

# THE EFFECT OF HARMFUL ZEOLITE WASTE AS REPLACEMENT ADDITION TO CEMENT ON HYDRATION AND PROPERTIES OF HARDENED CEMENT COMPOSITES

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## INTRODUCTION

Natural zeolites, natural alumo-silicate materials having a unique spatially networked structure with a specific structure of pores and channels of specific shape and size, beside other properties have the property of ion exchange<sup>1</sup>. If used in treatment and purification of wastewaters loaded with heavy metal ions (Pb, Cd, Cu, Zn, Cr, etc.), which are hazardous for the environment, they will form harmful zeolite waste. This harmful waste is, like all others, subject to laws and regulations on storing and disposal of such wastes in the natural environment. As the harmful admixture (heavy Me) released from the waste into the environment cannot be destroyed or changed by any chemical or thermal process, it has to be stabilized in some manner (converted into or bound in the form of an insoluble compound or matter, preventing its leaching into the environment even in the conditions of prolonged rinsing)<sup>2-5</sup>.

As the alumo-silicate component from zeolite can participate in cement hydration processes, the harmful zeolite waste, used as replacement addition to cement, can be bound, i.e. stabilized by hydration and solidification of such cement composites.

Stabilization processes are based on cement hydration processes yielding lime as the reaction product. This lime further reacts with the alumo-silicate component of zeolite. During cement hydration, due to very high pH, de-polymerized mono silicates and aluminates from zeolite form  $[\text{SiO}(\text{OH})_3]^-$  ions and  $[\text{Al}(\text{OH})_4]^-$  ions, which, together with  $\text{Ca}^{2+}$  ions and  $\text{SO}_4^{2-}$  ions (from gypsum) from the solution form reaction products that are the same as those of hydration of cement itself. Therefore, these reactions form C-S-H and C-A-H as well as  $\text{C}_3\text{A} \times 3\text{CaSO}_4 \times 32\text{H}_2\text{O}$  (ettringite) which transforms into  $\text{C}_3\text{A} \times \text{CaSO}_4 \times 12\text{H}_2\text{O}$  (monosulphate). Products formed by the above reactions are stable and insoluble. They are built into the already formed matrix of the cement composite, increasing its density, hardness, durability and stability<sup>2-6</sup>.

Therefore, in combined mixing of zeolite waste with cement and hydration, S/S processes take place, i.e. stabilization and solidification of the harmful admixture from the zeolite addition, with the twofold advantage of replacing (reducing) the cement content in the composite and prevention of migration of the harmful substance into the environment. The harmful admixture is diluted, being spread over the mass of the composite, and it also reacts by itself, becoming additionally fixed. It has been proved that  $\text{Zn}^{2+}$  as a harmful admixture is bound in the form of the compound  $\text{Ca} [\text{Zn}(\text{OH})_3 \times \text{H}_2\text{O}]$ , or  $\text{CaZn}_2(\text{OH})_6 \times 2 \text{H}_2\text{O}$ . It has also been proved that zinc salts retard cement hydration, as they prevent transport of water for hydration of  $\text{C}_3\text{S}$ <sup>5-6</sup>.

Our research has therefore been aimed at showing the justification for the use of harmful zeolite waste as replacement addition to cement and its effects on hydration processes and properties of newly formed hardened cement composites in practice.

## EXPERIMENTAL

### *Experimental materials and preparations of samples for measurements*

Silicate or Portland cement was of industrial make, CEMEX, Dalmacijacement, the CEM I type, marked PC-45B.

Natural zeolite, zeolite tuff came from D. Jesenje, Republic of Croatia, saturated by  $Zn^{2+}$ -ions, representing harmful zeolite waste, marked SZ.

Additive, plasticizer, water reducer.

Water for hydration (for microcalorimetical measurements), distilled water.

Samples used in microcalorimetical measurements were prepared by mixing the precisely determined mass of cement (4,000 - 2,000 g) with the precisely weighed amount of dry zeolite addition (0,000 - 2,000 g). The total mass of solid was 4,000 g. These mixtures contained 0,0 % - 50 % zeolite addition and were placed in a differential microcalorimeter, in the measurement sample holder. The constant addition of the plasticizer addition (0,3 mass % to the mass of solid, cement + zeolite) and the constant amount of water of 2,0 mL, i.e. the requested water/solid ratio,  $W/S = 0,5$ , obtained by dissolving water + additive, was set separately (in the syringe) of the microcalorimeter, above the dry sample in the measuring cell. The hydration reaction started when the aqueous solution was introduced into the dry mixture of cement and zeolite<sup>7-8</sup>. Measurements were made at 20°C in the interval of 48 hours.

