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The effect of zeolite on the properties and hydration of blended cements

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ABSTRACT

In this paper the properties and the hydration of cements containing natural zeolite, coming from the Metaxades area, Thrace, Greece, are studied. The experimental part comprises three stages. In the first stage a complete mineralogical characterization of the zeolite was performed. In addition, the pozzolanic reactivity of the zeolite was evaluated on the basis of the Chapelle test. In the second stage, the mechanical and physical properties of blended cements, incorporating 0%, 10% and 20% per weight of fine zeolite were determined. Finally, the hydration rate and products were studied by means of X-ray diffraction and FTIR spectroscopy, in combination with thermoanalytical methods (TG/DTG and DTA). As it is concluded, the examined zeolite consists mainly of heulandite type-II and is a pozzolanic material that contributes to the strength development of zeolite-cement mixtures, the consumption of $Ca(OH)_2$ formed during the hydration of Portland cement and the formation of cement-like hydrated products. Finally, the addition of zeolite up to 20% w/w does not significantly affect the physical and mechanical properties of the blended cements.

1. Introduction

Zeolitic tuffs have been widely used, as mixtures with lime, in construction since Roman times. Nowadays, there is much discussion concerning the pozzolanic activity of natural zeolites and their incorporation in blended cements [1–7]. The term pozzolana is associated with all siliceous/aluminous materials, which, in finely divided form and in presence of water, react chemically with $Ca(OH)_2$ in order to form compounds that possess cementitious properties.

Zeolites are framework aluminosilicate minerals with a cage-like structure that offers large (internal and external) surface areas. The high surface area is the basis of high reactivity. Heulandite type zeolites are among the most abundant and useful zeolites found in nature, with a Si/Al ratio ranging from 3 to 5, defining a solid solution between heulandite ($(Na,K)Ca_4(Al_9Si_{27}O_{72})\cdot 24H_2O$), and clinoptilolite or high-silica heulandite ($(Na,K)_6Al_6(Si_{30}O_{72})\cdot 20H_2O$) end members. Heulandite is determined as the mineral with a ratio $Si/Al < 4$, while clinoptilolite has a ratio $Si/Al > 4$. They are both monoclinic zeolite minerals, C2/m group, with the following unit cell parameters: $\alpha = 17.70$ Å, $b = 17.94$ Å, $c = 7.42$ Å, $\beta = 116^\circ\ 24'$ and $\alpha = 17.62$ Å, $b = 17.91$ Å, $c = 7.39$ Å, $\beta = 116^\circ\ 18'$, respectively [8]. Their structure is characterized by large, intersecting, open channels of ten and eight-member tetrahedral rings. The large, ten-member ring and the smaller, eight-member ring confine channels parallel to the *c* axis. In natural zeolites, these channels are predominantly occupied by Na, K, Ca and H_2O [9].

Previous works on the pozzolanic reactivity of zeolites (heulandite, clinoptilolite, mordenite) have shown that the zeolitic minerals are able to react with lime and produce cementitious phases [2,10,11].

Large zeolite deposits of potential economic interest, are present in the Metaxades area, situated in the western part of the Orestias basin in north-east Greece. They are mostly of Tertiary age and are deposited in shallow marine basins [12].

In this study, the properties and the hydration procedure of cements containing zeolite from the Metaxades area were monitored for periods up to 360 days. This work belongs to a research project aiming to the exploitation of Greek zeolites in construction technology.

2. Experimental

2.1. Materials

The zeolite, used in this work, comes from natural deposits at the Metaxades area, Thrace, Greece. Portland Cement (CEM I 42.5 N and I 52.5 N, according to EN 197-1) of industrial origin was used for the production of the mixtures. The chemical analysis of the materials are given in Table 1. The zeolite was ground in a ball mill. The fineness characteristics of the ground zeolite are given in Table 2. The fineness of CEM I 42.5 N and CEM I 52.5 N is 3700 and 4100 Blaine, respectively. Blended cements were

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Table 1
Chemical composition of the zeolite and the cement (% w/w).

