning electron microscope was used for studying the crystals and morphology of the cement stone surface. The evaluation of the properties of Portland-composite cement was carried out through a flowing and compressive strength tests.

The compressive strength data of the multi-component cements was determined on $40 \times 40 \times 160$ mm mortar prisms with water/cement ratio of 0.50 according to EN 196-1. Determination the workability of fresh cement mortars (consistence by flow table) was carried according to EN 1015-3. The mortars with weight ratio of cement to sand 1:3 were manufactured with constant W/C = 0.5 for sulphate and magnesia resistance tests. Mortar specimens of size $40 \times 40 \times 160$ mm were cured 24 hours in a climate air. After remoulding the specimens were kept 27 days in water, and then either in water (reference) or sodiums sulphate solution (10.0 mg SO_4^{2-} per litre) and magnesium chloride (10.0 mg Mg^{2+} per litre) for 365 days, respectively.

3. Results and discussion

Particle size distribution of cementitious materials used to produce composite cements was studied. The Blaine specific surface areas of CEM I 42,5R, GGBFS, zeolitic tuff and limestone powder were 3,960; 4,600, 12,000 and 10,060 cm^2/g . The particle size distribution of CEM I, the grain granulated blast furnace slag, the zeolitic tuff and of the limestone powder are presented in Figure 2.

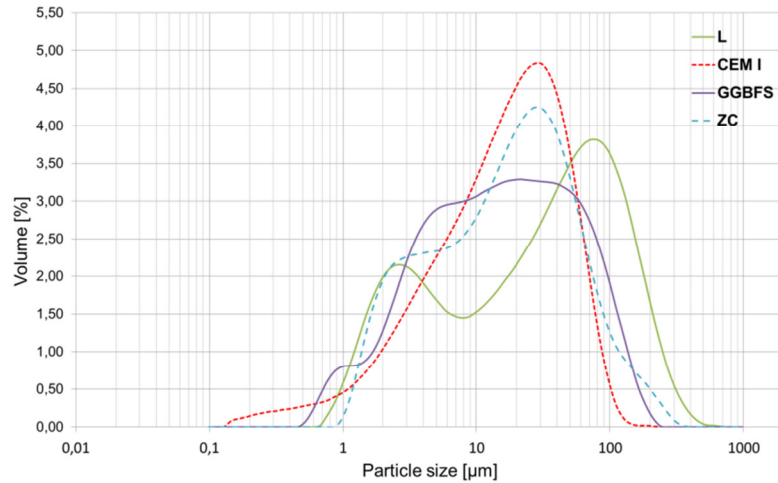
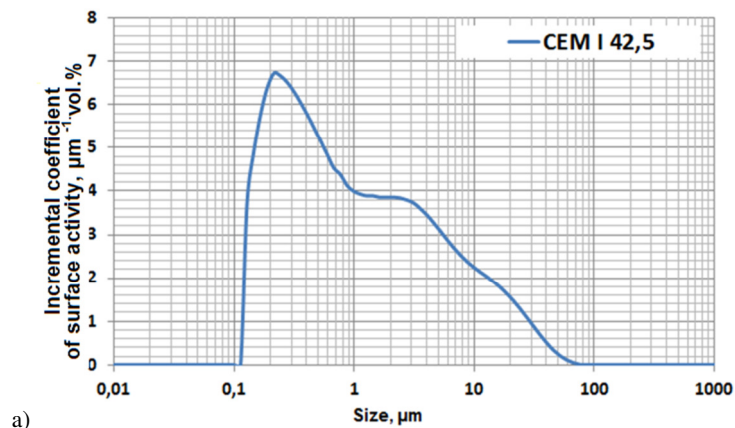


