# EFFECTS OF ZEOLITE INCORPORATION AND INERT FILLERS ON THE CURING OF CEMENT MORTARS

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## ABSTRACT

One of the main approaches to reducing the environmental impacts of the construction industry is the use of mineral additives reducing the use of cement in mortars and concretes for construction. The objects of this research are different cement composites with high content of inert mineral fillers (marble and quartz sand), the influence of zeolite incorporation on the microstructure, and low water-cement ratio, obtained after the hydration of white portland cement.

In this study, the evolution of the curing processes and the crystal formation during up to 120 days of water-curing are investigated. Moreover, the effects of replacing up to 10 wt. % of white cement with natural zeolite are studied. Attention was focused on the general microstructural development during curing with special attention on the evolution and morphology of pore space and the observed calcium silicate hydrates (C–S–H), portlandite, and carbonate-containing phases.

The phase composition (newly formed phases as well as the formation of C-S-H gel) is defined by using powder X-Ray diffraction and SEM. The experimental data shows that the cement composites with the inert marble filler as an additive lead to the creation of carbo-aluminates. The incorporation of up to 10 percent of clinoptilolite in concrete mixtures by mass of the total cementitious components is more efficient when used in lower strength mixes. A significant reduction in the workability of the fresh mortars is not observed, but the high surface area of zeolite reduces bleeding and accelerates setting without any strong effects on the other physical and technological properties of fresh mortars.

<u>Keywords</u>: cement mortar, mineral filler, zeolite additive, phase transformation.

## INTRODUCTION

In order to achieve an aesthetic and decorative surface of cement mortars and concretes, white or coloured portland cement and/or additive materials are used [1 - 3]. White decorative mortars and concretes have restrictions on: white colour of the binder and mineral additive, good workability, and a dense structure that does not have significant destructive processes at various atmospheric impacts. The properties of these cement compositions are determined by their microstructure [4], which consists of calcium-silicon, calcium-aluminium and other minerals, formed during the hydration process of the cementitious minerals [5]. The minerals have

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varying amounts of crystallization and structure-bound water - the type and composition of these hydrate phases depends on the presence of active and inert mineral additives in the binding system [6]. Most often, technogenic wastes are incorporated into cement mortars and concretes, whose role is to reduce the cost of the resulting composites, while maintaining or improving their durability to environmental impacts [7, 8].

Clinoptilolite is a zeolitic material that exhibits excellent pozzolanic activity - reaction with calcium hydroxide to form insoluble calcium silicates (cementitious phases) [9]. Its incorporation to the cement mortars has economic, engineering and durable effects typical for natural pozzolans. In comparison with light in colour pozzolans – silica fume, metakaolin, etc. the clinoptilolite is soft and ductile mineral. Moreover, it modifies the rheological behaviour of fresh mixes and takes an active part in the process of cement hydration. This predetermines the possibility of clinoptilolite incorporation in white cement mortars and concretes to produce architectural elements and details. Free of any additional pigments, the hardened white mortars have an ancient appearance, due to the characteristic colour of clinoptilolite.

The object of the study is cement compositions based on white portland cement, which are characterized by a high content of marble powder as an inert filler, natural zeolite (clinoptilolite) as a pozzolanic binder and a low water-to-cement ratio. The samples were prepared with different contents of the components, which affect their densities and strengths determined at 28 days or 120 days of curing.

Our previous research presents the results of mechanical, physical, chemical, XRD, SEM and thermal studies of the properties of cement mortars based on white cement, dry river sand and marble powder [10, 11] for decorative applications. The obtained results prove the formation of calcium-silicon hydrosilicates and establish the difficulties in identifying the formed hydrate phases and the influence of the zeolite additive, which provokes continued research in these systems based on cement binder.

The present work aims to study the influence of the: i) amount of marble powder (inorganic mineral filler); ii) natural zeolite (binder) - 10 % amount; iii) water-to-cement factor on the hydration and phase formation processes of hydrosulphate and hydro-

sulpho/carbonate calcium-silicate phases occurring in white cement mortars, the effect of inert filler and zeolite incorporation on the curing of cement mortars. The study was accomplished by physical-mechanical measurements - bulk density after immersion, adsorption after immersion, compressive strength, mercury intrusion porosimetry (MIP), powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials and Methods

The objects of research in the present work are cement solutions with different ratios of the main component - cement, aggregate and binder. The components of these mixes were: white cement type CEM I 52.5 N (Devnya Cement, Bulgaria), clinoptilolite (0 - 0.8 mm, Beli Plast deposite, Bulgaria) and clean washed and dried river sand as an aggregate.

