COMPRESSIVE STRENGTH AND MINERALOGICAL PROPERTIES OF CEMENT PASTE CONTAINING ZEOLITE

Tiana Milović [1]
Miroslava Radeka [2]
Mirjana Malešev [3]
Vlastimir Radonjanin [4]

UDK: 666.9.022.1 : 539.4
DOI:10.14415/konferencijaGFS 2016.040

Summary:. *Results of mineralogical characterisation and the compressive strength of pastes, at the age of 28 days, containing natural zeolite as partial replacement of cement are presented in this paper. Mixtures contain 0%, 10%, 20% and 30% of natural zeolite in relation to cement mass. All samples were prepared with water-to-binder ratio of 0.5. Consideration of a possible correlation between mineralogical properties (XRD, FTIR) and the compressive strength of pastes, at the age of 28 days, is a main goal of the research.*

Keywords: *Zeolite, paste, compressive strength, XRD analysis, FTIR spectorscopy.*

1. INTRODUCTION

Supplementary cementitious materials (SCMs) are natural or by-product materials which react with $Ca(OH)_2$, (CH), and form hydraulic compounds such as hydrated calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H) [1]. Natural zeolite belongs to the group of natural SCM, whose pozzolanic activity depends on several factors (chemical and mineralogical composition, particle size distribution, specific surface area, cation-exchange capacity, Si/Al ratio of the zeolite framework, etc) [2,3]. Many studies have promoted the use of the zeolite-bearing tuffs as SCMs due to their positive influence on the long term compressive strength and durability. Neverthereless, the variability in tuff′s mineralogical and physical properties results in limited understanding of pozzolanic activity of natural zeolites.
When zeolite comes in contact with $Ca(OH)_2$ or Ca^{2+}, in saturated high pH solution, OH^- ions begin the decomposition of zeolite framework, which leads to the formation of

[1] Tiana Milović, MSc. CE, University of Novi Sad, Faculty of Technical Sciences, Dept. of Civil Engineering and Geodesy, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia, e – mail: tiana.milovic@uns.ac.rs
[2] Miroslava Radeka, Dr. Prof., University of Novi Sad, Faculty of Technical Sciences, Dept. of Civil Engineering and Geodesy, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia, e – mail: mirka@uns.ac.rs
[3] Mirjana Malešev, Dr. Prof., University of Novi Sad, Faculty of Technical Sciences, Dept. of Civil Engineering and Geodesy, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia, e – mail: miram@uns.ac.rs
[4] Vlastimir Radonjanin, Dr. Prof., University of Novi Sad, Faculty of Technical Sciences, Dept. of Civil Engineering and Geodesy, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia, e – mail: radonv@uns.ac.rs

$[SiO(OH)_3]^-$ and $[AlO(OH)_4]^-$ groups. Those depolymerized species further enter the solution, react with Ca^{2+} and form C-S-H, C-A-H and C-A-S-H gels and AFm type calcium aluminate hydrates [3]. When the zeolite as SCMs is in question, C-A-S-H phase is of particular interest. The incorporation of Al into the C-S-H phase has great influence on mechanical properties and durability.
The experiments have been conducted to determine the effects of substituting cement with 0%, 10%, 20% and 30% natural zeolite per mass on the compressive strength and mineralogical properties of cement pastes.
In this paper, only the results of samples tested after 28 days of curing (research plan includes also the examinations after 60, 90, 180 and 365 days) are presented.

2. MATERIALS

The materials used in this study have been natural zeolite (particle diameter less than 125 μm) from the quarry from Igroš (Brus, Serbia) and Portland cement, CEM I 42.5 (Lafarge, Beočin, Serbia) which meets criteria of standard SRPS EN 197-1.
The chemical composition of natural zeolite is shown in Table 1. Ration Si/Al affects the stability of zeolite structure and in this case its value is 4.95 [2].

