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Mechanical and durability properties of concretes incorporating natural zeolite



Taras Markiv^a, Khrystyna Sobol^a, Małgorzata Franus^b, Wojciech Franus^{b,*}

^aDepartment of Civil and Environmental Engineering, Lviv Polytechnic National University, Ukraine

^bFaculty of Civil Engineering and Architecture, Lublin University of Technology, Poland

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ABSTRACT

This paper investigates the application of natural zeolite as a substitute of cement in concrete. It studies the mechanical and durability properties of concretes containing 10% of natural zeolite and superplasticizer, as well as 10% of natural zeolite, superplasticizer and an air-entraining agent in comparison to concretes without natural zeolite. The study shows that fresh concrete mixture containing zeolite due to its high surface area demands a higher dosage of superplasticizer to achieve the targeted slump flow. While concretes containing natural zeolite characterize a lower compressive strength until 90 days of hardening, the compressive strength exceeds the strength of the concretes without zeolite after 180 days. The results also reveal the considerable effectiveness of using a superplasticizer and an air-entraining agent in zeolite incorporating concretes on water penetration, drying shrinkage and freeze–thaw resistance of concretes.

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1. Introduction

Concrete is a fundamental component of modern infrastructure, which is why its strength and durability play an important role. The properties of concrete in most cases depend on Portland cement, which remains the main hydraulic binder in use today. It is known that a partial substitution of cement by pozzolans results in an increase in durability of the concrete and, as a result, the service life of concrete structures [1,2].

Among the most common natural pozzolanic materials such as fly ash and silica fume is zeolite, which is used in some regions of the world, because of its lower cost and accessibility

[3–5]. Although natural zeolites are crystalline, they show proper pozzolanic activity [6]. According to Uzal and Turanli [7] a lime reactivity of the clinoptilolite zeolite is comparable to silica fume, higher than fly ash and a non-zeolitic natural pozzolan. Therefore calcium hydroxide as a cement hydration product combines with natural zeolite consisting of reactive SiO₂ and Al₂O₃ to form calcium hydrosilicates [7,8]. It was confirmed by many researchers [1,6–8], that the pozzolanic reaction in pastes containing zeolite of clinoptilolite type considerably decreased the calcium hydroxide content. The reduction of free Ca(OH)₂ in the hardened concrete improves the durability and concrete becomes more resistant to lime leaching by flowing waters and to expansion due to sulfate attack [8,9]. Chan and Ji [10] concluded that zeolite is

* Corresponding author at: Faculty of Civil Engineering and Architecture, Lublin University of Technology, Nadbystrzycka 40, 20-618 Lublin, Poland. Tel.: +48 0815384416.

E-mail address: w.franus@pollub.pl (W. Franus).

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more effective than pulverized fuel ash but worse than silica fume in improving the compressive strength. A number of studies show that the optimal amount of zeolite replacement level is approximately 10% [11–13]. A higher amount of zeolite replacing cement in concrete causes reduction of compressive strength.

Najimi et al. [6] concluded that concretes incorporating zeolite are characterized by the reduction of the heat of hydration and consequently of thermal cracking and improved durability properties such as chloride ion penetration, corrosion rate, drying shrinkage and water penetration. Sabet et al. [14] and Ahmadi and Shekarchi [15] also reported that the incorporation of natural zeolite as a mineral admixture in concrete enhanced its durability properties. However, various types, structures and purities of natural zeolites influence concrete strength and durability in different ways and can lead in some cases to contradictory results in experimental studies. Moreover, properties of concretes with the addition of different types of zeolite located in various regions of the world are already partly researched, but there is very low researches in particular mechanical and durability properties of concretes relating to the zeolite tuffs from fields located in Ukraine.

The aim of this paper is to study the effect of natural zeolite coming from Sokyrnytsia (Ukraine) on the mechanical and durability properties of concrete. These properties include water absorption, water penetration, drying shrinkage, freeze and thaw resistance.

2. Materials and methods

The materials used in this study include a clinoptilolite type of natural zeolite and commercially available Portland cement CEM I 42.5R. The chemical composition of the natural zeolite and Portland cement are presented in Table 1. It was determined by X-ray spectrometer ARL 9800 XP. Zeolite in comparison with Portland cement is characterized by a higher amount of silica, alumina and iron oxides, which are responsible for the pozzolanic activity of zeolite.

The tests of Portland cement properties were carried out according to EN 196 [16]. The specific surface of Portland cement used in the study is 425 m²/kg. Water demand attains 27%, initial and final setting time are 200 and 260 min, respectively. The compressive strength of Portland cement CEM I 42.5R after 2 and 28 days is 30.5 and 55.0 MPa.

