

# MINERALOGICAL, MICRO-STRUCTURAL AND MECHANICAL PROPERTIES OF LIME MORTARS CONTAINING NATURAL ZEOLITE

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## ABSTRACT

In this paper, mineralogical, micro-structural and mechanical properties of lime mortars containing different percent of natural zeolite with binder to aggregate ratio 1:3 by volume at the age of 90 days were presented. Durability of the tested mortars was tested through their frost resistance. Although, the increase in the zeolite content led to the increase in compressive strength, only mixtures with 40% and 50% of lime replaced, showed higher strength than reference mixture. These results were in accordance to the X-ray diffraction and mercury intrusion porosimetry findings.

**Key words:** lime-putty, pozzolanic reaction, mercury intrusion porosimetry, natural zeolite

## INTRODUCTION

Lime-based mortars are one of the oldest building materials. They have been used for bedding and rendering of masonry buildings, together with stone blocks and building ceramics. In the last decades lime-based mortars are investigated in the scientific community due to the necessity for restoration of historical buildings and monuments, but also due to the development of energy efficiency strategies, and general policy for reduction of the greenhouse effect [1].

The most widespread lime-based mortar design is with maximum grain size of aggregate reaching usually 4 mm, while binder to aggregate ratio was between 1:4 to 1:3 (by volume). Veiga et al. reviewed the boundaries of physical and mechanical properties of lime mortars with different binder to aggregate ratio. For mixtures where this ratio was 1:3, boundaries for flexural strength were 0,2 and 0,8 MPa, for compressive strength 0.6 and 1.6 MPa, and for open porosity 27% and 35% [2].

Since lime mortars cannot harden in humid conditions, different potential pozzolanic additions, such as metakaolin, volcanic tuff, natural zeolites, crushed brick, etc., were applied in the past, when these mortars were used in humid environments. The paper presents the research regarding mineralogical, micro-structural and mechanical properties of lime-based mortars with partial replacement of lime with natural zeolite, found in Serbia.

## EXPERIMENTAL

Natural zeolitic tuff excavated in Igroš, near Brus (Serbia) was used in this study as a partial replacement for lime. Before application, it was ground to a fineness of 10% residue on 45  $\mu\text{m}$  sieve. The specific surface of the natural zeolite was 2.8  $\text{m}^2/\text{g}$ . The mineralogical composition of zeolite was determined by XRD analysis and shown in Table 2 [3].

**Table 1.** Chemical composition of the natural zeolitic tuff (wt.%) obtained by chemical analysis

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	CO <sub>2</sub>	L.O.I.
Natural zeolite	64.16	10.95	2.82	4.25	1.01	0.18	2.05	0.15	-	14.13
Lime	0.37	0.65	0.35	73.25	1.05	-	-	0	1.65	22.67

Pozzolanic reactivity, was determined via a modified Chapelle test. The result is expressed in mg of Ca(OH)<sub>2</sub> consumed in the reaction with 1 g of pozzolana over 24, 48, 72, 96 and 120 hours. Test results are presented in Table 2.

**Table 2.** Pozzolanic activity of natural zeolite obtained through a modified Chapelle test

Time of the test (days)	Consumed Ca(OH) <sub>2</sub> (mg/1 g pozzolana)
1	680.8
2	825.2
3	1073.1
4	1106.5
5	1129.0

Natural zeolite was used as a partial replacement of lime in lime-based rendering mortars for inner rendering layer. In these mortars lime-putty was used as a binder with approximately 50% of water. Chemical composition of lime, tested after drying, is shown in Table 1. Mixing proportions and composition of the tested mortars are shown in Table 3. Natural river sand with grain size between 0 and 4 mm has been used in all tested mixtures. Bulk density of the aggregate was 1610 kg/m<sup>3</sup> in loose state.

**Table 3.** Mixing proportions and composition of the mortar mixtures

Mixture	Lime (kg/m <sup>3</sup> )	Zeolite (kg/m <sup>3</sup> )	Sand (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	B/A (by volume)	B/A (by mass)	Partial replacement of lime (%)
1/3	190	-	1530	342	1:3	1:8.05	-
1/3-10	171	19	1530	342	1:3	1:8.05	10
1/3-20	152	38	1530	342	1:3	1:8.05	20
1/3-30	133	57	1530	342	1:3	1:8.05	30
1/3-40	114	76	1530	342	1:3	1:8.05	40
1/3-50	95	95	1530	342	1:3	1:8.05	50

Consistency of the fresh mortar was tested according to EN 1015-2, while the bulk density of the fresh mortar was tested according to EN 1015-6. After finalization of these tests, mortar was placed in formwork and cured in humid conditions for 5 days. After the samples have been removed from the formwork they were cured above water surface, with relative humidity of 95% up to the age of 28 days. At this age samples were divided in two groups. One group was cured in the same conditions up to the age of 90 days (RH100), while the other was placed in laboratory conditions (RH100/50). Reference mixture designated with 1/3, which was prepared using only lime-putty as a binder was cured in laboratory conditions (temperature of 20°C, relative humidity 50%) until the day of testing.

