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Zinoviy Blikharskyy[1], Taras Markiv[2], Danylo-Myroslav Sobol[1], Rafał Panek[3]

MECHANICAL PROPERTIES AND MICROSTRUCTURE OF CONCRETE INCORPORATING SYNTHETIC ZEOLITE

Lviv Polytechnic National University,
[1]Department of Building Constructions and Bridges,
[2]Department of Building Production.
Lublin University of Technology,
[3]Department of Building Materials Engineering and Geoengineering
taras.y.markiv@lpnu.ua

The effect of natural and synthetic zeolite on the microstructure of cement matrix and mechanical properties of concretes was studied in the article. Results show that the addition of these pozzolanic materials results in the increase both compressive and flexural strength after 28 days of hardening. The concrete incorporating 10 mass. % of synthetic zeolite Na-P1 characterizes the highest compressive and flexural strength that reaches 53.5 and 7.8 MPa and exceeds the strength of reference concrete by 18 and 24 %, respectively. This increase is the result of the improvement of the concrete on the microstructural level due to the formation of the additional amount of fibre-like crystals of hydrosilicates in the non-clinker part of the cement matrix providing its self-reinforcement.

Key words: microstructure, zeolitic tuff, synthetic zeolite, compressive strength, flexural strength, concrete

Introduction

Nowadays, the environmental problems are major issue resulting in world efforts aimed at implementation of the strategy of sustainable development in the construction. Portland cement concrete remains the most popular construction material with consumption of more than 12 billion ton/year and emitting approximately 3 billion tons of CO_2 per year (Kryvenko et al., 2024). To produce this amount, approximately 2 billion tons of Ordinary Portland Cement (OPC) is required. Some authors have estimated that the process of producing 1 ton of OPC generates about 1 ton of carbon dioxide, which results in cement industry being responsible for about 7 % of total worldwide CO_2 emissions (Kropyvnytska et al., 2022; Blikharskyy et al., 2021). Other impacts of cement production can include acid rain as a result of emissions of sulphur dioxide, nitrogen dioxide and nitric oxide; health risks caused by high concentrations of cement kiln dust, and the exhaustion of drinking water reserves.

Recent researches show that this harmful environmental impact can be reduced by incorporating reasonable amount of supplementary cementitious materials (SCMs) to reduce the proportion of cement in concrete. In recent decades, concrete that incorporates supplementary cementitious materials became a sustainable alternative to ordinary concrete. The use of industrial by-products and pozzolanic materials in concrete is becoming attractive because of it’s improved properties such as rheology, long-term strength and durability (Sanytsky et al., 2023). Among the most common pozzolanic SCMs such as fly ash and silica fume is zeolite. Zeolites are gaining interest due to their pozzolanic activity and filling effects. Novel synthetic zeolite obtained from fly ash will allow to reduce harmful environmental impact of thermal power plants and improve mechanical and durability properties of concretes conforming global demands towards sustainability (Grabias-Blicharz et al., 2022). This type of concrete is usually defined as “green” because it causes less environmental harm and has a better life cycle sustainability. Green concrete is defined as a concrete incorporating at least one component identified as a waste, or its production process does not have negative influence on the environment. In other words, green concrete can be considered as an environment friendly concrete and improves three pillars of sustainability: environmental, economic, and social impacts.

Synthetic zeolites are more widely used than natural zeolites because they are cleaner and the particles are more uniform in size. It should also be mentioned that synthetic zeolites are obtained from production waste (such as fly ash) and therefore help to reduce the amount of industrial waste (Wdowin et al., 2014). The fly ash is disposed at the landfill and can cause air and water pollution and, as a result, a potential risk to the people's health and significant stress to the economy and ecosystem (Scharff, 2014). According to the latest research, the addition of synthetic zeolite into cement paste enables to increase the compressive strength, density, and reduce the content of $Ca(OH)_2$ in the specimens (Vaitkevičius et al., 2015). The result is lower probability of corrosion, higher density and reduced porosity of hardened cement paste as well as subsequently reduced water permeability.

