



Article

The Effects of Natural Zeolite as Fly Ash Alternative on Frost Resistance and Shrinkage of Blended Cement Mortars

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Abstract: As the cement industry is responsible for 7% of the global CO₂ emissions, locally and abundantly available materials are vastly valorized, and their use is assuming a significant role in this domain. Over the last few decades, significant research in the development of supplementary cementitious materials (SCMs) derived from industrial wastes, such as fly ash (FA), has been conducted. However, facing environmental pressures, coal power plants are closing across the planet. Hence there is an urgent need to identify sustainable SCMs that can replace FA in the concrete industry. Furthermore, the usage of FA in cement-based composites does not often produce satisfactory results from the aspect of certain properties, such as freeze–thaw durability. Therefore, the application of natural zeolites (NZs) for these purposes has emerged as an area of interest in the civil engineering practice. This paper presents the results of experimental research regarding the influence of NZ, as a mineral admixture, on the basic physical and mechanical properties of cement mortars, with a focus on frost resistance and drying shrinkage. The amount of NZ was varied from 10 to 30% in relation to cement mass. The findings indicate that NZ positively influences the drying shrinkage reduction regardless of the replacement level, while the best results concerning frost resistance can be achieved in cement blends with 10% NZ.



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Keywords: natural zeolite; cement mortar; SCM; frost resistance; drying shrinkage; compressive strength; capillary water absorption; water absorption at atmospheric pressure; performance index

1. Introduction

Ordinary Portland cement (OPC) is a widely utilized building material. Nonetheless, several inherent disadvantages of OPC are challenging to overcome, including (i) high energy consumption, i.e., cost-effectiveness, (ii) natural resource consumption, a primary lack of availability of aggregates and (iii) emission of greenhouse gasses, such as CO₂.

The use of locally available waste materials as a partial alternate of aggregates/cement in the concrete design can notably reduce the environmental burden. These include fly ash (FA), silica fume, ground granulated blast furnace slag, and other calcined natural pozzolanic materials such as rice husk ash and metakaolin. In recent decades, substantial research on the possibilities to replace natural resources in cement-based composites with these by-products has been conducted.

The European Standard EN 206 provides the guidelines on how to design an appropriate concrete composition and achieve a durable structure conforming to the exposure classes identified therein. As the concrete rapidly deteriorates when exposed to severe environments (frost, sulfates etc.), it is essential to design a resilient concrete structure that continues to perform its intended functions, maintains its required strength and serviceability during the specified expected service life. Cement-based composites are, generally, porous materials able to entrain gas and liquids. The pores influence the properties of the material in various ways, e.g., compressive strength is related to the total porosity, the size of pores and their distribution, the size and form of the larger pores and their relations;

freeze–thaw resistance is controlled by the volume of both the air entrained in the pores and the space between the pores; drying shrinkage is a consequence of the loss of moisture from the fine pores in the concrete. In cold environments, the freeze–thaw durability is particularly important for a porous, brittle material such as concrete. Due to the volume expansion of concrete when it is subjected to lower temperatures, microcracks appear and act as an ingress path for aggressive ions. As a result, the durability of the concrete structure can significantly decrease. Numerous tests have been conducted all around the globe with concrete modified by active mineral admixtures to mitigate these problems.

Most of the researchers used FA as the major replacement of OPC. So far, it has been well established that FA contributes to the following: (i) reduces heat development at an early age [1], (ii) slows down the rate of hydration (pozzolanic reaction) [2], (iii) induces improved workability as a result of the rounded shape of FA particles [3], (iv) provides a higher long-term age strength by converting the calcium hydroxide into calcium silicate hydrate gel (C–S–H) [4], and (v) ensures a low permeability, i.e., it can reduce chloride ingress, thereby making concrete more durable [5]. As a result of a denser structure and the increase of the non-evaporable water content, Chen et al. [6] suggest that the fly ash-based concrete exhibits lower drying shrinkage than the traditional concrete.

Although FA is very frequently one of the main constituents of blended cement, there are certain studies documenting a disputable behavior of fly ash-based concrete subjected to freeze–thaw cycles [7–12]. Pedersen et al. [12] stated that FA commonly contains small amounts of unburnt carbon that can adsorb the air-entraining admixture (AEA), making it inactive, hence an additional amount of AEA is required to obtain a proper frost resistance. Generally, the damage caused by frost attack is determined by heat and moisture transport within the pore structure of the material. A detailed description of the mechanisms governing the frost resistance is out of the scope of this paper and is discussed elsewhere [13]. Essential for all these mechanisms is the existence of a “pumping effect” presenting an accelerated water uptake with the water content exceeding a critical value, caused by freezing–thawing at the restricted area resulting in the damage of the structure [14]. If the “pumping effect” can be decreased or eliminated, the frost damage will be avoided.

Since the shutdown of coal-fired power plants has already begun as planned in the USA as well as in Europe and Asia, it is necessary to find an alternative material to replace FA as a supplementary cementitious material (SCM) in blended cement composites that will have either the same or improved properties. Natural zeolites (NZs) have emerged as a potentially suitable substitute for FA as an SCM [15]. NZ is widely used in the cement industry as a cement blending material. However, its effects in cementitious systems have not yet been fully explored. Owing to the presence of reactive SiO_2 and Al_2O_3 , NZ contributes to the strength of concrete mainly by the pozzolanic reaction and the formation of additional C–S–H gel. This hydration product’s amount increases with time, thus enabling a decrease in the average pore size and, consequently, leading to lower open porosity, which results in improved properties of hardened cement-based composites. So far, it has been demonstrated that NZ addition up to the 10% cement replacement level increases the sulfate resistance, decreases the chloride permeability, shrinkage and water absorption, and improves the carbonation resistance of concrete [16]. These positive effects are explained by a high absorption capacity of NZ; hence it can cure the concrete internally and help to improve its permeability and durability [17].

This ability of NZ to reversibly absorb a significant amount of water within the porous framework [18] offers the possibility of decreasing the “pumping effect” in NZ blended cement and, consequently, raising the frost resistance. The use of NZ in cement composites production from the aspect of frost resistance and drying shrinkage has been scarcely investigated so far. Zheng et al. [19] documented that the frost resistance of concrete containing zeolite as a partial sand replacement is slightly lower in the early stage of freeze–thaw cycles, while in the middle and later stage, the frost resistance is higher than that of ordinary concrete. Bilim [20] determined that NZ as an SCM in the amount of 5% improved

the durability of mortar exposed to 50 freeze–thaw cycles, while the usage of NZ in the amount of over 10% led to a significant reduction in the mortars' strength. Regarding the influence of NZ on the drying shrinkage, Wang et al. stated [21] that the use of NZ at the selected sand replacement ratios can, due to the internal curing mechanism, successfully decrease the 28-day shrinkage of cement-based composite. Najimi et al. [22] found that, at the age of 90 days, the mortars with 15 and 30% NZ had lower values of drying shrinkage by 84% and 64% than those of the reference concrete. Shon and Kim [15] examined drying shrinkage of cement mortars blended with 0, 10 and 20% NZ as well as with 20% FA. The lowest drying shrinkage was detected in the mortar with 20% FA, then with 10 and 20% NZ, respectively, while the highest one was observed for the reference mortar.

Though the effects of NZ on the specific properties of blended cement mortars have been studied by different researchers, few studies quantify the possibility of its application from the aspect of certain properties which entail specifically frost resistance. The objective of this study is to investigate the effect of NZ, originating from one Serbian deposit, used as a partial substitute of OPC at various weight replacement rates, on compressive strength, flexural strength, capillary water absorption, water absorption at atmospheric pressure, drying shrinkage and frost resistance of blended cement mortars. In addition, this research analyzes and explores a solution for another concerning issue, i.e., the long-term uncertainty of FA availability due to the shutting down of coal power plants worldwide.

The obtained results indicate that the optimal cement replacement level by NZ can successfully decrease drying shrinkage and improve the frost resistance of cement mortar. Considering the reduction of the cement-related environmental burden and a possible decline in FA supply due to the closure of coal-fired power plants, NZ could offer an alternative solution and help to meet the demand of the construction industry. The NZ analyzed in this paper is the same one used for the purpose of the research reported by Radeka et al. [23], as well as Milović et al. [24], which deals with the soft water attack effects on phase composition and compressive strength of blended cement pastes, when cement is replaced with 0, 10, 20 and 30% of NZ.

