INFLUENCE OF THE NATURAL ZEOLITE ADDITION ON THE POZZOLANIC REACTION AND COMPRESSIVE STRENGTH DEVELOPMENT IN LIME BASED RENDERS

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ABSTRACT

During the last 30 years scientists have been regaining interest in lime based renders and mortars and their possible application in the resotration processes. Different locally available pozzolanic additions are often investigated as a way to improve the pure lime render properties, especially in increased relative humidity conditions. Study of the influence of the natural zeolite from Igroš (Brus) on the compressive strength of the lime based renders through the TG/DTA and FTIR analysis is presented in this paper. Results show that the natural zeolite from this location can improve the mechanical properties of the lime based renders when used in sufficient quantity and adequately cured.

Keywords: natural pozzolana, lime based renders, TGA, FTIR, compressive strength.

INTRODUCTION

Lime based mortars and renders have been used for masonry construction for many centuries, up to the second half of the XIX century when they were gradually replaced by hydraulic mortars, mainly cement based. The main advantages of air lime mortars were high deformability and vapor permeability, while their weaknesses were low compressive strength and slow hardening process (due to the nature of the carbonation process).

Renewed interest in these materials was initiated after the failures in several restoration works during XX century, due to the incompatibility of the applied hydraulic mortars of high strength with the originally used materials (masonry and mortars). Apart from the investigation of properties of air lime mortars and the regaining of lost knowledge on their preparation and testing, scientists were also interested in using different additions in order to improve their properties. The additions most frequently used in the past for these purposes are different types of pozzolanic materials [1]. By the definition, these siliceous or siliceous and aluminous materials, cannot be used as a binder on their own, but when finely divided and in the presence of calcium hydroxide and exposed to high relative humidity, form compounds possessing cementitious properties [2].

Zeolites, as microporous, hydrated alumina-silicate minerals, when finely graded, can also possess pozzolanic properties. Although, the application of natural zeolites from different locations as lime based mortar additions has already been studied in several papers, the relation between its reactivity and composition has not yet been precisely explained. It has been shown that finer grain size and easier cation exchange influence the reactivity of natural zeolites at the early ages, while further development of the reaction is mostly influenced by Si/Al ratio [3].

The most important zeolite excavation locations in Serbia are: Zlatokop (Vranje), Igroš (Kopaonik), Beočin (Fruška gora), Toponica and Slanci (near Belgrade) [4]. Zeolites from Zlatokop (Vranje) have been used in the investigation of the lime based mortars for the restoration of Viminacuim (archeological site in the eastern Serbia from the Roman period that used to be capital city of the province Upper Moesia), while the zeolites from Igroš (Brus) have been investigated as an addition to cement paste [5]. This paper presents part of the investigation of the development of the pozzolanic reaction in lime based renders with addition of different amounts of natural zeolite from Igroš, Brus.

EXPERIMENTAL

In this research three lime based render mixtures were used: one reference, containing only lime binder, water and sand, and two mixtures with natural zeolite used as partial replacement of lime in 10 % and 50 % by weight (designated as 1/3-10 and 1/3-50 respectively). Reference mixture (1/3) was designed with lime to aggregate volumetric ratio of 1:3 and enough water to achieve appropriate workability and flowability.

Lime putty produced by “Javor”, Veternik (Serbia) was used as a binder in all of the mixtures. This putty was produced by slaking of quicklime from “Jelen Do” quarry, Požega (Serbia) with water in excess. At the time of mixing the lime putty was one year old (preserved for 6 months by the producer, and then 6 months in sealed plastic containers). The content of active CaO and MgO was 95.43 %.

Natural zeolite excavated in Igroš, near Brus (Serbia) was used in this study. Originally, it contained grain sized up to 0,2 mm, which was the finest fraction available at the market. Before application zeolite was grounded to fineness of 10 % residue on 45 μm sieve. The Si/Al ratio of the zeolite in question was 5.86.The mineralogical composition of zeolite, determined by XRD analysis, is shown in Figure 1 [6]. XRPD patterns of the zeolite sample were recorded using Ital StructureAPD2000 diffractometer operating with CuK radiation (λ = 0.15418 nm) in the 2θ range 5–50.