Recent studies have shown that both natural and synthetic zeolites provide good mechanical and durability properties when used as SCMs (Blikharskyy et al., 2023; Sanytsky et al., 2021; Nagrockiene et al., 2016; Vaitkevičius et al., 2015). Even though the effects of these additions on mechanical properties of hardened systems were investigated, a few data are available on their influence on both concrete microstructure and its mechanical and durability properties (Shekarchi et al., 2023; Nas et al., 2018; Markiv et al., 2016; Sobol et al., 2015). However, the typical problems of most pozzolanic materials which influence their effectiveness and applications are variations in the compositions, sources and uniformity of the available materials. Therefore, new data can be useful for improving the current knowledge regarding both natural and synthetic zeolite effects on the microstructure and mechanical properties of "green concrete".

Therefore, the aim of this study is to investigate the influence of zeolitic tuff and synthetic zeolite on the microstructure and mechanical properties of concrete.

Materials and methods

Properties of Portland cement CEM I 42.5 R-N, which was used in this study, are presented in Table 1. The properties of Portland cement and aggregates were determined according to Ukrainian standards.

Table 1

Physical and mechanical properties of the cement

Specific surface, m^2/kg	Residue on sieve 008, %	Water demand, %	Setting time, min		Compressive strength, MPa		
			initial	final	2 days	7 days	28 days
390	2.8	29.0	150	240	29.5	39.3	53.5

As the fine aggregate the sand with fineness modulus of 1.6, bulk density of 1380 kg/m^3, voidage of 47.1 % and the content of dust and clay particles of 1.7 % was used. Bulk density, voidage, and the content of dust and clay particles of coarse aggregate (the fraction of 5-10 mm) were 1420 kg/m^3, 46.2 % and 0.3 %, respectively. 10 mass. % of Portland cement was replaced with synthetic zeolite Na-P1, Na-X and zeolitic tuff (Table 2). The size of the zeolitic tuff particles changed over a wide range of 0.01-2000 μm. The particles` size distribution of all two types of synthetic zeolite materials is very similar and is characterized by a monomodal curve with a maximum in the range from 26 to 30 μm. A polycarboxylate superplasticizer with a specific gravity of 1.06 and solid content of 20.4 % was used in the research.

Results and discussions

Growing environmental problems cause more and more serious consequences for the environment every year. Therefore, the replacement of the most energy- and resource-intensive component of concrete, namely Portland cement, is extremely relevant in the technology of modern concrete. The use of mineral additions is of practical interest which not only reduce the negative impact of the construction industry on the environment, but also increase the operational properties, durability and crack resistance of concrete.

Concretes with the addition of synthetic zeolites Na-P1 and Na-X and zeolite tuff (ZT) were studied. The degree of replacement for Portland cement was 10 %. Concrete compositions are given in Table 2. The consistency class of concrete mix was S4. In order to compensate the water, absorbed by the porous pozzolanic materials, which is necessary to ensure the designed consistency class for ease concrete compaction, an additional amount of superplasticizer was added. As can be seen from Fig. 1, fine-grained concrete with 10 mass. % synthetic zeolite Na-P1 is characterized by the highest compressive and flexural strength after 28 days of hardening. So, the compressive strength of Na-P1-10 concrete is 53.5 MPa, which exceeds the strength of the concrete R by 18 %, while the tensile strength at bending is 7.8 MPa, which is 24 % more compared to the reference concrete R.

The study of kinetics of the hydration and hardening processes of cement systems with pozzolanic materials, as well as the genesis of their microstructure, is of great importance, as it opens the way to scientific prediction of their properties. In this regard, the peculiarities of hydration of the following

Table 2

Mixture proportions of concretes (W/C=0,4)

Components of concrete/Designation	Reference concrete (R)	Na-P1-10	Na-X-10	ZT-10
C, kg	450	405	405	405
W, kg	180	180	180	180
S, kg	520	520	520	520
$G_{5\text{-}10}$, kg	1250	1250	1250	1250
Superplasticizer, %	0.6	1.0	1.0	1.0
Pozzolanic materials, kg	–	45	45	45

mixture proportions of concrete were studied by electron microscopy: reference concrete; 75 mass. % of CEM I+25 mass. % of zeolitic tuff; 75 mass. % of CEM I + 25 mass.% of synthetic zeolite Na-X; 75 mass. % of CEM I + 25 mass. % of synthetic zeolite Na-P1.