2. Materials and Methods

2.1. Materials

For the experimental investigation of the influence of NZ as an SCM in blended cement mortars on their basic physical and mechanical properties as well as frost resistance, the following component materials were used:

- OPC (CEM I 42.5R, Lafarge-BFC Serbia), standard EN 197-1 [25];
- NZ from a quarry in Igroš (Brus, Serbia) with particle size less than 125 μm ;
- CEN standard sand in accordance with EN 196-1 [26];
- Superplasticizer (HRWRA + SRA—High-Range Water-Reducing Admixture + Set-Retarding Agent) (Sika ViscoCrete 3070, Sika, Baar, Switzerland);
- Deionized water.

2.1.1. Characterization of Cement

OPC from Lafarge-BFC, Serbia, was used. The results of the examination of the physical properties of OPC, provided in Table 1, are in accordance with the requirements given in EN 197-1 [25].

Table 1. Physical properties and test methods for OPC.

Physical Property	Test Method	OPC
Density (g/cm ³)	EN 1097-7 [27]	3.13
Blaine specific surface (cm ² /g)	EN 196-6 [28]	4189
BET specific surface (m ² /g)	-	1.55
Fineness (wt.%), >45 µm	EN 196-6 [28]	4.89
Standard consistency (%)	EN 196-3 [29]	30.0
Initial setting time (min)	EN 196-3 [29]	200
Finish setting time (min)	EN 196-3 [29]	310
Soundness—Le Chatelier (mm)	EN 196-3 [29]	0.5

The chemical composition of OPC, Table 2, was determined by wet chemical analysis in accordance with EN 196-2 [30]. The loss on ignition (L.O.I.) was defined as a mass difference (expressed in mass percent) between the sample at 950 °C and 20 °C.

Table 2. Chemical composition of OPC.

Chemical Composition, (wt.%)	OPC
SiO ₂	20.98
Al ₂ O ₃	5.51
Fe ₂ O ₃	2.58
CaO	61.96
MgO	2.50
Na ₂ O	0.22
K ₂ O	0.74
SO ₃	3.60
L.O.I. *	1.35

* Loss on Ignition.

2.1.2. Characterization of Natural Zeolite

NZ from a quarry in Igroš (Brus, Serbia), with particle size less than 125 µm, was used as an SCM. The obtained physical properties of NZ, given in Table 3, were compared with the requirements for FA prescribed by the standard EN 450-1 [31]. NZ fulfilled the criteria for the initial setting time, soundness, the criteria for fineness characteristic of category N as well as the criteria for activity index. In that regard, NZ was classified as a pozzolanic material or mineral additive of type II.

Furthermore, the class of NZ pozzolanic activity was determined for the specimens prepared according to the procedure given in SRPS B.C1.018 [32]. Mortars were prepared with NZ, slaked lime and standard sand, with the following mass proportions: m_{sl}:m_{nz}:m_{qs} = 1:2:9 and water—binder ratio 0.6 (where: m_{sl}—mass of slaked lime; m_{nz}—mass of NZ; m_{qs}—mass of CEN standard sand). After compacting, the specimens were hermetically sealed and cured for 24 h at 20 °C, then for 5 days at 55 °C. Subsequently, a 24 h period was allowed for specimens' cooling process to reach 20 °C, followed by the compressive and flexural strength tests. The pozzolanic activity of NZ met the criteria for class 5 in accordance with SRPS B.C1.018 [32].

Compared to PC, NZ had a lower density and higher values of Blaine and BET specific surface areas. The first result implies that NZ blending could lower the overall specific gravity of the blended mortars, whereas the other two values indicate a prominent porous structure of NZ [24,33].

Table 3. Physical properties and test methods for NZ.

Physical Property	Test Method	NZ
Density (g/cm ³)	EN 1097-7 [27]	2.31
Blaine specific surface (cm ² /g)	EN 196-6 [28]	5393
BET specific surface (m ² /g)	-	78.16
Fineness (wt.%), >45 µm	EN 451-2 [34]	32.78
Standard consistency (%)	EN 196-3 [29]	40.6
Initial setting time (min)	EN 196-3 [29]	185
Finish setting time (min)	EN 196-3 [29]	302
Soundness—Le Chatelier (mm)	EN 196-3 [29]	0.5
Activity index, at the age of 28 days (% of control)	EN 450-1 [31]	85.60
Activity index, at the age of 90 days (% of control)	EN 450-1 [31]	90.00
Class of the pozzolanic activity	SRPS B.C1.018 [32]	Class 5

The chemical composition of NZ, shown in Table 4, was determined by energy-dispersive X-ray fluorescence, ED-XRF (Spectro XEPOS C, Boschstr. 10 D-47533 Kleve, Germany). The system uses a Silicon Drift Detector, band-pass filter, and focuses the X-ray from a binary Co/Pd alloy thicktarget anode (50 W/60 kV) combining polarized/direct excitation. The sample tray used for these measurements was with rotating positions for pellets. Measurements were carried out in a vacuum atmosphere, and Spectro XRF Analyzer Pro software was used. The samples for ED-XRF analysis were prepared in accordance with the pressed powder method. The observed materials (5 g) and the binding agent (Cereox wax, Fluxana) were mixed (1 g), and the 32 mm diameter pellets were formed. The pellets were formed under 10 tons load applied via a laboratory hydraulic press.

Table 4. Chemical composition of NZ.

Chemical Composition, (wt.%)	NZ
SiO ₂	62.78
Al ₂ O ₃	12.20
Fe ₂ O ₃	2.37
CaO	5.09
MgO	2.65
Na ₂ O	0.42
K ₂ O	0.74
P ₂ O ₅	0.05
SO ₃	0.01
Cl	0.05
L.O.I. *	12.36

* Loss on Ignition.

The sum of oxides, relevant for pozzolanic reaction (SiO₂, Al₂O₃ and Fe₂O₃) and shown in Table 4, higher than 70%, allows for NZ to be classified into a silicate mineral additive of type II conforming to EN 450-1 [31]. According to the loss on ignition result, NZ could not be classified into any category proposed by the standard EN 450-1 [31].

2.2. Mixture Compositions

Mixture proportions of the reference and three blended cement mortars, containing 10, 20 and 30% NZ as an SCM per cement mass, are provided in Table 5.

Table 5. Marks and compositions of mortar mixtures.

Mixture	C	CZ10	CZ20	CZ30
OPC, (g)	450	405	360	315
NZ, (g)	-	45	90	135
CEN standard sand, (g)	1350	1350	1350	1350
Superplasticizer, (g)	-	-	2.25	4.50
Deionized water, (ml)	225	225	225	225

2.3. Experimental Program

As part of the experimental research, the mineralogical characterization of NZ was conducted first, and then the following tests were performed on hardened mortar specimens:

- Compressive strength, at the age of 2, 7, 28, 60, 90 and 180 days;
- Flexural strength, at the age of 2, 7, 28, 60, 90 and 180 days;
- Capillary water absorption, at the age of 28 days;
- Water absorption at atmospheric pressure, at the age of 28 days;
- Drying shrinkage, at the age of 1, 3, 7, 14, 28 and 56 days;
- Frost resistance, the first cycle—out of 50 cycles in total—started at the age of 28 days.

2.4. Methods

The mineralogical characterization of NZ was performed by XRD analysis (Philips PW1710 device) under the following experimental conditions: monochromatic Cu K α radiation with 1.5418 Å wavelength in the 5–60° of 2 θ range, scan rate 0.02° and 0.5 s per step.

The compressive and the flexural strengths of mortars C, CZ10, CZ20 and CZ30 were determined in accordance with EN 196-1 [26] by testing the same specimens (3 standard prisms with dimensions 40 mm × 40 mm × 160 mm per mixture). At first, the flexural strength of the reference and NZ blended cement mortars was tested by Michaelis scales, and then the compressive strength on the halves of the broken prisms was determined. The hydraulic compression testing machine, with the range of 150 kN, was used for this purpose.

Capillary water absorption and the capillary water absorption coefficient were determined in accordance with the National standard SRPS U.M8.300 [35]. Three standard mortar prisms with dimensions 40 mm × 40 mm × 160 mm were used for this purpose per each mortar mixture. After 24 h of casting, specimens were demolded and cured for 7 days at 23 ± 2 °C and more than 90% relative humidity. Before testing, the samples were conditioned at standard laboratory air temperature and humidity for 21 days. Thereafter, a waterproof coating was applied to the sides of the prisms. The surface area subjected to water was 64 cm². Measurements were conducted after 1 min, 5 min, 15 min, 30 min, 1 h, 4 h, and 25 h. The results were expressed as water absorption in kg/m². The capillary water absorption coefficient after 25 h was calculated using Equation (1):

$$A = \frac{\Delta m_v}{\Delta \sqrt{t}} \quad (1)$$

where:

A—capillary water absorption coefficient, (kg/m²h^{0.5});

m_v —capillary water absorption, (kg/m²);

t—time of test duration, (h).