Table 1- Chemical composition of natural zeolite [2]

Chemical composition of natural zeolite from Igros [%]												
SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	P_2O_5	L.I.*	L.H.**	SO_3
62.30	12.59	0.23	1.20	4.80	1.94	0.22	0.70	0.63	0.016	11.06	4.59	0.05
* Loss on ignition ** Loss by heating												

The mixtures of Portland cement, combining 0%, 10%, 20% and 30% per mass of natural zeolite (samples are referred as C, CZ10, CZ20 and CZ30 respectively) have been used for pastes preparation (Tab. 2). Water/binder ratio (W/B=0.5) has been retained for all samples. The dimensions of paste samples have been 1x1x6 cm.

Table 2- Mix proportions for cement and cement-zeolite pastes

Mix proportions				
	C	CZ10	CZ20	CZ30
CEM I 42.5	450g	405g	360g	315g
Natural zeolite	-	45g	90g	135g
Deionized water	225g	225g	225g	225g
w/b ratio	0.5	0.5	0.5	0.5

3. METHODS

Mineralogical characterisation –via XRD analyses and FTIR spectroscopy
The XRD patterns have been acquired on Philips X-ray powder diffractometer type PW-1710 using copper anticathode with CuKα=1.54128Å and graphite monochromator. Powder XRD analyses have been performed in the 2θ(°) angle range from 5° to 50° with

a 0.02° step in experiments. The identification of the existing mineral phases has been acquired by comparing interpolate distances (d) and relative intensities (I) with literature data, or the appropriate card from the JCPDS files.

Fourier Transform Infra-Red (FTIR) analyses have been carried out using Thermo-Nicolet Nexus 670 FTIR spectrometer. For each measurement 32 scans and 32 background have been recorded with a resolution of 4.0 cm^{-1}. The spectra of all investigated samples have been measured using the KBr pellet technique. One of the advantages of using FTIR spectroscopy is a possibility to study the vibrational properties of amorphous as well as crystalline samples [4].

Compressive strength – The mechanical performance of the pastes has been estimated by measuring the compressive strength of samples (10 samples per mixture). All samples have been cured in accordance with standard SRPS EN196-1 [5], except for the condition related to the quality of curing water (deionized water have been used instead of tap water).

4. RESULTS AND DISCUSSION

Mineralogical characterisation
The main objective of this study is analyses of hydration products of paste made with and without zeolite as SCM, after 28 days of curing. The hydration process is very complex and mostly related to the structure and the amount of calcium silicate hydrate (C-S-H) gel.
Two methods have been used in order to achieve this goal: XRD and FTIR spectroscopy. XRD analysis is more convenient for the characterisation of compounds with crystal form, while FTIR spectroscopy is one of the most powerful techniques which is normally used for molecular characterization. It has turned out to be very useful to use it for characterisation of C-S-H, main hydration compound, with poor crystalline structure.

The XRD analyses of all samples (C, CZ10, CZ20 and CZ30) have shown the presence of different crystalline phases (Fig. 1). The most intensive peaks correspond to portlandite (calcium hydroxide-CH), ettringite, CSH (calcium silicate hydrate) and CAH (calcium aluminium hydrate) compounds, respectively.
CZ30 samples has had the lowest intensities of the peaks corresponding to portlandite. The characteristic peaks of clinoptilolite, the main component of zeolite, had not disappeared. Moreover, for CZ30 sample the intensities of the peaks corresponding to clinoptilolite have been a bit more pronounced than for samples CZ10 and CZ20. Usually a decrease in the intensity of CH-peaks in CZ30 sample indicates that pozzolanic reaction is more prominent. However, the presence of clinoptilolite implies that pozzolanic reaction is not the only reason for reduction in these peaks intensities.

FTIR analysis as a spectroscopic method has been used to study the chemistry of hydration process. In this paper, the comparison of spectra obtained for cement paste with spectra which have been obtained for cement pastes containing zeolite as SCM, has been performed.