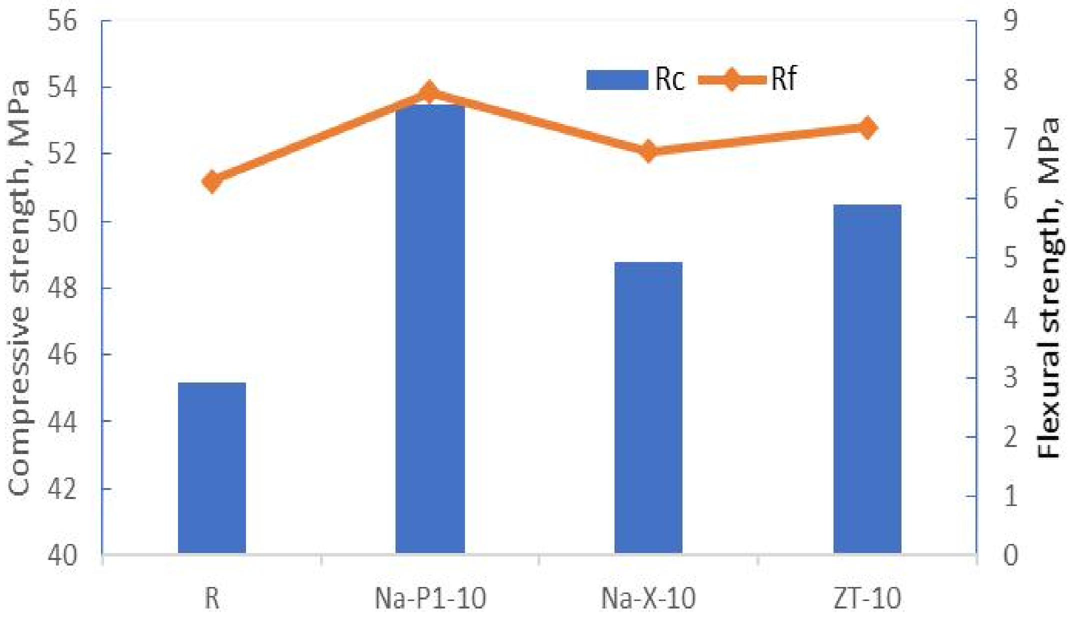
