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Iryna Kirakevych

PROPERTIES OF FRESH AND HARDENED SELF-COMPACTING CONCRETE CONTAINING SUPPLEMENTARY CEMENTITIOUS MATERIALS

Department of Building Production,
Lviv Polytechnic National University
iryna.i.kirakevych@lpnu.ua

This paper presents the properties of fresh and hardened self-compacting concrete (SCC) containing supplementary cementitious materials, such as complex sulphoaluminosilicate additive based on the metakaolin and gypsum, fly-ash and limestone microfiller. If sufficient gypsum is present the main hydration products in unclinker part is a thin crystals of ettringite. Ettringite is formed by a topochemical reaction in a closed space at the beginning of the formation of the cement matrix, which ensures the compaction of SCC. This is one of the major causes of increasing of the early strength of SCC containing supplementary cementitious materials. The SCC containing supplementary cementitious materials are characterized by such properties as obtaining workability concrete mixtures (slump flow 650-730 mm), high viscosity (T50=5-13 s), high strength (58-95 MPa), low porosity, high reliability and durability of structures.

Key words: self-compacting concrete, supplementary cementitious materials, metakaolin, fly-ash, limestone microfiller, polycarboxylate type superplasticizer.

Introduction

During the operation of reinforced concrete products, in order to avoid damage to the reinforcement, diagnostics of the stress-deformed state of structures should be performed (Blikharskyy, Khmil, Selejdak, Katunský, Blikharskyy, 2024). In monolithic structures with using concrete pumps high workability concrete mixtures are used. One of the most important properties of concrete mixture is its increased workability, which is due to the peculiarities of its transportation and laying technology, as well as the need to concrete the heavily reinforced structures (Sanytsky, Usherov-Marshak, Marushchak & Kabus, 2021). In this regard, the use and research of modified cement systems with the use of supplementary cementitious materials that provide the necessary rheological properties is of great practical interest (Sanytsky, Kropyvnytska, Heviuk, Sikora & Braichenko, 2021).

The water-cement ratio is directly related to the the hardening process of implementation. At the same time, for the creation a dense structure with high strength paste, it is necessary to provide hardening conditions, which is determined by low value of W/C (Sohail, Kahraman, Nuaimi, Gencturk & Alnahhal, 2021). Therefore, in order to achieve increased workability of Portland cement systems, highly effective new generation type of superplasticizers are added, which determines the need to study the processes of their structure formation, as well as the formation and genesis of the microstructure of cement paste (Aicin, 2003; Nivin, Jędrzejewska, Varughese & James, 2022).

Freshly placed concrete contains more water than it is necessary for complete hydration of cement, however, in most cases, in production conditions, already in the initial periods of hardening, a significant amount of water is lost due to evaporation, which leads to insufficient strength, increased porosity and deterioration of the structures and technical properties of concrete (Jasiczak, Wdowska & Rudnicki, 2008; Haufe, Vollpracht & Matschei, 2021). The use of supplementary cementitious materials, such as metakaolin or fly-ash makes it possible to increase the time of preservation of the ease of placing of the concrete mixture without significant impact on the terms of hardening of concrete (Switonski, Mrozik & Piekarski, 2004; Chousidis, Rakanta, Ioannou & Batis, 2015). Among the numerous advantages of using of some supplementary cementitious materials the following should be highlighted: a significant reduction in the amount of mixing water; the possibility of pumping of concrete mixtures over long distances; high workability of the concrete mixture without segregation; sufficient time for placing fresh concrete mixtures; high early and later strength, density and durability of concrete (Runova, Gots, Rudenko, Konstantynovskyi & Lastivka, 2018; Valcuende, Lliso-Ferrando, Ramón-Zamora & Soto, 2021). Therefore, it is advisable to investigate the effect of supplementary cementitious materials on the properties of fresh concrete mixture and hardened self-compacting concrete on their basis (Sanytsky, Kropyvnytska, Vakhula & Bobetsky, 2024; Krivenko, Petropavlovskyi & Kovalchuk, 2018).

The aim of this study is of properties of fresh and hardened self-compacting concretes containing supplementary cementitious materials.