The mineral composition of zeolitic tuff was determined by means of a powder X-ray diffraction method, using a PANalytical X'pert APD diffractometer (with a PW 3020 goniometer), a Cu lamp and a graphite monochromator. The analysis was performed at the angle range of 5–65° 2 θ . Philips X'Pert Highscore software was used to process the diffraction data. The identification of mineral phases was based on the PDF-2 release 2010 database formalized by the ICDD.

Powder X-ray diffraction patterns of the zeolite showed that clinoptilolite is the major crystalline phase. Zeolitic tuff also contains quartz as a minor impurity (Fig. 1a). The main components of the natural zeolite are identified as clinoptilolite, accompanied by other components.

The morphology of clinoptilolite and chemical composition in the field of main mineral components of the investigated materials was examined by scanning electron microscope SEM FEI Quanta 250 FEG, equipped with EDS. Clinoptilolite occurs in forms of thin plates in the range 10–30 μ m, sometimes of distinct hexagonal shapes (Fig. 1b).

According to the thermal analysis, in the first thermolysis phase of the zeolitic tuff, sample mass loss takes place in the temperature range of 20–200 °C (Fig. 2). It is associated with the release of physically-absorbed water. The second thermolysis phase of the sample occurs in the temperature range of 200–440 °C and corresponds to the emission of chemically bonded water, which is coordinatively and chemically linked to the crystal lattice of the mineral and forms aqua complexes with metal cations that enter the structure of the zeolite.

A shallow endothermic effect is observed in the temperature range of 440–580 °C, which relates to the dehydroxylation process of surface due to splitting off of OH– groups, which corresponds to a small weight loss in the TG curve.

In the high-temperature range of 580–1000 °C, the appearance of an endothermic effect in the DTA curve can be explained by a combination of several processes: a deeper surface dehydroxylation, destruction and a depreciation of the crystal structure of zeolite under high temperatures.

Mercury intrusion porosimetry (MIP) was used for determining the pore size distribution of natural zeolite. The tests were performed for pressures ranging from 0.1 to 200 MPa or pore radii from 10.0 to 3.8 $\times 10^{-3}$ μ m. The volume of mercury V [m³/kg] intruded at a given pressure P [Pa] gave the pore volume that can be accessed. The intrusion pressure was translated on equivalent pore radius R [m] following the Washburn equation:

Table 1 – Chemical and mineralogical phase composition of the cement and zeolite.

Portland cement (CEM I 42.5R)				Natural zeolite			
Chemistry	wt.%	Mineralogy	wt.%	Chemistry	wt.%	Mineralogy	wt.%
SiO ₂	20.17	C3S	59.76	SiO ₂	75.34	Clinoptilolite	60
Al ₂ O ₃	4.41	β -C2S	18.12	Al ₂ O ₃	8.77	Quartz	30
Fe ₂ O ₃	2.39	C3A	6.76	Fe ₂ O ₃	1.30	Other phases	10
CaO	63.45	C4AF	10.91	CaO	4.6		
MgO	2.41			MgO	0.55		
SO ₃	3.21			SO ₃	0.05		
Na ₂ O	0.17			Na ₂ O	1.22		
K ₂ O	1.02			K ₂ O	2.41		

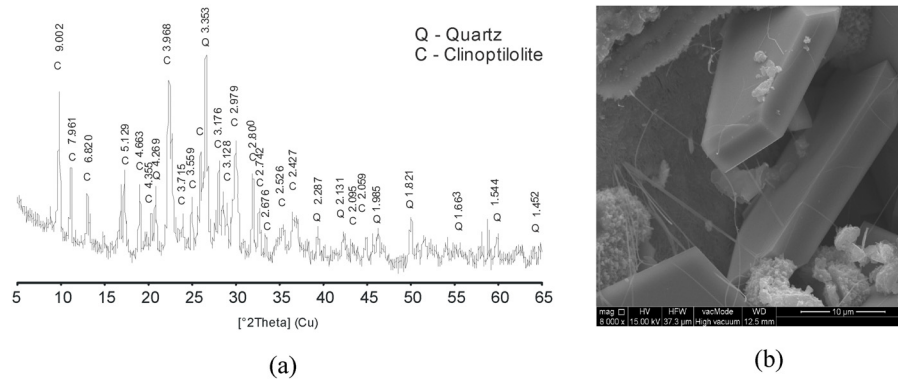


Fig. 1 – (a) XRD analyses of zeolitic tuff (clinoptilolite) (Q: quartz; C: clinoptilolite) and (b) SEM image of the lamellar grains of clinoptilolite (SEM, magnification 8000×).