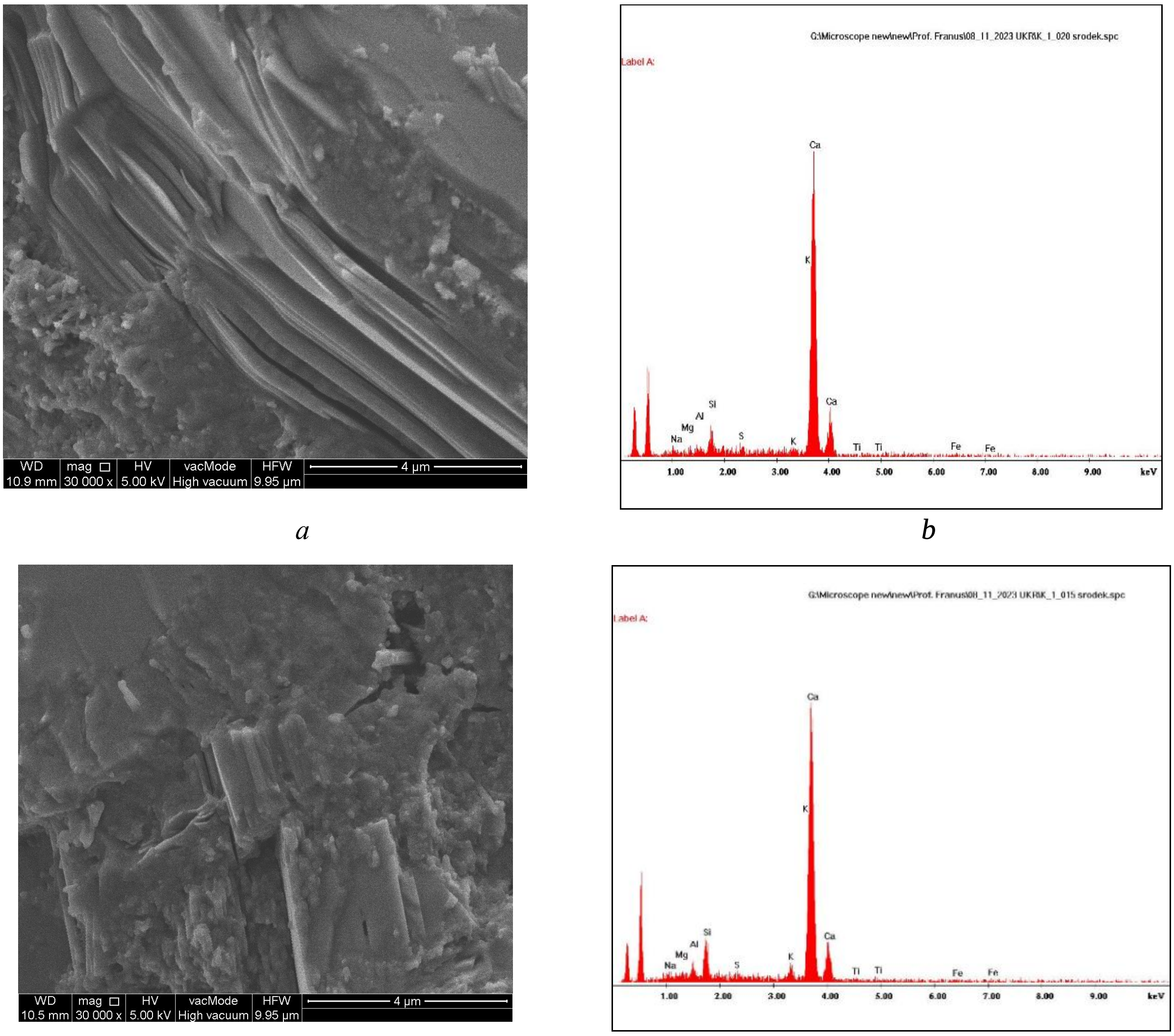


