CI&CEQ
Chemical Industry & Chemical Engineering Quarterly

Available on line at
Association of the Chemical Engineers of Serbia *AChE*
www.ache.org.rs/CICEQ

*Chem. Ind. Chem. Eng. Q.* 27 (4) 403–415 (2021) CI&CEQ

TIANA MILOVIĆ[1]
OGNJEN RUDIĆ[2]
SAEEDA OMRAN FURGAN[1]
MIROSLAVA RADEKA[1]
MIRJANA MALEŠEV[1]
VLASTIMIR RADONJANIN[1]
SEBASTIAN BALOŠ[1]
MIRJANA LABAN[1]

[1]Faculty of Technical Sciences, University of Novi Sad, Novi Sad, Serbia
[2]Institute of Technology and Testing of Building Materials (IMBT-TVFA), Graz University of Technology, Graz, Austria

SCIENTIFIC PAPER

**UDC 691.3:666.942**

# EFFECTS OF SOFT WATER ATTACK ON PORTLAND AND NATURAL ZEOLITE BLENDED CEMENTS

## Article Highlights

- Ordinary Portland cement was partially substituted in pastes with natural zeolite from Serbia
- Paste specimens were exposed to simulated soft water attack via leaching in deionised water
- Hydration products in blended cement pastes remained stable during leaching in deionised water
- Specimens with 10% of natural zeolite had the highest compressive strength values after 90 days

## Abstract

*The durability of concrete infrastructure is related to the properties of the applied concrete and the effects of the aggressive external environment on it. When concrete is directly exposed to soft water, the leaching of calcium ions from hardened cement or cement-based pastes occurs, causing reduction in strength and further deterioration of the concrete structure. This paper presents the experimental results of 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 natural zeolite. In order to simulate soft water attack in laboratory conditions, paste specimens were exposed to leaching in deionised water up to 180 days. The evaluation of the changes in phase composition (ettringite, portlandite, calcium silicate hydrate gel) due to calcium ion leaching was made based on X-ray diffraction analysis, Fourier-transform infrared spectroscopy and paste compressive strength tests. The presence of portlandite and ettringite after 180 days of exposure to deionised water indicates that leaching did not influence the stability of the hydration products in blended cement pastes. Moreover, blended cement paste with 10% of natural zeolite had a higher compressive strength than the reference one.*

*Keywords: Ca-clinoptilolite, compressive strength, deionised water, FTIR spectroscopy, leaching, XRD analysis.*

The environmental concerns related to the decrease of global warming and maintaining natural resources have renewed the interest for the replacement of Portland cement (PC) by supplementary cementitious materials (SCMs) with pozzolanic properties and low embodied $CO_2$ footprint [1]. Pozzolana additives have little or no cementing properties but will as powders react with calcium hydroxide when water is present. The availability of many industrial by-products (fly ashes from coal-fired electricity production, blast furnace slag, etc.), commonly used as SCMs, in large and consistent quantities, and their full exploitation in certain countries, has heightened the need for the use of local natural pozzolanic materials as zeolitised tuffs, vitreous pumices and ashes, diatomaceous earth, etc. [2]. Zeolitised tuffs are widely abundant in the world and present in almost every country. They contain fine microcrystalline zeolite that binds nonzeolitic minerals like clay minerals, feldspars and glasses [3]. Some of these phases have pozzolanic

---

Correspondence: M. Radeka, Faculty of Technical Sciences, University of Novi Sad, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia.
E-mail: mirka@uns.ac.rs
Paper received: 20 November, 2020
Paper revised: 17 February, 2021
Paper accepted: 20 March, 2020

https://doi.org/10.2298/CICEQ201120009M

properties (zeolite, clay minerals, glasses), while the others (quartz, feldspars) are inert. Natural zeolites (NZs) with Ca-clinoptilolite and Ca-heulandite as main mineral phases [4] dominate in Serbia. The use of NZs as SCMs is of importance because of their accessibility [3,5] proper pozzolanic activity [1,5], sulphate resistance [6], the ability to prevent the expansion due to alkali-aggregate reaction [5] and enhanced durability in terms of electrical resistivity, chloride diffusion, oxygen permeability and water absorption [5]. On the other hand, NZ blended cement requires more water [7] and the strength develops gradually over long time [5]. Most of these properties derive from NZs being pozzolanic materials which inherently change the microstructure of hydrated products. However, the reactivity of NZs in pozzolanic reactions as well as some specific durability properties depends primarily on zeolite-specific structure along with nonzeolitic mineral structure, among other parameters. One of the durability properties which has not been extensively researched is the leaching of concretes based on zeolite binder caused by the attack of soft water. A number of studies have been published on leaching of cement-zeolite composites; they are aimed at valorising the stabilisation of harmful wastes (*e.g.*, zinc-saturated zeolite [8]), immobilisation of heavy metals [9,10], solidification the intermediate-level radioactive waste [11], etc. Leaching caused by soft water appears when concrete structures are exposed to soft water attack, such as rainwater and other low ion content waters (found in lowland streams and rivers, as well as in mountainous areas in springs 12]). Leaching is present in concrete infrastructures such as hydro structures (dams, water tanks, and other allied structures [13]), tunnels [12,14], tanks, retaining walls, etc.

At the core of the leaching process under the aforementioned conditions is the diffusion of ionic species from the pore solution (mainly $Ca^{2+}$ and $OH^{-}$) to the surrounding soft water, caused by the concentration gradient [15]. Although leaching is a slow process under normal conditions [16], chemical processes considered during degradation also affect continuous, long-lasting zeolite blended cement hydration process.

The zeolite structure is a microcrystalline one, formed of $Si^{4+}$ and $Al^{3+}$ tetrahedrally coordinated by oxygen atoms and thus interconnected to form rings and channels of various sizes. These complex structures create different types of zeolite frameworks with an open network [3]. The substitution of $Si^{4+}$ by $Al^{3+}$ results in a negative excess charge of the framework balanced by exchangeable alkali (Na, K) and/or alkaline earth (Ca, Mg, Ba) ions [17] located in the channels together with variable amounts of water. The ions and the water are loosely bound to the framework. Therefore, the cations placed in the channels are exchangeable, while water is subject to reversible hydration. Therefore, the zeolite structure could be characterised as the one with: great surface area, varying Si/Al ratio, different types and amounts of exchangeable cations and water. $Ca^{2+}$ as an exchangeable cation dominates in Serbian NZs.

The influence of exchangeable cations, specifically $Ca^{2+}$, on hydration is the most prominent through the impact on the chemical reactions leading to the formation of hydrated products [18,19]. Zeolite pozzolanic reaction goes through the following steps: *i*) cation exchange, *ii*) dissolution, *iii*) breakdown and/or conversion of the zeolite into amorphous material, followed by *iv*) the precipitation of hydrated products [20]. The release of exchangeable cations from the zeolite framework has a crucial role on the reaction rate and hydration product assemblages [21]. Snellings *et al.* [21] have shown that $Na^+$ ion is more readily exchanged from $Na^+$-containing zeolite in comparison to $K^+$ and $Ca^{2+}$-containing zeolites. Alkali ions are more efficient in raising pore solution pH value than earth-alkali ions. The pH value of the pore solution determines the dissolution rate and formed hydrated assemblages. Several publications related to the dissolution where the reactant is the glassy phase documented that released $Ca^{2+}$ control the dissolution and precipitation of silica [19,22]. As reported by Newlands and Macphee [22] and Skibsted and Snellings [19], for the pore solution pH values greater than 11 (cement-relevant values) there is a tendency of aluminosilicate phases being formed as hydrated products (calcium silicate hydrate (C-S-H) or calcium (aluminate) silicate hydrate (C-(A)-S-H) gel with low calcium/silicon (Ca/Si) ratio) [23]. The formation of these products is highly productive concerning the physico-mechanical properties of concrete. Luke [24] showed that similar results were obtained for zeolite pozzolanic reaction. Namely, alkali contribution to the pore solution increased with the rise of zeolite content. The prevailing creation of C-S-H and C-A-S-H gels after the destruction of the aluminosilicate framework was also confirmed when the pore solution was alkaline.

