18. KONFERENCIJA SA MEĐUNARODNIM UČEŠĆEM
RIZIK I BEZBEDNOSNI INŽENjERING

RAZLIKE U PONAŠANJU CEMENTNE PASTE KOJA SADRŽI PRIRODNI ZEOLIT KAO SCM USLED DEJSTVA POŽARA KORIŠĆENJEM TGA/DTA U VAZDUHU I U ARGONU

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Rezime: U ovom radu su prikazani eksperimentalni rezultati termičke analize cementne paste koja sadrži 0%, 10%, 20% i 30% prirodnog zeolita kao SCM nakon dugotrajnog izlaganja mekoj vodi koja dovodi do ispiranja kalcijuma i povećane osetljivosti betonske konstrukcije na visoke temperature. Kako bi se simuliralo dejstvo meke vode u laboratorijskim uslovima , uzorci pasta su bili izloženi ispiranju u dejonizovanoj vodi tokom 365 dana. Nakon toga, ispitane su fizičke i hemijske promene cementnih pasta koje sadrže prirodni zeolit , pomoću TGA/DTA, pri atmosferskom pritisku na vazduhu i u argonu. Korišćena je kriva vreme-temperatura koja simulira standardnu ISO 834 požarnu krivu.

Ključne reči: prirodni zeolit, pasta, TGA/DTA, vazduh, argon, ISO 834, dejstvo meke vode

DIFFERENCES IN FIRE BEHAVIOR OF CEMENT PASTE CONTAINING NATURAL ZEOLITE AS SCM USING TGA/DTA IN AIR AND ARGON

Abstract: This paper presents the experimental results of the thermal analyses of cement paste containing 0%, 10%, 20% and 30% natural zeolite as SCM after long-term exposure to soft water which leads to leaching of calcium and increased sensitivity of the concrete structure to high temperatures. In order to simulate soft water attack in laboratory conditions, paste specimens were exposed to leaching in deionized water up to 365 days. Afterward, the physical and chemical changes of the cement pastes containing natural zeolite were determined using TGA/DTA at atmospheric pressure in the air and in argon. The used time–temperature curve simulated the ISO 834 standard fire curve.

Key words: natural zeolite, paste, TGA/DTA, air, argon, ISO 834, soft water attack

1. INTRODUCTION

In order to examine the fire behavior of concrete, it is necessary to understand the fire behavior of the cement matrix. The research in this field is mostly focused on the physical and mechanical properties of the concrete itself, although the phase composition and the thermal behavior of the cement matrix have an important role in determining the fire resistance of concrete. Thermogravimetric analysis/Differential thermal analysis (TGA/DTA) could be a useful device for evaluating the fire behavior of building materials [1]. This analysis can be used to monitor the mass loss in each sample as a result of temperature-induced mineral reactions (e.g. dehydroxylation reactions). Bakhtiyari et al. [1] used TGA at atmospheric pressure in the air to determined the mechanical properties and changes in the phase composition of the paste at elevated temperatures, like Terzić et al. [2], while Kushnir et al.[3] investigated the influence of high temperatures on concrete in argon atmosphere.

Although it is considered that ordinary concrete has high fire resistance, due to the exposure to i.e. accidental fire, it may experience numerous chemical and mineralogical changes, which can

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compromise the durability of post-fire structures [4]. Furthermore, when concrete structures are previously exposed to soft water attack for an extended period of time, they become significantly less durable due to calcium leaching and even more sensitive to high temperatures. Leaching caused by the exposure to pure or natural water with pH value close to neutral (salt free-distilled or deionized, rainwater, snow-melt water, water from the river, etc.) has been identified as very important for the structures exposed to external applications like concretes used in hydro structures (dams, water tanks, and other allied structures [5]), tunnels [6], tanks, retaining walls, etc.

Supplementary cementitious materials (SCMs), such as natural zeolites (NZs), have been used as partial replacement of Portland cement (PC) in concrete mixtures. Many physical and chemical changes (i.e. volatilization of water vapor from the system and de-alumination of zeolitic structure) could occur simultaneously during heating of NZs, such as the collapse of the microporous structure of NZ, melting of product and entrapment of gaseous products, etc. [7].