The chemical composition of used white portland cement CEM I 52.5 N, produced by Devnya Cement (Bulgaria), was (in wt. %): $SiO_2$ - 24.3; $Al_2O_3$ - 2.1; $Fe_2O_3$ - 0.2; CaO - 68.3; MgO - 0.3; $Na_2O$ - 0.13; $K_2O$ - 0.02; free lime - 1.9. Thus, the mineral composition, calculated by Bogue method was (in wt. %): $C_3S$ - 72.13; $C_2S$ - 15.28; $C_3A$ - 5.23; $C_4AF$ - 0.61.

The studied samples were prepared with marble powder as an aggregate and natural clinoptilolite as a binder, and 2% high range water reducer (HRWR), manufacturer Sika ViscoCrete 5-800. The additive is polycarboxylate based with a density of 1,07 g/cm3 (at 20 °C).

The used aggregate - marble powder was produced by White Marble Products AIAS S.A. (Greece) with the following chemical composition (wt. %): $CO_2$ + $H_2O$ - 45.7; $SiO_2$ - 0.12; $Al_2O_3$ - 0.38; $Fe_2O_3$ - 0.14; CaO - 32.9; MgO - 20.0; $Na_2O$ - 0.05; $K_2O$ - 0.19; MnO - 0.01. This chemical composition defines the mineral composition of dolomite $CaCO_3.MgCO_3$ and calcite $CaCO_3$.

The clinoptilolite was from the Beli Plas deposit, Bulgaria. Natural clinoptilolite is a mineral of volcanic activity origin forming large industrial deposits. The clinoptilolite tuff contains about 80 wt. % clinoptilolite and admixtures of montmorillonite, biotite, celadonite, low-cristobalite, calcite, quartz and feldspars. In the present studies, the natural clinoptilolite is thermally activated at 250°C [12].

The polydispersity of aggregate was: maximal size of grains - 2 mm; grains with sizes < 0.125 mm - 50.0 wt. %; grains with sizes < 0.063 mm - 35.0 wt. %.

After casting, the specimens (6 prisms, 40´40´160 mm) were stored in the moulds for 1 day in a moist atmosphere (> 95 % RH and 20°C). Then the demoulded specimens were stored under water (20ºC) until strength testing (28 and 120 days).

The experiments were carried out with two types of cement composites, which codes, type of used aggregate and compositions are shown in Table 1 - samples M: binder (white portland cement) + aggregate (marble powder) + water, and samples Mz: binder (white portland cement + zeolite) + aggregate (marble powder) + water. All samples were mixed with distilled water.

The methods used to study both the curing and effects of cement substitution with natural zeolite include physical-mechanical methods, mercury intrusion porosimetry (MIP), X-ray powder diffraction (PXRD) and scanning electron microscopy (SEM).

The MIP was carried out using Carlo Erba, Porosimeter Mod. 1520. The used pressure range was 1 - 150 atm corresponding to pore size range 50 - 15000 nm.

The powder X-ray diffraction (PXRD) measurements were made by D2 Phaser BrukerAXS, CuKα radiation (λ = 0.15418 nm) (operating at 30 kV, 10 mA) from 5 to 80° 2θ with a step of 0.05° (grinded sample with weight - 1.0 ± 0.1 mg and particle sizes below 0.075 mm. The database PDF (Powder Diffraction File, ICDD, 2001) was used for the determination of the phases and minerals present in the samples [13].

The microstructures were observed with Philips PH Model 515, regime of secondary electron emission. The fracture fragments of the samples with approximately flat surface of about 10´10 mm was dried for 12 hours at 60 ± 5ºC, then were coated with a thin layer of gold.

**RESULTS AND DISCUSSION**

**Physical-mechanical measurements**

The measured physical-mechanical properties of mortars were bulk density after immersion, spreading diameter, water adsorption after immersion, 28-day flexural and compressive strengths and 120-day compressive strength. The method of measuring and the average values of properties are shown in Table 2. Because of the different density of the samples, the adsorption after immersion is calculated in volume percentages.