When pH is close to a neutral value, the glass network is disrupted by $Ca^{2+}$ and aluminium leaching thus forming Si-O-Al species. In addition, in these conditions the dissolution process is slow so the modification of the glass surface and the formation of these species do not beneficially impact final material properties. Similar results were reported by Ragnarsdóttir [25], obtained by the analyses of dissolution kinetics of heulandite.

The progress in leaching depends on the stability of PC hydrated products (portlandite, aluminates, C-S-H gel) when $Ca^{2+}$ leach out due to the differences in concentrations between the pore solution and soft water. The most valuable hydrated product is C-S-H gel due to its large amount (50-70% by volume) and good mechanical properties [26,27]. At the start of the process, $Ca^{2+}$ originates from calcium hydroxide (portlandite) which is the most soluble hydration compound. As long as it is present in a crystalline form as portlandite it controls the solubility of C-S-H gel. The buffering effect of calcium hydroxide will keep C-S-H gel stable [28].

Besides the solid phase containing hydrated products, hydrated cement paste contains pores of different sizes. These pores comprise soluble ions making a highly basic pore solution ($pH>12.7$). The dissolution of portlandite occurs when $Ca^{2+}$ concentration in pores is lower than 22 mmol/l ($pH<12.5$) [29]. It presents a degradation mechanism (decalcification, calcium leaching) characterised by primarily dissolute portlandite followed by dissolution of cement hydrates (ettringite and C-S-H gel). C-S-H gel decalcifies in the range $8.8<pH<10.5$ depending on the Ca/Si mole ratio [29]. Actually, the Ca/Si ratio depends on $Ca^{2+}$ concentration in pore solution. A higher Ca/Si ratio corresponds to a higher pH value of pore solution. When C-S-H gel decalcifies, Ca/Si ratio decreases [26]. Leaching is divided into two phases: dissolution and diffusion [29]. The outward diffusion of $Ca^{2+}$ from the pore solution to the bulk is controlled by concentration gradient as well as by porosity and pore size distribution of concrete.

The addition of a SCM (natural pozzolans, by-product materials like ashes, glass, slags, silica fume) to PC plays an important role in the improvement of the resistance to decalcification. They form a denser structure (low porosity) [30], decrease portlandite content and form a more stable C-S-H structure (lower Ca/Si ratio) [2,18]. It was reported that the stopping of leaching could be efficiently achieved when the most effective pozzolan, silica fume, is used as a SCM [26]. However, the research presented in this paper focuses on the estimation whether Ca-clinoptilolite, as the main mineral phase in the utilized NZ, could affect leaching. It can be assumed to be the additional source of $Ca^{2+}$ and in this respect could have the buffering capacity. On the other hand, as a material with pozzolanic properties, it reduces porosity and refines the pore structure of binder, further mitigating the leaching process.

All these observations are significant in terms of knowledge that in this investigation NZ having prolonged hydration [19] will be exposed to concurrent processes: leaching and hydration.

The properties of hardened NZ blended cements also depend on the properties of other tuff constituents, such as clay. If clay particles are present, many properties of concretes are compromised primarily due to their size (~5 μm) and, consequently, high surface area, thus influencing hydration characteristics and the ability to strongly modify the flow behaviour of liquids [31].

This paper presents laboratory evaluation of NZ from a Serbian deposit [4] as a SCM in blended cement pastes regarding: *i*) characterisation of physical, chemical and mineralogical properties of NZ, *ii*) establishing whether the release of $Ca^{2+}$ during pozzolanic reaction will enable high pore solution pH value while the cement based pastes with NZ as a SCM are exposed to soft water and, consequently, C-S-H formation and stability and *iii*) determination of the compressive strength of reference and $Ca^{2+}$-containing NZ (NZ-Ca) blended cement paste after 28, 60, 90 and 180 days of exposure to soft water.

## MATERIALS AND METHODS

### Materials

#### *Physical and chemical properties of component materials and mixture compositions*

For the experimental investigation of the influence of NZ-Ca as an SCM in blended cement pastes on their properties, the following component materials were used:

- PC (CEM I 42.5R, Lafarge-BFC, Serbia), standard EN 197-1:2011 [32];
- NZ-Ca from a quarry in Igroš (Brus, Serbia) with particle size less than 125 μm;
- Deionised water.

The physical and chemical properties of PC and NZ-Ca were determined according to the methods prescribed in specified standards and presented in Tables 1 and 2, respectively.

The results provided in Table 1 indicate that the physical properties of PC are in accordance with the requirements given in EN 197-1:2011 [32]. The obtained physical properties of NZ-Ca were compared with the requirements for fly ash given in EN 450-1:2012 [37]. NZ-Ca fulfilled the criteria for the initial setting time, soundness, as well as the criteria for the fineness characteristic of category N. NZ-Ca

*Table 1. Physical properties and test methods for PC and NZ-Ca*

| Physical property | Test method | PC | NZ-Ca |
|---|---|---|---|
| Density (g/cm$^3$) | EN 1097-7:2008 [33] | 3.13 | 2312.0 |
| Blaine specific surface (cm$^2$/g) | EN 196-6:2010 [34] | 4190 | 5390 |
| BET specific surface (m$^2$/g) | - | 1.55 | 78.2 |
| Fineness - (wt. %) + 45 μm | EN 196-6:2010 [34]<br>EN 451-2:1995 [35] | 4.89$^a$ | 32.78$^b$ |
| Standard consistency (%) | EN 196-3:2005 [36] | 30.0 | 40.6 |
| Initial setting time (min) | EN 196-3:2005 [36] | 200 | 185 |
| Finish setting time (min) | EN 196-3:2005 [36] | 310 | 302 |
| Soundness - Le Shatelier (mm) | EN 196-3:2005 [36] | 0.5 | 0.5 |
| Activity index, at age of 28 days (% of control) | EN 450-1:2012 [37] | - | 85.60 |
| Activity index, at age of 90 days (% of control) | EN 450-1:2013 [37] | - | 90.00 |

$^a$Fineness of PC was determined in accordance with EN 196-6:2010 [34]; $^b$fineness of NZ-Ca was determined in accordance with EN 451-2:1995 [35]

also satisfied the criteria for activity index and was classified as a pozzolanic material or type II addition. The density of PC was higher than the one for NZ-Ca, Table 1, suggesting that NZ-Ca blending would lower the overall specific gravity of the blended pastes unlike that of the reference specimen. Additionally, higher values of Blaine finesse and BET surface area of NZ-Ca in comparison to PC indicated a prominent porous structure [38].

*Table 2. Chemical composition of PC and NZ-Ca; L.O.I. - loss of ignition*

| Chemical composition, (wt.%) | PC | NZ-Ca |
|---|---|---|
| $SiO_2$ | 20.98 | 62.78 |
| $Al_2O_3$ | 5.51 | 12.20 |
| $Fe_2O_3$ | 2.58 | 2.37 |
| CaO | 61.96 | 5.09 |
| MgO | 2.50 | 2.65 |
| $Na_2O$ | 0.22 | 0.42 |
| $K_2O$ | 0.74 | 0.74 |
| $P_2O_5$ | - | 0.05 |
| $SO_3$ | 3.60 | 0.01 |
| Cl | - | 0.05 |
| L.O.I. | 1.35 | 12.36 |

The chemical composition of NZ-Ca was determined by energy-dispersive X-ray fluorescence, ED-XRF (Spectro XEPOS C, Germany), while the one of PC was assessed by wet chemical analysis according to EN 196-2:2013 [39].