Fig. 2. Particle size distribution of the main constituents

On the differential curve of the particle distribution, the maximum for CEM I is $6.84 \mu\text{m}$, and for GGBFS, zeolite tuff and limestone powder – 3.35 , 4.38 and $3.96 \mu\text{m}$ accordingly. The volume mean diameter $D[4;3]$ for CEM I corresponds to $17.7 \mu\text{m}$, and for the mineral additives in the range of 28.6 to $71.9 \mu\text{m}$. Furthermore the surface area mean diameter $D[3;2]$ for CEM I shows a value of $3.79 \mu\text{m}$, those of the mineral additives lay in the range of 4.62 to $6.66 \mu\text{m}$. The maximum value for CEM I shown on the differential curve of the particle distribution, is $6.84 \mu\text{m}$; GGBFS, zeolitic tuff and limestone powder show maxima at 3.35 , 4.38 and $3.96 \mu\text{m}$ respectively (Figure 3). This indicates that the fine fraction determines the surface area of particles of the cementitious systems.



a)

Fig. 3. The surface distribution of CEM I 42,5 (a), GGBFS (b), zeolite tuff (c) and limestone powder (d)

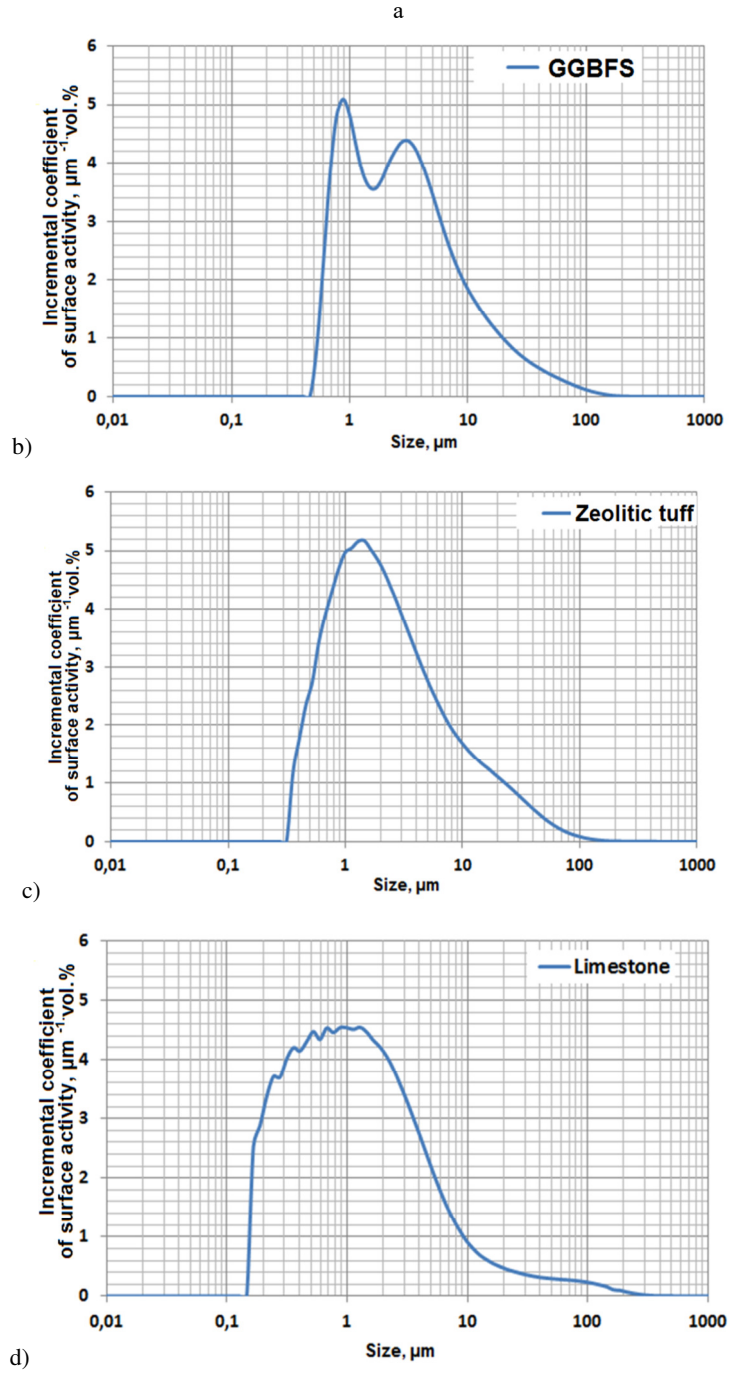


Fig. 3 (cont.). The surface distribution of CEM I 42,5 (a), GGBFS (b), zeolite tuff (c) and limestone powder (d)