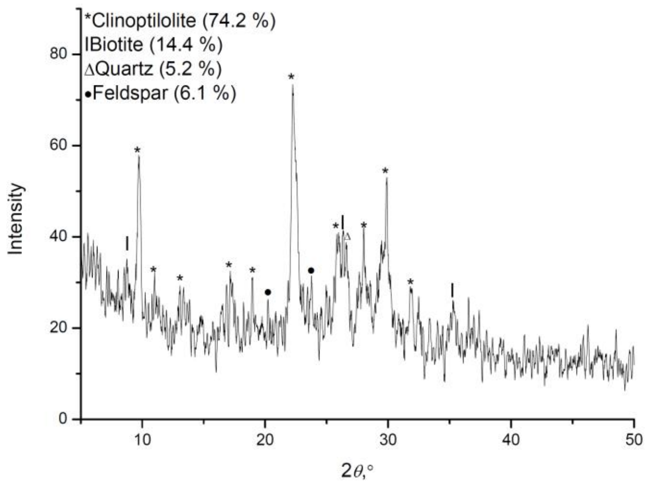

Figure 1. Mineralogical composition of zeolite (XRD analysis).

Table 1. Chemical composition of natural zeolite and river aggregate.

Component	Natural zeolite (%)	River aggregate (%)
CaO	4.25	4.21
SiO_2	64.16	80.49
Fe_2O_3+Al_2O_3	13.77	8.22
MgO	1.01	1.38
SO_3	0.15	0.02
K_2O	2.05	1.1

Natural river aggregate originating from Danube river (Serbia) graded 0/4 mm was used in the mixtures. Its bulk density amounted to 1610 kg/m^3.Chemical composition of the natural zeolite and aggregate, determined by chemical analysis according to SRPS EN 196-2:2015 and SRPS EN 1744-1:2014, is shown in Table 1.

Standardized prismatic samples (4×4×16 mm) were prepared for testing of the compressive strength of the mortars at the ages of 14, 28, 60 and 90 days. The samples were cured in the conditions of high relative humidity (RH=100 %) and temperature of 20±2 ˚C until tested. These conditions are more suitable for pozzolanic reaction, while they at the same time slow down the carbonation process. When the age of testing was reached the samples were dried for 72 hours at the temperature of 60 ˚C. After the cooling, compressive strength was determined following the standardized procedure according to the SRPS EN 1015-11:2008. At the ages of 28 and 90 days, after destructive testing sample material was additionally crushed and sieved through 0.09 mm sieve in order to separate the binder portion from the aggregates. Sieved material was used for testing of the development of the pozzolanic reaction through simultaneous differential thermal and thermogravimetric analysis (TG/DTA), and Fourier Transform Infrared (FTIR) Spectroscopy (at the age of 90 days). Thermal analysis was performed using a SDT Q-600 simultaneous DSC-TGA instrument (TA Instruments). The powdered samples (mass app. 10 mg) were heated in a standard alumina 90 µl sample pan. All experiments were carried out under air at a flow rate of 0.1 dm^3 min^{-1} with heating rate of 10 ˚C min^{-1}.The FTIR spectra were recorded in the range 4000–600 cm^{-1} with a resolution of 4 cm^{-1} at room temperature, using Nicolet iS10 (Thermo Scientific) spectrometer.

RESULTS AND DISCUSSION

Results of TG/DTA analysis are shown in Figure 2. The peak in the DTG curves positioned around 100 ˚C at the age of 28 days is observed for the mixture with 50 % of natural zeolite (1/3-50) and in much smaller degree for the mixture marked with 1/3-10 which indicates the decomposition of the hydrated phases, namely C-S-H (calcium-silicate-hydrate). Presence of the peak around 480˚C in both mixtures indicates decomposition of calcium hydroxide, that has not reacted completely at this age. Finally, peak between 600-800 ˚C shows the decomposition of calcium carbonate in both mixtures, although it is more present in the mixture with lower amount of zeolite.