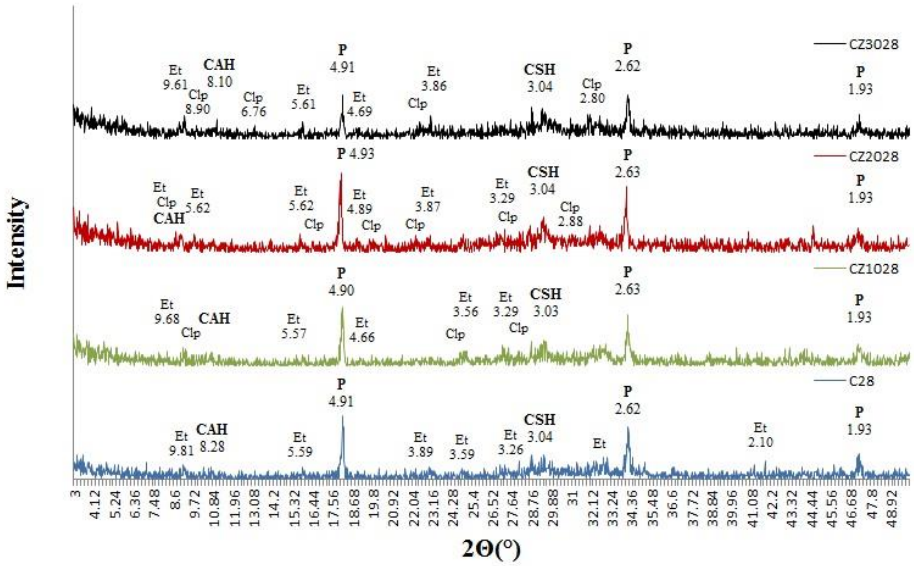

Figure 1- XRD patterns of the hardened cement paste and pastes of cement containing natural zeolite as SCM, after 28 days of hydration (P-portlandite, Et-ettringite, CSH-calcium silicate hydrate, CAH-calcium aluminium hydrate, Clp- clinoptilolite) [2]

FTIR spectra for all paste samples are presented in Fig. 2.

FTIR analysis of cement paste has indicated the existence of mid –IR bands referred to the presence of several molecular groups. The band at 3640 cm^{-1} is addressed to stretching vibrations of Ca-OH from portlandite. The presence of this compound has also been confirmed by XRD analysis. The band at ~3436 cm^{-1} is assigned to hydrogen bonded OH species adsorbed on the surfaces of the tested samples and is assigned to ν_1 vibration of hydrogen bonded OH group in H_2O. In contrast to portlandite, carbonates have not been indentified by XRD but their presence have been indicated by FTIR. The bands at 1423cm^{-1}, 875 cm^{-1} and 712 cm^{-1} point to its presence. This is probably caused by the reaction of atmosferic CO_2 with calcium hydroxide (band at ~875 cm^{-1}). This band corresponds to ν_3 vibration mode of CO_3^{2-}. The peak at ~3436cm^{-1} has been assigned to ν_1 vibration of hydrogen bonded OH group in H_2O. The identification of ettringite is not an easy task due to overlapping of its main bands. Namely, the band at 1100 cm^{-1} could be attributed to the presence of the SO_4^{2-} -vibration which could be assigned to the ettringite mineral phase. Also the band at ~3436 cm^{-1} denoted to hydrogen bonded OH group is characteristic of the water present in ettringite. The presence of ettringite has been confirmed by XRD. The absorption band at 1100 cm^{-1} and 1200 cm^{-1} have been allocated to sulfates. The sulfate compounds in portland cements are gypsum ($CaSO_4 \cdot 2H_2O$), hemyhydtrate ($CaSO_4 \cdot 0.5H_2O$) and anhydrite ($CaSO_4$). Calcium silicate hydrate presents the most important binding phase in hydrated portland cement. The main mid-IR bands for C-S-H gels appear at ~970 cm^{-1} (denoted to Si-O stretching vibrations of Q^2 tetrahedra), 660-670 cm^{-1} (Si-O-Si bending vibration, which is influenced by Si-O-Si angle) and band at 450-500 cm^{-1} (deformation of SiO_4

tetrahedra). These bands could be changed in frequency and/or intensity with the change of Ca/Si ratio. Namely, with the increase of Ca/Si ratio, the wavenumber decrease indicating the depolimerization of the silicate chains [6]. In the case of cement paste the band at 992.44 cm^{-1} has been noticed, which indicates that there has been a decrease of Ca/Si ratio and an increase of polimerization of the silicate chains compared to the FTIR specta of cement-zeolite paste samples (Figure 2).