Samples used to determine compressive and bending strength were prepared in the shape of standard prisms; measurements were performed according to the EN-197 standard.

## RESULTS AND DISCUSSION

Figure 1 (A and B) show the results of microcalorimetical measurements. The analysis of results presented, Fig. 1A, shows that all kinetic curves for all samples have the same or very similar shape.

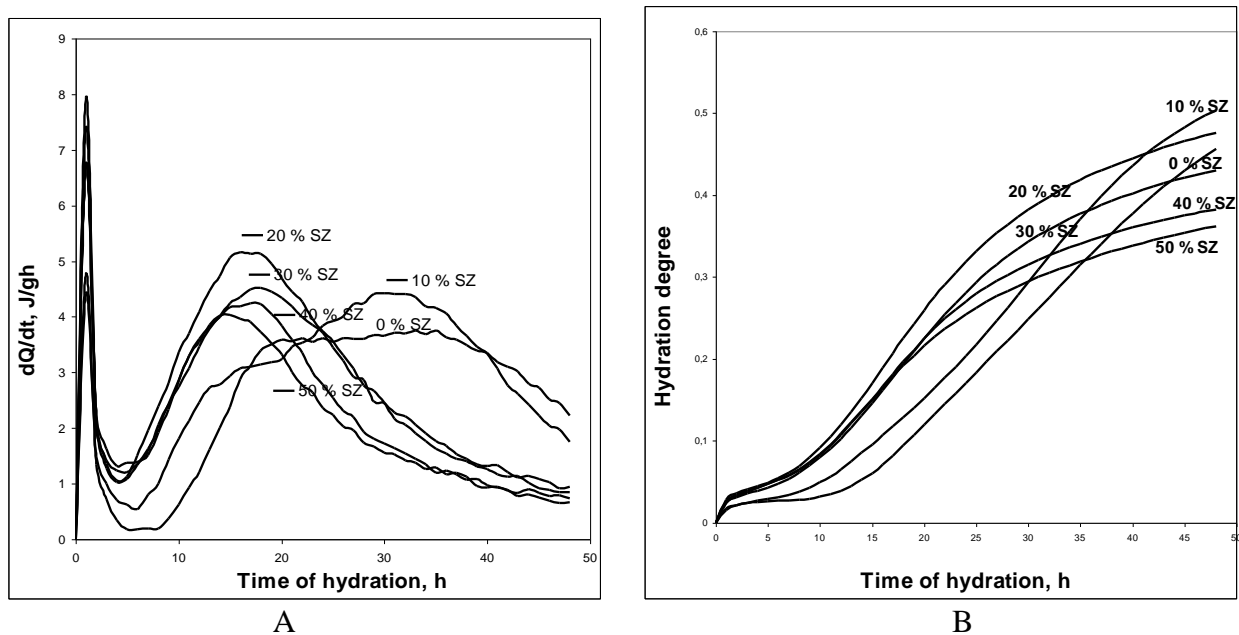


Figure 1. Microcalorimetical measurements of hydration kinetics (A) and hydration heats (B) of cement composites with (0-50 mass. %) of zeolite waste as the replacement addition.

The effects recorded (peaks) indicate the basic hydration processes, which means that the zeolite addition does not change the basic process mechanisms. The size and position of the peaks recorded relative to the temporal hydration axis show that the zeolite addition modifies the kinetic parameters of the process, shifting the peaks toward earlier times with increased amounts of zeolite waste added. The amplitude of the maximum decreases with the increased quantity of the addition. Such results agree with the reactions taking place in this reaction system (the content of the zeolite component in the conditions of high pH, the effect of the W/C ratio on the shift of hydration equilibrium, the effect of the harmful  $Zn^{2+}$ - admixture that retards hydration of  $C_3S$  etc.)<sup>6-8</sup>. Fig. 2. show that hydration heats (after 48 hours of hydration) become lower if the content of zeolite waste increases above 10 mass %. The maximum amount of hydration is found in the sample containing 10 mass % of zeolite waste. This is due to the shift of equilibrium and hydration kinetics (catalytic action of zeolite particles, the effect of zeolite component on the W/C ratio and equilibrium shift, and interactions in the conditions of hydration). Lowered values of hydration heat with the increased content of the zeolite waste in cement composite are due to the reduction of the thermally active matter – cement, owing to the increased content of zeolite as the replacement addition<sup>5,7,8</sup>.