The primary objective of this study is to investigate the differences in the phase composition changes (reaction to fire) of the cement paste containing 0%, 10%, 20% and 30% NZ as SCM after 365 days of exposure to soft water, using TGA/DTA (i) at atmospheric pressure in the air, and (ii) in an argon atmosphere. The used time–temperature curve simulated the ISO 834 standard fire curve.

2. MATERIALS AND METHODS

2.1. Materials

In order to evaluate the differences in fire behavior of cement paste containing NZ as SCM applying TGA/DTA in the synthetic air at atmospheric pressure and in the argon atmosphere, the following component materials were used for the preparation of the paste:

- Ordinary Portland cement CEM I 42.5R (Lafarge-BFC Serbia),
- NZ from a quarry in Igroš (Brus, Serbia) with particle size less than 125 µm,
- Deionized water.

Selected PC and NZ physical properties were determined according to the methods prescribed in specified standards and results are presented in Table 1.

Table 1 – Physical properties and test methods for PC and NZ

Physical property	Test method	PC	NZ
Density (g/cm^3)	SRPS B.B8.032 [8]	3.13	2.31
Blaine specific surface (cm^2/g)	SRPS B.C8.024 [9]	4189	5393
Activity index, at age of 28 days (% of control)	EN 450-1 [10]	-	85.6
Activity index, at age of 90 days (% of control)		-	90.0

The chemical composition of NZ was determined by X-ray fluorescence (XRF) spectroscopy. The instrument used for the XRF analysis is an ED-XRF spectrometer, manufacturer Spectro Xepos from Germany. The system uses a Silicon Drift Detector (SDD), band-pass filter and focuses the X-rays from a binary Co/Pd alloy thicktarget anode (50W/60kV) combining polarized/direct excitation. Sample tray used for these measurements was with rotating positions for pellets. Measurements were carried out in vacuum atmosphere and Spectro XRF Analyzer Pro software was used. The sample for ED-XRF analysis was prepared in accordance with the pressed powder method. Tested materials (5 g) and binding agent (Cereox wax, Fluxana) were mixed (1 g) and the 32 mm diameter pellet was formed. The pellet was formed under 10 tones load applied via a laboratory hydraulic press. The loss on ignition (LOI) of NZ was determined after exposing the sample in the amount of 2 g, to a temperature of 950°C for 1 h. The obtained results are shown in Table 2.

As shown in Table 2, the sum of the oxides that are relevant for pozzolanic reaction (SiO_2, Al_2O_3, and Fe_2O_3) is higher than 70% (77.35 %), allowing the classification of NZ into the type II addition conforming to EN 206-1 [11] and EN 450-1 [10]. Based on the LOI result, NZ could not be classified into any category proposed by the standard EN 450-1 [10].

Table 2 – Chemical composition of NZ

Chemical composition of NZ (%)					
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LOI
62.78	12.20	2.37	5.09	2.65	
Na_2O	K_2O	P_2O_5	SO_3	Cl^-	12.36
0.42	0.74	0.05	0.01	0.05	

The mineralogical characterization of NZ was performed by XRD analysis (Philips PW1710 device) under the following experimental conditions: monochromatic Cu Kα radiation with 1.5418 Å wavelengths in the 5–60° of 2θ range, scan rate 0.02° and 0.5 s per step. The diffraction pattern of the NZ is presented in Figure 1.

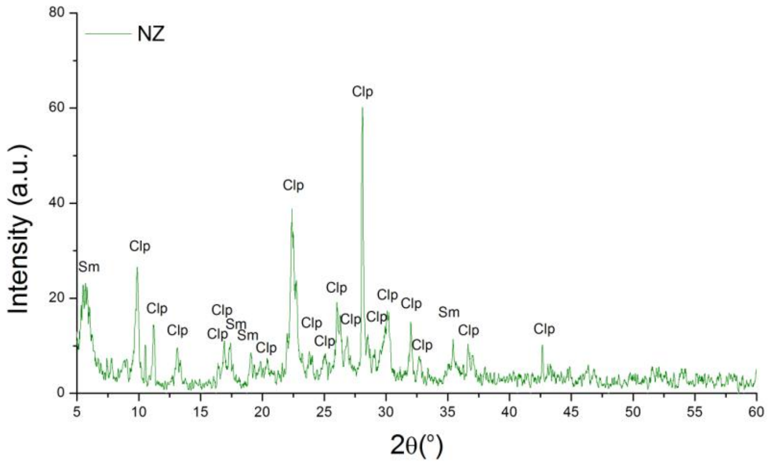

Figure 1 – XRD diffractogram of NZ (Clp - clinoptilolite, Sm - smectite)

According to the XRD analysis results, NZ consists mainly of clinoptilolite (type of NZ mineral), and smectite ("swelling" 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 [12].