$$P = - \frac{A\sigma_m \cos \alpha_m}{R} \tag{1}$$

where σ_m is the mercury surface tension (0.485 N/m), α_m is the mercury/solid contact angle (141.3° for all studied materials) and A is a shape factor (equal to 2 for the assumed capillary pores). Knowing the dependence of V vs. R, a normalized pore size distribution, $\chi(R)$, was calculated and expressed in the logarithmic scale:

$$\chi(R) = \frac{1}{V_{max}} \frac{dV}{d \log(R)} \tag{2}$$

The results of MIP indicate that porosity of zeolite is 54.7%. Graphical interpretation of obtained results shows that almost 65% of total pore volume of natural zeolite can be attributed to pores with diameter from 0.4 to 40 μm (Fig. 3). Regarding the quantitative aspect, the share of small pores in the range of 0.01–0.15 μm is relatively very low in investigated particle size of zeolite.

Particle size distribution (PSD) were measured using laser diffraction method on Mastersizer 2000 with Hydro G dispersion unit with the measuring range of 0.02 μm to 2 mm. Mie theory was applied for PSD determination with parameters equal to 1.52 for light refractive index and 0.1 for absorption coefficient [17,18]. Measurements were carried out at pump and stirrer speeds equal to 1750 and 700 rpm, respectively [19].

The bimodal PSD curve of the considered natural zeolite is presented in Fig. 4. Dominating grains are in the range of 0.01–90 μm with a maximum diameter of 25 μm and 90–2000 μm, the largest share of particles being 300 μm.

Commercially available polycarboxylate-based superplasticizer with a specific gravity of 1.05 and solid content of 20% and an air-entraining agent, based on abietate salts, with specific gravity of 1.015 and solid content of 4.4% were used in this study. The properties of aggregates used in the studies were tested according to PN-EN 1097 [20]. The results of investigations are reported in Table 2.

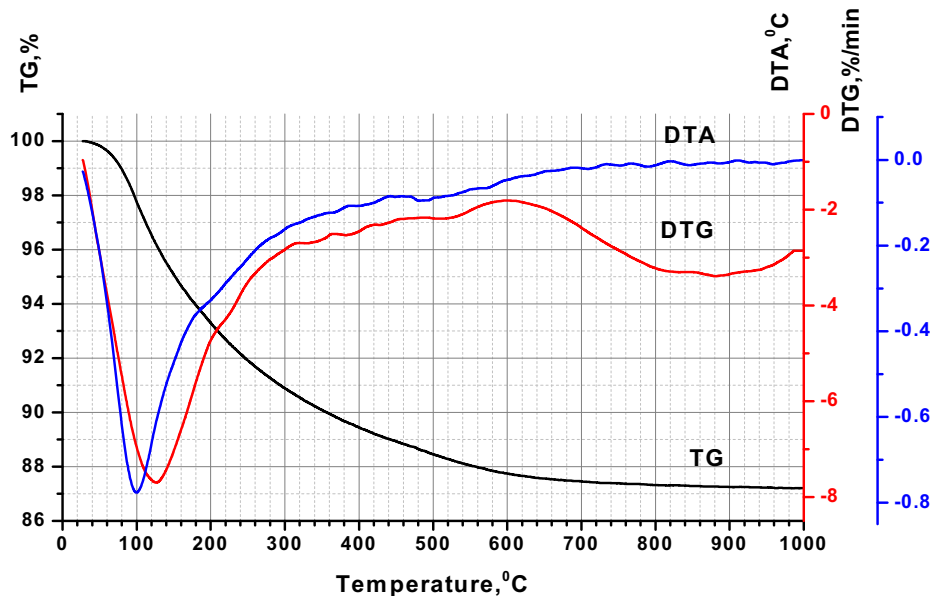


Fig. 2 – DTA diagrams of zeolitic tuff.

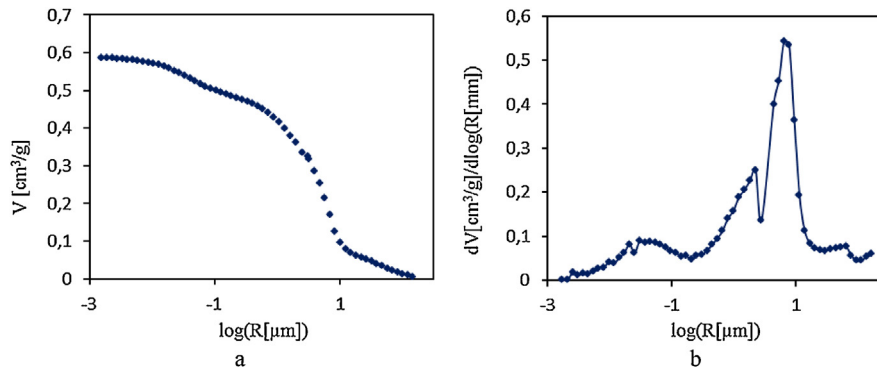


Fig. 3 – Cumulative pore volume (a) and pore radius (b) of natural zeolite.