Oxide	Zeolite	CEM I 42.5	CEM I 52.5
SiO_2	70.61	19.6	19.8
Al_2O_3	10.83	4.6	4.7
Fe_2O_3	0.48	3.7	3.8
MgO	0.62	3.2	3.2
CaO	3.52	60.0	60.3
Na_2O	0.52	0.16	0.16
K_2O	1.95	0.55	0.55
TiO_2	0.09	–	
SO_3	–	2.9	2.9

Table 2
Fineness characteristics of zeolite d_i: % w/w of the powder (particles) having diameter higher than *i*.

d_{20} (μm)	d_{50} (μm)	d_{80} (μm)
31	8.9	1.7

produced by replacing the Portland Cement with 10% w/w and 20% w/w of the ground zeolite.

The hydration process of the cements was studied according to the following procedure. The cements were mixed with water in order to prepare cement pastes. A water-to-cement ratio (W/C) of 0.4 was retained for all pastes and deionized water was used. After a period of 6 h the cement cores where put in polythene containers (vials), sealed hermetically and wet-cured at 20 °C. Samples hydrated for periods of 1, 2, 7, 28, 90, 180 and 360 days were subjected to acetone and isopropyl ether treatment and then dried for 24 h in vacuum.

2.2. Techniques

The zeolite used was studied by X-ray diffraction and FTIR spectroscopy, in combination with thermoanalytical methods (TG/DTG and DTA). These techniques were also applied in order to identify the hydrated products and evaluate the hydration rate.

X-ray powder diffraction patterns were obtained using a Siemens D-5000 diffractometer, with Ni-filtered, CuKa$_1$ radiation (λ = 1.5405 Å), operating at 40 kV, 30 mA. The IR measurements were carried out using a Fourier Transform IR (FTIR) spectrophotometer (Perkin Elmer 880). The FTIR spectra in the wavenumber range from 400 to 4000 cm^{-1}, were obtained using the KBr pellet technique. The pellets were prepared by pressing a mixture of the sample and dried KBr (sample:KBr approximately 1:200) at 8 tons/cm^2. Differential thermal analysis (DTA) and thermogravimetric analysis (TG/DTG) was obtained simultaneously using a Mettler Toledo 851 instrument. The samples were heated from 20 to1200 °C at a constant rate of 10 °C/min in an atmosphere of carbon dioxide free nitrogen, flowing in 50 cm^3/min.

Chapelle test is a quick test for the evaluation of the pozzolanic activity of a material. One gram of sample is added in 200 ml of distilled water followed by the addition of 1 g of $Ca(OH)_2$. The mixtures were then boiled for 16 h. After that the solution is filtrated and titrated with HCl solution (1 N) and phenolphthalein in order to find the amount of $Ca(OH)_2$ that has not participated in the pozzolanic reaction.

The compressive strength up to 360 days as well as the water demand and the setting time of the cements were determined according to EN 196-1 and EN 196-3, respectively.

3. Results and discussion

3.1. Characterization of zeolite

From the XRD study of the zeolite, it is concluded that the main mineral constituent belongs to heulandite group. K-feldspars (*d* = 3.21 Å), cristobalite (*d* = 4.0 Å) and quartz (*d* = 4.24 Å) are also present (Fig. 1).

The end members of the heulandite group have some differences in the diffractometer tracings. In heulandite, the higher peak is attributed to the (0 2 0) reflection (*d* = 8.99 Å), while in clinoptilolite the higher peak is attributed to the (0 0 4) reflection (*d* = 3.98 Å). Moreover, the thermal behavior of the end members of this zeolite group depends on whether the crystal structure is maintained or decomposed after heating overnight at 450 °C [11]. A complete lattice break down after heating at a temperature of 450 °C for 15 h, indicates the presence of heulandite, while the clinoptilolite crystal structure is kept unaffected. A partial framework break down indicates the presence of an intermediate member of the heulandite–clinoptilolite isomorphous series.

In order to identify the type of the Metaxades zeolites, their thermal behavior was examined [11]. Based on the fact that (i) the intensity of the (0 2 0) and (0 0 4) characteristic diffraction peaks decreases after heating the samples at 350 °C, for 15 h, and (ii) these peaks do not entirely disappear after heating the samples at 450 °C, it is concluded that this zeolite belongs to the heulandite type-II categorization (Fig. 1).

In the FTIR spectra of the raw sample (Fig. 2), the bands at exactly 1048 cm^{-1} as well as at 598.9 cm^{-1} confirm that the zeolite is heulandite type-II.

