*Проведеними дослідженнями встановлено вплив різних видів цементозаміщуючих матеріалів на фізико-механічні властивості та структуроутворення низькоемісійних багатокомпонентних цементів. Отримано результати гранулометричного складу основних складників багатокомпонентних цементів та проведена комплексна оцінка розподілу їх частинок за розмірами відносно об'єму та питомої поверхні. Доведено, що збільшення дисперсності цементозаміщуючих матеріалів призводить до зниження їх водовідділення та зростання активності, проте при цьому збільшується водопотреба, а також підвищуються енергозатрати на механічну активацію. Проведено порівняння ефективності механічної активації неклінкерних основних складників різної природи активності.*

*Експериментальними дослідженнями підтверджено, що вирішення проблеми підвищення гідравлічної активності гранульованих доменних шлаків досягається за рахунок зростання вмісту фракції до 10 мкм. Разом з тим, при одержанні високоактивних гранульованих доменних шлаків суттєво зростають енергозатрати на розмелення, особливо в кульових млинах. Слід відзначити, що в найближчі роки в цементній промисловості передбачається дефіцит якісних шлаків. Це визначає необхідність пошуку нових комбінацій цементозаміщуючих матеріалів, а саме природних цеолітів і золи-винесення, що характеризуються високими пуцолановими властивостями. Проведеними дослідженнями часткової та повної заміни гранульованих доменних шлаків у складі низькоемісійних цементів з показником клінкер-фактору 0,50 встановлено, що за рахунок оптимізації гранулометричного складу пуцоланових добавок забезпечуються необхідні показники ранньої та стандартної міцностей. При цьому з віком тверднення міцність в'яжучого суттєво зростає і через 90 діб перевищує стандартну міцність на 30 %. Це дозволяє стверджувати, що внаслідок пуцоланової реакції між високодисперсним цеолітом, золою-винесення та гідроксидом кальцію стимулюються процеси утворення гідратних фаз у міжзерновому просторі та відбувається ущільнення мікроструктури цементуючої матриці. Показано, що при використанні низькоемісіних багатокомпонентних цементів, модифікованих суперпластифікаторами полікарбоксилатного типу, забезпечуються технологічний, технічний, економічний та екологічний ефекти.*

*Таким чином, є підстави стверджувати про доцільність одержання клінкер-ефективних низькоемісійних багатокомпонентних цементів шляхом оптимізації гранулометричного складу цементозаміщуючих матеріалів різних видів з метою зменшення енергозатрат у технологічних процесах їх виробництва*

*Ключові слова: багатокомпонентні низькоемісійні цементи, цементозаміщуючі матеріали, гранульований доменний шлак, суперцеоліт, зола-винесення, клінкер-фактор*

UDC 666.94
DOI: 10.15587/1729-4061.2019.175472

# STUDY OF LOW-EMISSION MULTI-COMPONENT CEMENTS WITH A HIGH CONTENT OF SUPPLEMENTARY CEMENTITIOUS MATERIALS

**H. Ivashchyshyn**
Postgraduate Student*
E-mail: aiwaszczyszyn@gmail.com

**M. Sanytsky**
Doctor of Technical Sciences, Professor, Head of Department*
E-mail: msanytsky@ukr.net

**T. Kropyvnytska**
PhD, Associate Professor*
E-mail: tkropyvnytska@ukr.net

**B. Rusyn**
PhD, Assistant*
E-mail: brusyn@ukr.net

*Department of Building Production
Lviv Polytechnic National University
S. Bandery str., 12, Lviv, Ukraine, 79013

*Received date 18.06.2019*
*Accepted date 22.07.2019*
*Published date 30.08.2019*



## 1. Introduction

Implementation of the concept of low-carbon development is an important component of strategic goals of the global economy. Cement industry has made significant progress in terms of production efficiency and technological processes. However, level of environmental pollution caused by cement production is steadily rising. It amounts to 2.34 Gt $CO_2$/year, which relates to the current accelerating pace of construction in the world [1, 2]. One of the most effective methods of reducing $CO_2$ emissions in this sector consists in reduction of the clinker factor by means of a wider use of supplementary cementitious materials (SCMs) [3, 4]. This practice also contributes to reduction of concrete price, raises its strength at later age of hardening and durability. At the same time, with introduction of SCMs, slowdown of strength gain kinetics is observed in the products based on blended cements [5].

According to EN 197-1:2015, main components of the conventional cement family include additives of natural and technogenic origin having a hydraulic effect (granulated blast-furnace slag) and pozzolanic effect (zeolites and fly ash). Typically, SCMs contain reactive silicon dioxide and aluminum oxide which react with calcium hydroxide, and as a result, hydrosilicates and calcium hydroaluminates are formed. According to [6], granulated blast-furnace slag (GBFS) and fly ash (FA) are the most common supplementary cementitious materials of technogenic origin (487 and 225 Mt/year) and their use in the today's cement industry amounts 13.0 and 6.0 %, respectively. Natural pozzolans as supplementary cementitious materials have also found a wide use (75 Mt/year) and their reserve remains high enough [7]. According to EN 197-1:2015, level of clinker replacement and combination of various types of major components determine cement type. Cements CEM III/A, B, C containing of 36–95 wt. % granulated blast-furnace slag and CEM IV/B containing 36–55 wt. % pozzolanic additives can be defined as low-emission cements. Composite cements CEM V/A, B require a combination of supplementary cementitious materials having hydraulic and pozzolanic properties as high as 36–80 wt. %.

The technology of production of low-emission multi-component cements involves separate grinding or intergrinding of main components and blending of Ordinary Portland cement CEM I and SCMs of various types. In-depth interpretation of role of supplementary cementitious materials and their synergistic interaction contributes to the most effective realization of potential binding properties of low-emission multi-component cements. Advantages of such cement systems include high level of energy saving and low $CO_2$ emissions in their production combined with higher durability of concretes based on them. However, the degree of replacement with mineral additives is limited in multi-component cements because of a slow growth of their early strength caused by low reactivity of such components as compared to the clinker phases. In order to overcome these shortcomings and increase activity of main components, various approaches have been developed to create new types of low-emission cements. Significant acceleration of hardening of cement systems can be achieved by nanomodification and alkaline activation [8–11]. The reduced clinker factor of multi-component cements determines low heat of hydration of concrete which ensures their effective application in massive structures. Large content of highly active SCMs in composition of low-emission multi-component cements enables obtaining of corrosion-resistant concretes. Such concretes can be used in hydrotechnical and reclamation facilities exposed to various aggressive environment and in building structures with special requirements (pressure concrete pipes, etc.) [12, 13].

