

INFLUENCE OF NATURAL ZEOLITE ON SOME PROPERTIES OF MORTAR/CONCRETE

Tiana Milović¹

Miloš Šešlija²

Slobodan Šupić³

Suzana Vukoslavčević⁴

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Summary: Concrete is the most widely used construction material in the world, so in recent years more attention has been dedicated to its durability. This paper provides an overview of the results of different studies that examined the impact of natural zeolite on the properties of mortar/concrete (used as a partial replacement of cement), as well as a comparison with the results obtained in the experiments where fly ash has been used. Natural zeolite is volcanic or volcano-sediment material (there are zeolite deposits in Serbia), while fly ash is a by-product of coal combustion in thermal power plants.

Keywords: Natural zeolite, fly ash, mortar, concrete, compressive strength, durability

1. INTRODUCTION

Due to multiple advantages (such as its low price, adequate mechanical characteristics, its easy forming in various shapes and sizes, etc.) concrete is the most widely used construction material [1]. Despite mentioned advantages, the use of concrete causes environmental problems since the cement industry has been responsible for approximately 7% of the global CO₂ emission [1,2]. Also durability problems of concrete structures, especially in aggressive environment, can affect the lifespan of the structures [1,3]. In the USA during 2006 around 18-21 billion dollars were spent on concrete repair, rehabilitation and protection [3]. The use of natural or artificial (by products) pozzolans as partial replacement of Portland cement (PC) has economic and environmental benefits and positive effects on durability properties of concrete structures [1-4]. Natural zeolites are hydrated aluminosilicate minerals of alkali and alkaline earth metals. They consist of an open three-dimensional network of silicon-oxygen and

¹ Tiana Milović, MSc CE, PhD student, University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, Serbia, tel: +381604671261, e – mail: tiana.tatomirovic@gmail.com

² Miloš Šešlija, MSc CE, PhD student, University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, Serbia, tel: +381653990089, e – mail: slavijasrb@gmail.com

³ Slobodan Šupić, MSc CE, PhD student, University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, Serbia, tel: +381640914861, e – mail: slobodansupic@gmail.com

⁴ Suzana Vukoslavčević, MSc CE, PD student, University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, Serbia, tel: +381631737390, e – mail: suzanav@uns.ac.rs

aluminium-oxygen tetrahedra [1,4,5]. Crystals of natural zeolite have a honeycomb like structure with small channels and pores, which leads to its large surface area. Natural zeolites also have ability to adsorb and lose water up to 30% of their dry weight and exchange extraframework cations, without any change of crystal structure [4-6].

In recent years, zeolitic tuffs have been frequently used as pozzolanic material in China, Bulgaria, Cuba, Germany, Greece, Italy, Jordan, Russia, Turkey, USA, Iran, Spain and Serbia [1,2]. Large zeolite deposits of potential economic interest, in Serbia, are Beocin, Igros, Jablanica 1, Toponica and Zlatokop [7]. On the other hand, some by-products, such as fly ash (FA), can be used too as supplementary cementitious material (SCM) in concrete industry [8]. Only in Serbia about 5 million tons of FA is generated per year during coal combustion in thermal power plants [9].

2. POZZOLANIC REACTIVITY

Despite its crystalline structure, natural zeolite shows pozzolanic reactivity which is related to its large surface area and metastability, and depends of its chemical and mineralogical composition. Zeolite pozzolanic reaction starts in the presence of $\text{Ca}(\text{OH})_2$, liberated during the hydration of cement. In a high pH solution, hydroxyl ions (OH^-) attack NZ structure, and aluminosilicate network starts decomposing. The newly created species enter the solution, react with Ca^{2+} ions and form hydrated calcium silicate and calcium aluminate compounds. As a result, hydrated products improve the microstructure of hardened mortar/concrete due to pore refinement, enhancing durability and final strength of mortar/concrete [2,4,6]. The performance of NZ in mortar/concrete has been also compared with performance of other pozzolanic materials [1,10,11]. Poon et al. [10] found that the reactivity of NZ is higher than reactivity of fly ash, and a lower than silica fume's (SF). Also it was noticed that the degree of reaction of NZ in a paste with a higher percentage of replacement is lower than in a paste with a lower percentage of replacement [10]. According to Chan and Ji's [11] comparative study, pozzolanic reactivity of NZ is also between one of pulverized fuel ash (PFA) and silica fume.