Portland-composite cements obtained by mixing of Portland cement CEM I 42,5R, zeolite tuff and limestone powder in different proportions. According to the particle size distribution of Portland-composite cement ($SSA=4,250 \text{ cm}^2/\text{g}$) fraction $\emptyset 1, \emptyset 5, \emptyset 10, \emptyset 20$ and $\emptyset 60 \mu\text{m}$ are respectively 4.75, 18.58, 31.62 and 85.56%, and the grain size D_{10}, D_{50} and D_{90} corresponds to 2.13, 20.5 and $69.7 \mu\text{m}$ (Figure 4a). The maximum value of K_{isa} ($6.45 \text{ m}^{-1}\cdot\text{vol.}\%$) of CEM II/B-M(S-P-L) 32,5R achieved for a fraction $0.354 \mu\text{m}$, and for a fraction of $5 \mu\text{m}$ this coefficient decreases 2.3 times and with further particle size increasing is significantly reduced (Figure 4b).

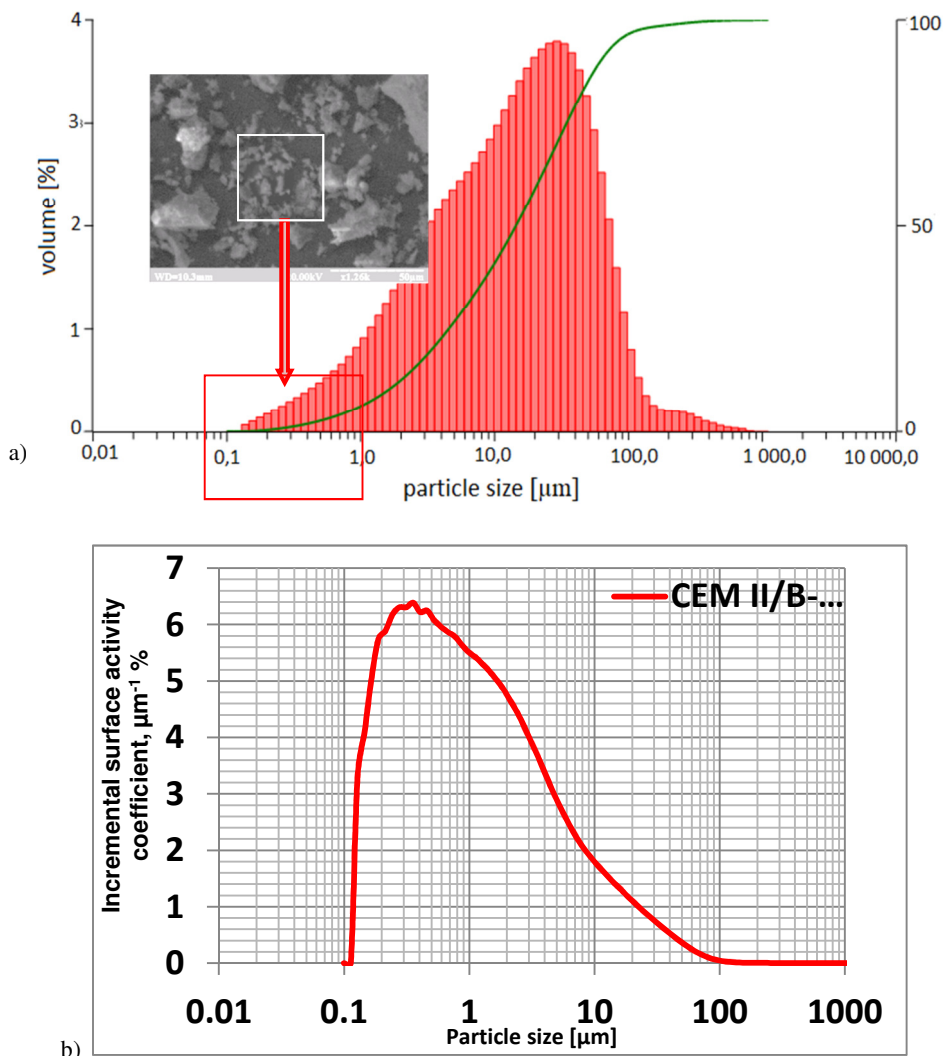


Fig. 4. Particle size distribution (a) and coefficient of incremental surface activity K_{isa} (b) of Portland-composite cement CEM II/B-M(S-P-L) 32,5R

Isoparameter lines of influence of zeolite tuff and limestone powder concentration after 28-days and 90-days mortars strength in quaternary Portland-composite cements is shown in Figure 5. From these diagrams, the optimal balance between non-clinker constituents that realize the workability more than 190 mm flow and 28-days compressive strength greater than 38.2 MPa is 17.5 mass.% GGBFS, 10.0 mass.% zeolite tuff and 7.5 mass.% limestone powder.

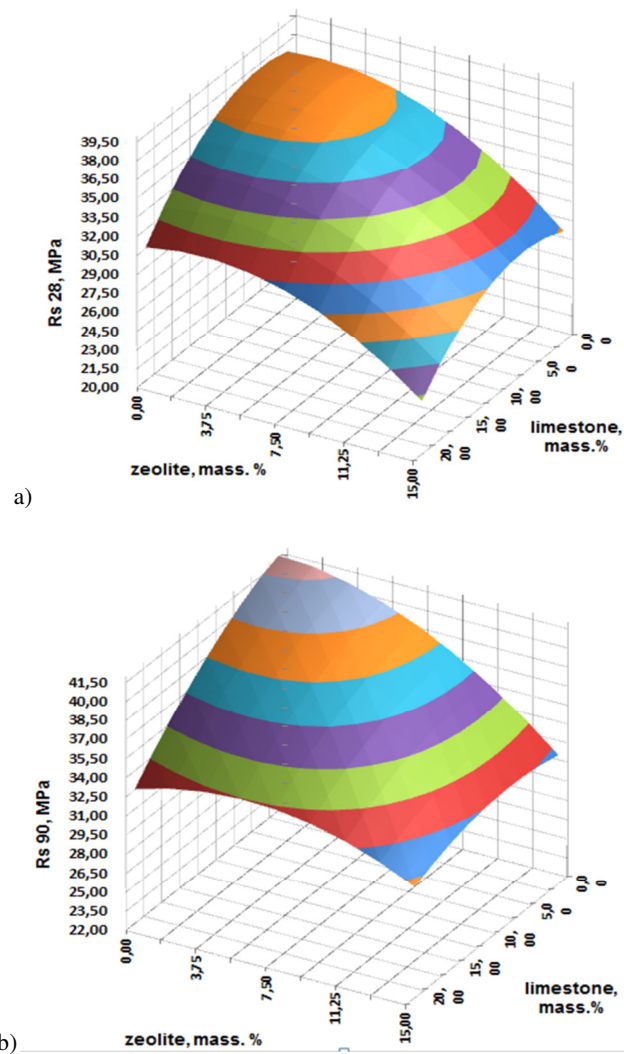


Fig. 5. The isoparametric lines of 28-days (a) and 90-days (b) compressive strength of Portland-composite cement CEM II/B-M