Considering the necessity of realizing main goals of the low-carbon development strategy, it is important that the studies aimed at determining the SCMs effect on physical and mechanical properties of low-emission multi-component cements with a clinker factor reduced to 0.50 were considered topical. Development of such cements makes it possible to create progressive models of rational use of natural raw materials, fuels and electric power, recycle production wastes and reduce greenhouse gas emissions. This approach addresses a series of important environmental, economic and social problems.

## 2. Literature review and problem statement

The results of studies [14] show that slag cements are characterized by low heat of hydration, resistance to corrosive chemical media, high water resistance of concrete and less shrinkage deformations compared to Portland cement of type I. However, there are unresolved issues related to slow kinetics of strength gain, substantial bleeding, concrete peeling caused by alternating freezing and thawing when using cements with a high GBFS content. This can be explained by low reactivity of GBFS ground in ball mills. This problem can be solved by raising the GBFS grinding fineness in more efficient grinding units.

This approach was used in [15] to improve technical properties of slag cements by increasing content of fine (up to 10 μm) fraction. Fine-dispersed particles of GBFS in such cements accelerate early hydration resulting in acceleration of the strength gain kinetics compared to similar cement compositions with a smaller content of fine GBFS fraction. At the same time, dense glassy structure and, as a consequence, increased abrasiveness of GBFS bring about a significant growth of power input during grinding at ball mills. For example, when doing GBFS dispersion higher, power inputs in grinding get higher compared to the Portland cement clinker. Natural pozzolans (zeolites) feature a high grindability and 2.5–3.0 times lower (compared to GBFS) power consumption in improvement of their efficiency. However, the increased amount of natural zeolite may cause a decrease in early strength of cements [16]. Pozzolanic activity of natural zeolites grows due to the increase in grinding fineness while bleeding drops. That is why cements containing highly dispersed zeolites are characterized by high water retentivity. Due to their microcellular framework structure, water demand of zeolites is higher than that of Portland cement CEM I. It should be noted that clinoptilolite mineral $(Na, Ca, K)_{2\text{-}3}Al_3(Al, Si)_2Si_{13}O_{36}\cdot 12H_2O$ is the main component of natural zeolite. Due to the ion-exchange products of such aqueous aluminosilicate of alkali metals from the group of zeolites, pH of the medium gets higher, that is, alkaline activation of the aluminosilicate component of SCMs is ensured [17].

Effectiveness of improving dispersity of artificial and natural pozzolans was confirmed by development of superfine active mineral additives belonging to super-pozzolans and providing accelerated bonding of calcium hydroxide being the product of hydrolysis of the alite phase of the Portland cement clinker. This interaction of super-pozzolans with the products of hydration of the Portland cement clinker leads to a decrease in porosity which helps to increase strength and corrosion resistance of concrete and determines its durability [18].

The high degree of dispersity of low-calcium fly ash and the appropriate chemical composition contribute to its widespread use in the cement industry as a SCMs. However, fly ash-containing cements are usually characterized by low early strength. On the other hand, fly ash causes a decrease in water demand of multi-component cements due to its spherical particles as this increases the mobility of the mixture ("roller bearing effect") [19].

Recently, shortage of granulated blast-furnace slag is observed in EU countries. In the future, fly ash from thermal power plants will also become scarce due to the transition to renewable energy sources. As was noted by the authors of [20], from a technical point of view, production and consumption of multi-component cements with a reduced content of Portland cement clinker is an alternative to one-component Portland cements. At the same time, as concerns GBFS and Portland cement clinker, the grindability coefficient which expresses growth of specific surface area in grinding is 10…12 and 15…20 $cm^2/(g·s)$, respectively, whereas 55…65 $cm^2/(g·s)$ for zeolite [21]. Therefore, in the case of intergrinding, soft materials are concentrated in the fine fraction while clinker and GBFS are concentrated in a coarser fraction. In this case, the SCMs fractions having higher reactivity are more conducive to growth of early strength of cements. Feasibility of using low-emission multi-component cements is determined by availability of their further upgrading to more efficient systems. It mainly depends on quantitative ratio of SCMs, their grinding fineness, ratio of dispersion of particles and uniformity of their distribution in the powder. Effectiveness of use of pozzolans based on natural zeolites was proved in [22, 23], however, combination of zeolite and fly ash was not disclosed as an alternative to the granulated blast-furnace slag. The authors of [24] have shown effectiveness of partial replacement of cement in compositions of concrete mixes with zeolite and fly ash. This measure ensures reduction of concrete cost. However, dispersity of FA and zeolite is not large enough to obtain a high technical effect since the content of 10 μm fractions for zeolite and FA is only 18.0 and 9.0 vol. %, respectively. At the same time, it is necessary to study influence of higher dispersity of SCMs on their properties, which are decisive in optimizing composition of the multi-component cements.

Therefore, there is a reason to consider that the insufficient certainty of influence of characteristics of supplementary cementitious materials of various types on physical and mechanical properties of low-emission multi-component cements and the features of their structure formation necessitates studies in this direction.

## 3. The aim and objectives of the study

The study objective was to determine criteria of surface and hydraulic activity of supplementary cementitious materials of various types, study their influence on technological and mechanical properties of low-emission multi-component cements and establish physical and chemical features of the processes occurring in their structure formation.

To achieve this objective, the following tasks were solved:

– study granulometric composition of SCMs of various dispersity, determine their effect on physical properties and optimize the SCMs blend by the method of mathematical planning of experiments;

– study physical and mechanical properties of multi-component cements with a high SCMs content, power intensity of the process of SCMs grinding to ensure high reactivity and the influence of superplasticizers of polycarboxylate type on strength of cementing systems.

## 4. Materials and methods used in studying low-emission multi-component cements with a high content of supplementary cementitious materials

### 4. 1. Experimental materials and equipment

The studies were performed using cement CEM I 42.5 R produced by PJSC Ivano-Frankivsktsement, Ukraine (*SSA*==3,590 $cm^2/g$) and ground granulated blast-furnace slag (*SSA*=3,750 $cm^2/g$) from ArcelorMittal Kryvy Rih Mining and Metallurgical Works, Kryvy Rih, Ukraine. Natural zeolite from Sokyrnytsia deposit, Ukraine (*SSA*=5,900 $cm^2/g$) and fly ash (FA) from Burshtyn TPP, Ukraine, (*SSA*=4,190 $cm^2/g$) were used as pozzolanic additives. Chemical composition of main components of the multi-component cement is presented in Table 1.

To ensure plasticity of the cement-sand mortars based on low-emission multi-component cements, a high-performance Master Glenium ACE 430 (BASF) polycarboxylate ether (PCE) superplasticizer was used.