Mercury intrusion porosimetry (MIP), compressive strength (according to EN 1015-11) and mineralogical composition using X-ray diffraction (XRD) analysis were tested at the hardened mortars at age of 90 days. Frost resistance was tested on mixtures designated as 1/3, 1/3-40 and 1/3-50. The number of cycles, the environmental conditions and duration were chosen according to EN 1015-21. MIP was measured using a Micromeritics PoreSizer 9310 that can generate a maximum pressure of 207 MPa. The mineralogical composition of natural zeolite and mortar mixtures was determined on powder samples by PANalytical Empyrean XRD (Malvern Panalytical Ltd.) with Cu-K $\alpha$  as the radiation source ( $\lambda = 1.540598 \text{ \AA}$  for K $\alpha_1$ ), accelerating voltage 45 kV, beam current 40 mA, diffraction angle  $2\theta$  in the range of 5° to 80° with a step scan of 0.01°.

## RESULTS AND DISCUSSION

Properties tested in fresh state are presented in Table 4 (bulk density) and Figure 1 (consistency using flow-table test). Calculated bulk density for all of the mixtures was 2062

kg/m<sup>3</sup>. Mixtures containing higher percentage of natural zeolite (over 30%) had lower values of the bulk density, which can be explained by differences in specific densities of lime and natural zeolite. These differences had no effect on the bulk densities with amount of natural zeolite lower than 20%. Increase in natural zeolite addition led to the increase in the flow diameter of the mixtures. Highest flow diameter was measured for the mixture containing 50% of natural zeolite as a replacement for lime.

**Table 4.** Bulk density of the mortars in fresh state

Mixture	1/3	1/3-10	1/3-20	1/3-30	1/3-40	1/3-50
$\gamma$ (kg/m <sup>3</sup> )	2056	2068	2066	2054	2040	2040

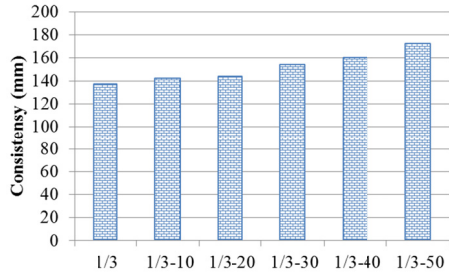


Figure 1. Flow-table test results

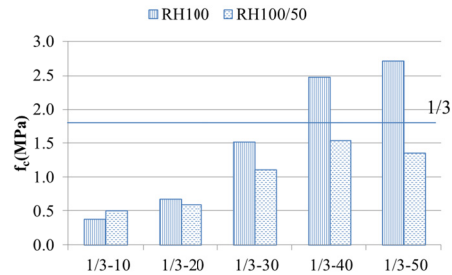


Figure 2. Compressive strength at the age of 90 days

Compressive strength of the all mixtures containing natural zeolite at the age of 90 days is presented in Figure 2. The increase of the natural zeolite addition led to the increase of compressive strength of the tested mixtures. Still, only mixtures containing 40% and 50% of lime replacement reached higher strength than reference mixture, that reached 1.77 MPa at this age. The change in the curing conditions at the age of 28 days, led to the decrease of compressive strength, that was more pronounced for the mortars with higher percent of lime replacement with natural zeolite. The highest reduction in strength was measured for the mixture designated as 1/3-50. This is explained by the carbonation process that takes place on the hydrated phases, after the samples are placed in laboratory conditions. This can be confirmed through results obtained by MIP and XRD analysis presented at Figures 3 and 4.