Figures 2 (A and B) show the results obtained for strength of cement composite mixtures with hazardous zeolite waste as replacement addition.

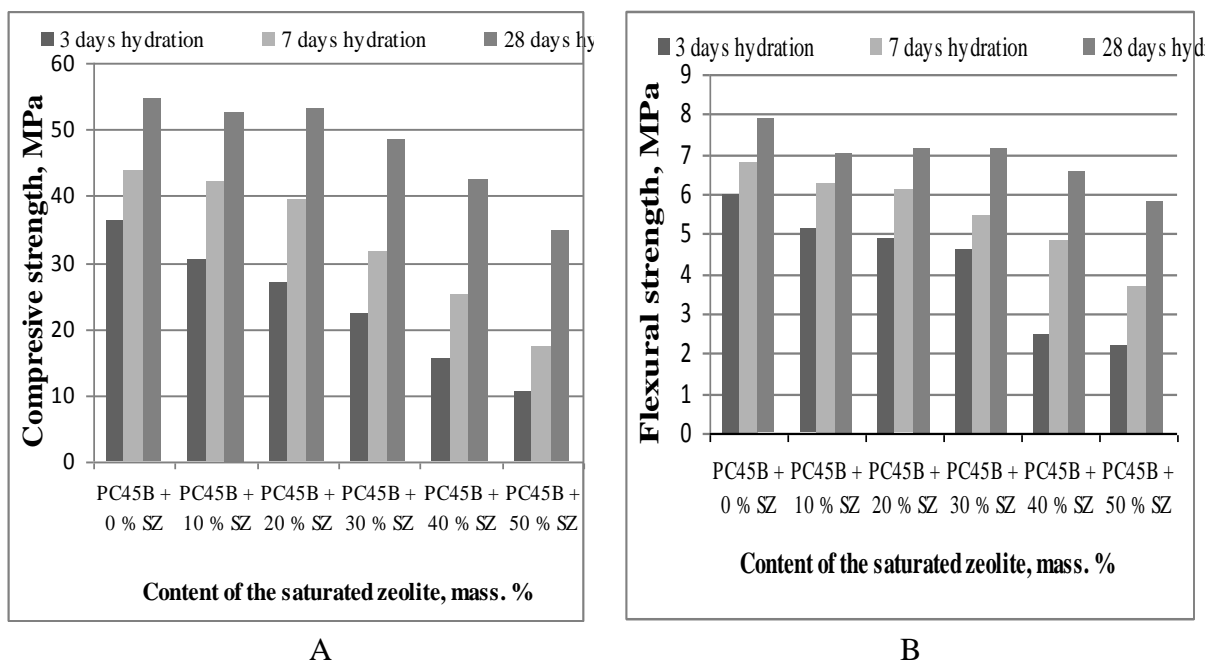


Figure 2. Compressive strength (A) and flexural strength (B) of cement composites relative to the amount of hazardous zeolite waste

Figure 2 (A and B) indicate that compressive, i.e. flexural strength depends on the amount of replacement addition to cement, i.e. the addition of zeolite waste to cement composites. The strength of the composite material decrease with the increased amount of replacement addition for all times of examination (3, 7, and 28 days). However, the strength decrease is most prominent after 3 days of hydration, less after 7 days, and the least after 28 days. This completely agrees with the role of the replacement addition, the reactions and interactions of the zeolite addition to the reaction system of cement and water, where the characteristic properties of zeolite come into effect, its chemical aluminosilicate composition that provides for a pozzolanic reaction with the products of hydration of the cement itself, and

its specific structure with highly developed reaction surface. Compressive strengths of the newly formed cement composites with the content of the replacement addition even as high as 30 mass % are only insignificantly lower than those of samples without the addition. This fact justifies the use of this replacement addition, reducing the need for costly cement, accompanied by cheaper production of cement composites of certain programmed properties that could be used in construction industry as new cement composites that at the same time permanently dispose of environmentally hazardous substances, which the contemporary world recognizes and attempts to do in a great number of scientific-research projects.