Table 1

Chemical composition of main components of the multi-component cement

| Main component | 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 |
| GBFS | 48.10 | 39.26 | 6.55 | 0.82 | 3.45 | 0.31 | 0.33 | 1.18 |
| Zeolite | 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 |

Studies of chemical composition of cements and supplementary cementitious materials were performed using ARL 9800 XP X-ray spectrometer (Thermo Electron SA, Switzerland). Granulometric composition was studied using Master Sizer 3000 laser particle analyzer (Malvern Panalytical, France). Specific surface area of main components and multi-component cements obtained therefrom was determined by the air permeability method according to EN 196-6:2018 [25]. Microstructure of the stone based on supplementary cementitious materials was studied using REM 106I scanning electron microscope (SELMI, Ukraine). To determine phase composition of the SCMs based stone, X-ray analysis was made using DRON-3 diffractometer (Burevestnik, USSR).

### 4. 2. The procedure for determining properties of samples

Physical and mechanical properties of low-emission cements with high content of supplementary cementitious materials were determined in accordance with current standards and conventional methods.

According to the results of laser granulometry using the developed methodology [26], differential coefficient of particle size distribution by specific 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, $A/V$, characterizes specific surface area *SSA*, $μm^2/μm^3=μm^{-1}$) for the content of each material fraction. This coefficient makes it possible to estimate distribution of the SCMs particle sizes over a specific surface area, which makes it possible to determine a degree of additional active interphase surface of SCMs.

Optimal ratio between SCMs was determined using the Scheffe simplex-lattice design ‘mixture-property’ to ensure a uniform spread of the experimental points in the factor space. The Gibbs concentration triangle was used to design and analyze the experiment plan. Indices of bleeding and water demand of supplementary cementitious materials were used as a target function.

To determine class of the cement strength, 40×40×160 mm prism specimens of cement-sand mortar were prepared based on CEN standard sand at C:S=1:3 ($W/C$=0.50) according to EN 196–1:2007. Specimens were cured in molds for 24 h in controlled temperature and humidity conditions. After extraction from molds and labeling, the samples were placed in water ($t_{water}$=20.0±±1.0 °C) for storage before testing after 2, 7 and 28 hours.

Activity indices of ground granulated blast-furnace slag were determined according to DSTU B V.2.7-302:2014 as the ratio (%) of compressive strength of the cement prisms made of 50 wt. % CEM I and 50 wt. % GBFS to compressive strength of cement prisms made of 100 wt. % CEM I compared at the same age.

## 5. Results obtained in the studies of influence of supplementary cementitious materials on physical and mechanical properties of the low-emission multicomponent cements

Specific surface area (by Blaine) at which main components have a sufficiently high reactivity was 3,600...3,900 cm$^2$/g for clinker, 4,000...4,500 cm$^2$/g for GBFS, 9,000...12,000 cm$^2$/g for zeolite and 4,000...4,500 cm$^2$/g for fly ash [19]. The results of laser granulometry studies obtained for CEM I 42.5 R and SCMs have made it possible to estimate contribution of individual fractions to the development of a specific surface area. As can be seen from Table 2, the original Portland cement CEM I 42.5 R most closely meets requirements and is characterized by a maximum content of fractions finer than 10 μm. This was reflected in the fact that the volume average diameter $D$ [4;3] of 24.85 μm corresponded to CEM I 42.5 R and diameters 27.40 μm, 47.30 μm and 60.70 μm corresponded to GBFS, zeolite and FA, respectively. The maximum average diameter by specific surface, $D$ [3;2], in the distribution of specific surface was 5.23 μm for CEM I 42.5 R and 6.28 μm, 11.00 μm and 13.10 μm for GBFS, zeolite and FA, respectively. It should be noted that the high index of specific surface area of zeolite is determined by structure of the clinoptilolite mineral which is a three-dimensional aluminosilicate lattice. Its structure specificity forms a developed system of micropores and channels.

It should be noted that granulometric composition of initial supplementary cementitious materials such as GBFS and zeolite ground in a ball mill was characterized by larger grain sizes compared to CEM I 42.5 R. Therefore, to increase content of reactive particles in SCMs, they were activated in a MV-25 laboratory vibration mill and the effect of dispersity of such supplementary cementitious materials on their properties was determined (Table 3). After 3 cycles of activation, specific surface area of GBFS and FA has increased by 1.6 and 1.9 times, respectively. It was characteristic for zeolite that its specific surface area has increased to 12,000 cm$^2$/g after 3 cycles, that is, such superfine zeolite can be classified as a super-zeolite (SZ) (Fig. 1).

Table 2

Granulometric composition of CEM I 42.5 R and SCMs

| Cement components | Ø <1 μm, % | Ø <5 μm, % | Ø <10 μm, % | Ø <20 μm, % | Ø <45 μm, % | D[3;2], μm | D[4;3], μm |
|---|---|---|---|---|---|---|---|
| CEM I 42.5 R | 4.92 | 24.46 | 43.41 | 66.33 | 90.32 | 5.23 | 24.85 |
| GBFS | 2.60 | 20.71 | 36.19 | 56.11 | 85.08 | 6.28 | 27.40 |
| Zeolite | 0.05 | 14.21 | 23.87 | 37.49 | 60.21 | 11.00 | 47.30 |
| FA | 0.55 | 9.07 | 22.13 | 39.39 | 64.68 | 13.10 | 60.70 |

Table 3

Dispersion of SCMs after mechanical activation

| Number of activation cycles in the vibration mill | Specific surface area, cm$^2$/g | | |
|---|---|---|---|
| | GBFS | Fly ash | Zeolite |
| 0 | 3,750 | 4,190 | 5,900 |
| 1 | 4,500 | 5,430 | 8,120 |
| 2 | 5,250 | 6,650 | 9,960 |
| 3 | 6,000 | 7,870 | 12,000 |

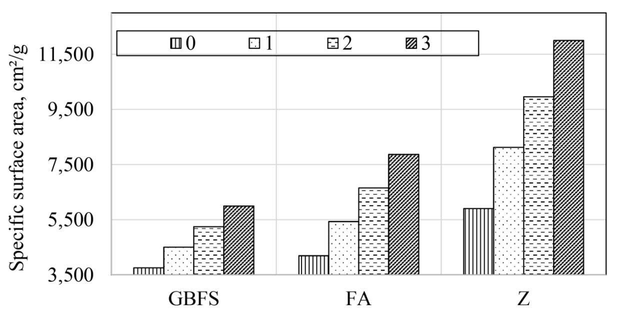
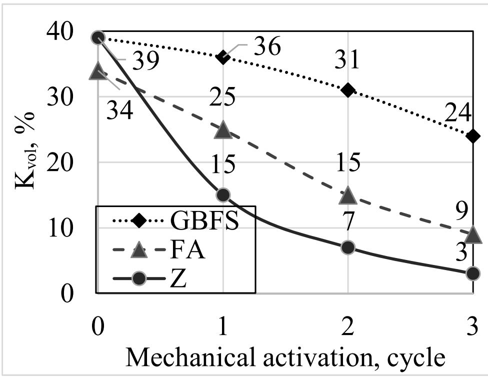