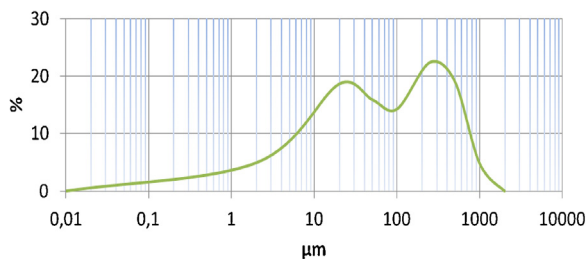


Fig. 4 – Particle size distribution of the natural zeolite.

The concrete mixture proportions are presented in Table 3. The control concrete mixtures without natural zeolite (ZOP, ZOPA) and two mixtures named as Z10P and Z10PA were made by replacing 10% of cement weight with natural zeolite. The consistency class of the concrete mixtures was S4.

The making and curing of specimens for strength tests were carried out according to PN-EN 12390-2 [21]. The strength tests of the specimens were conducted on days 1, 28, 56, 90 and 180 according to PN-EN 12390-3 [22]. The reported results are the averages of three specimens. Standard deviation(s) of results is

0.4–2.6 MPa. Water penetration, absorption and freeze–thaw tests were carried out according to PN-EN 12390-8 [23] and PN-EN 206:2014 [24], respectively.

Drying shrinkage was measured using 40 mm × 40 mm × 160 mm prisms. Three samples were prepared, demolded 24 h after casting, and stored in a room at temperature of 20 ± 2 °C and $50 \pm 4\%$ relative humidity. The length was measured using a comparator starting at the age of 24 h after casting and continuing up to 180 days.

3. Experimental results and discussion

3.1. Mechanical properties

The strength of concrete is an important characteristic that determines its quality as a building material. The use of natural zeolite decreased the workability of the concrete mixture. Loss of workability was compensated by using an extra amount of superplasticizer (Table 3). The higher water demand of concrete mixtures incorporating zeolite is caused by the porous microstructure of the natural zeolite. In order to increase the concrete's durability to freezing and thawing

Table 2 – Aggregate properties.

Aggregate type	Density (g/cm ³)	Bulk density (kg/m ³)	Voidage (%)	Dust and clay particles (%)	Fineness modulus
Fine (0–2 mm)	2.63	1440	45.2	1.5	2.0
Coarse (2–8 mm)	2.63	1400	45.1	0.5	–
Coarse (8–16 mm)	2.64	1450	45.8	0.3	–

Table 3 – Mixture proportions and air content results.

Mixture identification	Portland cement (kg/m ³)	Natural zeolite (kg/m ³)	Natural zeolite (% of cement)	Superplasticizer (% of cement)	Air-entraining agent (% of cement)	Air content (%)
ZOP	350	0	–	1.22	–	2.4
ZOPA	350	0	–	1.22	0.3	5.1
Z10P	315	35	10	1.64	–	2.4
Z10PA	315	35	10	1.64	0.3	4.0

Note: The followings are valid for all mixtures: fine aggregate = 660 kg/m³, coarse aggregate (2–8 mm) = 450 kg/m³ and coarse aggregate (8–16 mm) = 700 kg/m³; w/cm = 0.5.