The water absorption of mortars at atmospheric pressure was obtained according to the procedure described in the National standard SRPS B.B8.010 [36] by gradually immersing standard mortars' specimens in water (3 specimens with dimensions 40 mm × 40 mm × 160 mm per one mortar type). Before testing, the specimens were dried to the constant mass in a laboratory drying oven at 105 ± 5 °C and then cooled in a desiccator to the laboratory air temperature. Upon their removal from the desiccator, the mass of dried specimens was

recorded, and then the specimens were immersed in a container with distilled water up to $\frac{3}{4}$ of their height. After 1 h, the container was filled with water to half the height of the specimens, after 2 h up to $\frac{3}{4}$, and, finally, after 22 h, the specimens were completely immersed in water. The test lasted for four days. The results of water absorption were expressed as a percentage of the mass of the dry specimens.

The drying shrinkage of the reference and NZ blended cement mortars were determined in accordance with the method described in EN 12617-4: Chapter 6 [37]. The standard mortar prisms were used for this purpose.

The frost resistance of mortars was estimated in accordance with the National standard SRPS U.M1.016 [38]. A series of six standard mortar prisms with dimensions 40 mm \times 40 mm \times 160 mm was prepared for each mortar type. One half of every series (3 specimens) was exposed to the freeze–thaw cycling, while the other half (3 specimens) was used as an etalon. After 28 days of a standard treatment procedure, 3 specimens of each mortar were exposed to freeze–thaw cycles. Each cycle consisted of two phases: 4 h of freezing at -20 ± 2 °C in the air and at least 4 h of submersion in tap water at $+20 \pm 3$ °C. After 50 freeze–thaw cycles, the compressive strengths of the tested specimens were determined. The criterion for the frost resistance evaluation of mortar was a fall in compressive strength up to 25% in comparison to their corresponding etalons.

The climatic test chamber, type KKT-300 (Elektron, Banja Koviljača, Serbia) with an integrated environmental control system that can maintain relative humidity levels from 10% to 90% and temperature from -40 °C to $+160$ °C, was used for curing/conditioning the specimens for the capillary water absorption, water absorption at atmospheric pressure, drying shrinkage and frost resistance testing.

3. Results and Discussion

3.1. Mineralogical Characterization of Natural Zeolite

The diffraction pattern of the NZ is presented in Figure 1. According to the obtained results, NZ consists mainly of clinoptilolite (type of natural zeolite mineral) and smectite (known as “swelling” or “expandable” clay mineral). The presence of smectite in zeolite tuff, as a secondary component, can affect the properties of fresh and hardened NZ blended cement composites [24].

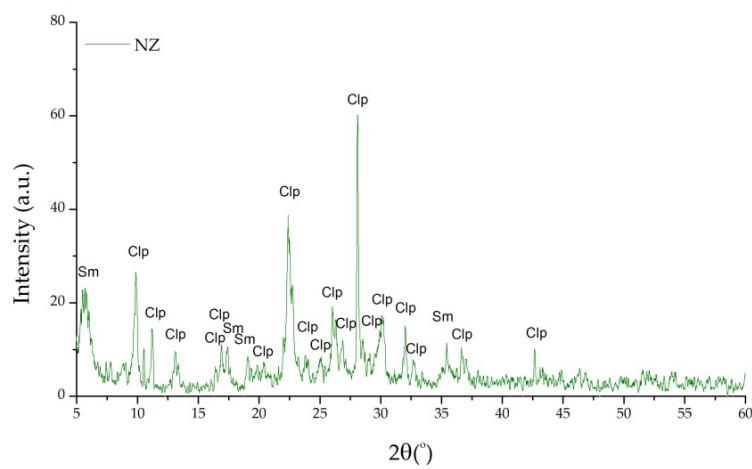


Figure 1. XRD diffractogram of natural zeolite (Clp—clinoptilolite, Sm—smectite).

3.2. Compressive Strength

The impact of the pozzolanic activity on the compressive strength of NZ blended cement was studied on the mortar specimens prepared according to EN 196-1 [26]. The average compressive strengths of blended cement mortars over time are presented in Figure 2. After analyzing these results, it can be seen that, generally, the mortar compressive strength decreased as the content of NZ increased for all ages, except in the case of mortars

with 10 and 20% NZ, at the age of 90 days, when their strengths were in the same range (difference between their strength values was about 5%). The reference mortar, C, had the highest compressive strength value up to the age of 60 days. In a later period, the compressive strengths of blended mortars with up to 20% NZ as an SCM were equal to or higher than the corresponding reference values. As in the case of NZ blended cement pastes [24], the obtained results indicate that NZ as an SCM contributes to mortar compressive strength development over time.

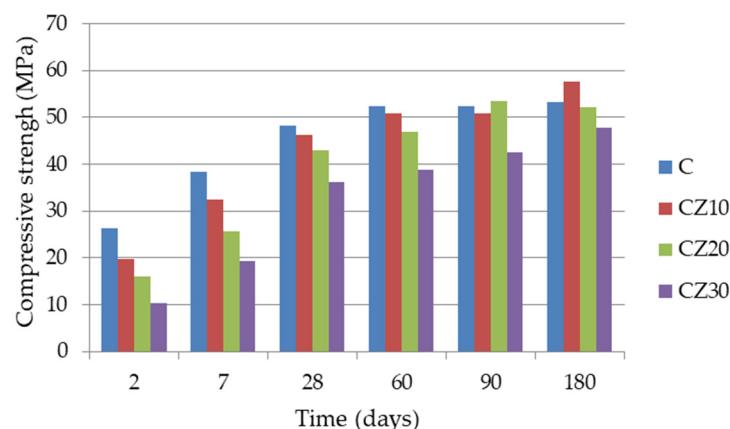


Figure 2. Average compressive strengths of tested mortars.

Although NZ fulfilled the requirements prescribed in EN 450-1 [31], except for loss on ignition, the authors decided to use the k-value concept for FA, defined in SRPS EN 206-1 [39], for the calculation of effective water to cement ratio ($\omega_{\text{eff}} = \text{water} / (\text{cement} + k \times \text{addition})$). The obtained values of ω_{eff} were 0.534, 0.568 and 0.631, for mortars CZ10, CZ20 and CZ30, respectively.

Specifically, at the ages of 28, 60 and 90 days, the compressive strengths of CZ10 were lower than their corresponding reference values by just 4%, 3% and 3%, respectively, while they exceeded the reference mortar ones by 8 % after 180 days

After 28 and 60 days, the relative strength of CZ20 was lower by 11 % and 10%, respectively, while, at the age of 90, it reached its reference strength value and remained in that range over time.

Although the compressive strengths of CZ30 were always lower than their corresponding reference values, an upward trend over time can be noticed, i.e., the difference between its compressive strength and the corresponding reference value decreased by 26%, 19%, and 10%, at the ages of 60, 90 and 180 days, respectively.

The results imply that the effect of NZ on blended mortar's compressive strength is related to the replacement level and the age of mortar specimens. Mortar compressive strengths at the age of 28 days were lower than those of the reference one for all levels of OPC substitution with NZ. This decrease in compressive strength may be attributed to the insufficient rate of NZ pozzolanic activity and the dilution effect. Namely, NZ met the criteria for the lowest class of pozzolanic activity according to [32], while the dilution effect was caused by the reduction in the OPC amount—further influencing a rise in the effective water to cement ratio and a decline in the number of hydration products. After 180 days, 10% substitution showed an improvement of 8% in compressive strength compared to the reference mortar due to a prolonged pozzolanic reaction of NZ and, consequently, the formation of additional C–S–H gel. The compressive strength of the mortar containing 20% NZ stayed in the range of the reference value, while the mortar containing 30% NZ had the compressive strength value lower than that of the reference one by 10%.