As shown in Table 2 the sum of $SiO_2$, $Al_2O_3$ and $Fe_2O_3$, which is relevant for pozzolanic reaction, is greater than 70% allowing the classification of NZ-Ca into silicate mineral additions conforming to EN 450-1:2012 [37]. Moreover, Si/Al ratio amounting to 4.9 indicates that NZ-Ca is rich in Si and, therefore, exhibits a high long-term pozzolanic activity. The alkali content does not exceed 5%. According to the loss of ignition results, NZ-Ca could not be classified into any category proposed by the standard EN 450-1:2012 [37].

The cation-exchange capacity (*CEC*) analysis results for NZ from Igroš, obtained by Kasic *et al.* [4], demonstrate the highest exchange capacity of calcium of all other cations (K, Na and Mg).

*Mixture compositions*

Table 3 summarises mixture proportions of the reference and three blended cement pastes, containing 10, 20 and 30% of NZ-Ca as an SCM per cement mass.

*Table 3. Mixture proportions for reference and blended cement pastes*

| Mixture | PC (g) | NZ-Ca (g) | Deionised water (ml) |
|---|---|---|---|
| C | 450 | - | 225 |
| CZ 10 | 405 | 45 | 225 |
| CZ 20 | 360 | 90 | 225 |
| CZ 30 | 315 | 135 | 225 |

## Experimental program

The following tests were conducted on hardened pastes:

- Mineralogical characterisation (XRD and FTIR), at the age of 28, 60 and 180 days, after the exposure to deionised water.
- Compressive strength, at the age of 28, 60, 90 and 180 days after the exposure to deionised water.

## Methods

The method for determining calcium leaching used in this study (leaching in deionised water) is less efficient than the one involving the exposure to 6 M

$NH_4NO_3$, which is a common practice method. The use of the method of leaching by water was selected to observe the impact of NZ-Ca in the conditions when pozzolanic reaction and leaching are concurrent processes. In this case, the "excess" of $Ca^{2+}$ could take part in the leaching process. In that way, the calcium leaching of both C-S-H gel and other products of hydration would be retarded.

### *Preparation of paste specimens*

The prism specimens with the dimensions of 10 mm×10 mm×60 mm were prepared to follow the influence of binder composition on mechanical and structural changes caused by the exposure to deionised water. These paste specimens were kept in moulds for 1 day and then submerged in deionised water for testing leaching up to the age of 28, 60, 90 and 180 days. Leaching was tested using polyethylene containers. Reference and each type of blended cement pastes were immersed in separate sealed containers filled with deionised water. The ratio of the volume of deionised water to the mass of pastes (L/S ratio) was 50. The leaching water was not renewed. The leaching water volume was maintained constant.

The leaching water pH values (Wissenschaftlich-Technische Werkstatten GMBH, Multi 3320) were determined after 28, 60 and 180 days of exposure to deionised water. The changes in pH value as a function of paste type and time are given in Table 4. The initial pH value of deionised water was 6.6 and was not de-aired.

*Table 4. Change of leaching water pH value with time*

| Paste type | 14 days | 28 days | 60 days | 180 days |
|---|---|---|---|---|
| C | 11.97 | 11.55 | 8.80 | 8.70 |
| CZ 10 | 11.94 | 12.18 | 12.02 | 11.90 |
| CZ 20 | 12.05 | 12.20 | 11.80 | 11.60 |
| CZ 30 | 9.98 | 9.26 | 8.60 | 8.40 |

The pH value showed the tendency to converge to constant values implying that solid and liquid phases are in equilibrium.

Compressive strength test was performed on paste specimens 10 mm×10 mm×60 mm, while the surface of ten degraded paste specimens (0.5 mm) was taken for mineralogical and structural analyses after the exposure to deionised water.

The degraded depth was determined by BSE-EDS analysis. For these analyses, the specimens (paste cross sections - 10 mm×10 mm) were prepared according to the following procedure: *i*) immersion into isopropyl alcohol for 7 days, *ii*) drying in a vacuum chamber for 8 hours, *iii*) impregnation with low viscosity epoxy resin, *iv*) polishing and *vi*) coating in gold. BSE-EDS analyses were performed by SEM-EDS device (JEOL, Tokyo). The EDS analyses were conducted at magnification of 1000, an acceleration voltage of 10 keV (software INCA 4.04, Oxford Instruments) and at specific depths (up to 0.6 mm from the surface of the specimens). Not less than 20 measurements were carried out in this region up to 0.6 mm. The collection time of each spectrum was 60 seconds. The results of EDS analyses were converted to oxide percentages and normalised to 100%.

Based on the results of EDS analyses, a profile of calcium oxide content was formed in the region up to 0.6 mm in depth from the surface of the specimen, Figure 1. The distances at which the content of calcium oxide converges to constant percentage values were regarded as the criteria for the transition from an altered zone to the sound one. The Figure 1 shows that this transition occurs at a distance of about 0.5 mm for all specimens. It can also be observed that the precipitation of $Ca(OH)_2$ appears (abrupt increase of CaO concentration) in the specimens with CZ 10, CZ 20 and CZ 30 on the outer surface that was exposed to leaching.

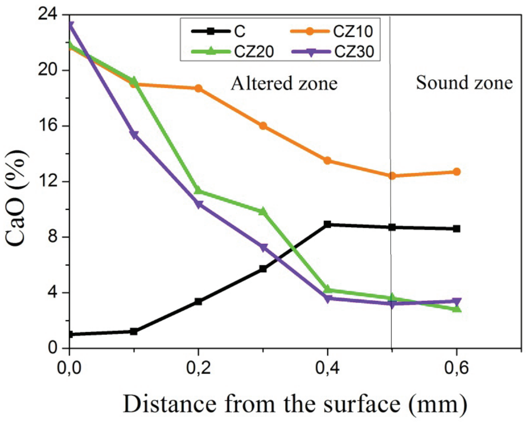

*Figure 1. Profiles of calcium oxide content determined by BSE-EDS analyses according to the distance to the paste's surfaces.*

The specimens from each mixture were denoted in the way specified in Table 3.

### *Methods for characterisation of NZ-Ca, PC and pastes*

XRD analysis was used for NZ-Ca and pastes characterisation, FTIR for NZ-Ca, PC and pastes, while compressive strength analysis was performed on paste specimens after the exposure to deionised water.

Mineralogical and structural analysis was performed by XRD analysis (Philips PW1710 device) under the following experimental conditions: monochromatic CuK$\alpha$ radiation with 1.5418 Å wavelength in the 10-60° of $2\theta$ range, scan rate 0.02° and 0.5 s per step. These investigations were complemented with FTIR (Thermo-Nicolet Nexus 670 FTIR spectrometer, spectral resolution of 4 $cm^{-1}$, range of 400–4000 $cm^{-1}$, 32-averaged scans per one measurement, KBr pellet technique) method, primarily in order to obtain an integral view of the structural changes of NZ-Ca blended cements.

After the exposure to deionized water during 28, 60, 90 and 180 days, 10 prism specimens per mixture were broken in flexure, and each half was tested for strength in compression by a hydraulic compression testing machine with a range of 50 kN. The characteristic compressive strength for every type of paste was determined as the average value of 20 test results.