3.2. Cement properties

Table 3 presents the water demand of cement paste and the setting time of the tested samples. The "water demand" is the quan-

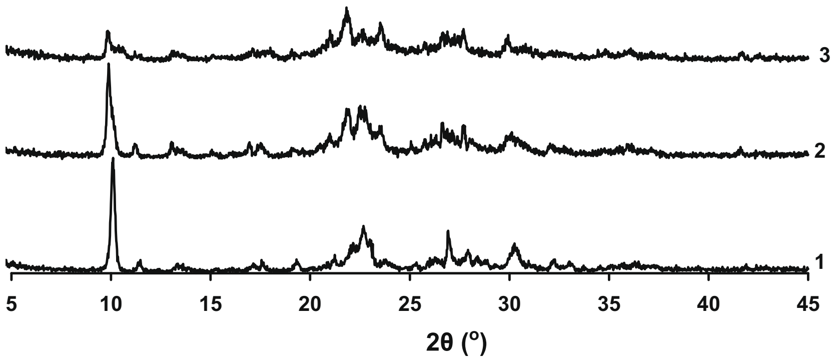

Fig. 1. XRD patterns of zeolite – 1: raw zeolite, 2: zeolite after 15 h at 350 °C, 3: zeolite after 15 h at 450 °C.

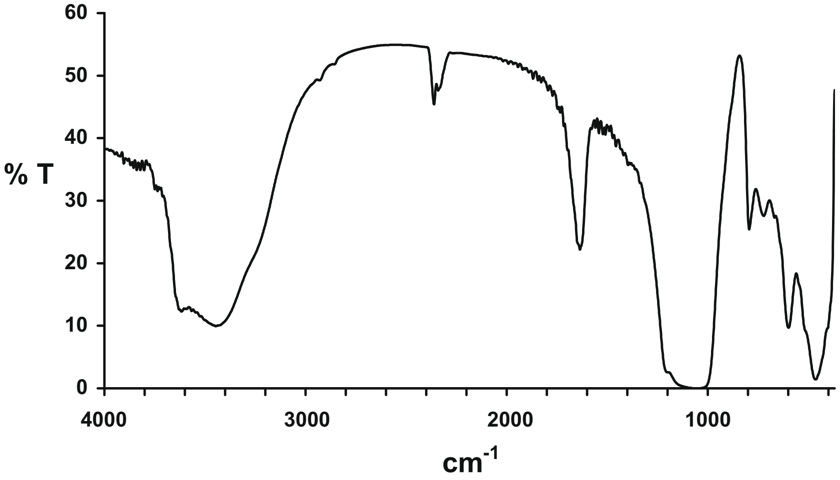

Fig. 2. FTIR spectra of raw zeolite.

tity of water that is required in order to prepare a cement paste of standard consistency as specified in EN 196-3. The blended cements demand more water than the relatively pure cements. The increase of the water demand is mainly attributed to the high fineness of zeolite (Table 2, d_{50} = 8.9 μm).

The initial and final setting time of zeolite cements is similar to the setting time of pure cement, in the case of CEM I 42.5 N (Table 3). In the case of CEM I 52.5 N, the addition of zeolite causes a slight increase of the setting time.

Figs. 3 and 4 show the compressive strength development of zeolite cements in relation to the cement replacement level, in the case of CEM I 42.5 N and CEM I 52.5 N, respectively. Concerning the use of CEM I 42.5 N, the addition of 20% w/w zeolite leads to lower cement strength at all ages, while the addition of 10% w/w zeolite seems to improve the 28 days and 90 days cement strength (Fig. 3). It is also observed that zeolite cements based on CEM I 52.5 N develop lower strength than pure cement at ages up to 28 days, while they develop higher strength than pure cement at the ages of 90, 180 and 360 days (Fig. 4).

Table 3
Physical properties of zeolite cements.

Sample	Water demand (w/w%)	Setting time (min)	
		Initial	Final
CEM I 42.5	25.6	125	185
CEM I 42.5 + 10% zeolite	27.4	120	180
CEM I 42.5 + 20% zeolite	28.4	125	175
CEM I 52.5	28.6	135	175
CEM I 52.5 + 10% zeolite	29.2	140	180
CEM I 52.5 + 20% zeolite	29.8	150	190

Fig. 5 shows the relative strength of zeolite cements in relation to curing age and the cement replacement level. The relative strength is the ratio of the strength of the zeolite cement to the strength of the pure Portland cement (PC), at each particular curing time. The strength development in PC is mainly depended on the hydration rate of clinker, while in PC-zeolite systems it depends on the combination of PC hydration and the pozzolanic activity of zeolite. Therefore, the relative strength versus time plots provide an insight into the rates of reaction in the blended system relative to the plain PC system [13]. According to the literature, the main factors that affect the strength development in blended cements are: (a) the filler effect, (b) the dilution effect and (c) the pozzolanic reaction of added materials with CH.