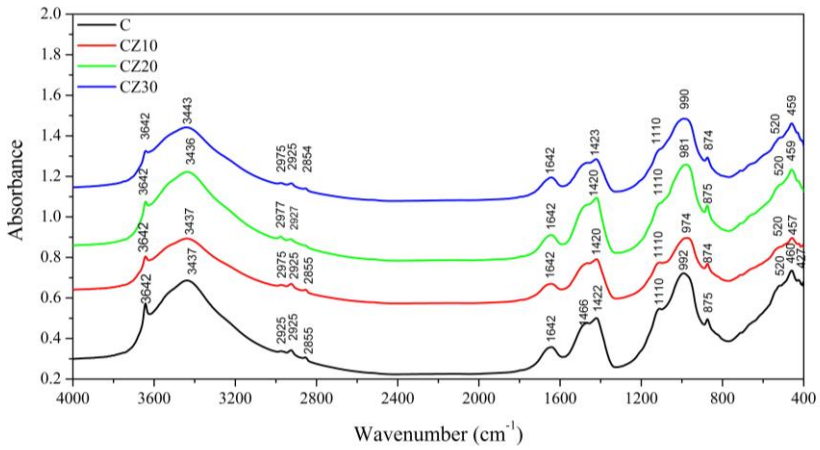

Figure 2- FTIR spectra of pastes after 28 days of hydration

The analysis of spectra for other, cement-zeolite pastes are also presented in Fig 2. The obtained data for these pastes are similar to the above presented ones for cement paste. Certain difference of the Si-O streching bend which was detected for cement paste has been noticed since it is shifted toward lower wavenumber values for CZ10, CZ20 and CZ30 pastes (974.05 cm^{-1}, 981.09 cm^{-1}, 990.05 cm^{-1}, respectively), which could be atributed to the increase of Ca/Si ratio. The largest shift of the mentioned Si-O streching band position has been found in the case of CZ10, suggesting that the zeolite phases decomposition has influenced the composition of C-S-H gel during hydration process.
The possible formation of amorphous C-A-S-H gel is difficult to distinguish from other species because of their unresolved bands (appearance of a shoulder at ~1200 cm^{-1}).
Additionally, based on the results of the comparative analysis of the obtained FTIR spectra, it can be noticed that there has been a decrease in the intensity of peaks characteristic of the portlandite and sulphates with the increase of the proportion of zeolite.
Compressive strength - The average compressive strengths of cement pastes containing 0%, 10%, 20% and 30% of zeolite as SCM, at the age of 28 days, are shown in figure 3, and table 3. The strength values have also been expressed as relative percentages of the 28-day reference paste compressive strength. Due to the dissipation of the measurement results, the standard deviations have been determined (Tab. 3).
CZ20 has the highest value in comparison to the compressive strength value of reference paste (C), (12.40% greater than C). The paste CZ10 has had compressive strength value for 8.51% greater than C, while CZ30 has not exceed the value of C (12.66% smaller than C).

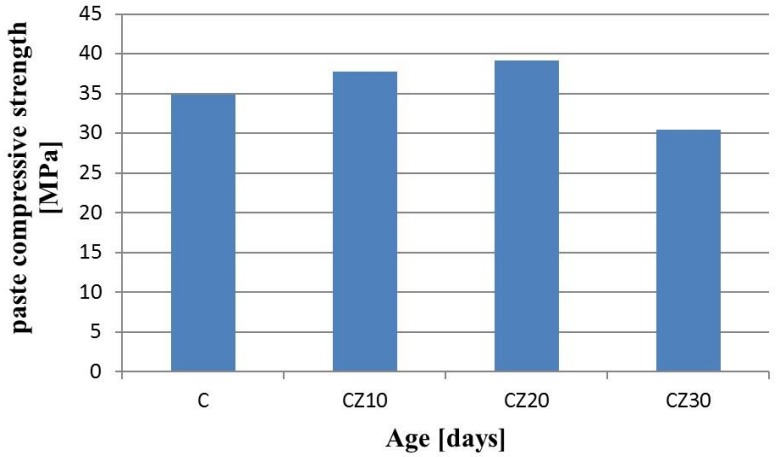

Figure 3- 28-day compressive strength of C, CZ10, CZ20 and CZ30 pastes

Table 3- 28-day compressive strength ($f_{cm,28}$) of cement and cement-zeolite pastes, the relation of compressive strength of cement-zeolite pastes and cement paste ($\Delta f_{cm,28}$) and standard deviations (σ)