**Powder XRD analysis**

The PXRD analysis was used to better evaluate and identify the phases contained in the investigated samples. The obtained results for raw material are shown in Fig. 1(a-c), 2(a-b), and Table 3.

Table 1. Codes and composition of mortars (wt. %).

| Mortar | Cement | Marble powder | Zeolite | Distilled water | Ratios (wt/wt) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | cement/ aggregate | water/ cement | water/ binder | water/ fines* |
| M | 1.0 | 3.0 | - | 0.4 | 1:3 | 0.50 | 0.40 | 0.353 |
| Mz | 0.9 | 3.0 | 0.1 | 0.4 | 1:3 | 0.60 | 0.40 | 0.353 |

*all particles with sizes below 125 μm*

Table 2. Physical and mechanical properties of studied mortars M and Mz.

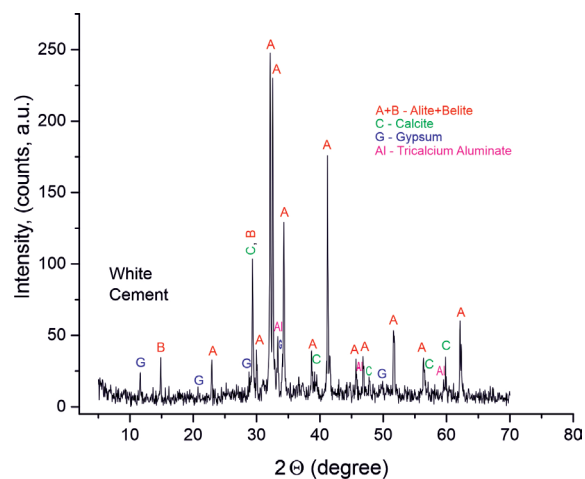| Property | Method | Units | Mortar | |
|---|---|---|---|---|
| | | | M | Mz |
| Bulk density after immersion | [16] | kg m$^{-3}$ | 2348 | 2330 |
| Spreading diameter | [14] | mm | 332 | 290 |
| Adsorption after immersion | [16] | mm$^3$ cm$^{-3}$ | 192.5 | 162.4 |
| 28-day Flexural strength | [15] | N mm$^{-2}$ | 11.51 | 9.79 |
| 28-day Compressive strength | [15] | N mm$^{-2}$ | 90.1 | 98.3 |
| 120-day Compressive strength | [15] | N mm$^{-2}$ | 106.2 | 109.0 |

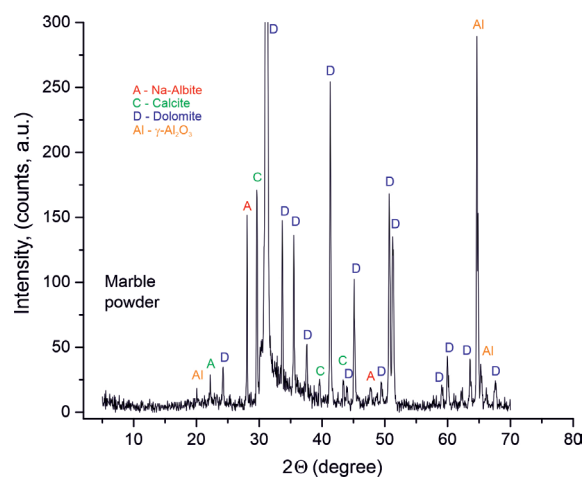Fig. 1(a). XRD pattern of raw sample - White Cement.



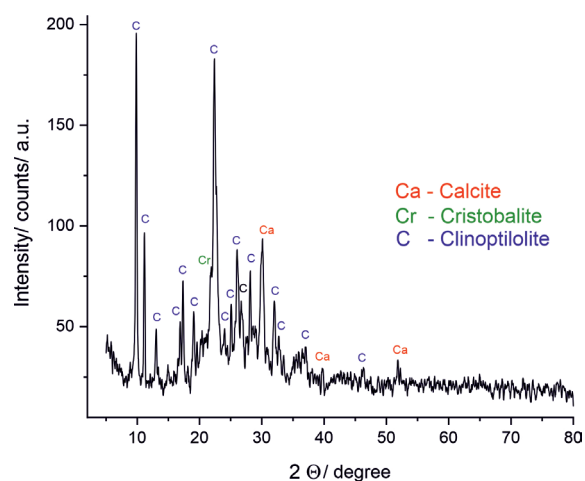Fig. 1(b). XRD pattern of raw sample - Marble powder.