## CONCLUSIONS

The study results indicate:

- harmful zeolite waste containing  $Zn^{2+}$ -ions as harmful admixture, if used as replacement addition to cement, does not affect the hydration mechanism of the cement – water reaction system, but does change, i.e. modify kinetic parameters of development of hydration processes in stabilization and solidification of cement composites
- harmful zeolite waste containing  $Zn^{2+}$ -ions as harmful admixture, if used as replacement addition to cement, favourably affects the properties of newly formed cement composites. It improves the microstructure, durability, and stability of newly formed cement composites, which is confirmed by values obtained for strength (compressive and flexural), which are much higher than expected in view of the quantity of costly cement replaced (0-50 mass %) as the main binder in cement composites. The quantities of replacement addition even as high as 30 mass % compare well with the strength of samples without additions.

## REFERENCES

- [1] B. Subotić, J. Bronić, A. Čizmek, T. Antonić i C. Kosanović, Zeoliti: svojstva, uporaba, istraživanje, *Kem. Ind.* 1994, **43**, 475-487
- [2] A. Jang i In S. Kim; Solidification and stabilization of Zn, Pb, Cd and Cu in Tailing Wastes using cement and fly ash, 2000, **13**, 1659-1662
- [3] C. Shi, J. Stegemann, R. Caldwell; An examination of interference in waste solidification through measurement of heat signature, *Waste Management*, 1997, **17**, 4, 249-255
- [4] M. Yousuf, A. Mollah, R. K. Vempati, T.- C. Lin and D. L. Cocks, The interfacial chemistry of solidification/stabilization of metals in cement and pozzolanic material systems. *Waste Management*, 1995, **15**, 2, 137-148
- [5] F. Olmo, E. Chacon, A. Irabien, Influence of lead, zinc, iron (III) and chromium (III) oxides on the setting time and strength development of portland cement, *Cem. Concr. Res.*, 2001, **31**, 1213-1219
- [6] F. Ziegler, C. Annette Johnson; The solubility of calcium zincate  $[CaZn_2(OH)_6 \cdot 2H_2O]$  *Cem. Concr. Res.*, 2000, **31**, 1327-1332
- [7] P. Krolo, R. Krstulović, P. Dabić, A. Bubić, Hydration and leaching of the cement zeolite composite, *Ceramics-Silikaty*, 2005, **49**, 3, 213-219
- [8] P. Dabić, P. Krolo, A. Žmikić, J. Zelić, Utjecaj dodataka na hidrataciju portland cementa, *Kem. ind.*, 2001, **50**, **11**, 623-629
- [9] C. S. Poon, L. Lam, S. C. Kou, Z. S. Lin, A study on the hydration rate of natural zeolite blended cement pastes, *Constr. Build. Mater.*, 1999, **13**, 427-432
- [10] A. Jang, In S. Kim, Solidification and stabilization of Pb, Zn, Cd and Cu in tailing wastes using cement and fly ash, *Minerals Engineering*, 2000, **13**, **14-15**, 1659-1662
- [11] EN-197, standard.

# DJELOVANJE ŠTETNOG ZEOLITNOG OTPADA KAO ZAMJENSKOG DODATKA CEMENTU NA HIDRATACIJU I SVOJSTVA OČVRSLIH CEMENTNIH KOMPOZITA

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## SAŽETAK

U radu je prikazan utjecaj štetnog zeolitnog otpada, koji sadrži  $Zn^{2+}$  ione, kao zamjenskog dodatka cementu, na hidrataciju cementa i svojstva očvrslih cementnih kompozita. Mjerenja su provedena određivanjem toplinskih učinaka reakcija hidratacije primjenom diferencijalne mikrokolorimetrije, te određivanjem tlačne i savojne čvrstoće očvrslih cementnih kompozita. Uzorci su mješavine cement + štetni zeolitni dodatak + voda, uz stalni udjel aditiva plastifikatora. Dobiveni rezultati pokazuju da štetni zeolitni otpad ne utječe na osnovne mehanizme hidratacije cementa ali modificira kinetiku hidratacijskih procesa, dok vrijednosti čvrstoća ukazuju na učinke iznosa zamjenskog dodatka u reakcijskom sustavu kao i same efekte pucolanske reakcije. Iz dobivenih rezultata može se zaključivati i o maksimalnim iznosima zamjenskih dodataka, koji se mogu dodavati u reakcijski sustav, a da se ne ugroze potencijalna vezivna svojstva cementnih kompozita za praktičnu uporabu.

Ključne riječi: prirodni zeolit, hidratacija cementa, mikrokolorimetrija, kinetika hidratacije, zamjenski dodatak,