2.2. Mixtures

Mixture proportions of the cement pastes, containing 0%, 10%, 20% and 30% NZ as SCM per cement mass, are provided in Table 3. The prism specimens with the dimensions of 10 mm×10 mm×60 mm were prepared and kept in moulds for 1 day and then were submerged in deionised water up to the age of 365 days. Reference and each type of blended cement pastes were immersed in separate sealed containers filled with deionised water.

Table 3 – Composition of paste mixtures

	C	CZ10	CZ20	CZ30
CEM I 42.5 R (g)	450	405	360	315
NZ (g)	-	45	90	135
Deionized water (g)	225	225	225	225

2.3. Methods

After 365 days of the previously described curing regime, specimens were taken from deionized water, crushed and sieved through a 125 µm sieve and then dried at 35°C to constant mass. The fire behavior of the pastes with NZ was investigated experimentally by means of Labsys Evo (Setaram) thermal analyzer using TGA/DTA. TGA was carried out to obtain the mass loss. Differentiation of the thermogravimetric data (mass loss rate) allows a better resolution and identification of m losses (DTA). During the experiment, the sample was placed in an alumina crucible whereas an empty one was used as a reference. The output information from each test was a change of sample mass (TGA) and mass loss rate (DTA), as a function of temperature. The TGA/DTA measurements were performed in the temperature range 25–1090°C which simulated the ISO 834 standard fire curve in the synthetic air at atmospheric pressure and in the argon atmosphere. The sample mass was about 30 mg.

3. RESULTS AND DISCUSSION

The TGA/DTA provides information on the chemical reactions and the materials degradation of the pastes due to the heating process. The results obtained by TGA/DTA measurements in the synthetic air at atmospheric pressure and in the argon atmosphere, in the temperature range of 25-1090°C, for the reference and blended cement pastes are presented in Figure 2.