3. COMPRESSIVE STRENGTH DEVELOPMENT

There have been several studies on the compressive strength development of cement paste/mortar/concrete containing NZ. However, it is still difficult to predict the influence of NZ as SCM on the properties of cement paste/mortar/concrete, including the strength development. Many parameters affect the strength and durability, such as w/cm ratio, weight percentage of cement replaced with NZ, the mineralogical and chemical composition of NZ, a purity level of NZ, its fineness, pozzolanic reactivity, etc [2,4,12]. In term of w/cm ratio, it seems that NZ contributes more to the compressive strength development at lower w/cm ratios. Poon et al. [10] investigated the effect of different w/cm ratios on zeolite modified cement pastes. It was found that lower w/cm ratio contributes more to the strength of the zeolite blended cement pastes [10]. According to Chan and Ji [11] the strength of concrete made with NZ (or PFA) as SCM was lower than that of the control concrete, when w/cm ratio was over 0.45. Ahmadi and Shekarchi

[12] found that concretes containing NZ with w/cm ratio of 0.40 had higher compressive strength than the control mixture at ages of 3, 7, 28 and 90 days. On other hand, when concretes were made with w/cm of 0.50 [1] contrary results were obtained. Up to 56 days curing period, mortars containing NZ from West Texas, made with w/cm of 0.48, showed slower compressive strength development, but exceeded strength of control mortar at the age of 91 days [13]. Several studies [10-14] have been conducted to examine the influence of different percentage of NZ blend ratios on the compressive strength development. Poon et al. [10] found that the NZ replacement (15% and 25%) did not increase 28-day compressive strength of the blended pastes. The 90-day compressive strength of fly ash cement paste was higher than that of cement paste with 25% NZ as SCM, control paste and cement paste with 15% NZ as SCM, respectively (Fig. 1).

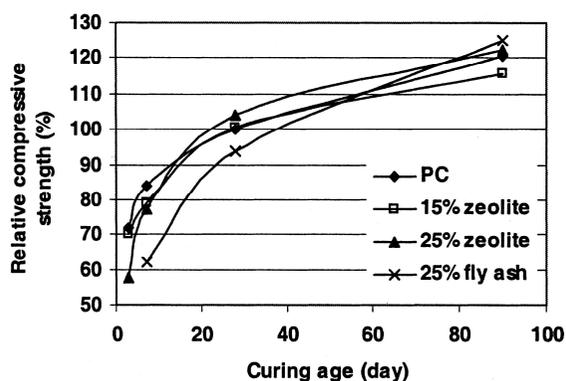


Figure 1. Relative compressive strength of zeolite cement pastes and fly ash cement pastes (w/cm ratio of 0.3) [10]

Based on the research results [13] it can be concluded that 20% replacement of PC with NZ is the optimum for mortars. Chan and Ji's [11] results showed that replacement of 15% of PC with NZ, by mass, resulted in 14% increase of concrete strength at 28-day compared with the control concrete. According to Ahmadi and Shekarchi [12] the compressive strengths of concretes with 5%, 10% 15% and 20% replacement of PC with NZ were 14%, 16%, 23% and 25% higher than that of the control concrete. Also in terms of 90-day compressive strength the optimum replacement level for NZ was 15% [12]. Canpolat et al [14] investigated the effects of NZ + FA as PC replacement materials on the properties of cement. Based on the results of their study, it seems possible to produce PC with substitution rate up to 20% NZ or 5% NZ + 5% FA and provide adequate strengths.

4. EFFECTS OF NZ ON SOME DURABILITY PROPERTIES

The most significant improvement of concrete containing NZ as SCM is not in compressive strength but in durability [15]. Due to pozzolanic reaction of NZ, formed

hydrated products fill the large capillary voids. As a result, microporous structure will be created and durability properties will be improved [2].