Fig. 1. Strength of concretes after 28 days of hardening

Electron microscopic studies were conducted for the purpose of in-depth study of the hardening processes and formation of the cement paste structure with pozzolanic materials. The microstructure of the reference cement paste based on CEM I, hydrated for 7 days under normal conditions, is characterized by a variety of forms (Fig. 2). At the initial stage of hydration, some crystals are at the stage of formation, whereas others already have clear shapes.



a *b* *c* *d*

Fig. 2. Microstructure (a, c) and EDS spectra (b, d) of concrete cement matrix based on CEM I, hardened for 7 days under normal conditions

In some places, blocks with a clearly defined parallel layered structure (Fig. 2, *a*) are observed, which according to microprobe analysis can be attributed to portlandite (Fig. 2, *b*).

The study of the microstructure of the cement matrix of concrete with the addition of synthetic zeolite Na-P1 showed the peculiarities of its hydration compared to the reference concrete. During the synthesis of this mineral component, its composition contains a certain amount of ash from which it is obtained. In the micrograph (Fig. 3, *a*), it is possible to observe various crystalline hydrate formations: plates of portlandite (Fig. 3, *b*), unreacted ash (Fig. 3, *c*), as well as calcium hydrosilicates (Fig. 3, *d*).

It is interesting to trace the process of ash particle interaction in cement (Fig. 4, *a*). A micrograph shows an ash particle, then a transition layer is visible, where calcium hydrosilicates and hydroaluminates are formed due to baring of the glassy phase (Fig. 4, *b*, *c*, *d*). This ensures an increase in the degree of fixation of ash particles in the mass of cement paste hydrates.

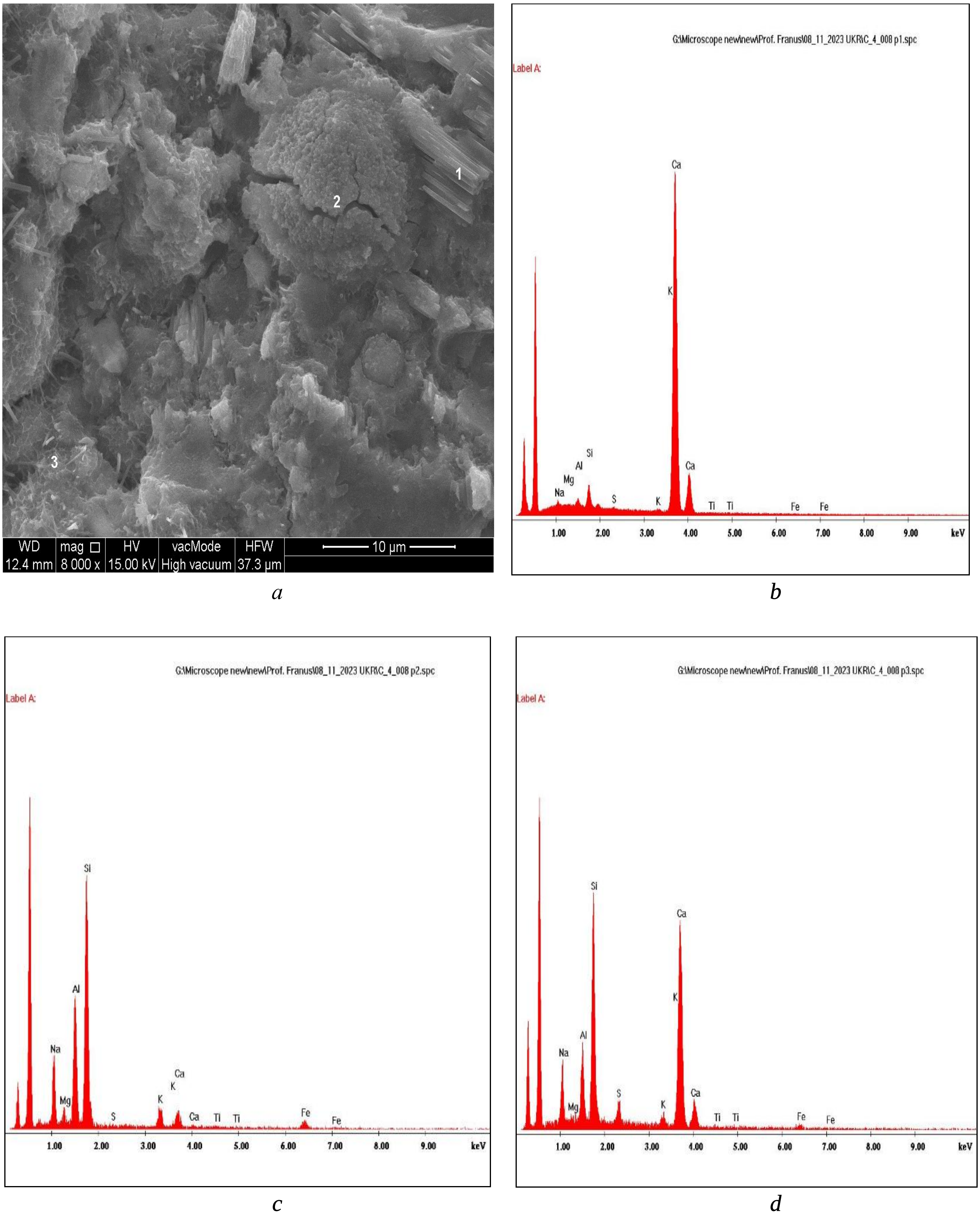


Fig. 3. Microstructure (a) and EDS spectra (b, c, d) of concrete cement matrix based on 75 mass. % of CEM I+25 mass .% of Na-P1, hardened for 7 days under normal conditions

Thus, the investigated zeolitic materials, which are the active elements of the cement matrix and have through-channel intracrystalline porosity, provide intensive nucleation. That is, when pozzolanic materials of the zeolite type are added into cement, the pozzolanic interaction occurs in the volume of each particle.