For 10% replacement of PC with zeolite, the relative strength at 1 day (Fig. 5) is almost 1 and this is mainly attributed to the filler effect that leads to an initial acceleration of PC hydration. For 20% replacement of PC with zeolite, at 1 day, the filler effect is surpassed by the dilution effect and this leads to lower relative strength than that observed in the case of 10% zeolite. The decrease of relative strength between 1 and 7 days is attributed to the dilution effect and the decrease is greater in the case of 20%

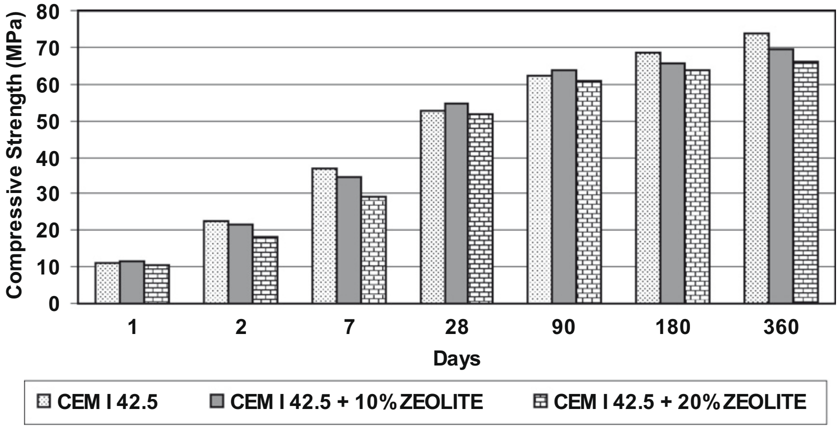

Fig. 3. Compressive strength development of zeolite cements in relation to the zeolite content (CEM I 42.5 N).

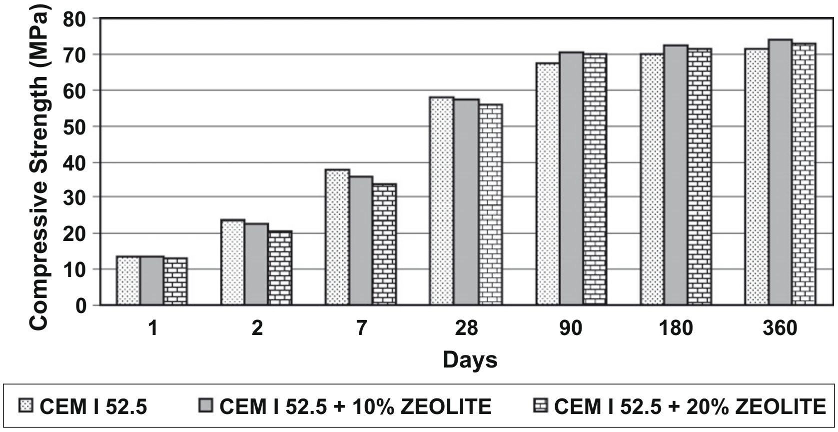

Fig. 4. Compressive strength development of zeolite cements in relation to the zeolite content (CEM I 52.5 N).

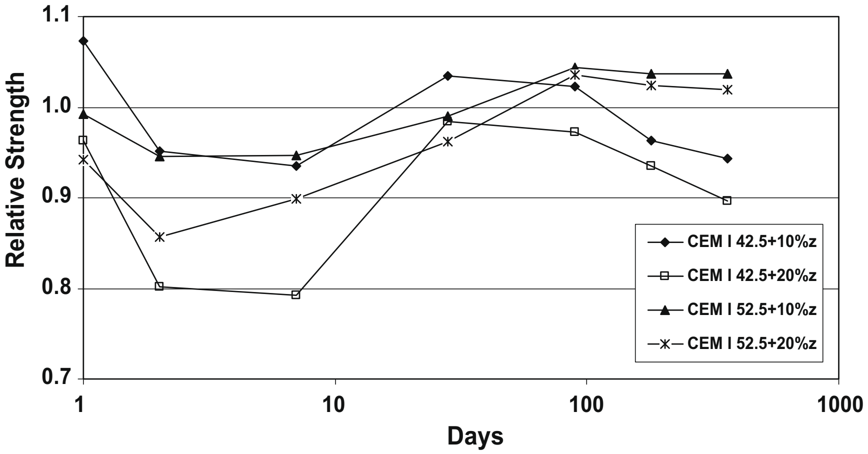

Fig. 5. Relative strength of zeolite cements.