Paste type	C	CZ10	CZ20	CZ30
$f_{cm,28}$ [MPa]	34.821	37.783	39.137	30.411
$\Delta f_{cm,28}$ [%]	**100.00**	108.51	112.40	87.34
σ [MPa]	± 5.211	± 7.288	± 5.523	± 6.832

5. CONCLUSION

The results obtained in this study for paste samples aged 28 days with binders comprising natural zeolite from Igroš, Serbia with 0%, 10%, 20% and 30% of cement per mass (samples C, CZ10, CZ20 and CZ30 respectively) allow the following conclusions:

- the ratio of Si/Al is 4.95,
- XRD analyses have determined that the main components in all hydrated paste samples (C, CZ10, CZ20 and CZ30) are portlandite, ettringite, C-A-H and C-S-H compounds. A significant decrease in the intensity of $Ca(OH)_2$ peaks in CZ30 sample indicates that the pozzolanic reaction has been rather prominent, but this has not been confirmed by the values of the compressive strength of these samples.
- the results of FTIR analysis have confirmed the results of XRD analyses, except in terms of CAH gel. Additionally, its results have indicated the presence of carbonates and the partly depolimerizied C-S-H gel in CZ10, CZ20 and CZ30 samples, in comparison to C sample.
- the value of compressive strength for samples CZ10 and CZ20 has exceeded the value of the referent sample, while the obtained value for the sample CZ30 has been 87 % of the referent one.

ACKNOWLEDGEMENTS

The work reported in this paper is a part of the investigation within the research project TR 36017 "Utilization of by-products and recycled waste materials in concrete composites in the scope of sustainable construction development in Serbia: investigation and environmental assessment of possible applications", supported by the Ministry of Education, Science and Technology, Republic of Serbia. This support is gratefully acknowledged.

REFERENCES

[1] Caputo, D. et al.: Some advances in understanding the pozzolanic activity of zeolites: The effect of zeolite structure. *Cement and Concrete Composites*, **2008.**, vol. 30, № 455-462
[2] Radeka, M. et al.: Effect of zeolite on basic physical properties, mechanical properties and frost resistance of cement mortars. *13th International Scientific Conference INDIS 2015*, 25-27 November 2015, Novi Sad, Serbia, № 260-272
[3] Perraki, Th. et al.: The effect of natural zeolites on the early hydration of Portland cement. *Microporous and Mesoporous Materials*, **2003.**, vol. 61, № 205-212
[4] Choudhary, H.K. et al.: Observation of phase transformations in cement during hydration. *Construction and Building Materials*, **2015.**, vol. 101, № 122-129
[5] SRPS EN 196-1: Methods of testing cement - Part 1: Determination of strength
[6] Yu, P. et al.: Structure of calcium silicate hydrate (C-S-H): Near-, Mid-, and Far-Infrared Spectroscopy. *J. Am. Ceram. Soc.*, **1999.**, vol. 82[3], № 742-748

ЧВРСТОЋА НА ПРИТИСАК И МИНЕРАЛОШКА КАРАКТЕРИЗАЦИЈА ЦЕМЕНТНЕ ПАСТЕ КОЈА САДРЖИ ЗЕОЛИТ

Резиме: *У раду су приказани резултати минералошке карактеризације као и резултати испитивања чврстоће при притиску цементних пасти, старости 28 дана, код којих је део цемента супституисан природним зеолитом. Мешавине садрже 0%, 10%, 20% и 30% природног зеолита у односу на масу цемента. Сви узорци су прављени са водо-везивним фактором 0.5. Циљ истраживања је да се размотри потенцијална корелација између минералошког састава (XRD, FTIR) и чврстоће при притиску пасти старости 28 дана.*

Кључне речи: *Зеолит, пасте, чврстоћа при притиску, XRD анализа, FTIR.*