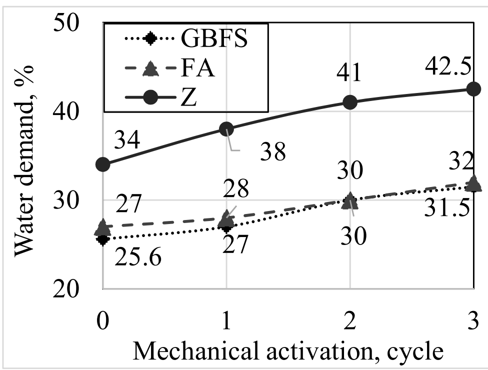

Fig. 1. Dispersity of SCMs after mechanical activation

It should be noted that granulated blast-furnace slags are characterized by high bleeding: for GBFS with specific surface area of 3,750 cm$^2$/g, bleeding coefficient ($K_{vol}$) was 38.9 % after 2 hours (Fig. 2, *a*). Reduction of the particle size contribute to stabilization of stratification of suspension with of GBFS added which has made it possible to reduce the coefficient of bleeding to 24.0 % with water demand increased by only 25 % (Fig. 2, *b*). After 3 cycles of mechanical activation of FA, coefficient of bleeding has decreased by 73 % and water demand increased by only 18 %. Fly ash was characterized by particles of regular spherical shape, which provided plasticizing effect due to the “roller bearing effect” [22]. It was noted that due to its porous structure, zeolite was characterized by high water demand which increased by 25 % with dispersity growth up to 12,000 cm$^2$/g and bleeding decreased to 3 %.

It should be noted that fly ash is a dusty, highly dispersed waste of thermal power plants. At the same time, fly ash from Burshtynska TPP features coarse inclusions of unburnt coal grains (sieve residue: 15 wt. % at 0.125 mm size). They significantly increase water demand and reduce efficiency of FA use. Therefore, further studies used separated fly ash (SFA) with a specific surface area of 4,300 cm$^2$/g.




*a*

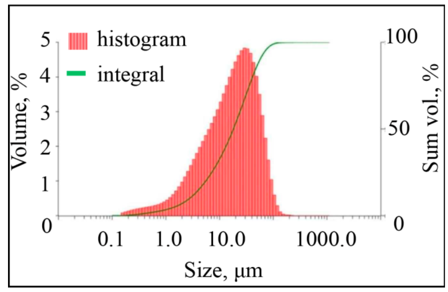



*b*

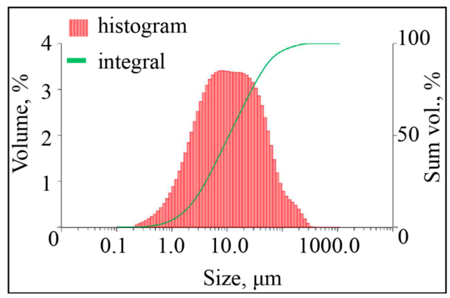
Fig. 2. Effect of mechanical activation on physical properties of SCMs: *a* — bleeding ($K_{vol}$); *b* — water demand (*WD*)

Results of laser granulometry of initial Portland cement CEM I 42.5 R, granulated blast-furnace slag (GBFS-3) and super-zeolite (SZ) mechanically activated in three cycles of grinding in the vibration mill and separated fly ash (SFA) are shown in Fig. 3. It can be seen that for GBFS-3 and SZ, there is a bimodal particle size distribution in volume with fractions of less than and more than 10 μm. As can be seen from Table 4, volume average diameter *D* [4; 3] for GBFS-3 was shifted to 23.70 μm and maximum of average diameter in specific surface, *D* [3; 2], to 4.50 μm. At the same time, content of up to 10 μm fractions for GBFS-3 (*SSA*=6,000 cm$^2$/g) has increased to 46.29 %. For SZ, average diameters *D* [4; 3] and *D* [3; 2] were displaced to 21.2 μm and 4.24 μm, respectively, content of up to 10 μm particles was increased to 52.16 %. Specific surface area of SFA slightly increased while average diameters *D* [4; 3] and *D* [3; 2] shifted to 41.80 μm and 7.22 μm. Content of up to 10 μm fractions for SFA increased from 22.13 % to 33.74 %.

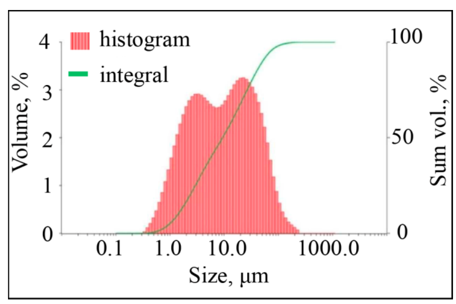
For a more complete estimation of SCMs dispersity according to the results of the obtained particle size distributions, determine their differential coefficients of particle size distribution by their specific surface area ($K_{isa}$). For example, for particles of initial CEM I 42.5 R, maximum of the $K_{isa}$ coefficient manifests itself for the particle size of 0.20 μm and 2.50 μm and makes 4.50 μm$^{-1}$·vol. % and 3.20 μm$^{-1}$ vol. %, respectively (Fig. 4, *a*). The highly dispersed GBFS-3 (*SSA*= =6,000 cm$^2$/g) and SZ (*SSA*=12,000 cm$^2$/g) prepared by mechanical activation were characterized by higher $K_{isa}$ coefficients compared to Portland cement CEM I. For GBFS-3, $K_{isa}$=5.80 μm$^{-1}$·vol. % for particle size of 2.13 μm (Fig. 4, *b*). For CZ, maximum $K_{isa}$=5.93 μm$^{-1}$·vol. % was reached at a particle size of 1.5 μm (Fig. 4, *c*). For separated fly ash, $K_{isa}$=3.47 μm$^{-1}$·vol. % was reached at a particle size of 2.42 μm (Fig. 4, *d*). It follows that about 80 % of specific surface area of CEM I 42.5 R and SCMs were determined namely by fine fractions up to 10 μm in size.