Materials and methods

Ordinary Portland cement CEM I 42.5 was used. Complex chemical admixtures (CCA) based on polycarboxylate type superplasticizer (PC) and alkali-metal salts (NaCNS and $Na_2S_2O_3$) were included in self-compacting concretes as modifiers. Limestone (LM) was used as microfiller and fly ash (FA), complex sulphoaluminosilicate additive (G) based on the metakaolin and gypsum were used as supplementary cementitious materials.

The workability of concrete mixtures was determined as the average of slump flow and the viscosity as the measure T50 time when the 500 mm circle is first reached.

Physico-mechanical tests of supplementary cementitious materials and concretes on their basis were carried out according to usual procedures. The evaluation of the properties of supplementary cementitious materials was carried out through a flowing and compressive strength tests. The physico-chemical analysis (electron microscopy) were used for investigation of supplementary cementitious materials hydration processes.

Results and discussions

The particle size distributions of CEM I 42.5, limestone microfiller, fly-ash and complex sulphoaluminosilicate additive are shown in Table. The limestone microfiller contains 60.1; 83.3 and 99.9 mass.% of particles with the size < 10; 20 and 60 μm correspondingly. The metakaolin additive contains 31.2; 56.0 and 90.0 mass.% of particles with the size < 10; 20 and 60 μm correspondingly. It should be noted that Portland cement CEM I 42.5 contains 10; 50 and 90 mass.% of particles with the size < 7.0; 18.7 and 50.7 μm correspondingly.

The characteristics of particle size distribution of Portland cement and supplementary cementitious materials

Material	<10 μm	<20 μm	<60 μm	D_{10}, μm	D_{50}, μm	D_{90}, μm
CEM I 42.5	25.32	52.80	94.60	7.00	18.70	50.70
Limestone	60.10	83.30	99.90	1.40	7.80	25.00
Metakaolin	31.20	56.00	90.00	2.30	16.70	58.00
Fly-ash	31.60	50.50	77.52	5.00	19.63	140.10

According to (Sanytsky, Rusyn, Kirakevych & Kaminskyy, 2023), the microstructure with finely dispersed hydrosilicates in cement paste has a positive effect on its strength; the presence of large-crystalline blocks of portlandite, hydroalumoferrites, calcium hydrosulfoalumoferrites in the microstructure negatively affects the strength of the paste. To increase the strength of cement paste, it is necessary to reduce the number and sizes of coarse-crystalline blocks of portlandite, hydroalumoferrites, calcium hydrosulfoalumoferrites in its microstructure, and simultaneously increase the amount of finely dispersed component, which results in a decrease of the water-cement ratio and more compact placement of the initial cementing grains in the "cement-water" system due to the use supplementary cementitious materials (Borziak, Plugin, Chepurna, Zavalniy & Dudin, 2019).

For the studied sample based on CEM I 42.5 with supplementary cementitious materials (6-20 mass.%) and without chemical admixtures, which hardened in air-dry conditions, the presence of a large number of pores is characteristic (Fig. 1, a). In addition, there is a large amount of finely dispersed amorphous hydrosilicate phases, which surround cement grains (Kropyvnytska, Sanytsky, Rucińska & Rykhlitska, 2019). During hardening in air-dry conditions, a small amount of hexagonal plates of calcium hydroxide is observed in some places (Kirakevych, Sanytsky, Shyiko & Kagarlitskiy, 2021).

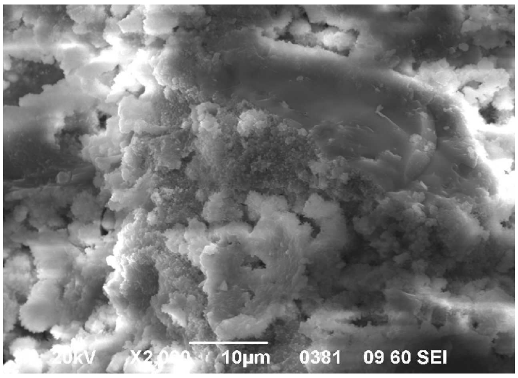
The addition of complex chemical admixtures based on polycarboxylate type superplasticizer and alkali-metal salts in the amount of 1.0 mass.% contributes to some compaction of the structure, but the porosity is still significant. Well-formed aggregates of $Ca(OH)_2$ hexagonal plates are observed in some places of the sample with the addition of complex chemical admixtures (Fig. 1, b). In air-dry conditions, in the structure of the studied sample with supplementary cementitious materials and complex chemical admixtures, pores are overgrown with needle-like crystals of calcium hydrosilicates and long prismatic crystals of ettringite (Gots, Berdnyk, Lastivka, Maystrenko & Amelina, 2023).