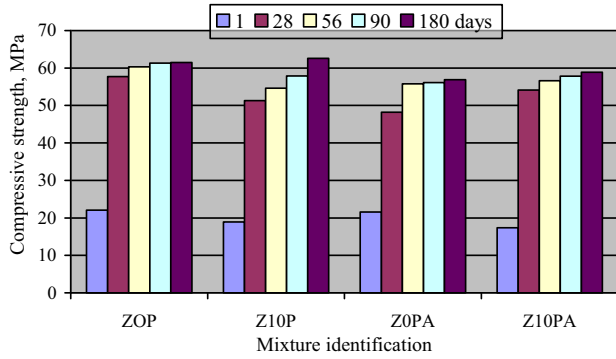


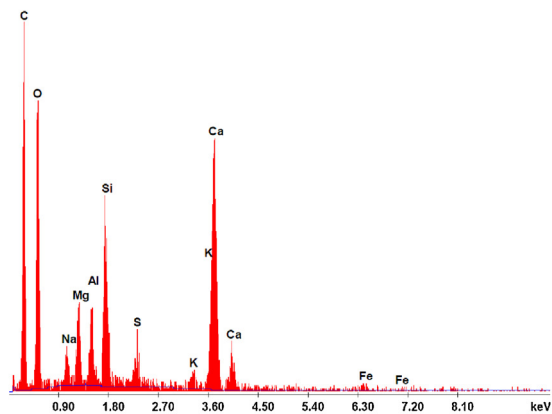
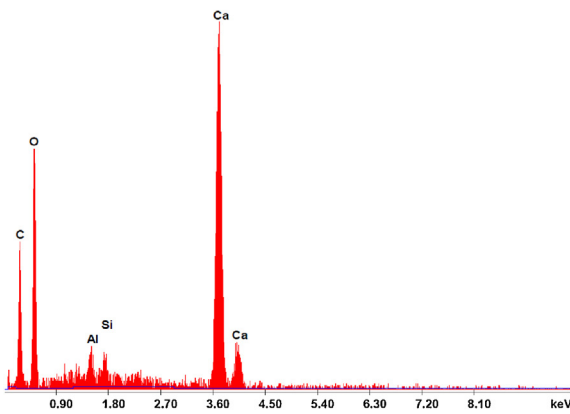
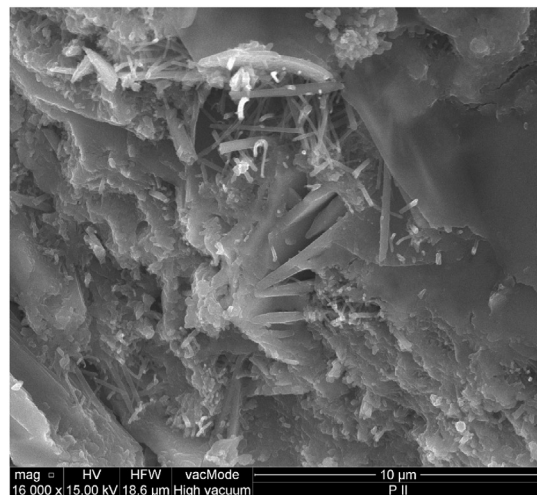
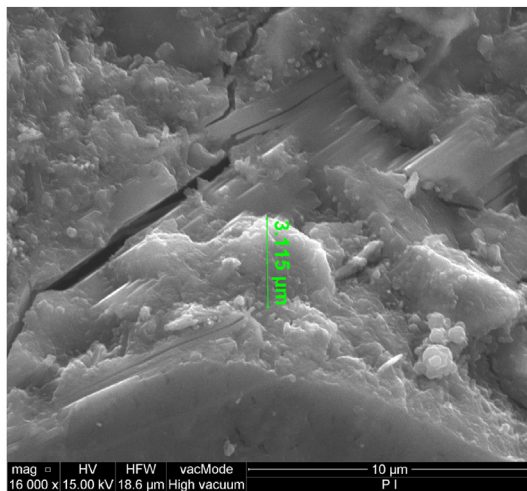
Fig. 5 – Compressive strength of concretes.

damage, an air-entraining agent was used. Air content of concretes ZOPA and Z10PA containing an air-entraining agent was 5.1 and 4.0%, respectively. It is almost two times higher in comparison with concrete without an air-entraining agent.

The compressive strength of concretes at w/cm ratio of 0.5 is presented in Fig. 5. It should be noted that the compressive strength of concretes incorporating zeolite and superplasticizer was lower than the control concrete (without zeolite) till 90 days of hardening. At the age of 1 day, the strength of the

concretes incorporating zeolite, superplasticizer, and air-entraining agent (Z10PA) was 19.4% lower than the control concrete ZOPA (without zeolite). It was found by Najimi et al. [6] and Chan and Ji [10] that at w/cm ratio higher than 0.45, the strength of the concretes incorporating zeolite was lower than that of the control concrete. However, as seen from the Fig. 5, the percentages of strength reduction were generally reduced with increasing the age. Over time, the strength of compared concretes was levelled. In the test conducted at day 180, the strength of concretes containing zeolite was found to be even greater than the strength of concretes without the zeolite. It should be noted that when zeolite is used in concrete the pattern is not retained when the percentage of concrete strength reduction does not correspond to the percentage content of zeolite in concrete.