For purpose of comparison, the X-ray diffraction lines of calcite at $d/n=0.303$, 0.249 nm, of the calcium hydroxide at $d/n=0.490$, 0.263 nm and of ettringite at $d/n=0.973$, 0.561 nm were chosen to follow up the variation in their intensities in the paste of the quaternary components mixed with a water/cement ratio of 0.4 and cured for 28 days (Figure 6). It was found that the intensity of the d-value lines of the calcium hydroxide is lower than those of the reference paste made of CEM I by around two folds. This is explained by the pozzolanic reactivity of the clinoptilolite present in the zeolite tuff used which promotes the binding of calcium hydroxide and form calcium silicate hydrates. Active forms of SiO_2 and Al_2O_3 in the composition of aluminum-containing pozzolana promote better binding of calcium hydroxide into low-basic calcium hydrosilicates, which indicates that the acceleration of pozzolanic reaction. This in turn affects the ultimate compressive strength, the permeability and chemical durability of quaternary zeolite-containing Portland-composite cements significantly.

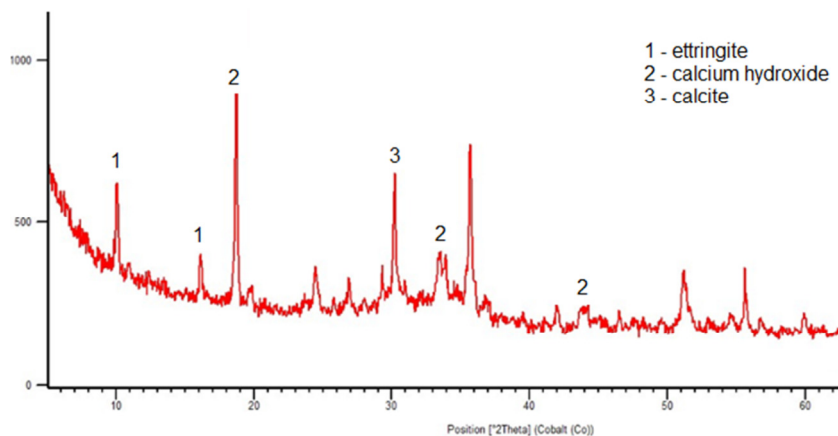


Fig. 6. X-ray diffraction lines of Portland-composite cement CEM II/B-M(S-P-L) 32,5R after 28 days of hardening

The dense structure of the hydrated solid phase is provided by AF_m - i AF_l - phases into gel-like C-S-H phase (Figure 7a). The use natural zeolite material containing clinoptilolite 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 quaternary zeolite-containing Portland-composite cements. According to EDX (Figure 7, b), the relative content of elements in interpore space in the sample of cement paste meets ettringite crystals. Fine particles of carbonate due to the effect of "fine powder" and chemical interaction with the products of hydration of alumo-containing phases with the formation of structurally active hexagonal AF_m -phases promote the synthesis of cement paste strength.

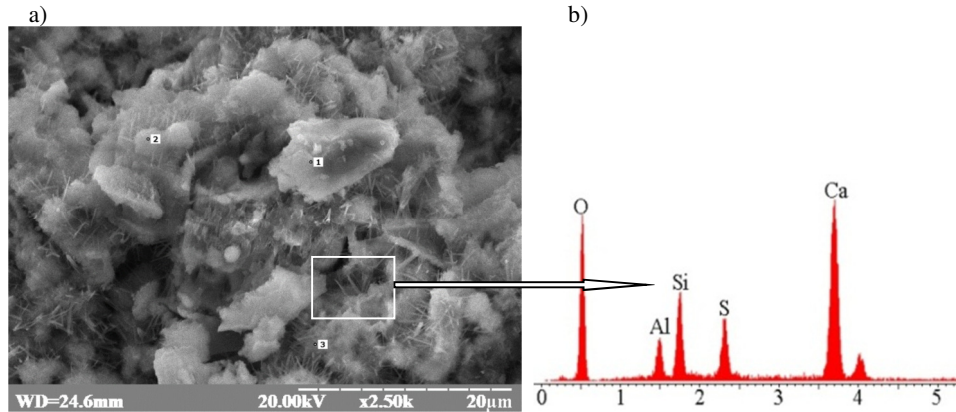


Fig. 7. SEM images (a) and EDX spectrum (b) of paste based on Portland-composite cement CEM II/B-M(S-P-L) 32,5R after 28 days of hardening