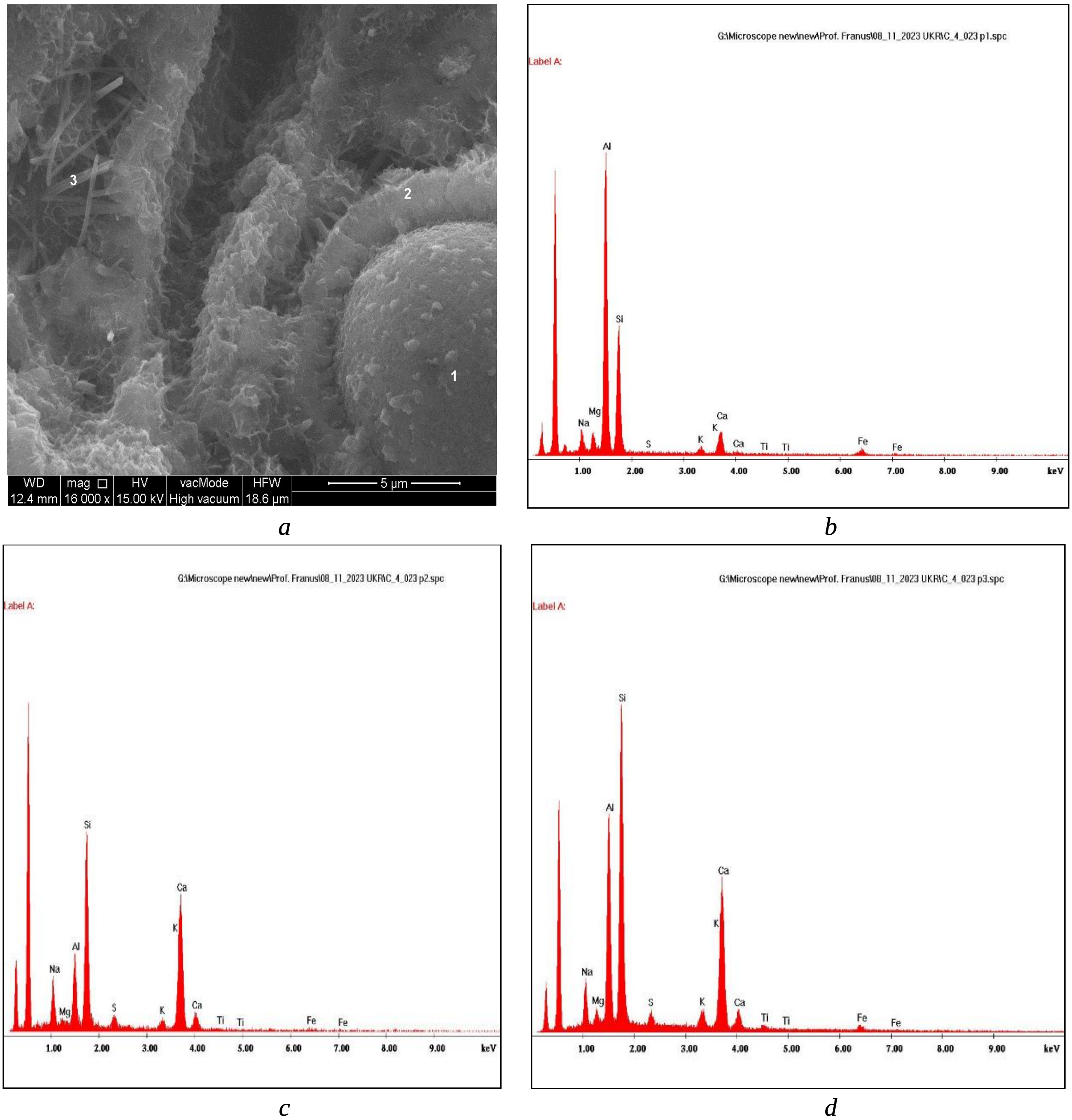


Fig. 4. Microstructure (a) and EDS spectra (b, c, d) of concrete cement matrix based on 75 mass. % of CEM I+25 mass .% of Na-P1, hardened for 7 days under normal conditions

At the same time, crystalline hydration products are released into the volume of the hardening system, resulting in the formation of a dense fine crystalline structure of cement paste with hydrosilicate fibres, which provide self-reinforcement of concrete at the microstructural level.

Conclusions

The article studied the effect of zeolitic materials on the mechanical properties and microstructure of cement matrix of concrete. It was established that the compressive strength of Na-P1-10 concrete exceeds the strength of the reference concrete by 18 %, while the tensile strength at bending by 24 %. The use of synthetic zeolite results in the formation of a tighter microstructure and fiber calcium hydrosilicates that are formed in the non-clinker part of the cement matrix due to the excellent pozzolanic activity provide its self-reinforcement.

References

Kryvenko, P., Rudenko, I., Sikora, P., Sanytsky, M., Konstantynovskyi, O., & Kropyvnytska, T. (2024). Alkali-activated cements as sustainable materials for repairing building construction: a review. *Journal of Building Engineering*, 109399. doi.org/10.1016/j.jobe.2024.109399

Kropyvnytska, T., Sanytsky, M., Heviuk, I., & Kripka, L. (2022). Study of the Properties of Low-Carbon Portland-Composite Cements CEM II/CM. In *International Scientific Conference EcoComfort and Current Issues of Civil Engineering* (pp. 230–237). Cham: Springer International Publishing. doi.org/10.1007/978-3-031-14141-6_22