Usage of scanning electron microscopy complemented the data on the structure formation of cement pastes. The microstructure of concrete ZOP was characterized by a large number of hydrate formations (Fig. 6). Some crystals had been already well formed and other ones were still forming and had a shape of small needle-like or plate-like formations. New crystals formed on top of the existing crystals, resulting in a stepwise growth of a number of layers of hydration products. Their morphology changed gradually with a reduction in the crystallization speed of hydrates. In some places, a part of



(a)

(b)

Fig. 6 – Microstructure and EDS spectra of Portland cement paste containing natural zeolite (b) and without zeolite (a).

densely composed hexagonal plates of calcium hydroxide changed. This was confirmed by the results of microprobe analysis (Fig. 6a). A high amount of clinoptilolite and an internal surface area of natural zeolites due to their porous microstructure as well as major alkali cations content in their compositions provide an excellent pozzolanic activity. It should be noted that the influence of the amount of K^+ and Na^+ cations in zeolite chemical composition on lime reactivity and as a result on pozzolanic activity was submitted by Sanytsky et al. [8] and Ghourchian et al. [25].

Usage of zeolite in concretes, which is a source of active Al_2O_3 and SiO_2 , provided the formation of additional quantities of fibre-like crystals of hydrosilicates and elongated crystals of ettringite. This resulted in the colmatation of pores and growth in the strength of the paste (Fig. 6b).

3.2. Water absorption and water penetration

Other important factors affecting concrete durability are water absorption and water penetration, which indirectly represent the porosity and also deliver information about pore structure of concretes. The water absorption and water penetration depth of concretes test results are presented in Fig. 7.

Water absorption of concretes containing natural zeolite and superplasticizer (Z10P), as well as the concrete incorporating natural zeolite, superplasticizer and air-entraining agent (Z10PA), was 5.3 and 4.9%, respectively. Their absorption was higher in comparison with concretes without zeolite (ZOP and ZOPA). It was connected with the water absorption of natural zeolite. Since it is higher in zeolite than in cement, the higher water absorption of concretes incorporating zeolite is inevitable.

The water penetration depth was tested at 28 days. The results show that designed concretes can be considered waterproof, because water penetration depth is lower than 20 mm. The concrete containing natural zeolite, superplasticizer and an air-entraining agent (Z10PA) showed the lowest water penetration depth of 3.5 mm. This can be explained by the positive influence of the pozzolanic reaction between natural zeolite and cement hydration products on the microstructure as well as the air-entraining agent on pore structure of concrete. Najimi et al. [6] observed similar dependences, but water penetration depth and water absorption of concretes were slightly higher at the same

water-to-cementitious ratio in comparison with concretes investigated in these studies.

3.3. Freeze–thaw resistance

The destruction of concrete in a water-saturated state at the alternate freezing and thawing is caused by complex physical processes that result in the deformation and mechanical destruction of concrete. The behaviour of concretes after 50, 100, and 150 freezing/thawing cycles were studied and the reduction of compressive strength is shown in Table 4. According to Sun and Scherer [26] and Coussy and Monteiro [27] the reduction of strength is observed due to stress developing in the material skeleton as the temperature decreases. Owing to higher thermal expansion ($50 \times 10^{-6} K^{-1}$ for ice versus $\sim 10 \times 10^{-6} K^{-1}$ for concrete) great internal tensile stress is developing causing the skeleton to crack. The crack will penetrate the surface of the concrete, then turn and remove a flake. As seen from Table 4, the concretes containing 10% of zeolite exhibited higher resistance to freezing and thawing damage compared to the concretes without zeolite. It is related with secondary CSH gel, which is formed due to the pozzolanic reaction and results in decrease of the capillary porosity of concrete incorporating zeolite. Vejmelková et al. [28] also reported that incorporating 10% of zeolite in concrete results in better resistance to freezing and thawing damage after 100 cycles compared to the concretes without zeolite. However, water-to-cementitious ratio was 0.45 and air-entraining agent was not used in that researches.

As it was mentioned above the usage of air-entraining agent is a very effective method of improving resistance to freezing and thawing cycles, because entrained air bubbles create sufficient free space to accommodate the volume of ice obtained after freezing water, but there are not enough researches concerning the effect of both zeolite and air-entraining agents on the frost resistance of concretes. It should be noted that the necessity of air-entraining agent usage for increasing resistance to freezing and thawing cycles was supposed by Bilim [29] in the research of mortar containing natural zeolite. As presented in Table 4, after 150 freezing/thawing cycles the lowest compressive strength reduction, 17.9%, was observed especially for concrete containing natural zeolite, superplasticizer and the air-entraining agent (Z10PA).