replacement of PC with zeolite. Between 7 and 90 days the relative strength shows a clear increase, due mainly to the pozzolanic reaction of the zeolite. The increase of the relative strength is greater in the case of the blended cements based on CEM I 52.5 N. The acceleration of the pozzolanic reaction between 7 and 90 days is also confirmed by TGA measurements (see Section 3.3). Between 90 and 180 days, there is a decrease of the relative strength, due to the cessation of the pozzolanic reaction. At 360 days, cements based on CEM I 42.5 N have developed the 90–95% of the pure cement's strength, while in the case of zeolite cements based on the CEM I 52.5 N, the strength is slightly higher than that of the relative pure cement. This fact confirms that even long-term cement strength is affected by the zeolite in a positive way.

3.3. Hydration rate and products in zeolite cement pastes

The evaluation of the hydration rate in zeolite cement pastes was based on the TG/DTG curves and consists of the following steps:

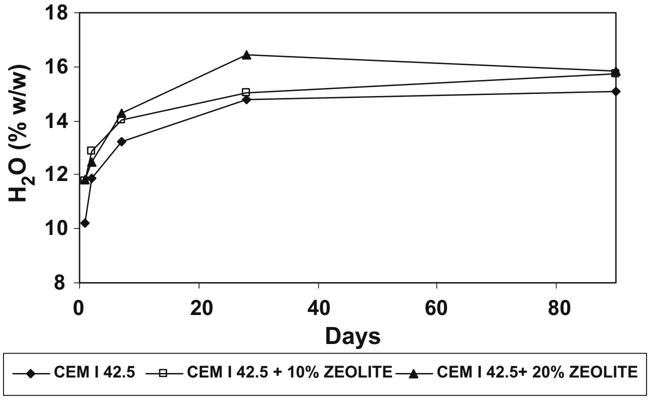

Fig. 6. Water of hydration products in zeolite cement pastes in relation to the hydration time.

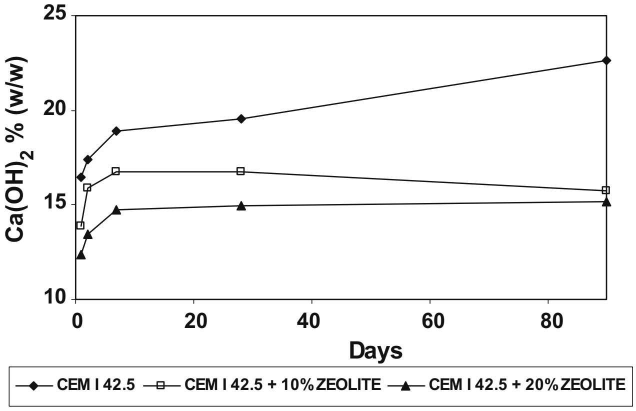

Fig. 7. $Ca(OH)_2$ in zeolite cement pastes in relation to the hydration time.

I. Determination of the total combined water: this is the total water incorporated in the cement paste. It corresponds directly to the weight loss up to 550 °C. The weight loss in the range 600–700 °C, if any, corresponds to the CO_2 of $CaCO_2$ (coming from the carbonation of $Ca(OH)_2$) and must be converted to the equivalent $Ca(OH)_2$ and then to equivalent H_2O.

II. Determination of the $Ca(OH)_2$: it is found by the weight loss in the range 400–550 °C, converted to calcium hydroxide and then added to the calcium hydroxide that has been carbonated.

III. Determination of water combined in the hydration products (other than calcium hydroxide): it corresponds directly to the weight loss up to 300 °C. Any changes of the water content in the hydration products indicate that the kind and/or the stoichiometry of these compounds have changed.

Figs. 6–8 present the water in the hydration products, the calcium hydroxide content and the total combined water of zeolite-CEM I 42.5 N pastes, in relation to the hydration age, respectively. The zeolite-CEM I 52.5 N pastes have a very similar behavior.