## RESULTS AND DISCUSSION

### Characterisation of XRD diffractogram of NZ-Ca sample and FTIR spectra of PC and NZ-Ca samples

*XRD diffractogram of NZ-Ca sample*

The mineralogical composition of NZ-Ca is complex, Figure 2. According to XRD analysis, the used NZ-Ca consists mainly of clinoptilolite $(Na,K,Ca)_5Al_6Si_{30}O_{72}18H_2O$) (JCPDS: 025-1349) and smectite $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2\cdot nH_2O$ (JCPDS: 29-1497), Figure 2. It is difficult to determine the influence of smectite on the characteristics of fresh and hardened pastes based solely on chemical composition. In general, smectite has several unique physicochemical properties important for the performances of fresh and hardened concretes based on NZ blended cements. The most significant ones are: *i*) large cation exchange capacity, *ii*) surface area that is chemically active and *iii*) cation hydration between smectite units. The most common smectite exchangeable ions are Ca, Mg, Na and H. The role of exchangeable cations is of importance for hydration characteristics [40]. The hydration capability of natural smectite clays influences swelling. The range from strongly swelling to non-swelling depends on the smectite clay species and on the ratio of Na and exchangeable Ca plus Mg ions. When smectite clays have Ca and Mg as predominant exchangeable cations, they are essentially non-swelling, while Na is susceptible to swelling by water adsorption. The highest adsorption sometimes occurs when approximately one quarter to one fifth exchangeable ions are Ca and Mg.

The influence of the properties of smectite as a secondary mineral phase in NZ-Ca on the pozzolanic reaction of clinoptilolite in NZ-Ca and leaching arises from the dependence of the decalcified cement pastes' properties on calcium concentration. Namely, it has been suggested [40] that smectite could also have an impact on certain properties related to pozzolanic activity (high cation exchange capacity, great specific surface area) and consequently on leaching. Calcium concentration could be disrupted locally on the spots in NZ-Ca where smectite is present due to: *i*) its own large cation exchange capacity and *ii*) the fact that $Na^+$ in the pore solution reduces the dissolution of $Ca^{2+}$ because of a common ion effect. These two effects could locally change pore solution pH values and calcium concentration.

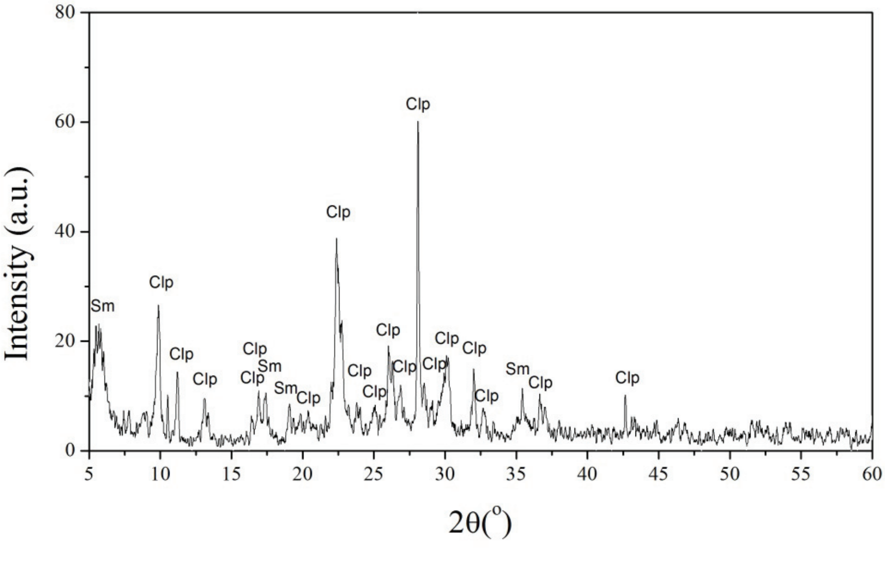

*Figure 2. XRD diffractogram of NZ-Ca (Clp - clinoptilolite; Sm - smectite).*

In addition, the presence of Na$^+$ can increase swelling which could influence the mechanical properties, specifically a decrease in the strength of CZ pastes.

#### *FTIR spectra of PC and NZ-Ca samples*

FTIR analysis of PC, Figure 3, revealed the absorption peaks at 460 and 520 cm$^{-1}$ related to the presence of Al-O bonds with Si-O. The peak at 993 cm$^{-1}$ is assigned to Si-O asymmetric vibrations characterising mainly $C_2S$ or $C_3S$ phases [41]. The absorption peak at 1110 cm$^{-1}$ (attributed to S-O bonds) was also registered, showing the presence of gypsum in cement. The absorption peaks observed at 874, 1422 cm$^{-1}$ as well as the group of peaks at 2850-3000 cm$^{-1}$ indicated the presence of C-O molecular group vibration, while the absorption peaks at 1643 and 3455 cm$^{-1}$ are characteristic of $OH^-$ and water molecules in the structure. The data obtained by the FTIR analysis of NZ-Ca, Figure 3, pointed to the presence of the Si-O stretching band at 1044 cm$^{-1}$. Its position is dependent on Si/Al ratio [42] since the peak position moves towards lower wavelengths with the reduction in the value of this ratio. The given peak is assigned to the asymmetric Si-O and Al-O stretching vibrations. Shoulders at 3623 and 1208 cm$^{-1}$ indicated the presence of the Si-OH stretching and Si-O-Si asymmetric stretching vibrations in the internal tetrahedra of NZ-Ca, respectively. The intensities of absorption peaks at 1422 and 720 cm$^{-1}$, characteristic of C-O molecular vibrations, can be ascribed to the carbonation of specimens during manipulation.

Al-O bonds and Si-O bonds generate vibration peaks at 460 and 520 cm$^{-1}$. Since the bands in the 500-800 cm$^{-1}$ interval of the FTIR spectra of NZ-Ca could be related to pseudo-lattice vibrations, the registered clinoptilolite absorption peaks at 600 cm$^{-1}$ implied the presence of a silica-rich structure. Three absorption bands at 3623, 3437 and 1637 cm$^{-1}$ are characteristic of isolated $OH^-$ stretching vibration, hydrogen-bonded $OH^-$ to oxygen ions and the usual bending vibration of zeolite water, respectively.

### **Characterisation and time evolution of specimens exposed to leaching by XRD diffractograms, and FTIR spectra for reference and NZ-Ca blended cement pastes**

#### *XRD diffractograms*

The assessment of the reaction products, performed by XRD analysis, contributed to the understanding of structural changes during hydration reactions, Figure 4. A noteworthy decrease in the intensity of portlandite (JCPDS: 073-5492), especially in the case of the pastes with the highest replacement ratio of NZ-Ca, (CZ 30), indicates a noticeable progression of the pozzolanic reaction. Nevertheless, portlandite was still present at the age of 180 days, in the case of all blended cement pastes. The noticed decline of clinoptilolite peaks with hydration time was associated with the decomposition of the zeolite phase. Small but notable peaks related to the clinoptilolite mineral phase could be distinguished, indicating the ongoing pozzolanic reaction continued up to 180 days especially in the case of the specimens with a higher content of NZ-Ca.

C-S-H (JCPDS: 03-0606) formation was detected, regardless of the age and exposure to deionised water, and was identified due to the existence of diffraction peaks at approximately 29.30 and 31.81° within the registered hump in the range of $2\theta$ 25-35°, Figure 4. Namely, the low intensity diffraction peak at $2\theta$ value 29.30° indicates the existence of a low crystallinity C-S-H mineral phase.