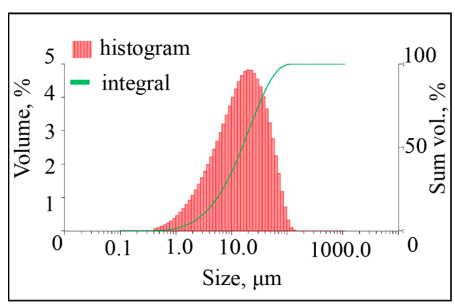

*a*




*b*




*c*




*d*

Fig. 3. The particle size distribution by volume: *a* — CEM I 42.5 R; *b* — GBFS-3; *c* — SZ; *d* — SFA

It is important to study the effect of increase in specific surface area on the strength activity index of the GBFS according to DSTU B V.2.7-302:2014. According to the obtained results of strength activity index in the hardening age of 7 and 28 days, it was established that GBFS in the range of specific surface area 3,750...5,250 cm$^2$/g belonged to class 3. Increase in dispersity up to 6,000 $cm^2/g$ has contributed to growth of the strength activity index up to 82 and 95 %, respectively, after 7 and 28 days of hardening which has made it possible to attribute GBFS-3 to class 2. It should be noted that value of the strength activity index of 70.4 % for GBFS-3 with the highest dispersion was reached after 4 days of hardening and only after 28 days for the initial GBFS with specific surface area of 3,750 $cm^2/g$ (Fig. 5). At the same time, an increase in specific surface area has involved significantly higher power consumption on grinding. For example, power intensity of GBFS grinding in a ball mill for the above range has increased from 50 to 140 kWh/t.

Table 4

Granulometric composition and specific surface area of SCMs after activation

| Cement components | SSA, $cm^2/g$ | Ø<1 μm, % | Ø<5 μm, % | Ø<10 μm, % | Ø<20 μm, % | Ø<45 μm, % | D[3;2], μm | D[4;3], μm |
|---|---|---|---|---|---|---|---|---|
| GBFS-3 | 6,000 | 4.66 | 30.66 | 46.29 | 67.81 | 88.46 | 4.50 | 23.7 |
| SZ | 12,000 | 5.12 | 38.46 | 52.16 | 68.79 | 90.12 | 4.24 | 21.2 |
| SFA | 4,300 | 1.67 | 16.98 | 33.74 | 52.88 | 75.30 | 7.22 | 41,.0 |

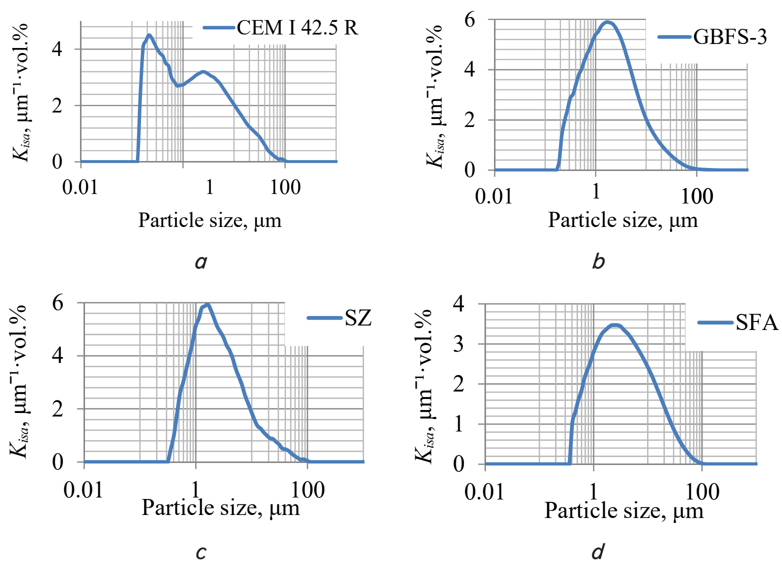



Fig. 4. The particle size distribution by surface area for: a – CEM I 42.5 R; b – GBFS-3; c – SZ; d – SFA

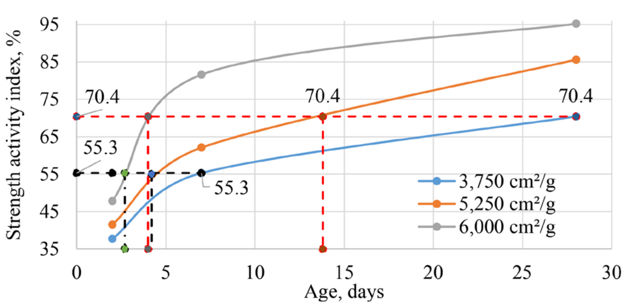



Fig. 5. Strength activity index of GBFS with various dispersity

Distribution of energy consumption for the production of cement in a dry way at averaged indices for a ball mill to obtain specific surface area of 3,500–4,000 $cm^2/g$ is given in Table 5. Energy consumption for SCMs production is significantly lower than that for the Portland cement clinker, so it is important to increase SCMs amount in compositions of multi-component cements. Mohs hardness number of the Portland cement clinker and granulated blast-furnace slag was 7 and hardness number of natural zeolite was 4. High dispersity of fly ash has provided possibility of its use after separation of coarse inclusions. Increased grindability of natural zeolites has made it possible to reduce power consumption on grinding in a ball mill to 20 kWh/t while increasing specific surface area from 5,900 to 12,000 $cm^2/kg$.

Solution of the problem connected with development of a technology of production of efficient low-emission multi-component cements is largely achieved by development of multimodal multi-component cements [22]. This technology is based on the use of supplementary cementitious materials of various sources and granulometric composition with high surface energy of fine-dispersed fractions in the non-clinker part of the system. Joint effect of supplementary cementitious materials on bleeding and water demand was studied by the method of Scheffe's simplex-lattice design "mixture-property". In the case of the three-component GBFS ($X1$):SZ ($X2$):SFA ($X3$) blend, one ratio corresponds to each point of the triangular diagram and each composition is characterized by the value of a certain property. Thus, taking into account significance of coefficients, the regression equations of water demand ($Y_{WD}$) and bleeding ($Yc_{vol}$) of the SCMs blend take the following form:

$$Y_{WD}=25.6889 \cdot X1+42.6344 \cdot X2+27.1253 \cdot X3-4.55349 \cdot X-1 \cdot X2-3.57167 \cdot X2 \cdot X3+11.012 \cdot X1 \cdot X2 \cdot X3;$$

$$Yc_{vol}=38.8826 \cdot X1+1.80989 \cdot X2+41.3281 \cdot X3-35.015 \cdot X1 \cdot X2-3.97862 \cdot X1 \cdot X3-26.1241 \cdot X2 \cdot X3+166.235 \cdot X1 \cdot X2 \cdot X3.$$

Fig. 6 presents an initial profile map of the response surface in the form of contour isolines of values of projections of the target functions $Y_{WD}$ and $Yc_{vol}$ on a three-component simplex.