The research results of construction and technical properties of Portland-composite cement with zeolite tuff CEM II/B-M(S-P-L) 32,5R in Table 1. The optimum particle size distribution of the finely ground zeolite tuff and limestone powder provided high early strength of the quaternary Portland-composite cement CEM II/B-M(S-P-L) 32,5R. This cement was characterized by a high-water retention capacity of 98.9%, a homogeneity and a stability of the mix without sedimentation; the bleeding of Portland-composite cement paste is 15.2%. Furthermore, the GGBFS and zeolite tuff, as well the reduced CaO content suggested the improved chemical resistance to aggressive natural waters and soils. Non-clinker constituents GGBFS and zeolite tuff after 365 days provide higher resistance into aggressive sulfate $R_{\text{sulphate}}/R_{\text{water}}=1.04$ and magnesia $R_{\text{magnesia}}/R_{\text{water}}=1.01$ environments. The lowering clinker factor ratio in CEM II/B-M (S-P-L) 32,5R reduces the CO₂ discharge in the cement production process 1.46 times/ 1 ton cement.

Table 1. Properties of Portland-composite cement CEM II/B-M(S-P-L) 32,5R

Property	Results
Loss on ignition, %	1.17
Sulfate content (as SO ₃), %	2.55
Water demand, %	29.0
High-water retention capacity, %	98.9
Bleeding, %	15.2
Segregation, %	3.9
Heat of hydration after 168 h, J/g	285
Sulphate resistance after 365 days	1.04
Magnesia resistance after 365 days	1.01

4. Conclusion

The rheological properties of the strength development of Portland-composite cement CEM II/B-M improve and its density increase due to the following factors: 1) the optimization of the particle size distribution of the constituents using the values of incremental coefficient of surface activity, 2) the effect of the hydraulic properties of the GGBFS combined with the pozzolanic action of the zeolite tuff, 3) the filling effect of the finely dispersed limestone powder, 4) the reduction in the clinker factor. Based on the results obtained, high quality quaternary zeolite-containing Portland-composite cements can be produced which advantage is to lower the energy consumption and CO₂ emission and the indication of a better sustainability.

References

- [1] Schneider M., Romer M., Tschudin M., Bolio H. Sustainable cement production present and future. *Cement and Concrete Research*, Vol. 41, 7, p. 642–650, 2011.
- [2] Sanytsky M., Kruts T., Kropyvnytska T., Rusyn B. Sustainable Green Engineered Composites Containing Ultrafine Supplementary Cementitious Materials. 14th International Congress on the Chemistry of Cement (ICCC 2015), Beijing, China, 1, p. 265.
- [3] Muller M., Ludvig H-M., Ben Haha M., Zajac M. Optimization of multi-component cements containing cement clinker, slag, V-fly ash, limestone. 19th Internationale Baustofftagung, 2015, Weimar, Germany, 1, p. 449–456.
- [4] Smrčková E., Bačuvčík M., Janotka I. Basic Characteristics of Green Cements of CEM V/A and V/B Kind. *Advanced Materials Research*, Vol. 897, p. 196–199, 2014.
- [5] Snellings R., Mertens G., Elsen J. Evaluation of the Pozzolanic Activity of Natural Zeolite Tuffs. 14th International Congress on the Chemistry of Cement (ICCC 2015), Beijing, China.
- [6] Kryvenko P., Sanytsky M., Kropyvnytska T., Kotiv R. Decorative multi-component alkali activated cements for restoration and finishing works. *Advanced Materials Research*, Vol. 897, p. 45–48, 2014.

Przesłano do redakcji: 24.11.2017 r.

Przyjęto do druku: 25.09.2018 r.