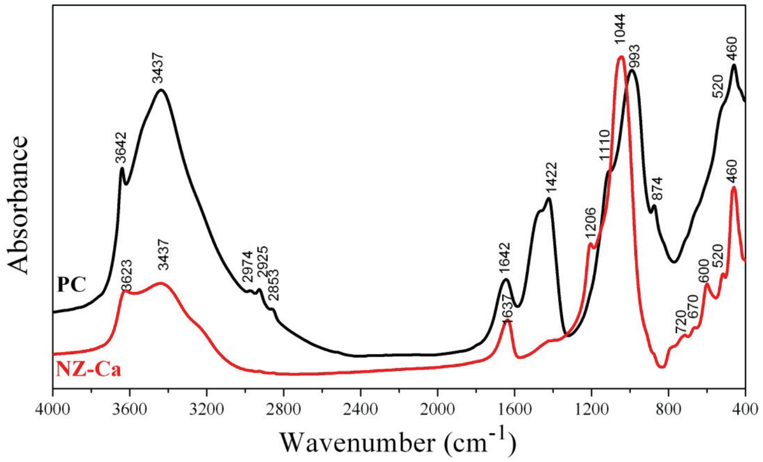

*Figure 3. FTIR spectra of PC and NZ-Ca.*

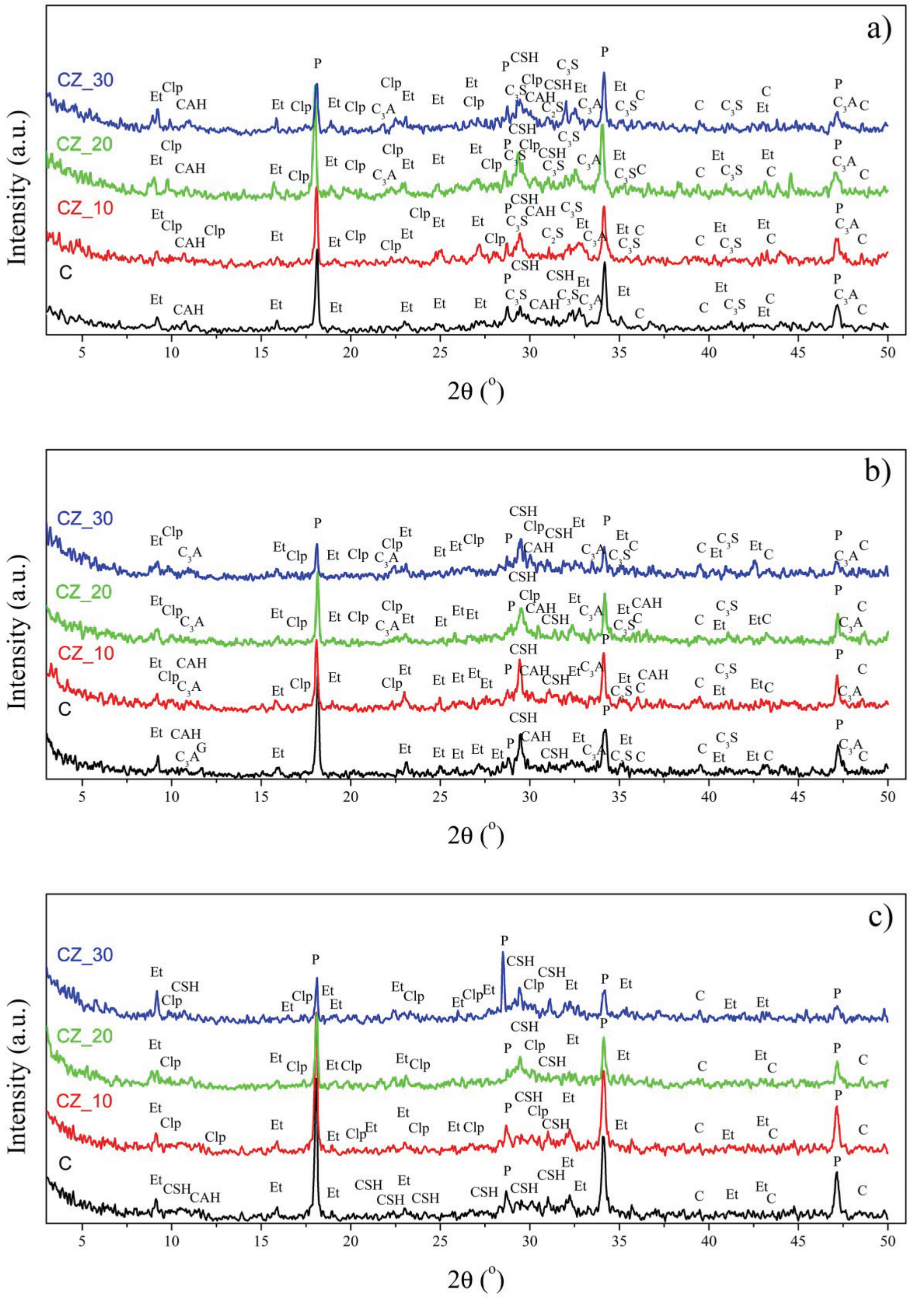

*Figure 4. XRD diffractograms of reference and blended cement pastes exposed to deionised water, at the age of: a) 28, b) 60 and c) 180 days (P - portlandite, Et - ettringite, C-S-H - calcium silicate hydrate, C-A-H - calcium aluminium hydrate, Clp - clinoptilolite, C - calcite, $C_3S$ - alite, $C_3A$ - calcium aluminate (JCPDS: 38-1429)).*

Besides the C-S-H phase, the presence of alite (JCPDS: 49-0442) and calcium aluminate (JCPDS: 38-1429) was confirmed up to 28 days of hydration, suggesting the existence of non-reacted cement grains. Moreover, a distinguished occurrence of ettringite (Et) (JCPDS: 41-1451) up to the age of 180 days and exposure to deionised water could be clearly noticed, Figure 4. According to Duchesne and Bertron [29], ettringite is unstable under pH value of 10.7. Its presence up to 180 days indicates that the exposure to deionised water as a leaching medium did not reduce pore solution pH value under the above-mentioned value. The presence of ettringite could also be explained by the availability of sulphate ions due to the specific zeolite feature to absorb $SO_3$ through alumina in zeolite structure [43]. Additionally, the occurrence of calcium carbonate (JCPDS: 01--0837) suggests the carbonation process took place during the manipulation with specimen in the course of its preparation.

*FTIR spectra*

The information acquired by XRD analysis was complemented with FTIR analysis, Figure 5. In order to obtain an integral view of the structural changes and the formation of the reaction products during hydration process and exposure to deionised water, it was most important to monitor the intensity decrease of the main absorption peak at 1044 cm$^{-1}$ caused by Ca clinoptilolite decomposition and the changes in the position and the intensity of FTIR bands at around 970 cm$^{-1}$ assigned to C-S-H gels [44]. Unfortunately, the peak at 1044 cm$^{-1}$ was not distinguished mainly because of the overlapping with the peaks related to the formation of C-S-H gel. Changes of a very complex C-S-H gel structure with a variable Ca/Si ratio can be tracked through the shifting of wavelength value in comparison to bands centered at ~970 cm$^{-1}$. Bulatovic *et al.* [45] obtained band value at ~969 cm$^{-1}$ for the curing process up to 180 days in tap water for the same type of cement supplied by the same producer. This value changes to lower wavelength values when the Ca/Si ratio increases, indicating depolymerisation or, in this test, a rise of Ca$^{2+}$ in C-S-H gel structure. On the other hand, a decrease in Ca/Si ratio is assigned to the wavelength values higher than the main position, indicating polymerisation [46,47]. The exposure to leaching conditions leads to the reduction of Ca/Si ratio [29].