Table 5

Energy consumption in production of CEM I 42.5 R and SCMs

| Process | Power consumption in material production, MJ/t | | |
|---|---|---|---|
| | CEM I 42,5 R | SZ | GBFS |
| Crushing and delivery of raw materials | 25 | 24 | 16 |
| Drying and milling of raw material | 160 | 52 | 152 |
| Burning | 3,250 | – | – |
| Grinding* (kWh/t) | 152 (42) | 72 (20) | 180 (50) |
| Total power consumption | 3,587 | 147 | 348 |

*Note: * – ball mill*

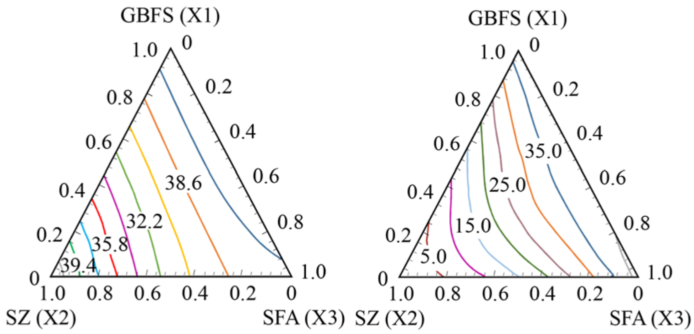



Fig. 6. Isolines of influence of composition of SCMs based on GBFS, super-zeolite and fly ash on: *a* — bleeding; *b* —water demand

Strength of the artificial stone based on the GBFS-SZ-SFA (1:1:1) system was 12.0 MPa after 180 days of curing. The fine-dispersed particles of the super-zeolite caused an increase in the medium pH compared to the initial zeolite, which has contributed to GBFS activation in the curing process. According to the data of raster electron scanning microscopy (Fig. 7, *a*), interaction inside the GBFS-SZ-SFA system has caused appearance of a zone of crystal accretion among particles having size of up to 5 µm after 180 days of hardening. A considerable amount of contacts between grains has contributed to formation of a dense structure with low porosity and had a significant impact on physical and mechanical properties of the artificial stone with a high content of supplementary cementitious materials.

Analysis of data of the X-ray phase analysis of the hydrated GBFS-SZ-SFA system presented in Fig. 7, *b* indicates presence of lines of sufficiently high intensity of β-$SiO_2$ (*d/n*=0.425; 0.334 nm). During hydration of the active GBFS glassy phase, formation of CSH phases occurs in the composition of the three-component SCMs blend and calcite (*d/n*=0.303; 0.228 nm) is observed. Because super-zeolite with a high content of fine fraction was used, a slight line of calcium hydrocarboaluminate (*d/n*=0.76; 0.38 nm) was additionally appearing.

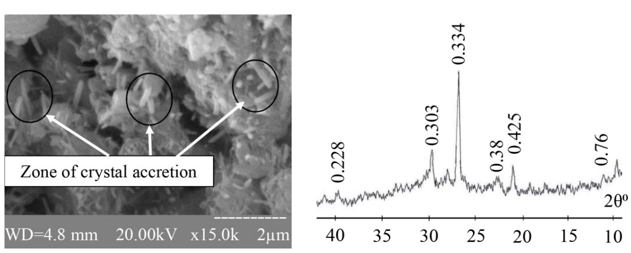



Fig. 7. Stone on the basis of the GBFS-SZ-SFA system after 180 days of hardening: *a* — microstructure; *b* — phase composition

The results of determining physical and mechanical properties of low-emission cements obtained by mixing Portland cement CEM I 42.5 R with mineral additives GBFS and the SZ+SFA blend are given in Table 6. It can be seen that there was a significant slowdown of strength gain of blended cements at an early age. It is noteworthy that the strength activity index of the ternary pozzolanic cement CEM IV/B (50 wt. % CEM I 42.5 R; 27 wt. % SZ, 23 wt. % SFA) exceeded the analogous index of slag cement CEM III/A [27]. With increase in the age of hardening, the difference in strength of CEM IV/B in comparison with Ordinary Portland cement CEM I decreased and the strength activity index of CEM IV/B became the highest after 90 days. It is also worth noting significantly lower power consumption on grinding the pozzolanic cement compared to the slag cement.

Increase in efficiency of low-emission pozzolanic cement CEM IV/B is largely achieved due to the use of superplasticizers of new generation. The flow table (*FT*) test has shown an increase from 144 to 280 mm with addition of 1.0 % PCE to composition of a cement-sand mortar based on pozzolanic cement at *W/C*=0.5. Thus, the technological effect obtained by addition of the superplasticizer was Δ*FT*=94 % without reduction of compressive strength. Due to the water-reducing effect (Δ*W/C*=20 %), the technical effect (Δ$R_c$) was 31, 27 and 27 % after 2, 7 and 28 days, respectively, (Fig. 8). The environmental impact of reducing $CO_2$ emission of the multi-component cement was 47 % since carbon dioxide emissions were reduced from 865 kg/ton of cement (CEM I, clinker factor – 0.95) to 456 kg/ton of cement (clinker factor – 0.50). The high-performance polycarboxylate superplasticizer of PCE type can increase technical and economic indices of this low-emission multi-component cement.

Table 6

Influence of SCMs on physical and mechanical properties of low-emission cements

| Main components, wt. % | | | | SSA, cm²/g | Compressive strength in the age, day, MPa / Strength activity index, % | | | | Power consumption for grinding, kWh/t |
|---|---|---|---|---|---|---|---|---|---|
| CEM I | GBFS-3 | SZ | SFA | | 2 | 7 | 28 | 90 | |
| 100 | – | – | – | 3,590 | 22.8 / 100 | 37.4 / 100 | 45.5 / 100 | 52.3 / 100 | 42 |
| 50 | 50 | – | – | 4,350 | 10.5 / 46 | 30.3 / 81 | 43.2 / 95 | 51.8 / 99 | 91 |
| 50 | – | 27 | 23 | 7,520 | 11.9 / 52 | 32.5 / 87 | 43.7 / 96 | 54.4 / 104 | 31 |

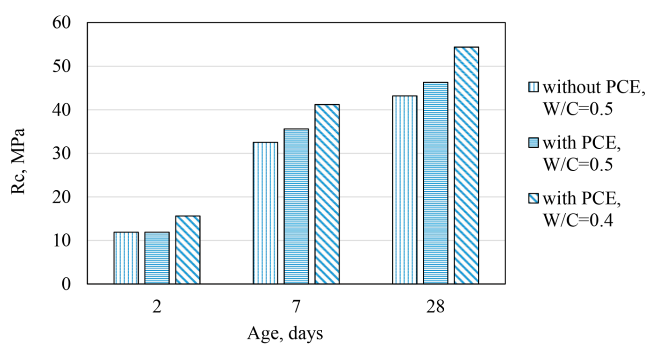



Fig. 8. Influence of PCE superplasticizer on compressive strength of low-emission ternary pozzolanic cement

Thus, the technology of production of low-emission multi-component cements with high SCMs content meets the principles of the strategy of sustainable development in construction and is a practical solution of the problem of reducing costs, power consumption and $CO^2$ emissions in the building production.