For the studied sample based on CEM I 42.5 with supplementary cementitious materials (6-20 mass.%) and without chemical additives during hardening under normal conditions, the presence of a small amount of pores is characteristic. It is known that pores are open and closed. Pores of the first type are initially formed between cement grains, which are in a limited geometric volume. Under normal conditions of hardening, they are filled with water and growth of hydrate compounds occurs in them, primarily tangle-fibrous crystals of calcium hydrosilicates (Fig. 1, c). Other pores are characterized by the presence of a large number of hexagonal prismatic crystals and their drusen. The surfaces of these crystals are not clear, which indicates their growth from solution (Valcuende, Parra, Marco, Garrido, Martínez & Cánoves, 2012).

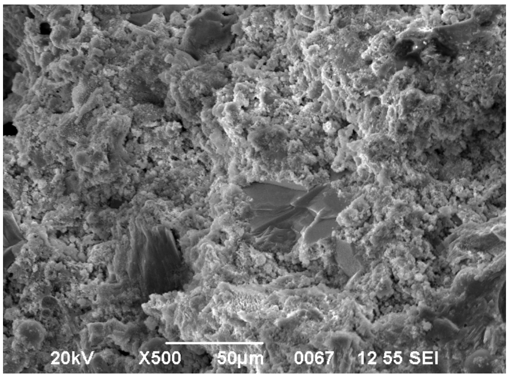
The paste based on CEM I 42.5 with supplementary cementitious materials (6-20 mass.%) and complex chemical admixtures (1.0 mass.%) based on polycarboxylate type superplasticizer and alkali-metal salts during hardening under normal conditions is characterized by a rather dense microstructure with a large number of pores that are either already overgrown with hydrated formations or are in the stage of overgrowth. It is important to have parallel oriented prismatic, lamellar and fibrous crystals with perfect cleavage in the direction of their growth (Ting, Wong, Rahman & Meheron, 2021). The size of the crystals that make up the blocks can reach up to 10 μm. Their splitting takes place in different ways: along the cleavage plates and across (Sun & Wu, 2022).

It should be noted that with the time of hardening, the gradual growth of these crystals into polysynthetic twins, differently oriented in the volume of the paste, occurs. A rhythmic layer-by-layer crystallization of compounds occurs in a similar way on each grain of the binder (Fig. 1, d). The microstructure of the studied cement paste is characterized by the presence of pores that are almost completely overgrown with fibrous crystals of calcium hydrosilicates, as well as short prismatic hexagonal crystals of $Ca(OH)_2$ (Shi, Shi, Zhao & Wan, 2015).

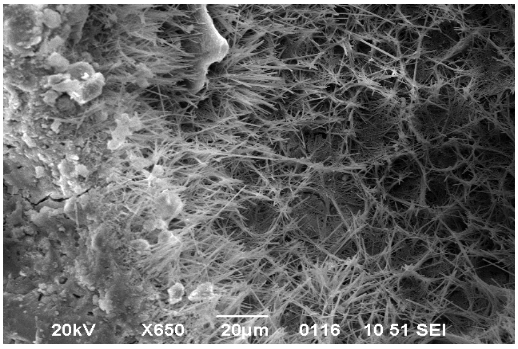
The morphology, crystal structure and composition of hydration products can be very different. With sufficient gypsum (as a component of the complex sulphoaluminosilicate additive) under favorable conditions, ettringite is the main hydration product in the unclinker part. At the same time, ettringite crystals are small, since ettringite was formed in a closed space by a topochemical reaction only after the formation of the cement matrix. Ettringite is formed in the form of thin crystals, which ensures the compaction of the SCC cement matrix. This is one of the main reasons for increasing the early strength of SCC based on supplementary cementitious materials (Ivashchyshyn, Sanytsky, Kropyvnytska & Rusyn, 2019).