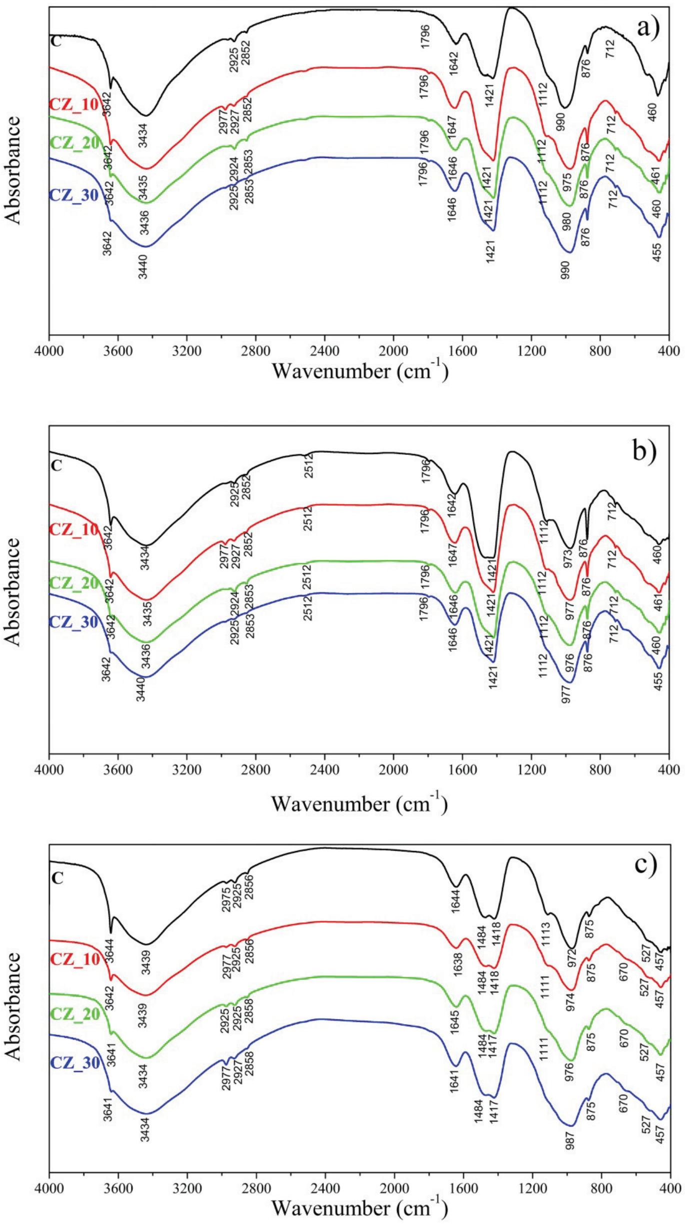

Figure 5. FTIR spectra of reference and blended cement pastes exposed to deionised water, at the age of: a) 28, b) 60 and c) 180 days.

The obtained value of the absorption band at ~990 $cm^{-1}$ for reference paste (C) at the age of 28 days and the exposure to deionised water, Table 5, Figure 5, had higher wavenumbers in comparison to 970 $cm^{-1}$ at later ages, implying leaching and, consequently, a decrease in Ca/Si ratio. Gained wavelength values for blended cement paste CZ 10 were more stable than the reference and other blended pastes up to the age of 180 days and exposure to deionised water, Table 5, implying that $Ca^{2+}$ originating from NZ-Ca, succeeded to keep the pore solution buffered by calcium hydroxide during leaching. The observed shifting in band position at ~970 $cm^{-1}$ had the highest peak value obtained for CZ 30 28 (990 $cm^{-1}$) indicating a greater level of polymerisation/leaching, *i.e.*, lower Ca/Si value in C-S-H gel structure. CZ 20 28 (981 $cm^{-1}$) and CZ 10 28 (974 $cm^{-1}$) displayed lower values than C 28 (990 $cm^{-1}$), pointing to a higher Ca/Si ratio value in C-S-H gel. The shift of absorption peak position to lower values for C 60 (973 $cm^{-1}$) indicated that C-S-H structure was less affected by leaching and a new equilibrium was established between pore solution and solid phase [26]. These processes lead to the dissolution of NZ and precipitation of products reflecting Ca/Si ratio in C-S-H gel structure. A similar direction of changes was obtained for CZ 30 pastes at the age of 60 and 180 days in comparison to CZ 30 28, Table 5.

*Table 5. Changes of C-S-H absorption peak values ($cm^{-1}$) with time*

| Paste type | Age (days) | | |
|---|---|---|---|
| | 28 | 60 | 180 |
| C | 990 | 973 | 972 |
| CZ 10 | 974 | 977 | 974 |
| CZ 20 | 981 | 976 | 976 |
| CZ 30 | 990 | 977 | 987 |

The absorption bands at ~3640, ~3435 and ~1646 $cm^{-1}$ were ascribed to different vibrational modes of the O-H molecular group. The stretching vibrations of Ca-OH from portlandite were indicated due to the absorption band at ~3640 $cm^{-1}$, while the absorption bands at ~3435 $cm^{-1}$ and ~1646 $cm^{-1}$ were associated to the presence of hydrogen-bonded $OH^{-}$ group. Özen *et al.* [48] assigned absorption bands at ~3435 and ~1646 $cm^{-1}$ to bending and stretching deformation of zeolitic water.

Distinctive ettringite bands are generally assigned to 1100 and 610 $cm^{-1}$. The presence of a weak shoulder, Figure 5, at ~1111 $cm^{-1}$ could be assigned to ettringite or gypsum [49]. The presence of carbonates was noted due to the occurrence of the absorption bands at ~1421, ~876 and ~711 $cm^{-1}$ [47]. The intensity of the peaks at ~1421 and ~876 $cm^{-1}$ was the highest at the age of 60 days and exposure to deionised water.

### The effect of leaching on compressive strength of pastes

The optimal replacement ratio of cement by NZ-Ca is defined depending on desired properties. Namely, in this investigation the criteria to achieve the resistance to leaching in deionised water is maintaining: *i*) the unchanged Ca/Si ratio in C-S-H gel and *ii*) the stability of C-S-H gel and ettringite. Heukamp *et al.* [50] indicated that decalcification of C-S-H gel to low Ca/Si ratio leads to a decrease in the cohesion of pastes, while decomposition of ettringite leads to an increase in porosity.

The optimal replacement ratio estimated following these criteria does not have to counterpart to the one obtained for the best compressive strength, as a traditional criterion of acceptance for concrete [51].

The average compressive strengths of cement pastes containing 0, 10, 20 and 30% of NZ-Ca as an SCM, exposed to deionised water in various time periods, are presented in Figure 6.

By analysing the presented results, the following findings have emerged:

- The pastes containing 10% of NZ-Ca had the highest compressive strength values, while the pastes with 30% of NZ-Ca had the lowest ones;
- The increase in the compressive strength of blended cement pastes was less prominent up to the exposure of 60 days, while later it was more pronounced, especially for CZ 10 and CZ 30 pastes. On the other hand, the reference cement paste, C, did not show a significant increase in compressive strength in the time period after 60 days;
- The compressive strengths of CZ 10 were almost always higher than the corresponding values of the reference paste. At the age of 90 and 180 days compressive strengths of CZ 10 increased by 9 and 12%, respectively, when compared to their corresponding reference values, Figure 6b;
- The compressive strengths of CZ 20 were very close to their corresponding reference values for all ages and periods of exposure to deionised water, Figure 6b. Although the compressive strengths of CZ 30 paste were always lower than their corresponding reference values, an upward trend over time could be noticed; *i.e.*, the difference between compressive strength and corresponding reference value decreased by 16 and 10% at the age of 90 and 180, respectively.