The derived conclusions are in line with those obtained for NZ blended cement pastes, for the age of 180 days, reported by Milović et al. [24]. It should also be taken into account that the increase in the amount of NZ in the blended cement mortars entails a higher amount of smectite, a secondary mineral phase in NZ determined by XRD analysis. Norvell

et al. [40] reported that smectite (montmorillonite) clay reduced the compressive strength of blended cement concretes, which could be one of the potential reasons that led to a fall in mortar's compressive strength with NZ content rise, alongside the dilution effect.

Based on the obtained experimental results, the recommended level of substitution of OPC with NZ, regarding the long-term compressive strength (from 60 to 180 days), is up to 20%, and that is in accordance with the results reported by Jana [41], indicating that the optimal compressive strength of mortars with NZ as an SCM can be achieved (up to 56 days) within the range of 10–20% OPC substitution with NZ. Furthermore, Bilim [20] found that the mortars containing up to 30% clinoptilolite exhibited comparable or higher strength results compared to the control mixture at all curing times (up to 90 days). Furthermore, Shon and Kim [15] reported that the mixtures containing 10 and 20% NZ showed a slower strength development up to 56 days curing period but exceeded the strength of reference mixture at 91 days. Considering that Bilim [20], as well as Shon and Kim [15], examined the compressive strength of NZ blended mortar prisms with dimensions 40 mm × 40 mm × 160 mm, made with CEM I 42.5R (water to binder ratio of 0.5) and ASTM Type I Portland cement (water to binder ratio of 0.48), respectively, their results of strength activity index after 28 days alongside the results obtained in our own experimental research are presented in Figure 3. It can be noticed that the obtained results correspond to those reported by the other authors [15,20].

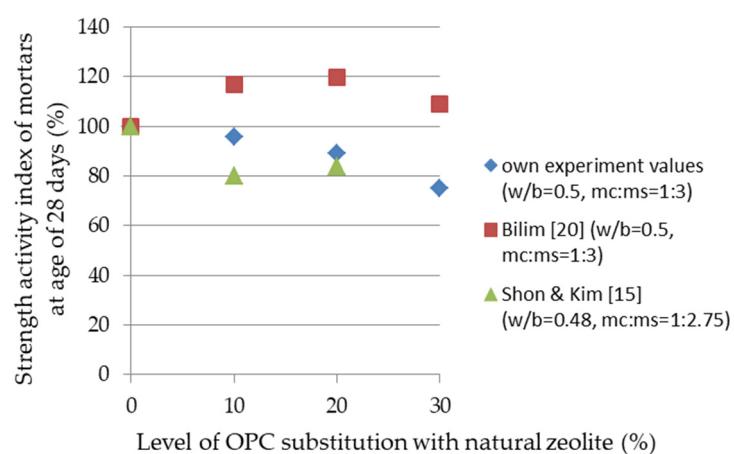


Figure 3. Presentation of the strength activity index results of our own research, as well as the results reported by other authors [15,20], for the age of 28 days (w/b—water to binder ratio, mc—mass of cement, ms—mass of sand).

3.3. Flexural Strength

The flexural strengths of the reference and NZ blended cement mortars over time are presented in Figure 4. It can be observed that the flexural strength decreased as the content of NZ rose. This was particularly noticeable until the age of 28 days. As in the case of mortars' compressive strength, there was a slight increase in the flexural strength (about 5%) of the mortar with 20% NZ in comparison with that of 10%, at the age of 90 days. The reference mortar, C, had the highest flexural strength up to the age of 90 days. In a later period, the flexural strengths of blended mortars with 20 and 30% NZ as an SCM were lower than those of the reference one by 8% and 9%, respectively, while the mortar with 10% NZ reached the corresponding reference value, i.e., its flexural strength value was comparable with that of the reference one.

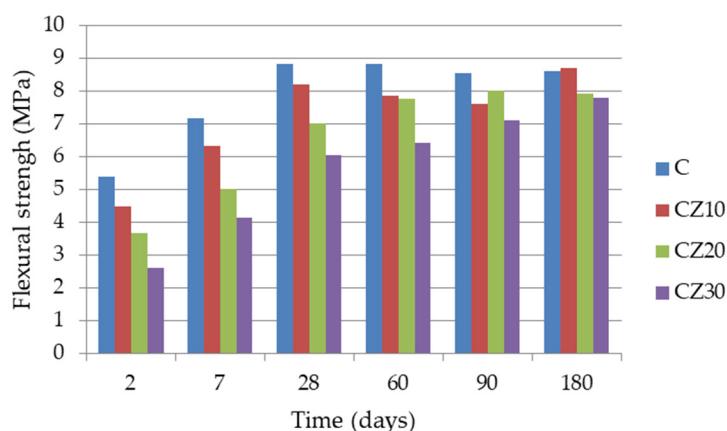


Figure 4. Average flexural strengths of tested mortars.

At the ages of 28, 60 and 90 days, the flexural strengths of CZ10 were lower than their corresponding reference values by just 7%, 11% and 11%, respectively, while they reached those of the reference mortar ones after 180 days.

Although the flexural strengths of CZ20 and CZ30 were always lower than the values of their reference ones, an upward trend over time can be noticed. After 28, 60 and 90 days, the relative flexural strengths of CZ20 were lower by 21%, 12% and 6%, respectively, while they remained at the same level thereafter. Furthermore, the difference between the flexural strengths of CZ30 and their corresponding reference values decreased by 32%, 27%, 17% and 9%, at the ages of 28, 60, 90 and 180 days, respectively.

It can be noticed that the mortars with 20 and 30% NZ as an SCM had a similar rate of flexural strength development, i.e., an intensive gain in flexural strength until the age of 90 days was observed, while CZ30 was shown to have reached the flexural strength value of CZ20 at the age of 180 days.

The obtained results imply that the effect of NZ on the flexural strength is related to the amount of mineral replacement, as in the case of mortars' compressive strength. Since the mortar with 10% OPC replacement by NZ reached the reference value after 180 days, and its flexural strength at the age of 28 days was just 7% lower than that of the reference mortar, the recommended level of substitution of OPC with the applied NZ, regarding the flexural strength, is up to 10%. On the other hand, Bilim [20] found that the mortars containing up to 30% clinoptilolite exhibited comparable or higher flexural strength values compared to the control mixture even at the early ages. It should be taken into account that the NZ used by Bilim [20] had a higher Blaine specific surface ($9660 \text{ cm}^2/\text{g}$) than that of the one used in this research ($5393 \text{ cm}^2/\text{g}$).

3.4. Capillary Water Absorption

One of the factors affecting blended cement composite durability is, generally, water absorption, which indirectly represents the porosity. The change in the kinetics of capillary water absorption of the reference and NZ blended cement mortars are shown in Figure 5. Based on the shape of the diagrams, the following can be observed:

- Mortar CZ30 showed the largest capillary water absorption. The amount of capillary water absorbed by this mortar varied significantly over time in relation to other mortars;
- With a rise in the level of substitution of OPC with NZ, the capillary water absorption increased as well. The first contributing factor may be the presence of smectite (a secondary mineral component in the applied zeolite tuff) due to the cation hydration between smectite units, which is one of its unique physico-chemical properties [24]. The second reason could be a low rate of pozzolanic activity of the applied NZ (class 5) together with the dilution effect, which could lead to the lower amount of C-S-H gel formation in the mortar at the age of 28 days (i.e., a higher permeability);

- The capillary water absorption graphic of mortars C, CZ10 and CZ20 had a bilinear form. The turning point for the mortars C and CZ10 was 15 min, while for the mortar CZ20, it was 1 h. The slope of the first part of these curves indicates a strong absorption of water in the initial period;
- The capillary absorption of mortar CZ30 is represented as a linear function, with no pronounced changes in the kinetics of water absorption;
- During the investigated time (25 h), the capillary water absorption did not stop, which indicates that the saturation of capillary pores was not reached. This conclusion could be applied to all tested mortars;
- The smallest capillary water absorption was observed for the reference mortar C. Its curve has the smallest slope, which indicates that the saturation would be reached soon.

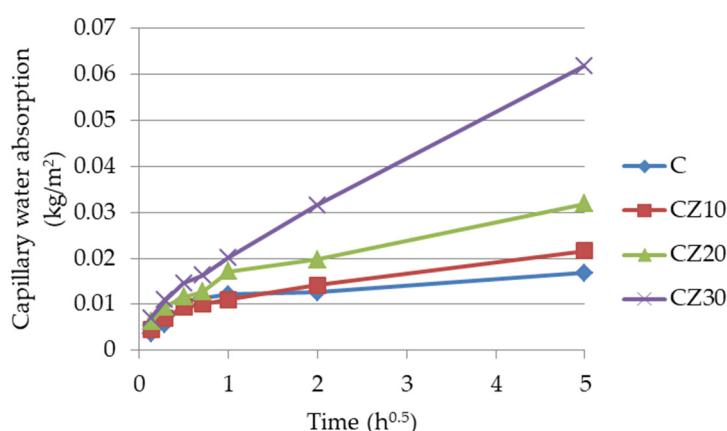


Figure 5. Capillary water absorption of examined mortars.