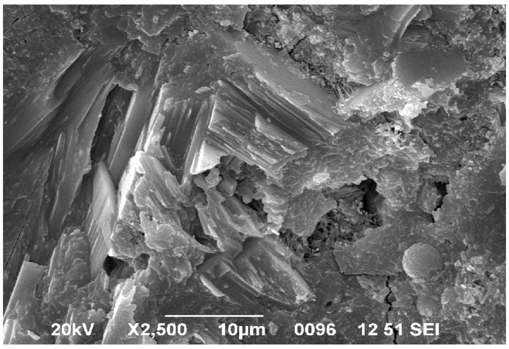
a



b



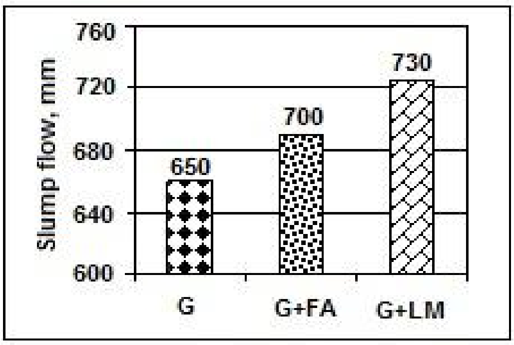
c



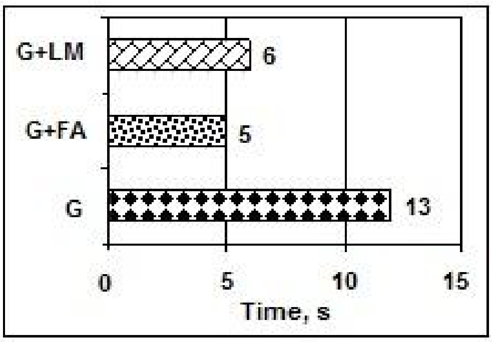
d

Fig. 1. SEM images of cement paste with supplementary cementitious materials \ in air-dry conditions (a, b) and in normal conditions (c, d) after 28 days

The using complex chemical admixtures and supplementary cementitious materials provide the increasing of slump flow of concrete mixture up to 650 mm (with complex sulphoaluminosilicate additive). The concrete mixture with using limestone microfiller characterizes the highest flowability 730 mm (Fig. 2, a). This is due to the fact that it ensures the optimal distribution of particles of supplementary cementitious materials, as a result of which water is not located in the voids, but between the grains of the material, acting as a lubricant, which creates excellent conditions for the gliding of particles, minimizing internal friction and increased flowability with the same W/C ratio (W/C=0.35) (Looney, Leggs, Volz & Floyd, 2022). It should be noted that the high-flowable concrete mixture with fly ash is characterized by the T50 time when the 500 mm circle is first reached is 5 s, with limestone microfiller and with complex sulphoaluminosilicate additive – 6 and 13 s respectively.



a



b

Fig. 2. The slump flow (a) and viscosity (b) of concrete mixtures based on limestone microfiller (LM) and supplementary cementitious materials (G – complex sulphoaluminosilicate additive based on metakaolin, FA – fly ash)

Dispersed limestone microfiller and supplementary cementitious materials provide compaction of the concrete matrix due to the effect of "fine powders" and an increase in strength as well as play an active structure-forming role due to the creation of additional hydrated phases. These compounds are hydrosilicates of the CSH (B) type, structurally active AFm-phases – calcium hydrocarbonates and AFt-phases – ettringite, which are characterized by binding properties in the composition of the unclinker part. Strength of concrete (C:S:G=1:1,52:2,04) with complex sulphoaluminosilicate additive and limestone microfiller after 2; 7 and 28 days of hardening is respectively 59.0; 67.0 and 68.0 MPa (Fig. 3) and with the additive of limestone microfiller 77.1; 80.1; 89.0 MPa, what gives the reason to attribute these concretes to rapid-hardening high strength concretes based on self-compacting mixtures.