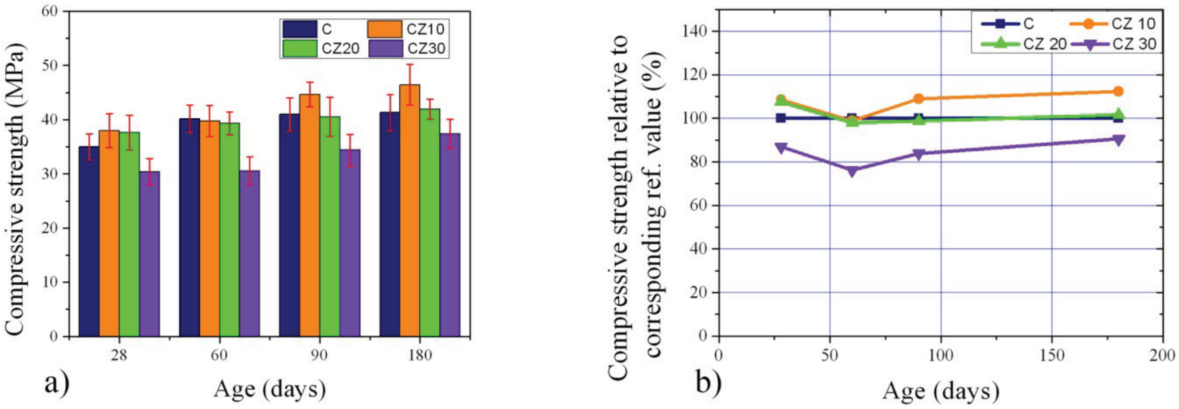

*Figure 6. Average compressive strengths of pastes: a) versus time and b) relative to corresponding reference value, versus time.*

Given that leaching is a very slow process that starts from the surface in contact with deionised water, the abrupt decrease of compressive strength for 60 days of exposure to deionised water, for all levels of cement replacement, could not be dominantly assigned to leaching. Due to a prolonged pozzolanic reaction of NZ-Ca, the appearance of these features could be related to the continuous expansion of the mean NZ-Ca cell volume causing a lower density of hydrated products and, consequently, compressive strength decrease. Bish [52] reported that the mean Ca-clinoptilolite cell volume continuously expanded resulting in lower density of pastes, while examining the dissolution process of 6 natural and 3 cation-exchanged (Ca, K, Na) clinoptilolites in pozzolanic reactions. Therefore, a decline in pastes density will impact a drop in compressive strength of zeolite blended cements. The density of zeolite blended cement pastes declined as the dosage of NZ rose. In addition, the contribution of the type of smectite clay determined by XRD analysis as a component of NZ-Ca was not clarified.

The effect of NZ-Ca pozzolanic reaction was noticeable at the age of 90 days, when the compressive strength of CZ 10 paste exceeded the reference value.

Good compressive strength results obtained for CZ 10 specimens along with their XRD and FTIR results indicate the importance of avoiding a fall in $Ca^{2+}$ concentration in the pore solution. The very existence of ettringite and portlandite mineral phases after 180 days of examination points to a structural stability of investigated paste samples during leaching in deionised water. Their presence in these specimens indicates that a high pH value (above 11.5) of pore solution will not drop within the test conditions. Furthermore, the constant Ca/Si ratio of C-S-H gel - being observed as almost not altered values of wavelength numbers (around 970 $cm^{-1}$, Table 5) and attributed to the presence of C-S-H gel (specifically for CZ 10 pastes) - implies that the effect of C-S-H gel decalcification was negligible during the exposure to deionised water. In addition, the compressive strength for CZ 10 was the highest.

The statements discussed in the paper as the results of the investigation suggest that the structural stability of cement-based material with NZ-Ca as an SCM after the exposure to deionised water is most likely caused by the existence of sufficient buffering capacity, regardless of the observed diffusion and leaching of $Ca^{2+}$ from paste specimens to deionised water.

## CONCLUSION

Based on the presented results, the following conclusions can be drawn:

- Natural Ca-exchanged clinoptilolite containing smectite as a secondary component can be classified as a pozzolanic material, type II addition;
- The presence of portlandite and ettringite in paste at the age of 180 days and the exposure to the deionised water was identified by XRD and FTIR analyses, indicating that pH value in that moment was not lower than 10.7. This implies that leaching in deionised water did not influence the stability of the hydration products. The results of the FTIR analysis confirmed that up to 180 days of exposure, the blend containing 10% Ca-exchanged clinoptilolite had an almost constant Ca/Si ratio value, thus confirming a buffering effect of calcium ions.
- The paste specimens showed the compressive strength of blended cement pastes was less prominent up to 60 days of exposure to deionised water, while it was more pronounced later in comparison to reference specimens. The replacement level of Ca-exchanged clinoptilolite in cement pastes up to 20% did not cause the reduction of compressive

strength. Even more, with the replacement level up to 10% of natural zeolite, compressive strengths were higher than in the reference cement pastes.

## Acknowledgment

This research has been supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia through the project No. 451-03-68/2020-14/200156: “Innovative scientific and artistic research from the FTS domain”.

## REFERENCES

[1] M. Najimi, J. Sobhani, B. Ahmadi, M. Shekarchi, Constr. Build. Mater. 35 (2012) 1023-1033

[2] M.C.G. Juenger, R. Snellings, S.A. Bernal, Cem. Concr. Res. 122 (2019) 257-273

[3] G. Mertens, R. Snellings, K.V. Balen, B. Bicer-Simsir, P. Verlooy, J. Elsen, Cem. Concr. Res. 39 (2009) 233-240

[4] V.D. Kasić, V. Simić, D. Životić, A.S. Radosavljević--Mihajlović, J.N. Stojanović, Hem.Ind. 71 (2017) 49-60

[5] B. Ahmadi, M. Shekarchi, Cem. Concr. Compos. 32 (2010) 134-141

[6] J. Małolepszya, E. Grabowska, Procedia Eng. 108 (2015) 170-176

[7] C. Bilim, Constr. Build. Mater. 25 (2011) 3175-3180

[8] P. Krolo, R. Krstulović, P. Dabić, A. Bubić, Ceram.-Silik. 49 (2005) 213-219

[9] M. Vyšvaril, P. Bayer, Procedia Eng. 151 (2016) 162-169

[10] C. Napia, T. Sinsiri, C. Jaturapitakkul, P. Chindaprasirt, Waste Manage. 32 (2012) 1459-1467

[11] I. Plecas, S. Dimovic, I. Smiciklas, Prog. Nucl. Energy 48 (2006) 495-503

[12] M. Otieno, M. Alexander, J. du Plessis, J. S. Afr. Inst. Civ. Eng. 59 (2017) 57-67

[13] B. Anand, S.N. Sharma, in Recent Advancements in Mineral and Water Resources, R.N. Tiwari Ed., Excellent Publishers, New Delhi, 2016, p. 155

[14] G. Vu, T. Iskhakov, J.J. Timothy, C. Schulte-Schrepping, R. Breitenbücher, G. Meschke, Materials 13 (2020) 1-17

[15] N. Marinoni, A. Pavese, M. Voltolini, M. Merlini, Cem. Concr. Compos. 30 (2008) 700-705