Capillary water absorption coefficients were determined in accordance with the procedure given in the National standard SRPS U.M8.300 [35]. In the period between 0 h and 25 h from the beginning of the capillary water absorption test, only the mortar with 30% NZ had a linear dependence on capillary water absorption, while the reference mortar C along with CZ10 and CZ20 had nonlinear dependences. In both cases, the capillary water absorption coefficient (for the period between 0–25 h) was calculated as described in Section 2.2.

The values of the capillary water absorption coefficient, as well as their correlation with the level of substitution of OPC with NZ, are provided in Figure 6. As NZ content rose by 10, 20 and 30%, the capillary water absorption coefficient value increased by 28%, 89% and 266%, respectively, in relation to the reference value. It can also be observed that there was a strong nonlinear correlation ($R^2 = 1$ for third-degree polynomial presented in Figure 6) between the capillary water absorption coefficients and NZ content, which can be described as a very good exponential relationship ($R^2 = 0.9538$).

The obtained results of capillary water absorption are similar to those reported by Vejmelkova et al. [42], i.e., liquid water transport parameters increased with the increasing dosage of NZ in the blended binder, and for lower NZ contents, up to 20%, the values of water absorption coefficient were still acceptable.

Based on the presented results, it can be concluded that the recommended level of OPC substitution with the applied NZ is up to 10% in regard to capillary water absorption of blended cement mortars.

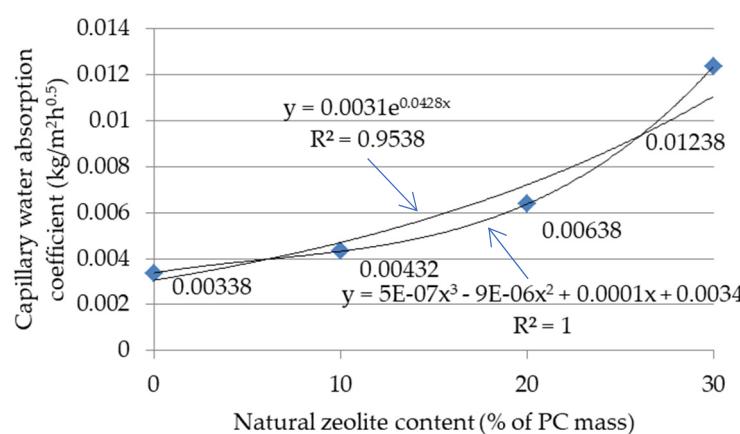


Figure 6. Correlation between capillary water absorption coefficients and natural zeolite content.

3.5. Water Absorption at Atmospheric Pressure

The results of water absorption at atmospheric pressure of the reference and NZ blended cement mortars, presented in Figure 7, are expressed as the percentage of the mass of dry specimens. The reference mortar, C, had the lowest value of water absorption. With an increase in the level of substitution of OPC with NZ, the water absorption grew, as well. Mortars CZ10, CZ20 and CZ30, had higher water absorption values by 26%, 35% and 52%, respectively, than that of the reference one.

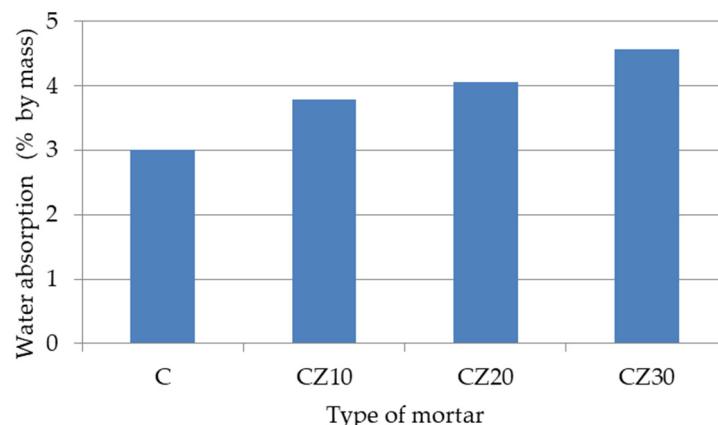


Figure 7. Water absorption of examined mortars at atmospheric pressure.

Although there was a strong nonlinear relationship ($R^2 = 1$ for third-degree polynomial presented in Figure 8, as in the case of capillary water absorption) between the water absorption of the reference and NZ blended cement mortars at atmospheric pressure and the levels of NZ content, this correlation can also be described as a very good linear one ($R^2 = 0.9606$).

The impact of NZ, as an SCM in cement mortars and concretes, on water absorption at atmospheric pressure has been investigated in previous research. Bilim [20] reported that mortars ($w/cm = 0.5$) incorporating up to 20% NZ (clinoptilolite) had lower water absorption values compared to the reference one, while those with 30% NZ showed a higher water absorption relative to the reference value. Ahmadi and Shekarchi [43] found that the concretes containing up to 20% NZ (clinoptilolite) had less water absorption than the reference concrete ($w/cm = 0.4$). However, the tests conducted by Valipour et al. [44] showed that the concrete with 30% NZ had the lowest absorption, followed by 10%, and that concrete with 20% NZ was in the same range as the control. Furthermore, Najimi et al. [22] found that the reference concrete had the lowest value of water absorption, followed by the one with 30% NZ, while the concrete with 15% NZ as an SCM had the

highest value. Due to the scattering of the reported results, no general recommendation can be given when it comes to the amount of OPC that would be substituted with NZ in terms of water absorption at atmospheric pressure. Instead, it is necessary to do preliminary tests with the specific NZ. Thus, such tests were carried out and reported in this paper, i.e., the recommended level of OPC substitution with the used NZ is up to 10%.

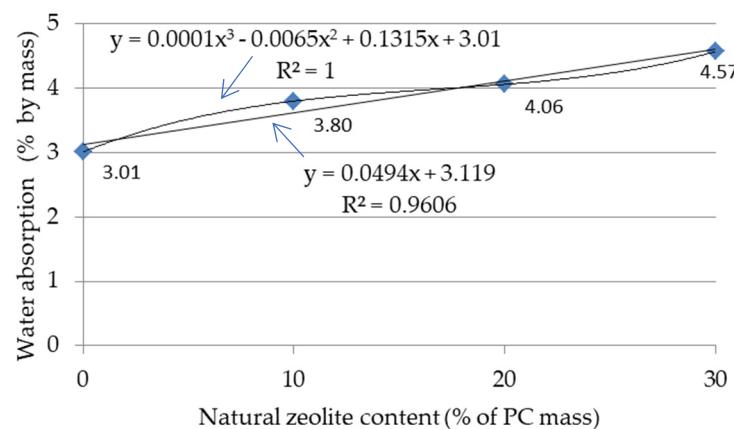


Figure 8. Correlation between water absorption of mortars at atmospheric pressure and natural zeolite content.

3.6. Drying Shrinkage

Drying shrinkage refers to the volume decrease over time due to the release of water into the environment as a consequence of the moisture migration when the material is exposed to a lower environmental relative humidity than the one in the pore system. This property is being measured while hydration is still ongoing. In these circumstances, the presence of autogenous shrinkage caused by water loss during hydration cannot be omitted [45,46]. To avoid the shrinkage and the accompanying cracking, the moisture loss during the binder hydration needs to be compensated [47]. Several strategies have been developed to compensate for the water loss due to the hydration process [48]. Self-curing is one of the suggested methods. This method is usually related to the use of prewetted lightweight aggregates as a source of water during hydration. The efficiency of these internal curing materials depends on their absorption-desorption properties [49]. The desorption properties of water are primarily governed by pore size distribution. The release of water is easier when the pores are coarse. The NZ pore structure is also promising for use as a lightweight aggregate for self-curing. Bílek et al. [50] demonstrated that NZ used as a powder might have a twofold role: as a reactive admixture and for self-curing.