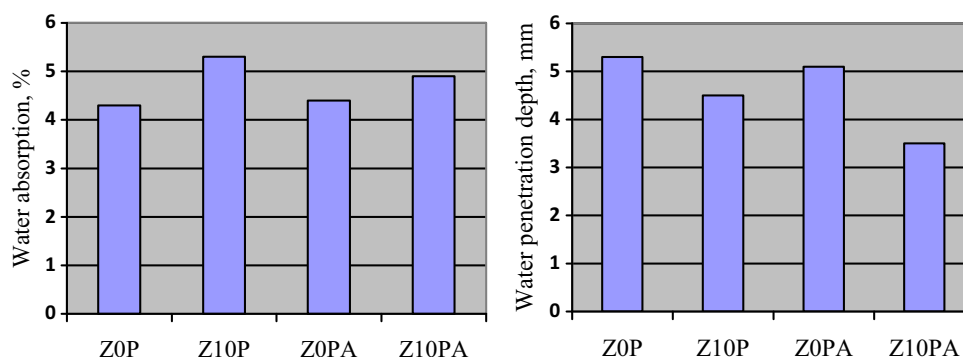


Fig. 7 – Water absorption and water penetration of concretes at 28 days.

Table 4 – The compressive strength (MPa) of the concretes.

Concretes identification	Freeze-thaw cycles	Compressive strength		Compressive strength reduction compared to the concrete without cycles (%)
		Without cycles	After freeze-thaw cycles	
NZOP	50	56.9	49.3	-13.3
	100	58.0	41.7	-28.1
	150	58.5	36.3	-37.9
NZ10P	50	54.8	48.2	-12.0
	100	55.8	44.5	-20.2
	150	54.6	40.6	-25.6
NZOPA	50	53.6	50.2	-6.3
	100	54.0	42.5	-21.2
	150	53.1	37.4	-29.5
NZ10PA	50	54.8	52.6	-4.0
	100	55.3	49.5	-10.4
	150	55.1	45.19	-17.9

At the same time, a dramatic decrease of compressive strength was obtained for concretes without zeolite ZOP and ZOPA, 37.9 and 29.5%, respectively.

3.4. Drying shrinkage

Shrinkage occupies an important place among the deformation properties of concrete and affects the quality and durability of structures and facilities. The investigation of the effect of natural zeolite on drying shrinkage deformations and moisture loss were carried out on fine-grained concretes. Mixture proportions of fine-grained concretes were as in the concretes described in Table 3 (cement:sand = 1:1.88; (cement + zeolite):sand = 1:1.88), except that coarse aggregate was not used and water to cementitious ratio was 0.41. The dosage of superplasticizer and air-entraining agent is presented in Table 3 and depends on the mixture proportion. The drying shrinkage of fine-grained concretes is plotted versus age in Fig. 8a. The results show that the application of natural zeolite considerably decreases shrinkage. The drying shrinkage of Z10P and Z10PA was about 2.6 and 5.4 times lower, respectively, than the control concretes ZOP and ZOPA after 180 days. Fig. 8b presents the drying shrinkage plotted versus the moisture loss of the samples. It should be noted that in samples with up to 2.7% moisture loss, the drying shrinkage of concretes containing zeolite Z10P and Z10PA was about

3 times lower than that of the control concretes without zeolite ZOP and ZOPA, but with moisture loss growth the drying shrinkage of concretes ZOP and ZOPA increases significantly. According to the obtained results, the drying shrinkage of concretes incorporated natural zeolite, at 4.5% moisture loss, was already about 6 times lower than the control concretes without zeolite.

This can be attributed to the internal curing ability of natural zeolite as a porous material which absorbs a part of water in fresh state of concrete. Ghourchian et al. [25] reported that the porosity of zeolite accessed through entrances larger than about 100 nm is sufficiently high to provide efficient internal curing. According to the results of MIP, presented in Fig. 3, majority of zeolite grains pores in particle size distribution range of 0.01-2000 μm (Fig. 4) are larger than 100 nm. Therefore, zeolite, used in this study, is suitable for internal curing of concretes, because of absorbed water can gradually migrate out of natural zeolite during drying of hardened concrete compensating its self-desiccation.

Najimi et al. [6] observed that the drying shrinkage of mixtures containing natural zeolite at 15 and 30% Portland cement replacement levels were also slightly lower than that of the control mixture, whereas contrary results were obtained by Jana [11] and Kasai et al. [30].