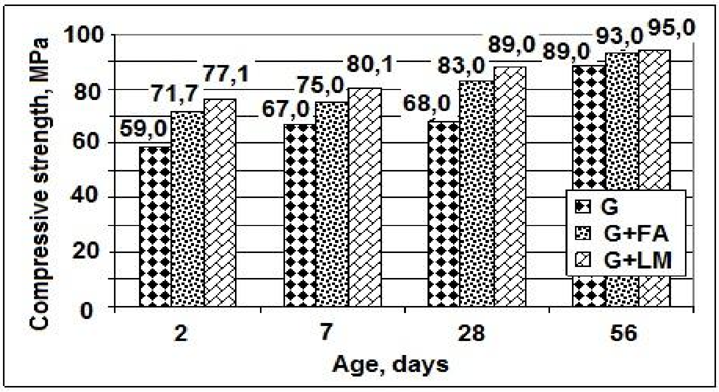


Fig. 3. Compressive strength of self-compacting concretes based on supplementary cementitious materials

The SCC with using limestone microfiller and supplementary cementitious materials (complex sulphoaluminosilicate additive and fly-ash) are characterized by dense structure and high technical properties.

Conclusions

Limestone microfiller and supplementary cementitious materials, such as complex sulphoaluminosilicate additive (based on the metakaolin and gypsum) and fly-ash have been researched for its further application in self-compacting concrete. The SCC (C:S:G=1:1,52:2,04) on the basis of supplementary cementitious materials with polycarboxylate type superplasticizer (PC) and alkali-metal salts are characterized by such properties as obtaining mobile concrete mixtures (increasing of slump flow of concrete mixture up to 650-730 mm), high viscosity (time to get the slump flow of 500 mm T50=5-13 s), high early strength and strength after 28 days – 89-95 MPa (class C50/60), low porosity, high reliability and durability of structures.

Prospects for further research

Highly dispersed mineral additives of pozzolanic action provide binding of portlandite in C-S-H phases, which contributes to the colmatations of pores with the age of hardening, such a structure of cement paste in concrete ensures an increase in its properties. During the hydration process in the superplasticized cement matrix with supplementary cementitious materials in the unclinker part, there is a process with the formation of ettringite crystals by a topochemical reaction, which ensures the compaction of the cement matrix of the SCC. The use of supplementary cementitious materials for self-compacting concrete will contribute to the design of structures of buildings with high strength, low porosity, high reliability and durability.

References

Blikharskyy, Y., Khmil, R., Selejdak, J., Katunský, D., Blikharskyy, Z. (2024). RC Beams with an middle phase of reinforcement damage. *System safety: Human – Technical facilyty – Environmental,* 6 (1), 184-191. Retrieved from: https://doi.org/10.2478/czoto-2024-0020.

Sanytsky, M., Usherov-Marshak, A., Marushchak, U. & Kabus, A. (2021). The effect of mechanical activation on the properties of hardened Portland Cement. *Lecture Notes in Civil Engineering*, 100, 378-384. Retrieved from: https://doi.org/10.1007/978-3-030-57340-9_46.

Sanytsky, M., Kropyvnytska, T., Heviuk, I., Sikora, P. & Braichenko, S. (2021). Development of rapid-hardening ultra-high strength cementitious composites using superzeolite and N-C-S-H-PCE alkaline nanomodifier. *Eastern-European Journal of Enterprise Technologies*, *5* (6 (113), 62-72. Retrieved from: https://doi.org/10.15587/1729-4061.2021.242813.

Sohail, M., Kahraman, R., Nuaimi, N., Gencturk, B. & Alnahhal, W. (2021). Durability characteristics of high and ultra-high performance concretes. *Journal of Building Engineering,* 33, 101669. Retrieved from: https://doi.org/10.1016/j.jobe.2020.101669.

Aicin, P. (2003). The durability characteristics of high performance concrete. *Cement and Concrete Composites,* 25 (4-5), 409-420. Retrieved from: https://doi.org/10.1016/S0958-9465(02)00081-1.

Jasiczak, J., Wdowska, A. & Rudnicki, T. (2008). Betony ultrawysokowartościowe, właściwości, technologie, zastosowanie: *Stowarzyszenie Producentow Cementu,* Krakow. Retrieved from: https://www.researchgate.net/publication/342720481_Betony_ultrawysokowartosciowe__wlasciwosci_technologie_zastosowania_UltraHigh_Performance_Concretes_Properties_Technology_Applications.

Switonski, A., Mrozik, L. & Piekarski, P. (2004). Creating structure and properties of high performance concrete. *University of Science and Technology in Bydgoszcz*. Retrieved from: https://depot.ceon.pl/bitstream/handle/123456789/12475/Creating%20structure%20and%20properties%20of%20high%20performance%20concrete3.pdf?sequence=1&isAllowed=y.