The evaluation of the effect of NZ on drying shrinkage dilatations was carried out on standard mortar specimens. The obtained results are presented in Figure 9. As it can be seen, the application of NZ as an SCM in blended cement mortars led to a decrease in drying shrinkage, especially at later ages. At the age of 28 days, the drying shrinkage of CZ10 and CZ20 was slightly lower or similar to that of the reference mortar, C, respectively, while it was higher for CZ30. After 56 days, the highest shrinkage value was registered for the reference mortar and the lowest one for CZ20. As reported by Najimi et al. [22], NZ as a porous material absorbs water in a fresh state. Later on, water could be gradually released and transported out of the NZ structure during drying through the hardening process. This presents a positive influence of the NZ structure on drying shrinkage. However, the presence of smectite as a secondary mineral phase in zeolite tuff, which may swell due to its interlayer absorption, could adversely affect this mortar performance. This finding is consistent with that of Norvell et al. [40], who determined that smectite (montmorillonite) clay significantly increases drying shrinkage.

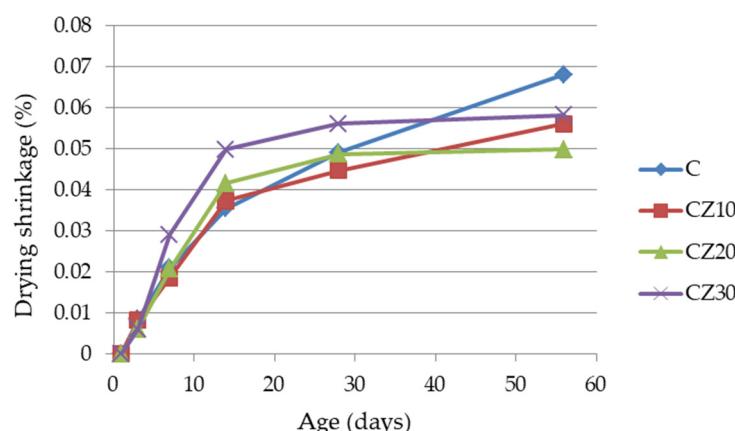


Figure 9. Drying shrinkage of reference and blended cement mortars.

Based on the diagram trends in Figure 9, it can be concluded that the drying shrinkage of CZ20 and CZ30 mortars tended to converge to final values, while the shrinkage of the reference mortar and CZ10 did not show that tendency during the investigation period. Considering that the drying shrinkage dilatations of all tested mortars at the age of 56 days were in the range of 0.05–0.1% (i.e., 0.5–1.0 mm/m), they can be classified as mortars with medium drying shrinkage [51]. Therefore, it can be deduced that NZ as an SCM (up to 30%) positively affects drying shrinkage reduction, although this influence is minor because the reference and blended cement mortars remained in the same category. The recommended level of the OPC substitution with NZ (up to 30%) is in accordance with the results reported by Najimi et al. [22], i.e., the drying shrinkage of concrete specimens containing 15 and 30% NZ were about 84% and 64% of the control one after 90 days, respectively. Shon and Kim [15] also reported that the lowest drying shrinkage was detected in the mortars with 10 and 20% NZ, respectively, while the highest one was observed for the reference mortar. These results are in contrast with the one reported by Jana [41], who observed that the drying shrinkage of NZ mixtures at 10 and 20% OPC replacement levels were similar or slightly higher than that of the control mixture, whereas by replacing 30% of OPC with NZ, the drying shrinkage was about 20% higher than the control mixture. However, it is important to bear in mind that those tests were performed on mortar bars after just 7 days of their moist-curing.

In previous research, Milović et al. [24] reported that XRD patterns showed small but notable peaks related to the clinoptilolite mineral phase, indicating the presence of unreacted NZ in blended cement pastes even at the age of 60 days. Hence, there is a possibility that the NZ used in this research contributed to the reduction of shrinkage due to its potential self-curing property. Wen et al. [52] demonstrated that zeolite powder (up to 8% as an SCM), as a self-curing material, had a good curing effect, which increased internal relative humidity and reduced the shrinkage of self-compacting concrete.

3.7. Frost Resistance

There are two approaches to avoid the damage caused by a frost attack. The first one is to decrease/avoid the “pumping effect” and consequently decrease/avoid developed stresses. The other one is to increase the strength of the material and make it able to resist the developed stresses.

After 50 freeze–thaw cycles, the compressive strength values of the reference and NZ blended cement mortars along with their etalons, which were not exposed to freeze–thaw cycling were determined. The obtained results are shown in Table 6. To evaluate the frost resistance of NZ blended cement mortars, the criterion is explained in Section 2.2. was applied. Mortars C and CZ10 met the aforementioned criterion, unlike mortars CZ20 and CZ30. Mortar CZ10 had the smallest drop in strength (−5%), followed by the reference C

mortar (-10%), while mortars CZ20 and CZ30 had the highest decline of strengths (-36% and -30% , respectively).

Table 6. Results of frost resistance examination of all mortar types after 50 freeze–thaw cycles.

Mortar Type	Compressive Strength, (MPa)		Compressive Strength Reduction, (%)	Fulfillment of Criterion " $<25\%$ "
	Etalon	Test-Specimen after 50 Cycles		
C	52.29 (± 0.65)	47.19 (± 1.08)	9.75	+
CZ10	50.83 (± 1.10)	48.23 (± 1.00)	5.12	+
CZ20	46.88 (± 0.94)	30.21 (± 0.95)	35.56	-
CZ30	38.85 (± 0.95)	27.29 (± 0.18)	29.76	-

The most likely causes of good frost resistance detected in CZ10 are good strength values and the ability of the NZ pore structure to absorb the extra amount of water found in the material [18] at the points where the saturation with water is achieved, i.e., the “pumping effect”. If the over-saturation does not exist, the possibility of the specimen damage during freeze–thaw cycles will be minimized. Furthermore, it can be noticed that among the examined NZ blended cement mortars, the one with 10% NZ had the lowest value of capillary water absorption coefficient.

Therefore, this is where the use of NZ in blended cement could have a prominent role. Based on the obtained results, it can be concluded that the substitution of OPC with NZ up to 10% produces a positive effect on frost resistance, while this substitution in the amount equal to or higher than 20% has a negative influence which is not acceptable. Similar conclusions were presented by other researchers [20,42]. Vejmelková et al. [42] reported that the substitution of cement with up to 10% NZ decreases open porosity and subsequently improves the freeze–thaw resistance of concrete. According to Bilim [20], NZ in the amount of 5% improved the freeze–thaw resistance (after 50 cycles) of blended cement mortar with the decrease in compressive strength of only 6% in comparison to the control mortar for which the decline of compressive strength reached 12%. However, the amount of over 10% of NZ led to a significant reduction in the strength, e.g., for the level of 10%, the decrease of compressive strength was 24%. The obtained results [20] were explained by the formation of secondary C-S-H gel as a result of the NZ pozzolanic reaction. Consequently, there is not enough free space to accommodate the volume increase due to ice formation in mortar. As a solution, Bilim [20] suggested the utilization of air-entraining agents in order to improve the frost resistance of the NZ containing cement mortar.

Finally, it was not possible to clarify the role of smectite and its contribution to the obtained values of the NZ blended cement mortars' frost resistance.

3.8. Performance Index

In order to describe the performance of NZ in blended cement mortars as an SCM, a quantitative evaluation of all examined properties at the age of 28 days was performed simultaneously, using the concept of a performance index [53].

Numerical values can be assigned to the mechanical and physical characteristics as well as the durability properties of the material by applying the concept of a performance index. These values can serve as a quantitative tool for making final decisions on the optimal amount of replacement of OPC with NZ in blended cement mortars. If the values of the performance index of NZ blended mortars are higher than 1.0, then they have better performance compared to the reference mortar to which the value of 1.0 is assigned. Otherwise, they have an inferior subject property.

Based on the compressive strength, flexural strength, capillary water absorption, water absorption at atmospheric pressure, drying shrinkage and frost resistance test results, performance indexes were calculated for each type of the tested mortar. The obtained

results are presented in Figure 10 (Note: since the index value referring to capillary water absorption obtained for the CZ30 mortar was negative, it was adopted to be 0).