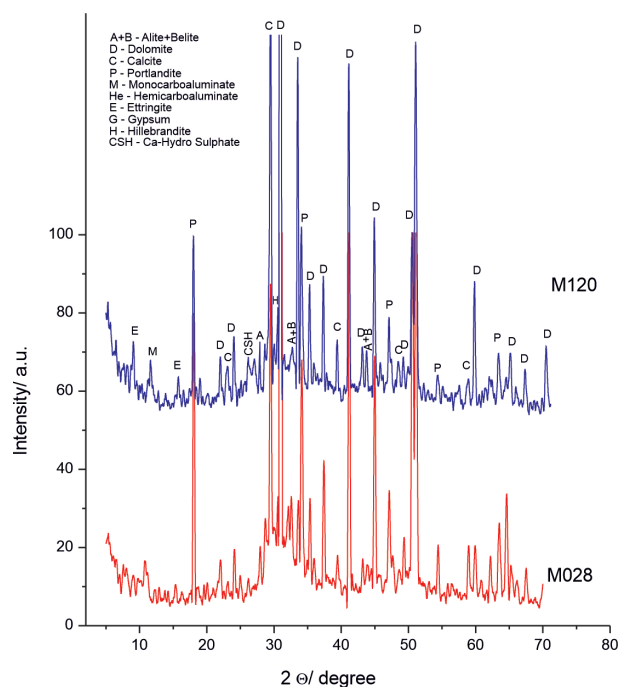Fig. 1(c). XRD pattern of raw sample - Clinoptilolite.

Fig. 2(a). XRD pattern of M-samples - marble powder + white cement (reference samples).
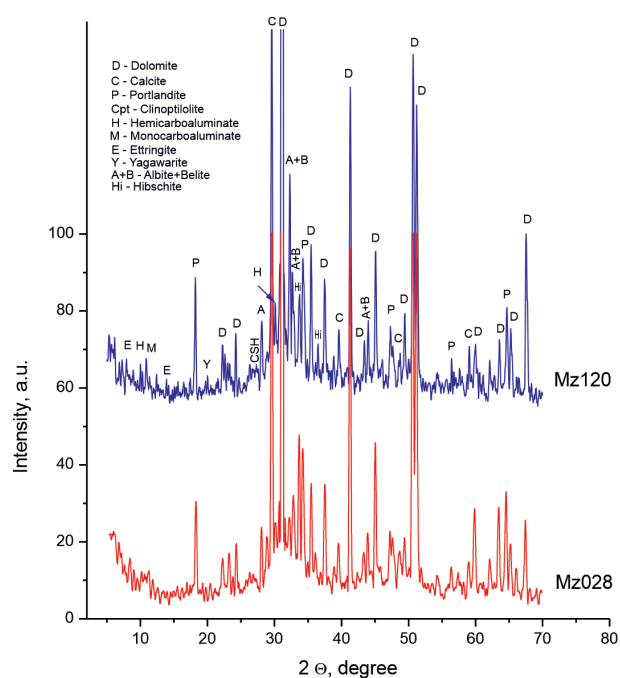
Fig. 2(b). XRD pattern of Mz-samples - marble powder + 90 % white cement + 10 % natural zeolite.

Table 3. Results from PXRD analysis of raw materials (white portland cement, marble powder, and natural zeolite) and M028, M120, Mz028, and Mz120.