## 6. Discussion of the results obtained in the study of low-emission multi-component cements with high content of supplementary cementitious materials

According to the results of particle size distribution analysis of components of multi-component cements, granulated blast-furnace slag, natural zeolite, and fly ash are characterized by an insufficient content of fine (up to 10 μm) fraction (Table 2). This causes not sufficiently high coefficients of their surface activity and hence slowdown of strength gain kinetics of cements based on these additives.

Type and amount of supplementary cementitious materials substantially determine water demand and the bleeding of the multi-component cements. Technological optimization by means of combination of mineral additives of various granulometric composition, namely: GBFS, super-zeolite and separated fly ash enables control of the processes of early structure formation and to a large extent provides necessary rheological and mechanical properties of multi-component cements. For example, water demand for GBFS and fly ash is 25.6 % and 27.0 %, respectively (Fig. 2, *b*). At the same time, natural zeolite is characterized by increased water demand (34.0 %). On the other hand, GBFS and fly ash have high bleeding (39.0 and 34.0 %, respectively) (Fig. 2, *a*).

Of particular interest is comparison of the effect of mechanical activation on the SCMs characteristics. The results of measuring the specific surface area shown in Fig. 1 confirm that GBFS has lower grindability compared to fly ash and natural zeolite. It was found in the study of the effect of SCMs dispersity that it is natural to increase the water demand and reduce the coefficient of bleeding of the supplementary cementitious materials while increasing their specific surface area.

Mechanical activation of GBFS makes it possible to compensate for the effect of reduced hydraulic activity by increasing content of active particles up to 10 μm in size. Analysis of the effect of mechanical activation on GBFS dispersity allows us to conclude that the increase in amount of active microparticles up to 10 μm helps to increase early strength of slag cement with GBFS content of 50 wt. % (Fig. 5). This is due to the increase in the amount of reactive GBFS particles and compaction of the cement stone microstructure.

Replacement of the clinker component of the SCMs has a particular effect on workability and bleeding of low-emission multi-component cements which leads to a change in indices of construction and technical properties of concretes and mortars based on them. It was established that super-zeolite has the decisive influence on bleeding and water demand of the three-component system while SFA and GBFS had almost the same effect. Increase in the content of SZ to 67 wt. % in the SZ+SFA blend provided reduction of the bleeding coefficient to 7.3 %. At the same time, these indicators were 30.9 and 35.7 % for the same content of GBFS and SFA, respectively On the other hand, SZ has a high water demand (36.0 %), so combination of super-pozzolana and SCMs having opposite properties makes it possible to ensure optimal rheological properties of the low-emission multi-component cement (Fig. 6, *a*, *b*).

Compressive strength of low-emission ternary pozzolanic cement CEM IV/B (clinker factor – 0.50) is gaining, especially with the age of hardening, power consumption for grinding is reduced to 31 kWh, and $CO_2$ emissions are reduced by 47 % compared to Portland cement CEM I 42.5 R and amount 456 kg/t. Compressive strength of such low-emission multi-component cement after 90 days of hardening is 2.1 MPa higher than that of CEM I 42.5.

Thus, use of technologically optimized multi-component cements with several major components becomes a rational solution of the problem of improving power efficiency of building production. The strategy of such development implies that the combination of several components of various sources, in particular, SCMs of pozzolanic action based on super-zeolite and separated fly ash, reduces to a greater extent $CO_2$ emissions and saves material resources. This approach also involves optimization of properties (workability, standard and early strength, durability, cost, environmental impact). The ternary pozzolanic cement CEM IV/B with a reduced up to 50 % clinker factor is an innovative binder with a combination of the above properties. Its production provides significant savings of fuel and energy resources and reduction of $CO_2$ emissions since energy consumption for production of such cement are much lower compared to that of CEM I cement. At the same time, early strength of low-emission multi-component CEM IV/B cement is lower than that of CEM I cement. Therefore, in order to fully evaluate effectiveness of the developed cement, it is necessary to conduct a study of the effect of hardening activators on kinetics of strength gain of concretes based on this cement which determines direction of further development of this study.

## 7. Conclusions

1. The studies have shown that supplementary cementitious materials of coarse grinding are usually obtained when ball mills are used. They are characterized by a small amount of reactive particles compared to CEM I 42.5 R Portland cement. Increase in SCMs dispersity significantly affects their physical properties, namely leads to reduction of bleeding without a sharp increase in water demand. Due to the increase in amount of up to 10 μm fraction, the surface activity factor (Kisa) of SCMs is in the range of 3.47...5.93 $\mu m^{-1}$·vol. % and reaches Kisa values of Portland cement: 4.50 and 3.20 $\mu m^{-1}$·vol. %. It was established by the method of three-factor mathematical experiment planning that the separated fly ash and GBFS have a similar effect on water demand and the coefficient of bleeding in the GBFS-SZ-SFA system. In order to obtain indices of bleeding and water demand corresponding to the values of CEM I 42, R, the ratio between SZ and SFA (1.2:1.0) was optimized for the non-clinker part of the multi-component cement.

2. The results obtained in the studies of physical and mechanical properties of low-emission multi-component cements indicate that to reduce power consumption for preparation of highly active supplementary cementitious materials, it is most effective to combine SZ and SFA. When SCMs are optimized, the strength activity index of the ternary pozzolanic cement are 48, 72 and 91 % after 2, 7 and 28 days of hardening, respectively and energy consumption on grinding is reduced to 31 kWh/t. The use of Master Glenium 430 ACE superplasticizer of new generation provides a high plasticizing effect (ΔFT=94 %) of low-emissive pozzolanic cement (clinker factor – 0.50). Due to the significant water-reducing effect (ΔW/C=20 %), early strength of such three-component cement increases by 30 %. Thus, composition of multi-component cement with content of SZ and SFA (1.2:1.0) in the amount of 50 wt. %, modified 1.0 % PCE which corresponds to the concept of low-emission development of the cement industry was technically and economically substantiated at this stage of the study.