Chloride permeability - Sabet et al. [6] investigated the effects of NZ and FA on durability properties of self-consolidating high performance concrete (SCHPC). Acid-soluble chloride was measured in accordance with ASTM C1152 after 90 days of exposure to the salt solution. Incorporation of 10% and 20% NZ led to decrease of the effective diffusion coefficient by more than two times (for 4.3×10^{-12} and 4.9×10^{-12} m/s², respectively) compared to the control mix. Use of fly ash (10% and 20%) also caused reductions in effective diffusion coefficient (from 7.9×10^{-12} to 4.7×10^{-12} and 3.2×10^{-12} m/s², respectively) but less than NZ [6]. According to Chan and Ji [11] NZ and PFA had a similar effect on chloride ions ingress into high performance concrete. The effectiveness of NZ or PFA on improving the resistance of chloride ingress decreased with reducing w/cm ratio and increased with higher replacement level [11]. However, Ahmadi and Shekarchi [12] found that at 10-20% NZ there was a marked decrease in diffusion coefficient compared to the control concrete.

Sulfate resistance – Shon and Kim [13] examined the effect of NZ as SCM on sulfate resistance of mortars in accordance with ASTM C 1012. One control mixture and three test mixtures (with 10% NZ, 20%NZ and 20% FA as SCM) were prepared under laboratory conditions. Control samples showed low initial expansion, up to 28 days, and then a rapid increase up to 180 days. Mixture with 20% FA had the lowest value of expansion compared with mixures containing 20% NZ and 10% NZ. Also it was found that relative compressive strength (strength of mortar sample exposed to 1 M Na₂SO₄ solution / strength of mortar cured in tap water) of all samples was sharply increased at early age, and then decreased after 14 days. After 56 days of exposure in Na₂SO₄ solution, the compressive strength ratios were about 0.98, 1.01, 1.00 and 1.19 for control, 20% FA, 10% NZ and 20% NZ mixture, respectively [13]. Karakurt and Topcu [8] also evaluated the volume expansion of different cement mortars immersed in 10% Na₂SO₄ solution for 26 weeks in accordance with ASTM C 1012. Based on the results, it can be concluded that NZ-, FA-, ground granulated blast furnace slag (GBFS)- blended cements are more durable than ordinary PC, under sulfate attack. Compressive strength variation of sulfate-resistance test samples was also investigated. At the end of 26 weeks ZSBC-10 (blended cement with 10% NZ and GBFS) and ZSFBC (blended cement with 10% NZ, GBFS and FA) had the highest values of compressive strength, approximately 66 Mpa [8].

5. CONCLUSION

The use of natural zeolite as partial replacement of cement in mortar and concrete has been widely studied in recent years. Based on research results related to pozzolanic properties of natural zeolite, cited in the paper, the following conclusions are derived:

- Pozzolanic reactivity of natural zeolite is related to its large surface area and metastability, and depends of its fineness and chemical and mineralogical composition. Compared to fly ash, NZ shows higher pozzolanic reactivity.
- Lower w/cm ratio contributes more to the strength of cement pastes /mortars /concretes containing natural zeolite as SCM (recommended w/cm ≤ 0.45 [11]).

- Mortars and concretes containing 15-20% NZ reach suitable compressive strength (but less than FA), improve the sulfate resistance (less than FA) and the resistance of chloride ingress (more than FA).
- Based on results, it seems possible to produce PC with substitution rate of 5% NZ + 5% FA and provide adequate strengths [14].
- Compressive strength variation of sulfate-resistance test samples was also investigated and At the end of 26 weeks ZSBC-10 (blended cement with 10% NZ and GBFS) and ZSFBC (blended cement with 10% NZ, GBFS and FA) had the highest values of compressive strength [8].

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УТИЦАЈ ПРИРОДНОГ ЗЕОЛИТА НА НЕКА СВОЈСТВА МАЛТЕРА/БЕТОНА

Резиме: Бетон је најчешће употребљаван грађевински материјал на свету, стога се последњих година све више пажње посвећује његовој трајности. У овом раду је дат преглед резултата различитих истраживања у којима је испитан утицај природног зеолиита, када се користи као парцијална замена цемента, на својства малтера/бетона, као и поређење са резултатима добијених приликом примене електрофилтерског пепела. Природни зеолит је вулкански или вулканско-седиментни материјал (у Србији постоје налазишта зеолиита), док је електрофилтерски пепео нус производ сагоревања угља у термоелектранама.

Кључне речи: Природни зеолит, електрофилтерски пепео, малтер, бетон, чврстоћа на притисак, трајност.