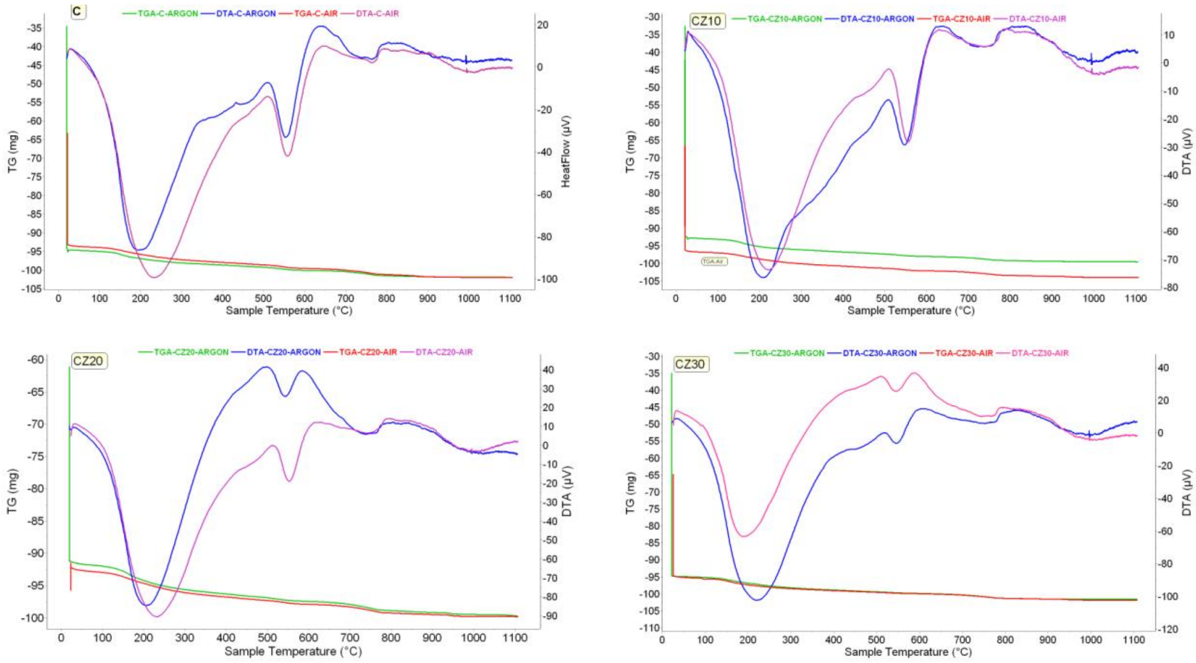

Figure 2 – Results of TGA/DTA for reference and blended pastes

As can be seen from this figure, the first endothermic peak occurs in the temperature range 25-350°C, which represents the evaporation of the free water and dehydration of some hydration products. This peak is very pronounced for each samples and may point to the participation of clinoptilolite in the pozzolanic reactions by forming secondary hydration products (for example C-A-S-H). It can be seen that the mass loss in the case of samples with 10% and 20% of NZ are higher in the case of testing under argon compared to air, while in the case of the reference sample and the sample with 30% of NZ, the opposite is the case, the mass losses are higher in the case of air. Also, the peaks in the case of argon were shifted to lower temperature values compared to the air in all samples except at samples with 30% NZ. This may indicate a strengthening of bonding in the case of air. The TGA results show also that the maximum rate of mass loss occurs at this temperature range which may indicate that there are the most products in this temperature range or that they are the most sensitive.

The next significant endothermic peak appears around 520-550°C (temperature range 450-650°C) and it belongs to the $Ca(OH)_2$ (portlandite) decomposition [13]. The differences between the samples in this temperature range are not significant, when observing argon and air atmospheres, except in the case of reference sample. The mass loss due to the decomposition of $Ca(OH)_2$ was decreased as the amount of NZ increases within the cement paste, in both cases, argon and air atmosphere. This decrease of $Ca(OH)_2$ phenomena usually represents the pozzolanic reactions that lead to a decrease in portlandite quantity leading to the formation of C–S–H and aluminates [13] or calcium leaching.

The shallow endothermic peak about 750°C belongs to the decomposition of calcium carbonate ($CaCO_3$) [14]. The carbonation of the paste is an event that may take place during the preparation of the paste, caring of the samples or during the grinding of the paste previous to the TGA measurement. The mass loss of samples in the temperature range 650-850°C are given in Table 4. As can be seen, the largest amounts of carbonate are detected in the reference sample, but there is no significant difference in the atmosphere, whether it is air or argon, for each samples except for reference sample.

The TGA/DTA curves show a continuous mass loss during heating and after 850°C, due to the removal of free water, dehydration and dehydroxylation of the pastes. The little exothermic peak at approximately 1000°C for each observed samples and each atmosphere may indicate the formation of new phases in the structure.

Mass loss for each paste by selected ranges as well as in total is given in Table 4. Obtained data on the mass losses in the temperature range 25-1090°C indicate that the total amount of products in samples CZ10, CZ20 and CZ30 are smaller in regard to reference sample C in air atmosphere while in an argon atmosphere it is the opposite.

Table 4 – Mass loss of pastes (%) at different temperature ranges

	Atmosphere	25-350°C	350-450°C	450-650°C	650-850°C	850-1090°C	Total
C	Argon	11.89	1.90	3.93	4.85	0.74	23.31
	Air	14.15	2.24	4.59	5.58	1.73	28.30
CZ10	Argon	14.12	2.10	3.74	4.07	0.53	24.56
	Air	13.66	2.13	3.78	4.30	1.52	25.39
CZ20	Argon	15.37	2.02	3.21	4.56	1.76	26.92
	Air	13.57	1.93	3.10	4.27	1.36	24.22
CZ30	Argon	12.62	1.87	2.88	4.60	0.39	22.34
	Air	14.08	1.80	2.75	4.40	1.47	24.51

4. CONCLUSION

Based on the analysis of the obtained experimental results, in a term of the reaction to high temperature in air and neutral atmosphere of the cement paste containing 0%, 10%, 20% and 30% NZ as SCM after 365 days of exposure to soft water, due to the phase composition changes determined via TGA/DTA at atmospheric pressure in the air, and in an argon atmosphere, the following can be concluded:

- The maximum mass loss of the sample is at the first temperature range (25-350°C). It may indicate on participated of NZ in the pozzolanic reaction because these are the temperatures at which certain hydration products are degraded.
- The effect of soft water on observed samples perhaps may be best analyzed across the temperature range corresponding to the decomposition of portlandite (450-650°C) where it is seen that the mass loss in samples with NZ is less than the reference one and decreases with an

increase in the proportion of NZ, which may indicate on pozzolanic reactions but also on leaching of calcium ions.