Runova, R., Gots, V., Rudenko, I., Konstantynovskyi, O. & Lastivka, O. (2018). The efficiency of plasticizing surfactants in alkali-activated cement mortars and concretes. *MATEC Web of Conferences 230*, 03016. Retrieved from: https://doi.org/10.1051/matecconf/201823003016.

Sanytsky, M., Kropyvnytska, T., Vakhula, O. & Bobetsky, Y. (2024). Nanomodified ultra high-performance fiber reinforced cementitious composites with enhanced operational characteristics. *Proceedings of CEE 2023*, 438, 362-371. Retrieved from: https://doi.org/10.1007/978-3-031-44955-0_36.

Nivin, P., Jędrzejewska, A., Varughese, A. & James, J. (2022). Influence of pore structure on corrosion resistance of high performance concrete containing metakaolin. *Cement – Wapno – Beton*, 27 (5), 302-319. Retrieved from: https://doi.org/10.32047/CWB.2022.27.5.1.

Valcuende, M., Lliso-Ferrando, J., Ramón-Zamora, J. & Soto, J. (2021). Corrosion resistance of ultra-high performance fibre-reinforced concrete. *Construction and Building Materials* 306, 124914. Retrieved from: https://doi.org/10.1016/j.conbuildmat.2021.124914.

Chousidis, N., Rakanta**.,** E**.,** Ioannou**,** I. & Batis, G. (2015). Mechanical properties and durability performance of reinforced concrete containing fly ash**.** *Construction and Building Materials***.** 101, 810-817. Retrieved from: https://doi.org/10.1016/j.conbuildmat.2015.10.127.

Haufe, J., Vollpracht, A. & Matschei, T. (2021). Performance test for sulfate resistance of concrete by tensile strength measurements: Determination of test criteria. *Crystals*, 11 (9)*, 1018*. Retrieved from: https://doi.org/10.3390/cryst11091018.

Krivenko, P., Petropavlovskyi, O. & Kovalchuk, O. (2018). A comparative study on the influence of metakaolin and kaolin additives on properties and structure of the alkali activated slag cement and concrete. *Eastern-European Journal of Enterprise Technologies*, 6 (91), 33-39. Retrieved from: https://doi.org/10.15587/1729-4061.2018.119624.

Sanytsky, M., Rusyn, B., Kirakevych, I. & Kaminskyy, A. (2023). Architectural self-compacting concrete based on nano-modified cementitious systems. *International Conference Current Issues of Civil and Environmental Engineering Lviv - Košice – Rzeszów. Proceedings of CEE,* 372–380. Retrieved from: https://doi.org/10.1007/978-3-031-44955-0_37.

Borziak, O., Plugin, A., Chepurna, S., Zavalniy, O. & Dudin, O. (2019). The effect of added finely dispersed calcite on the corrosion resistance of cement compositions. *IOP Conf. Series: Materials Science and Engineering,* 708, 012080. doi: 10.1088/1757-899X/708/1/012080.

Kropyvnytska, T., Sanytsky, M., Rucińska, T., & Rykhlitska, O. (2019). Development of nanomodified rapid hardening clinker-efficient concretes based on composite Portland cements. *Eastern-European Journal of Enterprise Technologies*, 6 (102), 38-48. Retrieved from: https://doi.org/10.15587/1729-4061.2019.185111.

Kirakevych, I., Sanytsky, M., Shyiko, O. & Kagarlitskiy, R. (2021). Modification of cementitious matrix of rapid-hardening high-performance concretes. *Theory and Building Practice*. 3 (1), 79-84. Retrieved from: https://doi.org/10.23939/jtbp2021.01.079.

Gots, V., Berdnyk, O., Lastivka, O., Maystrenko, A. & Amelina, N. (2023). Corrosion of basalt fiber with titanium dioxide coating in NaOH and $Ca(OH)_2$ solutions. *AIP Conf. Proc.* 2490, 050010. Retrieved from: https://doi.org/10.1063/5.0122739**.**

Valcuende, M., Parra, C., Marco, E., Garrido, A., Martínez, E. & Cánoves, J. (2012). Influence of limestone filler and viscosity-modifying admixture on the porous structure of self-compacting concrete. *Constr. Build. Mater.,* 28 (1), 122-128. Retrieved from: https://doi.org/10.1016/j.conbuildmat.2011.07.029.