In the case of 10% zeolite, the decrease of $Ca(OH)_2$ content after 7 days indicates that the $Ca(OH)_2$ consumed in the pozzolanic reaction is more than the $Ca(OH)_2$ produced through the hydration reactions of the calcium silicate cement compounds. In the case of 20% zeolite, the $Ca(OH)_2$ content remains practically constant after 7 days, indicating that almost all of the $Ca(OH)_2$, produced afterwards, is consumed in the pozzolanic reaction. The water in hydration products is slightly higher in zeolite pastes, indicating that there is not great differentiation as far as the hydration products are concerned. As it is expected, the total combined water is lower in zeolite blended pastes, due to the lower $Ca(OH)_2$ content.

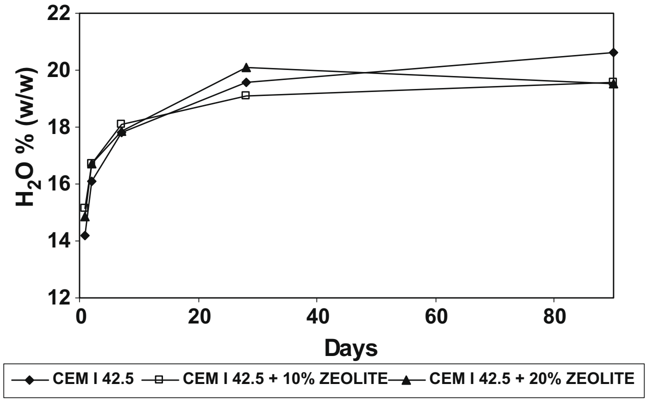

Fig. 8. Total combined water in zeolite cement pastes in relation to the hydration time.

The pozzolanic reactivity of zeolites has been related to their structure and composition. As it was reported, less siliceous zeolites seem to be more effective in reacting with Ca^{2+}, while more siliceous zeolites seem to be more effective in the development of compressive strength [14]. This is in agreement with our results. The studied zeolite has a hifh Si/Al ratio (approximately 4) and its contribution to the development of strength (Figs. 3 and 4) is more intense than its contribution to the consumption of $Ca(OH)_2$, (Fig. 7).

All pastes were examined by means of XRD in order to identify the hydration products in relation to the age of hydration and the zeolite content. As it is known, the principal hydration products in blended cements are essentially similar to those in pure Portland cement. Of course, in blended cement pastes, $Ca(OH)_2$ content is lowered, both by the dilution of clinker and the pozzolanic reaction. The hydration products of Portland cement do not have very clear diffraction peaks, due mainly to their semi-amorphous nature and the overlapping of the peaks of the hydrated and anhydrous compounds. Modifications of the composition of hydration products may probably occur in blended cements, but they cannot be clearly evaluated by means of XRD.

Fig. 9 shows the XRD patterns of the blended cement pastes after 6 months of hydration. In all samples, the only crystalline product is portlandite, while the anhydrous clinker phases have almost completely reacted. As it is seen, the characteristic peaks of zeolite have been completely disappeared, while the decrease of the $Ca(OH)_2$ content in the blended cement pastes is much higher than that justified by the dilution effect. These facts indicate that zeolite has reacted with $Ca(OH)_2$.

Fig. 10 presents the XRD patterns of zeolite cement pastes in relation to hydration age (sample: CEM I 52.5 N + 20% zeolite). A gradual increase of $Ca(OH)_2$ ($d \sim 4.9$, 3.1, 2.6, 1.9, 1.8 Å) content, accompanied by a corresponding decrease of the anhydrous calcium silicate compounds ($d \sim 5.9$, 3.01, 2.8, 2.7, 2.6, 2.4, 2.3, 2.2 Å) was observed, during the first 7 days of hydration. At higher age, the peaks of the cement anhydrous compounds are almost vanished. Since there is a clear decrease of the $Ca(OH)_2$ content, it is concluded that it was consumed in the pozzolanic reaction of the zeolite. This is also confirmed by the decrease of the main