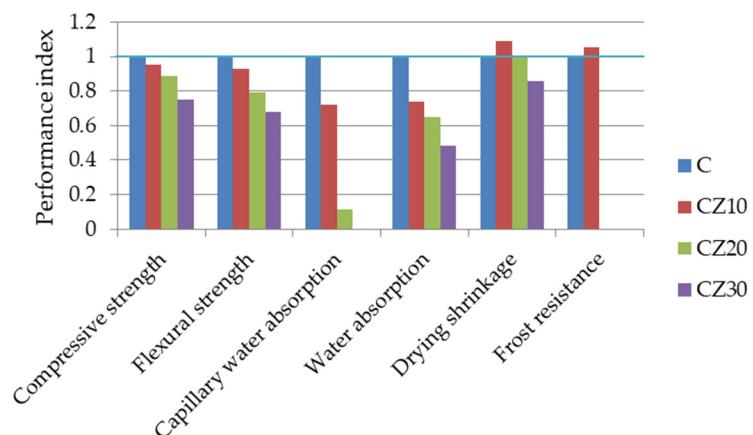


Figure 10. Performance index for each tested property of mortars.

It can be noticed that mortars CZ20 and CZ30 possess performance index value 0 regarding the frost resistance because those mortars did not meet the criterion described in [38]. Furthermore, only the mortar with 10% NZ had a higher performance index in terms of drying shrinkage (1.09) and frost resistance (1.05) compared to the reference value (1.0), while the performance index of mortar CZ20 was in the range with the reference value in terms of the drying shrinkage. Furthermore, mortar CZ10 held the values of compressive and flexural strength performance indexes in the range of or slightly lower than those of the reference mortar. As for the capillary water absorption and the water absorption at atmospheric pressure, performance indexes of CZ10 were lower than those of the strengths for that same mortar type. Regarding CZ10 mortar as well as CZ20 and CZ30, the performance index values were lower in the case of capillary water absorption and water absorption at atmospheric pressure than in the case of compressive and flexural strengths.

The sums of the performance indexes of C, CZ10, CZ20 and CZ30 were 6.0, 5.49, 3.46 and 2.77, respectively. Therefore, the optimal replacement of OPC with NZ is 10% regarding the concept of the performance index.

4. Conclusions

- Based on the presented results, the following conclusions can be drawn:
- NZ, containing clinoptilolite (a type of NZ) as a primary component and smectite clay as a secondary, can be classified as a pozzolanic material, type II addition;
- NZ as an SCM contributes to the compressive strength development over time, i.e., it can be used for the substitution of OPC up to 20% in blended cement mortars, as the decrease in compressive strength at the age of 28 days is about 10%;
- NZ as an SCM also contributes to the flexural strength development over time, i.e., it can be used for the substitution of OPC up to 10% in blended cement mortars, as the decrease in flexural strength at the age of 28 days is about 7%;
- In regard to the capillary water absorption of blended cement mortars, the recommended level of OPC substitution with NZ is up to 10%. With a rise in the level of NZ in cement mortars (up to 30%), capillary water absorption increases, and so do the values of capillary water absorption coefficients;
- The water absorption of cement mortars at atmospheric pressure requires preliminary tests with the specific NZ before offering a recommendation, as the findings reported in the literature are divergent. In terms of the water absorption of blended cement mortars, the recommended level of OPC substitution with the used NZ is up to 10%;

- NZ as an SCM positively affects drying shrinkage reduction, although this influence is minor because the reference and blended cement mortars remained in the same category;
- The substitution of OPC with up to 10% NZ beneficially impacts mortar's frost resistance, even better than in the case of the reference cement mortar. However, the amount of NZ equal to or higher than 20% has a negative effect which is not acceptable.

In terms of all examined properties (frost resistance, compressive strength, flexural strength, drying shrinkage, capillary water absorption and water absorption at atmospheric pressure) of blended cement mortars, the optimal level of OPC substitution with the investigated NZ is up to 10%, which is also confirmed by the application of the performance index concept.

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References

1. Azmee, N.M.; Shafiq, N. Investigating the Impacts of Ultra-Fine Calcium Carbonate in High-Volume Fly Ash Concrete for Structural Rehabilitation for Sustainable Development. *Sustainability* **2019**, *11*, 4671. [[CrossRef](#)]
2. Hemalatha, T.; Ramaswamy, A. A review on fly ash characteristics—Towards promoting high volume utilization in developing sustainable concrete. *J. Clean. Prod.* **2017**, *147*, 546–559. [[CrossRef](#)]
3. Solak, A.M.; Tenza-Abril, A.J.; Saval, J.M.; García-Vera, V.E. Effects of Multiple Supplementary Cementitious Materials on Workability and Segregation Resistance of Lightweight Aggregate Concrete. *Sustainability* **2018**, *10*, 4304. [[CrossRef](#)]
4. Sahmaran, M.; Li, V. Durability properties of micro-cracked ECC containing high volumes fly ash. *Cem. Concr. Res.* **2009**, *39*, 1033–1043. [[CrossRef](#)]
5. Liu, J.; Liu, J.; Huang, Z.; Zhu, J.; Liu, W.; Zhang, W. Effect of Fly Ash as Cement Replacement on Chloride Diffusion, Chloride Binding Capacity, and Micro-Properties of Concrete in a Water Soaking Environment. *Appl. Sci.* **2020**, *10*, 6271. [[CrossRef](#)]
6. Chen, H.; Chen, Q.; Xu, Y.; Lawi, A.S. Effects of silica fume and Fly ash on properties of mortar reinforced with recycled-polypropylene. *Constr. Build. Mater.* **2022**, *316*, 125887. [[CrossRef](#)]
7. Naik, T.R.; Kraus, R.N.; Ramme, B.W.; Chun, Y.M. Deicing salt-scaling resistance: Laboratory and field evaluation of concrete containing up to 70% Class C and Class F fly ash. *J. ASTM Int.* **2005**, *2*, 93–104. [[CrossRef](#)]
8. Hasholta, M.T.; Christensen, K.U.; Pade, K. Frost resistance of concrete with high contents of fly ash - A study on how hollow fly ash particles distort the air void analysis. *Cem. Concr. Res.* **2019**, *119*, 102–112. [[CrossRef](#)]
9. Lu, Z.; Feng, Z.; Yao, D.; Li, X.; Ji, H. Freeze-thaw resistance of Ultra-High performance concrete: Dependence on concrete composition. *Constr. Build. Mater.* **2021**, *293*, 123523. [[CrossRef](#)]
10. Uysal, M.; Akyuncu, V. Durability performance of concrete incorporating Class F and Class C fly ashes. *Constr. Build. Mater.* **2012**, *34*, 170–178. [[CrossRef](#)]
11. Karakurt, C.; Bayazjt, Y. Freeze-thaw resistance of normal and high strength concretes produced with fly ash and silica fume. *Adv. Mater. Sci. Eng.* **2015**, *2015*, 830984. [[CrossRef](#)]
12. Pedersen, K.H.; Jensen, A.D.; Skjøth-Rasmussen, M.S.; Dam-Johansen, K. A review of the interference of carbon containing fly ash with air entrainment in concrete. *Prog. Energy Combust. Sci.* **2008**, *34*, 135–154. [[CrossRef](#)]
13. Fagerlund, G. *A Service Life Model for Internal Frost Damage in Concrete*; Report TVBM (3119); Division of Building Materials, LTH, Lund University: Lund, Sweden, 2004; pp. A1-25–A1-31.