| No | Description | Sample | Identified phases (name, ICDD card number; formula) |
|---|---|---|---|
| | Minerals of raw materials and their relics in samples | | |
| 1. | white portland cement, M028, M120; Mz028, Mz120 | | belite ($C_2S$), #49-1673 - $Ca_2SiO_4$ |
| | | | alite ($C_3S$), #11-0593 - $Ca_3SiO_5$ |
| | | | calcite, #47-1743 - $CaCO_3$ |
| | white Portland cement | | tricalcium aluminate ($C_3A$), #38-1429 - $Ca_3Al_2O_6$ gypsum, #33-0311 - $CaSO_4.2H_2O$ |
| | marble powder, M028, M120; Mz028, Mz120 | | dolomite, #36-0426 - $CaMg(CO_3)_2$ Mg-rich calcite, #43-0697 - $CaCO_3$ |
| 2. | Newly formed phases | | |
| 2.1. | hydrate phase | M028, M120 Mz028, Mz120 | portlandite (CH), #44-1481 - $Ca(OH)_2$ |
| 2.2. | hydrosilicates - CSH, forming of main oxides CaO, $SiO_2$, $OH^-$ and/or crystal water $H_2O$ | M028, M120 Mz028, Mz120 | hillebrandite, #29-0373, #42-0538 - $Ca_2SiO_3(OH)_2$ |
| 2.3. | hydrosilicates - CSAH, forming of main oxides CaO, $Al_2O_3$, $SiO_2$, $OH^-$ and/or crystal water $H_2O$ | M028, M120 Mz028, Mz120 | yugawaralite, 39-1372 - $CaAl_2Si_6O_{16}.4H_2O$ |
| | | Mz028, Mz120 | hibschite, 45-1447 - $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$; (x = 0.2-1.5) |
| 2.4. | $OH^-$ and $HCO_3^-/CO_3^{2-}$ phases | Mz028, Mz120 | monocarboaluminate, #41-0219 - $Ca_4Al_2(OH)_{12}(CO_3).5H_2O$ |
| | | M028, M120 | hemicarboaluminate, #41-0221 - $Ca_4Al_2(OH)_{12}(OH)(CO_3)_{0.5}.4H2O$ |
| 2.5. | $OH^-$ and $HSO_4^-/SO_4^{2-}$ phases | M028, M120 Mz028, Mz120 | ettringite, 41-1451 - $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$ |
| | | M028, M120 Mz028, Mz120 | calcium hydrogensulphate, #85-1271 - $Ca(HSO_4)_2$ |

The XRD analysis of the raw materials (Fig. 1, Table 3) confirms the original data regarding the main minerals present in the composition of white cement, marble flour and natural clinoptilolite.

The X-ray powder diffraction was used in order to confirm the previously obtained results as well as to better evaluate the investigated samples [11]. The obtained results from the XRD analyses of the phase composition of samples of mortar M - M028, M120 and of mortar Mz - Mz028, Mz120, contain new-formed phases of hydration of relict cement minerals and the marble powder. X-ray measurements present a complex diffraction pattern with well crystallized phases such as dolomite, calcite, portlandite, but also those with low peak intensity - the newly formed phases from the CSH/CSAH gel. The XRD analysis (Table 3) show the presence of two groups of minerals in the studied samples: (i) relict minerals from the initial composition: belite, albite, anorthite, Mg-rich calcite, gypsum, dolomite, tricalcium aluminate and (ii) new formed minerals: portlandite, yugawaralite, hillebrandite, hemi- and monocarboaluminate, ettringite and hibschite.

The identification of components from raw components in the samples' compositions is associated with insufficient water in the systems, which results in an incomplete hydration of the raw minerals.

**Scanning electron microscopy and mercury intrusion porosimetry**

The surface structures of the studied samples are shown in Fig. 3(a-d). The micrographs indicate stable and dense structures and crackings (Micro crack), even at 28 days of curing, so there are no empty spaces for the growth of new minerals. The CSH/CSAH gel probably forms fine grained crystal aggregate with structural parameters under the limit of PXRD detection.

Due to wall effects, different cement-to-water ratio and empty space these areas are filled with crystal hydrates with different morphology: plate crystals (portlandite), needle crystals (ettringite) and fine crystal aggregates (CSH gel).

The replacement of 10 wt. % white cement with zeolite leads to the formation of shrinkage cracks caused by low water-cement ratios, in the bulk of the material

(Figs. 3(b) and 3(d)).

The addition of zeolite increases the 28-day compressive strength of SCMs. Despite its dense structure, the curing of SCMs continues when these mortars are immersed in water. The increase in compressive strength and the evolution of total porosity, based on MIP experiments (Fig. 4) are comparable to those of mortars M and Mz. The porous space is interconnected by voids and cracks through which the water can penetrate deeply, thereby continuing the processes of hydration and crystallization.