- The mass loss of samples with NZ at temperature range 650-850°C, related to reference sample, may indicate on less tendency blended samples towards carbonization.
- The mass change for extremely high temperatures are very similar between the observed samples for a suitable atmosphere. It can also be observed at this high temperatures that the mass loss is significantly higher in air atmosphere compared to argon for all samples except for the one with 20% NZ.
- Total mass losses are smaller in samples containing NZ compared to the reference sample, which may indicate on a lower sensitivity of samples with NZ to high temperatures. It can also be observed that the losses in the air atmosphere are higher compared to the neutral atmosphere (argon) for observed samples except for those with 20% NZ, which is especially noticeable at very high temperatures (over 850°C).

For a better understanding of the fire behavior of NZ blended cement paste, in addition to thermal analysis, some other analyzes of the microstructure should be done, such as XRD, FTIR etc.

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6. REFERENCE

[1] Bakhtiyari, S., Allahverdi, A., Rais-Ghasemi, M., Zarrabi, B.A, Parhizkar, T.: *Self-compacting concrete containing different powders at elevated temperatures – Mechanical properties and changes in the phase composition of the paste*, Thermochimica Acta 514, 2011, pp. 74–81.

[2] Terzić, A., Pezo, L., Mijatović, N., Stojanović, J., Kragović, M., Milić, Lj., Andrić, Lj.: *The effect of alternations in mineral additives (zeolite, bentonite, fly ash) on physico-chemical behavior of Portland cement based binders*, Construction and Building Materials 180 ,2018, pp. 199–210.

[3] Kushnir, A.R.L., Heap, M.J., Griffiths, L., Wadsworth, F.B., Langella, A., Baud, P., Reuschl´e, T., Kendrick, J.E., Utley, J.E.P.: *The fire resistance of high-strength concrete containing natural zeolites*, Cement and Concrete Composites 116, 2021, 103897.

[4] Li, Y., Mi, T., Liu, W., Dong, Z., Dong, B., Tang, L., Xing, F.: *Chemical and mineralogical characteristcs of carbonated and uncarbonated cement pastes subjected to high temperatures*, Composites Part B 216, 2021, 108861.

[5] Anand, B., Sharma, S.N: *Leaching corrosion of concrete due to soft water attack*, Recent Advancements in Mineral and Water Resources, Editor: Rabindra N. Tiwari, Publisher: Excellent Publishers, New Delhi, 2016, pp. 155-161. ISBN: 978-93-84935-84-9

[6] Otieno, M., Alexander, M., du Plessis, J.: *Soft water attack on concrete tunnel linings in the Ingula pumped storage hydro-power scheme: Assessment of concrete resistance and protection*, J. S. Afr. Inst. Civ. Eng 59(3), 2017, pp. 57-67.

[7] Duvarcı, Ö.Ç., Akdeniz, Y., Özmıḫcı, F., Ülkü, S., Balköse, D., Çiftçioğlu, M.C.: *Thermal behaviour of a zeolitic tuff*, Ceramics International 33, 2007, pp. 795–801.

[8] SRPS B.B8.032:1980 - *Testing of natural stone - Determination of bulk density, density, coefficient of density and porosity.*

[9] SRPS B.C8.024:1964 - *Determination of specific surface of Portland cements.*

[10] BS EN 450-1:2012 - *Fly ash for concrete Definition, specifications and conformity criteria.*

[11] SRPS EN 206-1:2011 - *Concrete - Part 1: Specification performance, production and conformity.*

[12] 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. 27, 2021, pp. 403–415.

[13] Rudžionis Ž. et al.: *Natural zeolite powder in cementitious composites and its application as heavy absorbents*, Journal of Building Engineering 43, 2021, 103085, doi: 10.1016/j.jobe.2021.103085

[14] Shariful Islam M, Mohr B.J, VandenBerge D: *Performance of natural clinoptilolite zeolite in the cementitious materials: A comparative study with metakaolin, fly ash, and blast furnace slag*, Journal of Building Engineering 53, 2022, 104535, doi: 10.1016/j.jobe.2022.104535