14. Ducman, V.; Škapin, A.S.; Radeka, M.; Ranogajec, J. Frost resistance of clay roofing tiles: Case study. *Ceram. Int.* **2011**, *37*, 85–91. [[CrossRef](#)]
15. Shon, C.-S.; Kim, Y.-S. Evaluation of West Texas natural zeolite as an alternative of ASTM Class F fly ash. *Constr. Build. Mater.* **2013**, *47*, 389–396. [[CrossRef](#)]
16. Nas, M.; Kurbetci, S.; Nayir, S. Investigation on Strength and Durability Properties of Concrete Containing Zeolite. In Proceedings of the 13th International Congress on Advances in Civil Engineering, Izmir, Turkey, 12–14 September 2018.
17. Tran, Y.T.; Lee, J.; Kumar, P.; Kim, K.H.; Lee, S.S. Natural zeolite and its application in concrete composite production. *Compos. Part B Eng.* **2019**, *165*, 354–364. [[CrossRef](#)]
18. Snellings, R.; Mertens, G.; Elsen, J. Calorimetric evolution of the early pozzolanic reaction of natural zeolites. *J. Therm. Anal. Calorim.* **2010**, *101*, 97–105. [[CrossRef](#)]
19. Zheng, X.; Zhang, J.; Ding, X.; Chu, H.; Zhang, J. Frost resistance of internal curing concrete with calcined natural zeolite particles. *Constr. Build. Mater.* **2021**, *288*, 123062. [[CrossRef](#)]
20. Bilim, C. Properties of cement mortars containing clinoptilolite as a supplementary cementitious material. *Constr. Build. Mater.* **2011**, *25*, 3175–3180. [[CrossRef](#)]
21. Wang, Q.; Zhang, J.; Ho, J.C.M. Zeolite to improve strength-shrinkage performance of high-strength engineered cementitious composite. *Constr. Build. Mater.* **2020**, *234*, 117335. [[CrossRef](#)]
22. Najimi, M.; Sobhani, J.; Ahmadi, B.; Shekarchi, M. An experimental study on durability properties of concrete containing zeolite as a highly reactive natural pozzolan. *Constr. Build. Mater.* **2012**, *35*, 1023–1033. [[CrossRef](#)]
23. Radeka, M.; Milović, T.; Malešev, M.; Radonjanin, V.; Laban, M. Hydration process and compressive strength of cement pastes containing natural zeolite. *Build. Mater. Struct.* **2016**, *59*, 29–45. [[CrossRef](#)]
24. Milović, T.; Rudić, O.; Furgan, S.O.; Radeka, M.; Malešev, M.; Radonjanin, V.; Baloš, S.; Laban, M. Effects of soft water attack on Portland and natural zeolite blended cements. *Chem. Ind. Chem. Eng. Q.* **2021**, *27*, 403–415. [[CrossRef](#)]
25. SRPS EN 197-1:2013; Cement. Composition, Specifications and Conformity Criteria for Common Cements. Institute for Standardization of Serbia: Belgrade, Serbia, 2013.
26. SRPS EN 196-1:2008; Methods of Testing Cement—Part 1: Determination of Strength. Institute for Standardization of Serbia: Belgrade, Serbia, 2008.
27. SRPS EN 1097-7:2008; Tests for Mechanical and Physical Properties of Aggregates, Part 7: Determination of the Particle Density of Filler—Pycnometer Method. Institute for Standardization of Serbia: Belgrade, Serbia, 2008.
28. SRPS EN 196-6:2011; Methods of Testing Cement, Part 6: Determination of Fineness. Institute for Standardization of Serbia: Belgrade, Serbia, 2011.
29. SRPS EN 196-3:2010; Methods of Testing Cement, Part 3: Determination of Setting Times and Soundness. Institute for Standardization of Serbia: Belgrade, Serbia, 2010.
30. SRPS EN 196-2:2015; Methods of Testing Cement. Chemical Analysis of Cement. Institute for Standardization of Serbia: Belgrade, Serbia, 2015.
31. SRPS EN 450-1:2014; Fly Ash for Concrete, Part 1: Definition, Specifications and Conformity Criteria. Institute for Standardization of Serbia: Belgrade, Serbia, 2014.
32. SRPS B.C1.018:2015; Non-Metallic Mineral Raws—Pozzolanic Materials—Constituents for Cement Production—Classification, Technical Conditions and Test Methods. Institute for Standardization of Serbia: Belgrade, Serbia, 2015.
33. Sabet, F.A.; Libre, N.A.; Shekarchi, M. Mechanical and durability properties of self consolidating high performance concrete incorporating natural zeolite, silica fume and fly ash. *Const. Build. Mater.* **2013**, *44*, 175–184. [[CrossRef](#)]
34. SRPS EN 451-2:2010; Method of Testing Fly Ash, Part 2: Determination of Fineness by Wet Sieving. Institute for Standardization of Serbia: Belgrade, Serbia, 2010.
35. SRPS U.M8.300:1985; Determination of the Capillary Water Absorption of Building Material and Coatings. Institute for Standardization of Serbia: Belgrade, Serbia, 1985.
36. SRPS B.B8.010:1981; Testing of Natural Stone—Determination of Water Absorption. Institute for Standardization of Serbia: Belgrade, Serbia, 1981.
37. SRPS EN 12617-4:2010; Products and Systems for the Protection and Repair of Concrete Structures, Test Methods—Part 4: Determination of Shrinkage and Expansion. Institute for Standardization of Serbia: Belgrade, Serbia, 2010.
38. SRPS U.M1.016:1992; Concrete—Method of Test for Resistance of Concrete against Freezing and Thawing. Institute for Standardization of Serbia: Belgrade, Serbia, 1992.
39. SRPS EN 206-1:2011; Concrete—Part 1: Specification Performance, Production and Conformity. Institute for Standardization of Serbia: Belgrade, Serbia, 2011.
40. Norvell, K.; Stewart, J.G.; Juenger, M.; Fowler, D. Influence of Clays and Clay-Sized Particles on Concrete Performance. *Mater. Civ. Eng.* **2007**, *19*, 1053–1059. [[CrossRef](#)]
41. Jana, D. A new look to an old pozzolan: Clinoptilolite—A promising pozzolan in concrete. In Proceedings of the 29th Conference on Cement Microscopy, Quebec, PQ, Canada, 20–24 May 2007; pp. 168–206.
42. Vejmelková, E.; Koňáková, D.; Kulovaná, T.; Keppert, M.; Žumár, J.; Rovnaníková, P.; Keršner, Z.; Sedlmajer, M.; Černý, R. Engineering properties of concrete containing natural zeolite as supplementary cementitious material: Strength, toughness, durability, and hygrothermal performance. *Cem. Concr. Compos.* **2015**, *55*, 259–267. [[CrossRef](#)]

43. Ahmadi, B.; Shekarchi, M. Use of natural zeolite as supplementary cementitious material. *Cem. Concr. Compos.* **2010**, *32*, 134–141. [[CrossRef](#)]
44. Valipour, M.; Pargar, F.; Shekarchi, M.; Khani, S. Comparing a natural pozzolan, zeolite, to metakaolin and silica fume in terms of their effect on the durability characteristics of concrete: A laboratory study. *Constr. Build. Mater.* **2013**, *41*, 879–888. [[CrossRef](#)]
45. Zhang, J.; Han, Y.D.; Gao, Y.; Luosun, Y. Integrative study on the effect of internal curing on autogenous and drying shrinkage of high-strength concrete. *Dry. Technol.* **2013**, *31*, 565–575. [[CrossRef](#)]
46. Lura, P.; Jensen, O.M.; van Breugel, K. Autogenous Shrinkage in high-performance cement paste: An evaluation of basic mechanisms. *Cem. Concr. Res.* **2003**, *33*, 223–232. [[CrossRef](#)]
47. Castro, J.I.; Lura, P.; Rajabipour, F.; Henkensiefken, R.; Weiss, J. Internal curing: Discussion of the role of pore solution on relative humidity measurements and desorption of lightweight aggregate (LWA). In *Advances in the Material Science of Concrete Session at the ACI Spring 2010 Convention*; American Concrete Institute: Detroit, MI, USA, 2010; pp. 89–100.
48. Radlinska, A.; Rajabipour, F.; Bucher, B.; Henkensiefken, R.; Sant, G.; Weiss, J. Shrinkage mitigation strategies in cementitious systems: A closer look at differences in sealed and unsealed behavior. *Transportation Research Record. J. Transp. Board* **2008**, *2070*, 59–67. [[CrossRef](#)]
49. Ghouchian, S.; Wyrzykowski, M.; Lura, P.; Shekarchi, M.; Ahmadi, B. An investigation of the use of zeolite aggregates for internal curing of concrete. *Constr. Build. Mater.* **2013**, *40*, 135–144. [[CrossRef](#)]
50. Bílek, V.; Mosler, T.; Keršner, Z.; Schmid, P. The possibility of self-curing concrete. In *Innovations and Developments in Concrete Materials and Construction*; Hewlett, P.C., Dhir, R.K., Csetenyi, L.J., Eds.; University of Dundee: Dundee, UK, 2002; p. 51.
51. Morgan, D.R. Compatibility of concrete repair materials and systems. *Constr. Build. Mater.* **1996**, *10*, 57–67. [[CrossRef](#)]
52. Wen, C.; Chen, J.; Liu, Q. Research on Influence of Zeolite Powder on Internal Humidity and Autogenous Shrinkage of Self-Compacting concrete. *Adv. Eng. Res.* **2017**, *121*, 195–200. [[CrossRef](#)]
53. Kayali, O.; Ahmed, M.S. Assessment of high volume replacement fly ash concrete—Concept of performance index. *Constr. Build. Mater.* **2013**, *39*, 71–76. [[CrossRef](#)]