## References


1. Miller, S. A., John, V. M., Pacca, S. A., Horvath, A. (2018). Carbon dioxide reduction potential in the global cement industry by 2050. Cement and Concrete Research, 114, 115–124. doi: https://doi.org/10.1016/j.cemconres.2017.08.026
2. Andrew R. M. Global $CO_2$ emissions from cement production. Earth System Science Data. 2018. Vol. 10, Issue 1. P. 195–217. doi: https://doi.org/10.5194/essd-10-195-2018
3. Scrivener, K. L., John, V. M., Gartner, E. M. (2018). Eco-efficient cements: Potential economically viable solutions for a low-$CO_2$ cement-based materials industry. Cement and Concrete Research, 114, 2–26. doi: https://doi.org/10.1016/j.cemconres.2018.03.015
4. Bolte, G., Zajac, M., Skocek, J., Ben Haha, M. (2019). Development of composite cements characterized by low environmental footprint. Journal of Cleaner Production, 226, 503–514. doi: https://doi.org/10.1016/j.jclepro.2019.04.050
5. Lothenbach, B., Scrivener, K., Hooton, R. D. (2011). Supplementary cementitious materials. Cement and Concrete Research, 41 (12), 1244–1256. doi: https://doi.org/10.1016/j.cemconres.2010.12.001
6. Kumar, P. R., Reddy, C. S., Baig, M. S. (2014). Zmiany wytrzymałości na ściskanie betonu, w którym część cementu zastąpiono dodatkami mineralnymi. Cement Wapno Beton, 1, 8–16.
7. Chlądzynski, S., Garbacik, A. (2007). Wlasciwosci cementow wieloskladnikowych CEM V z duza iloscia dodatkow mineralnych. Budownictwo, Technologie, Architektura, 2, 60–64.
8. Chung, S.-Y., Abd Elrahman, M., Sikora, P., Rucinska, T., Horszczaruk, E., Stephan, D. (2017). Evaluation of the Effects of Crushed and Expanded Waste Glass Aggregates on the Material Properties of Lightweight Concrete Using Image-Based Approaches. Materials, 10 (12), 1354. doi: https://doi.org/10.3390/ma10121354
9. Krivenko, P., Sanytsky, M., Kropyvnytska, T. (2018). Alkali-Sulfate Activated Blended Portland Cements. Solid State Phenomena, 276, 9–14. doi: https://doi.org/10.4028/www.scientific.net/ssp.276.9
10. Krivenko, P., Petropavlovskyi, O., Kovalchuk, O. (2018). A comparative study on the influence of metakaolin and kaolin additives on properties and structure of the alkaliactivated slag cement and concrete. Eastern-European Journal of Enterprise Technologies, 1 (6 (91)), 33–39. doi: https://doi.org/10.15587/1729-4061.2018.119624
11. Savchuk, Y., Plugin, A., Lyuty, V., Pluhin, O., Borziak, O. (2018). Study of influence of the alkaline component on the physico-mechanical properties of the low clinker and clinkerless waterproof compositions. MATEC Web of Conferences, 230, 03018. doi: https://doi.org/10.1051/matecconf/201823003018
12. Smrčková, E., Bačuvčík, M., Janotka, I. (2014). Basic Characteristics of Green Cements of CEM V/A and V/B Kind. Advanced Materials Research, 897, 196–199. doi: https://doi.org/10.4028/www.scientific.net/amr.897.196
13. Kropyvnytska, T., Semeniv, R., Ivashchyshyn, H. (2017). Increase of brick masonry durability for external walls of buildings and structures. MATEC Web of Conferences, 116, 01007. doi: https://doi.org/10.1051/matecconf/201711601007
14. Shamshad, A., Mohammad, Sh., Sirajuddin, A. (2016). Use of Ultrafine Slag in High Strength Concrete. International Journal of Science and Research, 5 (10), 1341–1344.
15. Oles'ko, M. (2018). Vliyanie razmera chastits granulirovannogo domennogo shlaka na gidratatsiyu shlakoportlandtsementa i ego svoystva. Tsement i ego primenenie, 6, 86–92.
16. Markiv, T., Sobol, K., Franus, M., Franus, W. (2016). Mechanical and durability properties of concretes incorporating natural zeolite. Archives of Civil and Mechanical Engineering, 16 (4), 554–562. doi: https://doi.org/10.1016/j.acme.2016.03.013
17. Sokoltsov, V., Tokarchuk, V., Sviderskiy, V. (2015). Hardening peculiarities of blended cements with silicate admixtures of different origin. Eastern-European Journal of Enterprise Technologies, 3 (11 (75)), 9–14. doi: https://doi.org/10.15587/1729-4061.2015.43460
18. Chen, J. J., Li, L. G., Ng, P. L., Kwan, A. K. H. (2017). Effects of superfine zeolite on strength, flowability and cohesiveness of cementitious paste. Cement and Concrete Composites, 83, 101–110. doi: https://doi.org/10.1016/j.cemconcomp.2017.06.010
19. Sabet, F. A., Libre, N. A., Shekarchi, M. (2013). Mechanical and durability properties of self consolidating high performance concrete incorporating natural zeolite, silica fume and fly ash. Construction and Building Materials, 44, 175–184. doi: https://doi.org/10.1016/j.conbuildmat.2013.02.069
20. Muller M., Ludvig H-M., Ben Haha M., Zajac M. (2015). Optimization of multi-component cements containing cement clinker, slag, fly ash, limestone. 19th Internationale Baustofftagung (IBAUSIL 19). Weimar, 449–456.
21. Ludwig, H.-M. (2012). Future cements and their properties. Cement International, 4, 81–89.
22. Sanytsky, M. A., Sobol, Kh. S., Markiv, T. Ye. (2010). Modyfikovani kompozytsiyni tsementy. Lviv: Vyd-vo Lviv. politekhniky, 130.
23. Krivenko, P. V., Sanytsky, M., Kropyvnytska, T., Kotiv, R. (2014). Decorative Multi-Component Alkali Activated Cements for Restoration and Finishing Works. Advanced Materials Research, 897, 45–48. doi: https://doi.org/10.4028/www.scientific.net/amr.897.45
24. Gucluer, K., Gunaydin, O., Unal, O., Bilen, S. (2016). Use of Natural Zeolite with Fly Ash In Conventional Concrete Production. Journal of Multidisciplinary Engineering Science and Technology, 3 (2), 4119–4122.
25. EN 196-6: 2018. Methods of testing cement - part 6: Determination of fineness (2018). Comite Europeen de Normalisation.
26. Sanytsky, M., Kropyvnytska, T., Kruts, T., Horpynko, O., Geviuk, I. (2018). Design of Rapid Hardening Quaternary Zeolite-Containing Portland-Composite Cements. Key Engineering Materials, 761, 193–196. doi: https://doi.org/10.4028/www.scientific.net/kem.761.193
27. Dean, S. W., Bentz, D. P., Durán-Herrera, A., Galvez-Moreno, D. (2012). Comparison of ASTM C311 Strength Activity Index Testing versus Testing Based on Constant Volumetric Proportions. Journal of ASTM International, 9 (1), 104138. doi: https://doi.org/10.1520/jai104138