The positive effect of natural zeolite on mechanical properties of concretes is also confirmed by the results of

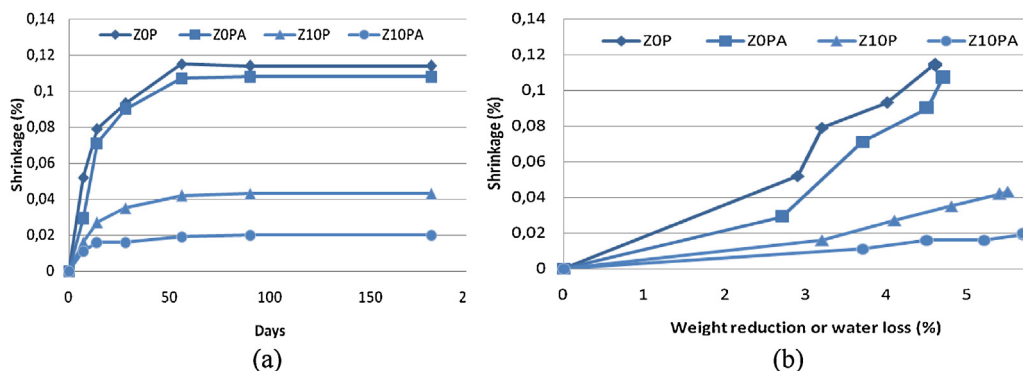


Fig. 8 – Drying shrinkage versus age (a) and drying shrinkage versus moisture loss (b).

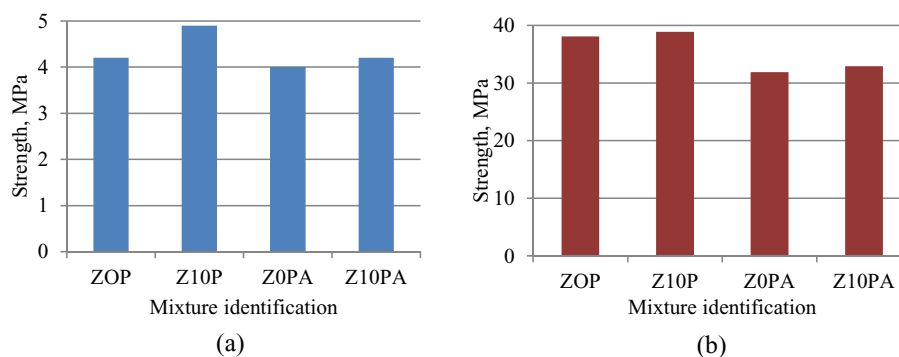


Fig. 9 – Flexural (a) and compressive (b) strength of fine-grained concretes after 180 days of hardening.

strength tests of fine-grained concretes specimens after drying shrinkage measurements. The obtained results are presented in Fig. 9.

According to Fig. 9a, flexural strength of concrete Z10P containing zeolite is 16% higher in comparison with control concrete ZOP. Air-entraining agent usage in concretes ZOP and Z10P provides 4 and 17% strength reduction of concretes both ZOPA and Z10PA, respectively. Similar trends were observed under compressive strength test. As shown in Fig. 9b, replacing 10% of cement by zeolite also causes slight increase in compressive strength of concretes Z10P and Z10PA in comparison with the control concretes ZOP and ZOPA.

Thus, the application of natural zeolite as a partial substitute of cement in concrete and rational technological solutions in the design of concrete mixtures allow to obtain materials with improved properties and durability. The usage of zeolite in concretes leads to technical, economical and ecological advantages as well as sustainable construction due to conserving energy and resources and reducing environmental pollution impact associated with cement production.

4. Conclusions

This paper considers the issues of development of effective concrete containing natural zeolites. The most important conclusions are as follows:

1. Proposed approaches allow implementing technologies of modified concretes with the required properties, obtained by the simultaneous introduction of an active mineral additive such as natural zeolite and chemical admixtures of plasticizing and air-entraining action in construction industry.
2. Investigations of mechanical properties of concretes show that the substitution of cement by zeolite resulted in some reduction of strength until 90 days of hardening, but after 180 days compressive strength of concretes containing zeolite exceeds the strength of concrete without zeolite.
3. Introduction of zeolite and chemical admixtures in concrete permits modifications of the phase composition of cement hydration products with the formation of an extra amount of calcium hydrosilicates, hydrogelenite and ettringite and also improves the pore structure of concrete.

4. Incorporation of cement replacement materials, such as zeolite in spite of its pores structure, in combination with chemical admixtures makes them effective components of concrete, which results in the increase of resistance to freezing and thawing damage, decrease of drying shrinkage, water penetration depth and results in the improved durability of concretes.

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