An additional explanation for the increase in compressive strength is the pozzolanic activity of zeolite. Its active amorphous $SiO_2$ and $Al_2O_3$ react with the portlandite and form variable additional C-S-H crystals. The morphological picture of the samples confirms postulates in the processes of dissolution and hydration
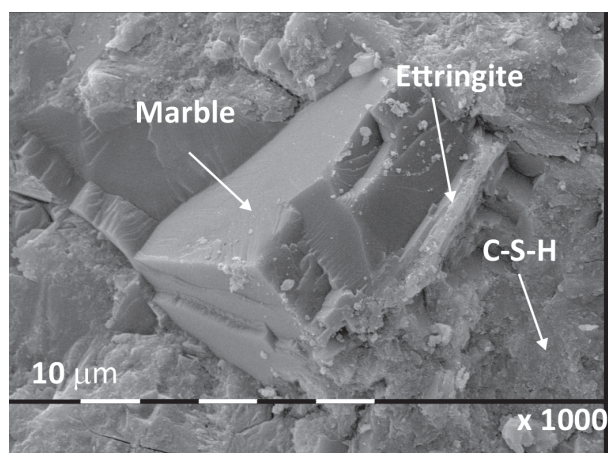


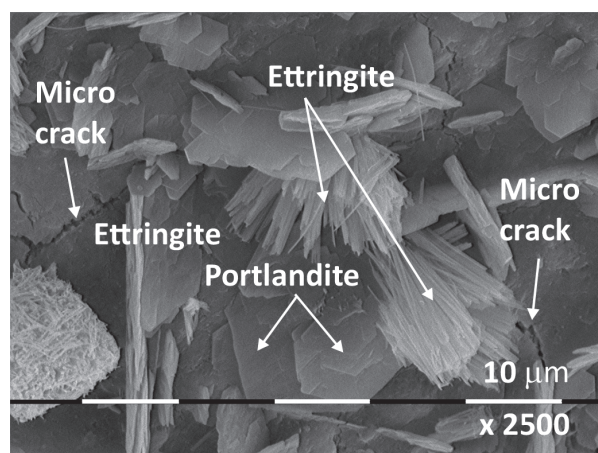Fig. 3(a). SEM micrograph of crystal hydrated phase of sample M at 28 days of water curing.



Fig. 3(b). SEM micrograph of crystal hydrated phase of sample M at 120 days of water curing.
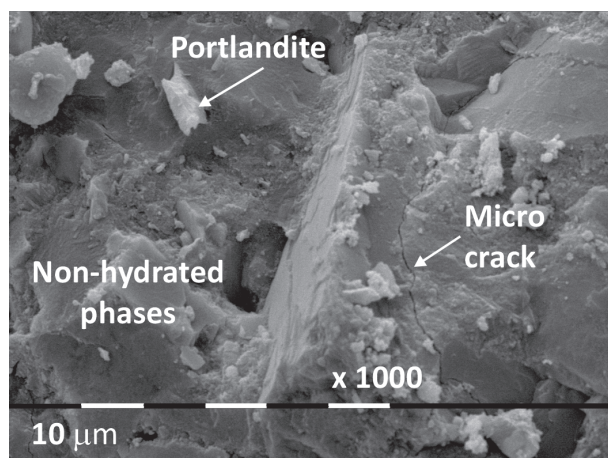


Fig. 3(c). SEM micrograph of crystal hydrated phase of sample Mz at 28 days of water curing.
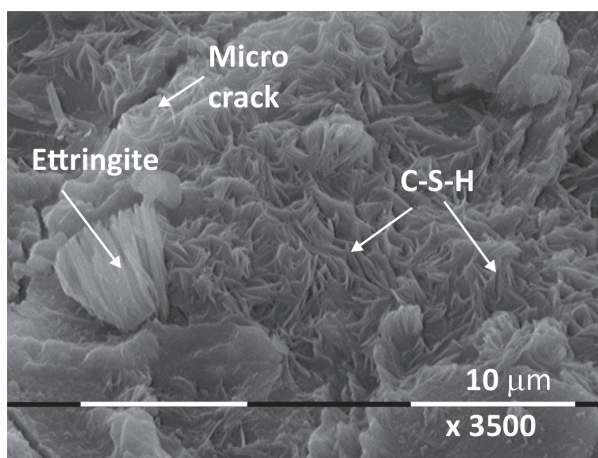