Blikharskyy, Z., Sobol, K., Markiv, T., & Selejdak, J. (2021). Properties of concretes incorporating recycling waste and corrosion susceptibility of reinforcing steel bars. *Materials*, *14*(10), 2638. doi.org/10.3390/ma14102638

Sanytsky, M., Kropyvnytska, T., & Ivashchyshyn, H. (2023). Sustainable modified pozzolanic supplementary cementitious materials based on natural zeolite, fly ash and silica fume. In *IOP Conference Series: Earth and Environmental Science* (Vol. 1254, No. 1, p. 012004). IOP Publishing. doi 10.1088/1755-1315/1254/1/012004

Grabias-Blicharz, E., Panek, R., Franus, M., & Franus, W. (2022). Mechanochemically assisted coal fly ash conversion into zeolite. *Materials*, *15*(20), 7174. doi.org/10.3390/ma15207174

Wdowin, M., Franus, M., Panek, R., Badura, L., & Franus, W. (2014). The conversion technology of fly ash into zeolites. *Clean Technologies and Environmental Policy*, *16*, 1217–1223. https://link.springer.com/article/10.1007/s10098-014-0719-6

Scharff, H. (2014). Landfill reduction experience in The Netherlands. *Waste Managment*, *34*, 2218–2224. https://doi.org/10.1016/j.wasman.2014.05.019

Vaitkevičius, V., Vaičiukynienė, D., Kantautas, A., Kartovickis, A., & Rudžionis, Ž. (2015). Blended cements produced with synthetic zeolite made from industrial by-product. *Materials Science*, *21*(1), 136–142. doi: 10.5755/j01.ms.21.1.5635

Blikharskyy, Z., Markiv, T., Turba, Y., Hunyak, O., Blikharskyy, Y., & Selejdak, J. (2023). Mechanical and fracture properties of air-entrained frc containing zeolitic tuff. *Applied Sciences*, *13*(16), 9164. doi.org/10.3390/app13169164