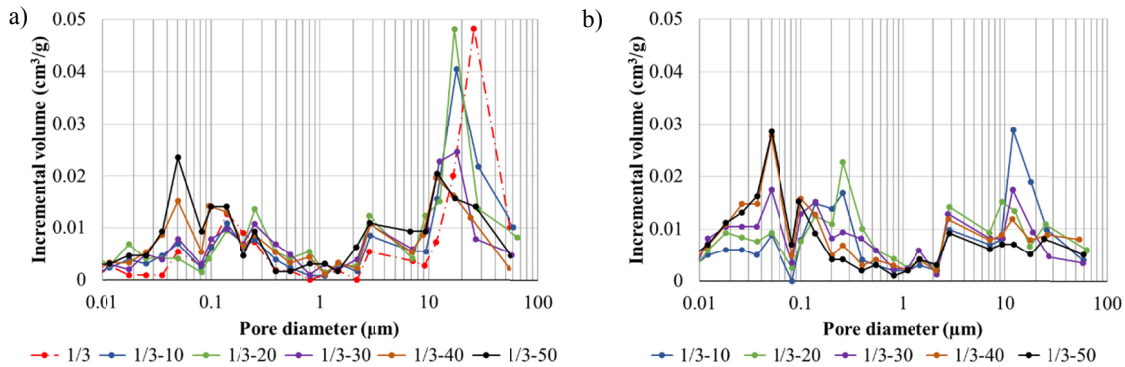


Figure 3. Mercury intrusion porosimetry test results at the age of 90 days: a) samples cured in combined conditions (RH100/50), b) samples cured in humid conditions (RH100)

The reference mixture is presented in Figure 3 by bimodal pore size distribution, that is usual for mortars prepared with lime – putty as a binder. The most pronounced pore diameters were between 0.1 - 0.2 µm and between 20 - 40 µm. With the increase of natural zeolite addition, the larger pores are reduced, while small pore diameters between 0.04 – 0.06 µm are developed. Due to the transition from humid to laboratory curing conditions at the age of 28

days, the amount of larger pores is increased, and pore size distribution of mixtures with 10 and 20 percent of lime replacement is very similar to the reference mortar. The reduction of smaller pores is visible for mortars designated as 1/3-40 and 1/3-50, but it is less emphasized.

The XRD patterns of the chosen mortar mixtures show that the mixture containing 20% of natural zeolite as lime replacement cured in humid conditions contains higher amount of portlandite than other presented mixtures. In this mixture part of the portlandite reacts with natural zeolite forming calcium-aluminate-hydrate, but since the curing conditions are not beneficial for carbonation reaction, there is a higher amount of non-reacted portlandite. This is not the case with the samples from the same mixture, cured in combined conditions (1/3-20 RH100/50), where the portlandite peaks are reduced, as well as peak related to calcium-aluminate-hydrate. Due to larger amount of natural zeolite in the mixture 1/3-50, the amount of portlandite is small both in the samples cured in humid and combined conditions.

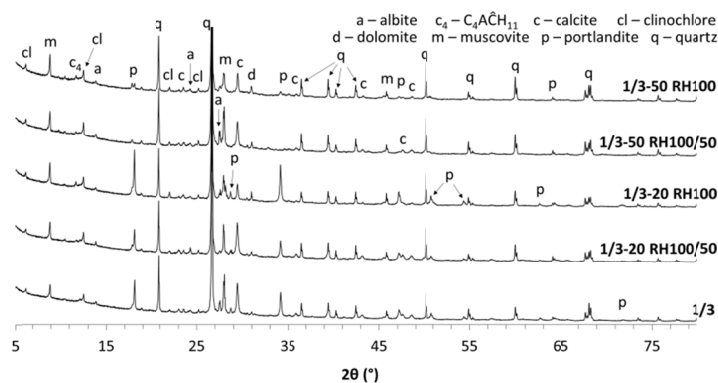


Figure 5. XRD patterns of the selected mortar mixtures at the age of 90 days

## CONCLUSION

The influence of natural zeolite addition to lime-based mortars was investigated through preparation and testing of lime-based mortars with different percentage of lime replaced with natural zeolite, cured in two different manners. According to the obtained results, in order to achieve positive effect of the pozzolanic reaction on the properties of lime-based mortars, higher percentage of natural zeolite should be used (40% or 50% of replacement). These mortars should be applied only in humid environmental conditions, since the products of pozzolanic reactions are included in carbonation reaction, if the relative humidity of the environment is reduced under 65%. None of the tested mortars showed good frost resistance, but the compressive strength after the finalization of the test was higher for mixtures designated as 1/3-40 and 1/3-50 than for the reference mixture.

## REFERENCES

- [1] T. Schlegel, A. Shtiza, Lime carbonation, environmental footprint of seven mortars placed on the European market, *Proceedings of the 16<sup>th</sup> international brick and block masonry conference*, 2016, 931-936 G
- [2] R. Veiga, Air lime mortars: What else do we need to know to apply them in conservation and rehabilitation interventions? A review, *Construction and Building Materials*, 2017, 157, 132-140.
- [3] M. Aškračić, M. Vyšvařil, D. Zakić, A. Savić, B. Stevanović, Effects of natural zeolite addition on the properties of lime putty-based rendering mortars. *Construction and Building Materials*, 2021, 270, 121363. ISSN: 0950-0618