Fig. 3(d). SEM micrograph of crystal hydrated phase of sample Mz at 120 days of water curing.
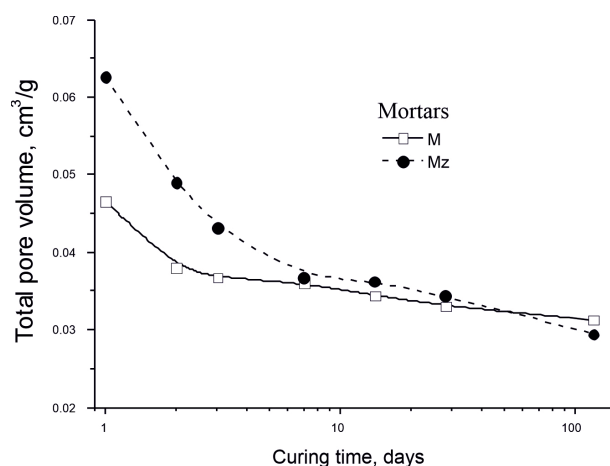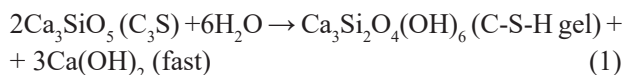
Fig. 4. Evolution of total porosity during water curing.

of cement minerals. When cement minerals hydrate without the presence of zeolite (Fig. 3(a) and 3(b)) the registered surface is covered with various crystalline products - platelets crystals of portlandite, needle-like crystalline ettringite and small crystals of C-S-H gel grown in the voids between portlandite particles. The replacement of 10 wt. % cement with zeolite (Fig. 3(c) and 3(d)) impedes the cement hydration due to lack of water. The products of hydration without the presence of both portlandite and ettringite cover a smaller area of the surface and shrinkage cracks begin to appear. The C-S-H gel has a significantly finer crystalline structure with interpenetrating crystal forms. This picture corresponds to the XRD data and their analysis (Fig. 2 and Table 3).
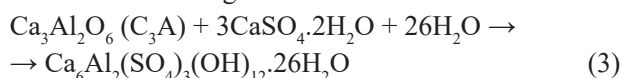
The results obtained from the PXRD, SEM, and MIP measurements make it possible to determine the main phases formed during the hydration of the cementitious solutions at low water-cement ratios and the use of marble flour as an aggregate and natural zeolite (clinoptilolite) as an additive of up to 10 % of the cement's amount. On their basis, the influence of marble powder and clinoptilolite on the microstructure of cement solutions was analyzed.

According to the results of PXRD and SEM analysis, the following reaction mechanism scheme of samples hydration have been defined as the main chemical reactions (1) and (2):
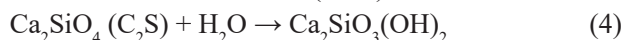
$$2Ca_3SiO_5 (C_3S) + 6H_2O \rightarrow Ca_3Si_2O_4(OH)_6 \text{ (C-S-H gel)} + 3Ca(OH)_2 \text{ (fast)} \quad (1)$$

$$2Ca_2SiO_4 (C_2S) + 4H_2O \rightarrow Ca_3Si_2O_4(OH)_6 \text{ (C-S-H gel)} +$$

$$+ Ca(OH)_2 \text{ (slow)} \quad (2)$$

When gypsum is added to the cement, ettringite is formed during the hydration process.
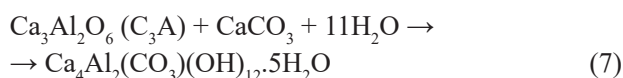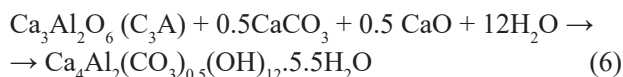
Formation of ettringite
$$Ca_3Al_2O_6 (C_3A) + 3CaSO_4.2H_2O + 26H_2O \rightarrow$$
$$\rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O \quad (3)$$

Formation of hillebrandite (CSH)
$$Ca_2SiO_4 (C_2S) + H_2O \rightarrow Ca_2SiO_3(OH)_2 \quad (4)$$