Sanytsky, M., Usherov-Marshak, A., Kropyvnytska, T., & Heviuk, I. (2021). Performance of multicomponent Portland cements containing granulated blast furnace slag, zeolite, and limestone. *Cement-Wapno-Beton= Cement Lime Concrete*, *25*(5), 416–427. doi.org/10.32047/CWB.2020.25.5.7

Nagrockiene, D., & Girskas, G. (2016). Research into the properties of concrete modified with natural zeolite addition. *Construction and Building Materials*, *113*, 964-969. DOI: 10.1016/j.conbuildmat.2016.03.133

Shekarchi, M., Ahmadi, B., Azarhomayun, F., Shafei, B., & Kioumarsi, M. (2023). Natural zeolite as a supplementary cementitious material – A holistic review of main properties and applications. *Construction and Building Materials*, *409*, 133766. doi.org/10.1016/j.conbuildmat.2023.133766

Nas, M., & Kurbetci, S. (2018). Mechanical, durability and microstructure properties of concrete containing natural zeolite. *Comput. Concr*, *22*(5), 449–459. DOI: 10.12989/cac.2018.22.5.449

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*, 554-562. doi.org/10.1016/j.acme.2016.03.013

Sobol, K., Markiv, T., Terlyha, V., & Franus, W. (2015). Peculiarities of hydration processes of cements containing natural zeolite. *Budownictwo i Architektura*, *14*(1), 105–113. doi:10.35784/bud-arch.1674

З. Я. Бліхарський[1], Т. Є. Марків[2], Д.-М. Соболь[1], Р. Панек[3]
Національний університет “Львівська політехніка”,
[1] кафедра будівельних конструкцій та мостів,
[2] кафедра будівельного виробництва,
Люблінський технічний університет,
[3] кафедра інженерії будівельних матеріалів та геоінженерії

МЕХАНІЧНІ ВЛАСТИВОСТІ ТА МІКРОСТРУКТУРА БЕТОНУ З СИНТЕТИЧНИМ ЦЕОЛІТОМ

У статті досліджено вплив додаткових цементуючих матеріалів на мікроструктуру цементної матриці та механічні властивості бетонів. Серед найпоширеніших матеріалів пуцоланової природи активності, таких як зола і мікрокремнезем, важливе значення має цеоліт, який широко використовується в бетоні завдяки його невисокій вартості та доступності. Незважаючи на кристалічну природу, цеоліти характеризуються необхідною пуцолановою активністю. Синтетичні цеоліти використовуються ширше, ніж природні цеоліти, оскільки вони чистіші, а частинки однорідніші за розміром. Деякі синтетичні цеоліти отримують із відходів виробництва (наприклад, золи), що дає змогу зменшити кількість промислових відходів і знизити потенційні ризики для здоров'я людей, економіки та екосистеми. Результати показують, що додавання цих пуцоланових матеріалів приводить до підвищення як міцності на стиск, так і на розтяг при згині через 28 днів твердіння. Бетон із вмістом 10 мас. % синтетичного цеоліту Na-P1 характеризується найбільшою міцністю на стиск і на розтяг при згині, яка становить 53.5 і 7.8 МПа і перевищує міцність контрольного бетону на 18 і 24 % відповідно. Це є результатом регулювання структури бетону на мікрорівні. Досліджувані цеолітові матеріали, будучи активними елементами цементної матриці і маючи наскрізно-канальну внутрішньокристалічну пористість, забезпечують інтенсивне зародкоутворення. Тобто у разі введення до цементу пуцоланових матеріалів цеолітового типу пуцоланічна взаємодія відбувається в об'ємі кожної частинки. Кристалічні новоутворення виділяються в об'єм системи, що твердне, внаслідок чого формується щільна дрібнокристалічна структура цементного каменю з волокнами гідросилікатів, які забезпечують самоармування цементної матриці бетонів.

Ключові слова: мікроструктура, цеолітовий туф, синтетичний цеоліт, міцність на стиск, міцність на розтяг при згині, бетон.