Ting, M., Wong, K., Rahman, M. & Meheron, S. (2021). Deterioration of marine concrete exposed to wetting-drying action. *J. Clean. Prod,* 278, 123383. Retrieved from: https://doi.org/10.1016/j.jclepro.2020.123383.

Sun, Y. & Wu, X. (2022). Two types of corrosion resistant high-performance concrete: ECC and EPS concrete. *Advances in Civil Function Structure and Industrial Architecture.* Retrieved from: https://www.taylorfrancis.com/chapters/edit/10.1201/9781003305019-38/two-types-corrosion-resistant-high-performance-concrete-ecc-eps-concrete-yixin-sun-xinyi-wu.

Shi, Z., Shi, C., Zhao, R. & Wan, S. (2015). Comparison of alkali-silica reactions in alkali-activated slag and Portland cement mortars. *Materials and Structures*. 48, 743-751 Retrieved from: https://doi.org/10.1617/s11527-015-0535-4.

Ivashchyshyn, H., Sanytsky, M., Kropyvnytska, T. & Rusyn, B. (2019). Study of low-emission multicomponent cements with a high content of supplementary cementitious materials**.** ***Eastern-European Journal of Enterprise Technologies*.** 4(6-100), 39–47. Retrieved from: https://doi.org/10.15587/1729-4061.2019.175472.

Looney, T., Leggs, M., Volz, J. & Floyd, R. (2022). Durability and corrosion resistance of ultra-high performance concretes for repair. *Construction and Building Materials*, 345, 128238. Retrieved from: https://doi.org/10.1016/j.conbuildmat.2022.128238.

І.І. Кіракевич
Національний університет „Львівська політехніка”,
кафедра будівельного виробництва

ВЛАСТИВОСТІ СВІЖОЗАФОРМОВАНОГО ТА ЗАТВЕРДІЛОГО САМОУЩІЛЬНЮВАЛЬНОГО БЕТОНУ, ЩО МІСТИТЬ ДОДАТКОВІ ЦЕМЕНТУЮЧІ МАТЕРІАЛИ

У статті представлені властивості свіжозаформованого та затверділого самоущільнювального бетону, що містить вапняковий мікронаповнювач та додаткові цементуючі матеріали, такі як добавка алюмосилікатна добавка на основі метакаоліну та гіпсу, зола-винесення. Під час процесу гідратації в цементній матриці з додатковими цементуючими матеріалами в неклінкерній частині відбувається реакція з утворенням кристалів етрингіту шляхом топохімічної реакції, що забезпечує ущільнення самоущільнювального бетону. Морфологія, кристалічна структура і склад продуктів гідратації можуть бути дуже різними. При наявності достатньої кількості гіпсу (як компонента алюмосилікатної добавки) основним продуктом гідратації в неклінкерній частині є кристали етрингіту. Ці кристали етрингіту є дрібними, тому що вони утворилися в результаті топохімічної реакції в замкнутому просторі під час утворення цементної матриці. Етрингіт утворюється у вигляді тонких кристалів, що забезпечує ущільнення цементної матриці та є однією з основних причин підвищення ранньої міцності самоущільнювального бетону, що містить додаткові цементуючі матеріали. Утворення вторинного дрібнодисперсного етрингіту при взаємодії активного оксиду алюмінію з кальцію гідроксидом та двоводним гіпсом в неклінкерній частині в’яжучого за рахунок топохімічних реакцій забезпечує компенсацію усадки та приріст міцності цементуючої системи. Використання додаткових цементуючих матеріалів в складі самоущільнювального бетону забезпечує одержання високорухливих бетонних сумішей (розплив конуса бетонної суміші становить 650-730 мм) високої в’язкості (час отримання розпливу 500 мм становить 5-13 с), а затверділі бетони на їх основі характеризуються високою міцністю (58-95 МПа), низькою пористістю, високою надійністю і довговічністю конструкцій.

Ключові слова: самоущільнювальний бетон, додаткові цементуючі матеріали, метакаолін, зола винесення, вапняковий мікронаповнювач, полікарбоксилатний пластифікатор.