Formation of Yagawarite (CSAH)
$$Ca_3Al_2O_6 (C_3A) + 6SiO_2 + 6H_2O \rightarrow$$
$$\rightarrow CaAl_2Si_6O_{16}.4H_2O + 2Ca(OH)_2 \quad (5)$$
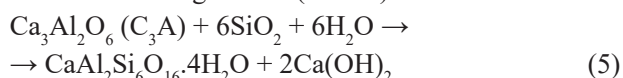
The use of marble white powder (Mg-rich calcite) increases the content of carbon ions [17 - 19]. They participate in the formation of the hydrated phases, which is verified by the presence of hemi-, and monocarboaluminate:

$$Ca_3Al_2O_6 (C_3A) + 0.5CaCO_3 + 0.5 CaO + 12H_2O \rightarrow$$
$$\rightarrow Ca_4Al_2(CO_3)_{0.5}(OH)_{12}.5.5H_2O \quad (6)$$

$$Ca_3Al_2O_6 (C_3A) + CaCO_3 + 11H_2O \rightarrow$$
$$\rightarrow Ca_4Al_2(CO_3)(OH)_{12}.5H_2O \quad (7)$$

When comparing our own results from previous studies of the PXRD analysis of cement mortars without zeolite addition [10, 11] with the current studies of mortars with zeolite (clinoptilolite) addition, it can be noted that a greater variety of newly formed hydrated
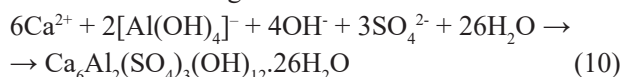
phases is registered during the identification of the phase composition. In the presence of up to 10 % of clinoptilolite in the cement, and despite the reduced amount of water, phases such as yugawaraite and hibschite are formed in addition to hillebrandite (Fig. 2, Table 3). The greater variety of CSH and CSAH phases is the result of the high sorption capacity of the implemented zeolite and its pozzolanic activity due to the presence of active $SiO_2$ and $Al_2O_3$ from the zeolite additive [20, 21].

The hydration of the minerals from the cement clinker occurs during increased alkalinity of the solutions under the influence of the zeolite additive. In solutions with an alkaline reaction, it becomes possible to dissolve the zeolite tuff with the formation of the following anions according to reactions (8) and (9) [22]:
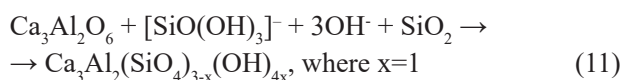
$$\equiv Si–O–Si\equiv + 8OH– \rightarrow 2[SiO(OH)_3]^- + H_2O \quad (8)$$

$$\equiv Si–O–Al\equiv + 7OH^- \rightarrow [SiO(OH)_3]^- + [Al(OH)_4]^- \quad (9)$$

In the presence of octahedral and tetrahedral fragments of the lattice structure of the zeolite and $Ca^{2+}$ of the cement, pozzolanic reactions are possible in the presence of water. This creates an opportunity for the formation of natural centres of crystallization, and leads to the growth of hydrated calcium aluminosilicate compounds (CSAH), which is partially illustrated by the following possible reactions (10) and (11) [23]:

Formation of Ettringite
$$6Ca^{2+} + 2[Al(OH)_4]^- + 4OH^- + 3SO_4^{2-} + 26H_2O \rightarrow$$
$$\rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O \quad (10)$$

Formation of Hibschite
$$Ca_3Al_2O_6 + [SiO(OH)_3]^- + 3OH^- + SiO_2 \rightarrow$$
$$\rightarrow Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}, \text{ where } x=1 \quad (11)$$

The PXRD results, together with the identification of the newly formed crystal hydrate phases, suggest that the amount of bound water in their structure is in short supply. The basis for such an assumption is the initial water-cement ratio and the presence of the zeolite additive in the compositions of the cement mortars of the second series. As other authors mention, zeolite facilitates the formation of a dense and strong structure due to its well-defined sorption properties [10, 22].

The scanning electron microscopy studies of the morphology of the cement mortars from the two series of samples also confirm the obtained results.

## CONCLUSIONS

The hydration process of white cement mortars is characterized with low content of crystal water, portlandite and calcium silicate hydrates. During the curing process, an autogenous shrinkage is realized due to self-desiccation and a low water-binder ratio. Regardless of the formed very dense structure, the cement mortars have open and continuous porosity. The water penetrates through these capillaries, thus the processes of delayed hydration and pozzolanic reaction are realized. The replacement of part of white cement with natural zeolite reduces the density of the hardened mortars, but both the quantity and variety of new crystal products are increased.

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