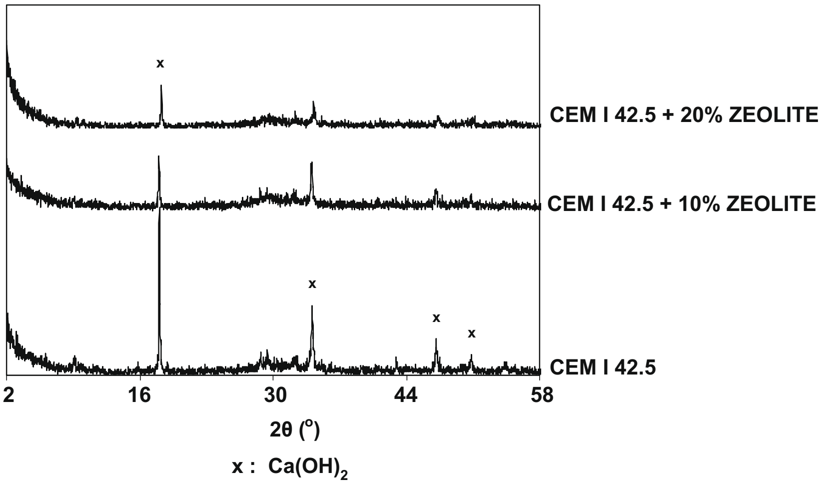

Fig. 9. XRD patterns of pastes after 6 months of hydration, in relation to zeolite content.

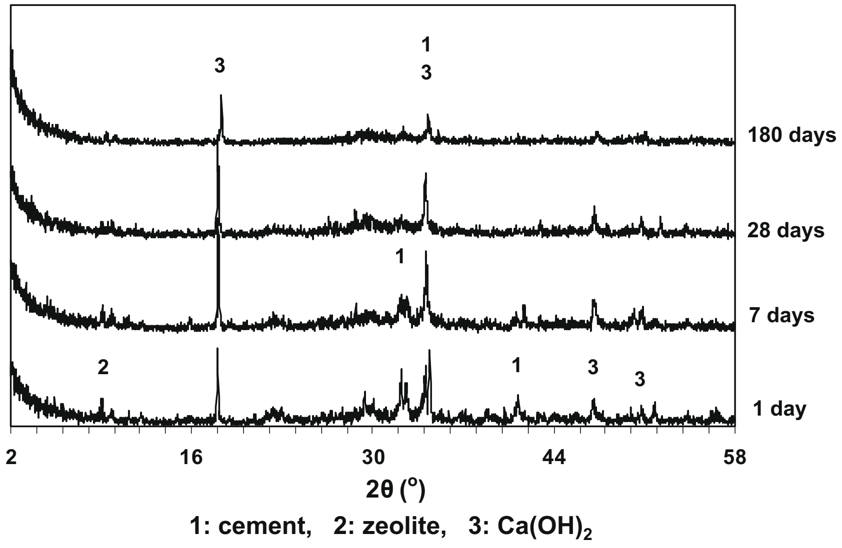

Fig. 10. XRD patterns of zeolite cement pastes in relation to hydration age (sample: CEM I 52.5 N + 20% zeolite).

zeolite peaks, especially after 28 days. The gradual increase of the background in the range 2θ: 25–35° is attributed to the formation of calcium silicate hydrates. The small peaks, observed after 6 months of hydration, at d = 3.39, 4.21 and 7.29 Å may be associated to gismodine ($CaAl_2Si_{12}O_8{\cdot}4H_2O$), a common product of the pozzolanic reaction.

The results drawn from each one of the above monitoring techniques are in good accordance with each other. It is confirmed that natural zeolite from Metaxades is a pozzolanic material that contributes to the strength development of zeolite-cement mixtures, the consumption of $Ca(OH)_2$ formed during the hydration of Portland cement and the formation of cement-like hydrated products.

4. Conclusions

The following conclusions can be drawn from this study:

- A complete mineralogical characterization of zeolites, from the Metaxades area in Greece, was performed using a combination of techniques. The material consists mainly of heulandite type-II. The total content of SiO_2, Al_2O_3 and Fe_2O_3 was approximately 82% w/w, which is typical of some other pozzolanic materials used in cement industry.
- The examined zeolite shows a good pozzolanic reactivity (0.64 g of $Ca(OH)_2$ per g of zeolite, according to Chapelle test).
- The blended cements demand more water than the relatively pure cements. The initial and final setting time of zeolite cements is almost similar to the setting time of pure cement.
- The addition of zeolite up to 20% w/w delays the strength development during the first 28 days. However at 360 days, cements based on CEM I 42.5 N have developed more than 90–95% of the pure cement's strength, while in the case of zeolite cements based on the CEM I 52.5 N, the strength is slightly higher than that of the relative pure cement.
- The incorporation of zeolite in cement contributes to the consumption of $Ca(OH)_2$ formed during the cement hydration and the formation of cement-like hydrated products.

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