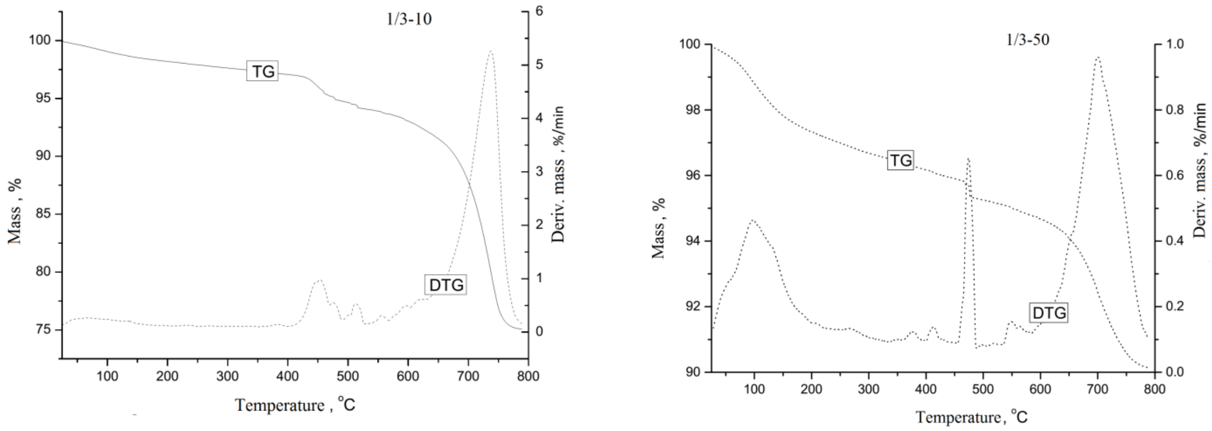

Figure 2. TG/DTA thermograms for the mixtures with 10 and 50 % of natural zeolite as lime replacement at the age of 28 days.

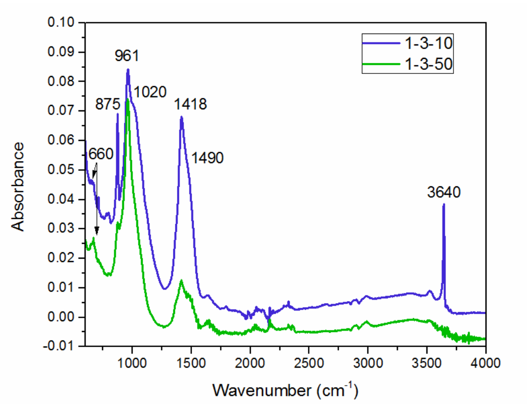

Figure 3. FTIR spectra of mixtures 1/3-10 and 1/3-50 at the age of 90 days.

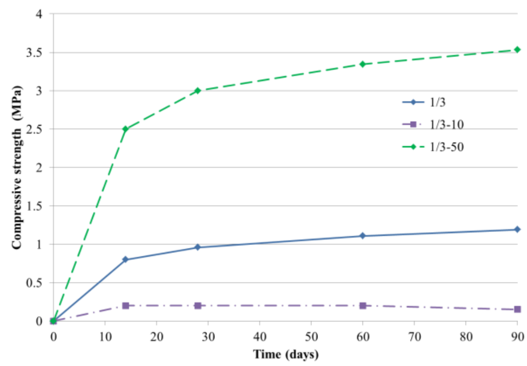

Figure 4. Compressive strength of the mixtures 1/3, 1/3-10 and 1/3-50 at different ages.

Figure 3 shows the FTIR spectra of both mixtures containing zeolite at the age of 90 days. Peak at 3640 cm^{-1} indicates that portlandite ($Ca(OH)_2$) is still present in the mixture marked 1/3-10, while it is not the case with the mixture 1/3-50. Similarly, higher peaks at 875 and 1418 cm^{-1} show more pronounced presence of calcium carbonate in the mixture with lower zeolite content. Peaks around 1000 cm^{-1} in both mixtures are of siliceous nature, and originate from the aggregate particles that were not removed from the samples by sieving. Results of the compressive strength measurements at different ages are presented in the Figure 4. For the mixture marked as 1/3-10 it can be seen that the compressive strength reached at the age of 14 days, did not change until the final testing age. This could be explained by the low quantity of natural zeolite in this mixture that induced the finalization of the pozzolanic reaction at the early ages. On the other hand, compressive strength of the mixture 1/3-50 continuously grew up to the age of 90 days with higher increment at the early ages. Since the FTIR spectra showed no presence of portlandite at the final age of testing it is expected that the pozzolanic reaction is finalized and that mixture has reached the maximum strength at this age. This assumption should be confirmed by testing the samples at the age of 180 or 360 days. When the compressive strength values are compared with the reference mixture it can be noticed that the mixture 1/3-10 reached 6 times lower strength and mixture 1/3-50 2.9 times higher strength at the age of 90 days.

CONCLUSION

The DTA results show that the natural zeolite from the location Igroš (near Brus) in the presence of calcium hydroxide and high relative humidity conditions forms C-S-H phases that are responsable for the compressive strength gain of the tested mixtures. In the case of the mixture with addition of 10 % of natural zeolite this incerease is not high enough to compete with the products of the carbonation reaction in the pure lime mortar (reference mixture). Results of the FTIR spectra show that the pozzolanic reaction was finalized by the age of 90 days for the mixture containing 50 % of natural zeolite, which could be confirmed by the testing of the compressive strenght at the ages of 180 or 360 days. Overall results show that the natural zeolite from this location can be used as an addition for the lime based renders after more detailed investigation on the optimum zeolite content and the duration of the curing.

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