[16] P. Faucon, P. Le Bescop, F. Adenot, P. Bonville, J.F. Jacquinot, F. Pineau, B. Felix, Cem. Concr. Res. 26 (1996) 1707-1715

[17] G. Kirov, L. Filizova, Geokhim. Mineral. Petrol. 49 (2012) 65-82

[18] B. Lothenbach, K. Scrivener, R.D. Hooton, Constr. Build. Mater. 41 (2011) 1244-1256

[19] J. Skibsted, R. Snellings, Cem. Concr. Res. 124 (2019), Paper 105799

[20] D. Caputo, B. Liguori, C. Colella, Cem. Concr. Compos. 30 (2008) 455-462

[21] R. Snellings, G. Mertens, J. Elsen, J. Therm. Anal. Calorim. 101 (2010) 97-105

[22] K.C. Newlands, D.E. Macphee, Adv. Appl. Ceram. 116 (2017) 216-224

[23] K.C. Newlands, M. Foss, T. Matchei, J. Skibsted, D.E. Macphee, J. Am. Ceram. Soc. 100 (2017) 1941-1955

[24] K. Luke, in Proceedins of 12th International Congress on the Chemistry of Cement, Montreal, Canada, 2007

[25] K.V. Ragnarsdóttir, Geochim. Cosmochim. Acta 57 (1993) 2439-2449

[26] C. Alonso, M. Castellote, I. Llorente, C. Andrade, Cem. Concr. Res. 36 (2006) 1583-1594

[27] W. Kunther, S. Ferreiro, J Skibsted, J. Mater. Chem., A 5 (2017) 17401-17412

[28] P. Feng, C. Miao, J.W. Bullard, Cement Concrete Comp. 49 (2014) 9-19

[29] J. Duchesne, A. Bertron, in Performance of Cement-Based Materials in Aggressive Aqueous Environments, State-of-the-Art Report, M. Alexander, A. Bertron, N. De Belie Eds., RILEM TC 211-PAE, 2013, pp. 91-112

[30] D. Vaičiukynienė, A. Kantautas, G. Krušinskas, A. Kielė, Ž. Rudžionis, Chem. Ind. Chem. Eng. Q. 22 (2016) 285-292

[31] J.K. Norvell, J.G. Stewart, M.C.G. Juenger, D.W. Fowler, J. Mater. Civ. Eng. 19 (2007) 1053-1059

[32] BS EN 197-1, Cement, Composition, specifications and conformity criteria for common cements, 2011

[33] BS EN 1097-7, Tests for mechanical and physical properties of aggregates, Part 7: Determination of the particle density of filler – Pycnometer method, 2008

[34] BS EN 196-6, Methods of testing cement, Part 6: Determination of fineness, 2010

[35] BS EN 451-2, Method of testing fly ash, Part 2: Determination of fineness by wet sieving, 1995

[36] BS EN 196-3, Methods of testing cement, Part 3: Determination of setting times and soundness, 2005

[37] BS EN 450-1, Fly ash for concrete, Part 1: Definition, specifications and conformity criteria, 2012

[38] F.A. Sabet, N.A. Libre, M. Shekarchi, Constr. Build. Mater. 44 (2013) 175-184

[39] BS EN 196-2, Methods of testing cement, Chemical analysis of cement, 2013

[40] I.E. Odom, Phil. Trans. R. Soc. Lond. A 311 (1984) 391--409

[41] M. Horgnies, J.J. Chen, C. Bouillon, in Proceedings of 6th International Conference on Computational Methods and Experiments in Materials Characterisation, Siena, Italy, 2013, p.251

[42] G. Rodriguez-Fuentes, A.R Ruiz-Salvador, M .Mir, O. Picazo, G. Quintana, Microporous Mesoporous Mater. 20 (1998) 269-281

[43] K. Sobol, T. Markiv, V. Terlyha, W. Franus, Pecularities, Bud-arch 14 (2015) 105-113

[44] F. Puertas, S. Goñi, M.S. Hernández, C. Varga, A. Guerrero, Cem. Concr. Compos. 34 (2012) 384-391

[45] V. Bulatović, M. Melešev, M. Radeka, V. Radonjanin, I. Lukić, Constr. Build. Mater. 152 (2017) 614-631

[46] P. Yu, R.J. Kirkpatrick, B. Poe, P.F. McMillan, X. Cong, J. Am. Ceram. Soc. 82 (1999) 742-748

[47] Y. Kocak, E. Tascı, U. Kaya, Constr. Build. Mater. 47 (2013) 720-727

[48] S. Özen, M.C. Göncüoglu, B. Liguori, B. de Gennaro, P. Cappelletti, G.D. Gatta, F. Iucolano, C. Colella, Constr. Build. Mater. 105 (2016) 46-61

[49] M.Y.A. Mollah, W. Yu, R. Schennach, D. L. Cocke, Cem. Concr. Res. 30 (2000) 267-273

[50] F.H. Heukamp, F.-J. Ulm, J.T. Germaine, Cem. Concr. Res. 33 (2003) 1155-1173

[51] A. Neville, Concrete: Neville's Insights and Issues, Thomas Telford Publishing, London, 2006, 75-78

[52] L.D. Bish, Clays Clay Miner. 32 (1984) 444-452.

TIANA MILOVIĆ[1]
OGNJEN RUDIĆ[2]
SAEEDA OMRAN FURGAN[1]
MIROSLAVA RADEKA[1]
MIRJANA MALEŠEV[1]
VLASTIMIR RADONJANIN[1]
SEBASTIAN BALOŠ[1]
MIRJANA LABAN[1]

[1]Fakultet tehničkih nauka, Univerzitet u Novom Sadu, Trg Dositeja Obradovića 6, 21000 Novi Sad, Srbija
[2] Institute of Technology and Testing of Building Materials (IMBT-TVFA), Graz University of Technology, Graz, Austria

NAUČNI RAD

# UTICAJ DEJSTVA MEKE VODE NA PORTLAND CEMENT I MEŠAVINU PORTLAND CEMENTA I PRIRODNOG ZEOLITA

*Trajnost infrastrukture spravljene od betona dovodi se u vezu sa svojstvima samog betona i uticajima koje agresivna spoljašnja sredina ima na njega. Kada je beton direktno izložen dejstvu meke vode, dolazi do ispiranja jona kalcijuma iz očvrsle cementne paste odnosno paste na bazi cementa, što dovodi do smanjenja čvrstoće i dalje devastacije strukture betona. U ovom radu su prikazani rezultati eksperimentalnog istraživanja uticaja dejstva meke vode na fazni sastav i čvrstoću pri pritisku pastā na bazi cementa, kada se cement supstituiše sa 0, 10, 20 i 30% prirodnog zeolita. Kako bi se simuliralo dejstvo meke vode u laboratorijskim uslovima, uzorci pastā su bili izloženi ispiranju u dejonizovanoj vodi u periodu od 180 dana. Procena promena faznog sastava (etringit, portlandit, kalcijum-siliko-hidratni gel) nastalih usled ispiranja jona kalcijuma urađena je na osnovu rezultata rendgenostrukturne analize, infracrvene spektroskopije i čvrstoće pri pritisku pasta. Prisustvo portlandita i etringita nakon 180 dana izlaganja dejstvu dejonizovane vode ukazuje da ispiranje nije uticalo na stabilnost produkata hidratacije u pastama na bazi cementa. Štaviše, cementna pasta sa 10% prirodnog zeolita imala je veću čvrstoću pri pritisku u odnosu na referentnu.*

*Ključne reči: Ca-klinoptilolit, čvrstoća pri pritisku, dejonizovana voda, FTIR spektroskopija, ispiranje, XRD analiza.*