Zeolite blended cements: evaluation of their hydration rate by means of thermal analysis

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Abstract In this work, the hydration rate and products of blended zeolite cements were studied for periods up to 360 days. Thermoanalytical methods (TG/DTG and DTA) were applied in order to evaluate the hydration rate of blended cements, while. X-ray diffraction and FTIR spectroscopy were used in order to identify the hydrated products. As it is concluded 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. The pozzolanic reaction of the zeolite is rather slow during the first days of hydration but it is accelerated after the 28 days.

Keywords Cement · Zeolite · Hydration

Introduction

Portland cement is mainly composed of calcium silicates and calcium aluminates, which react with water, in the presence of gypsum, producing a variety of hydrated compounds. Cement hydration is a complex physico-chemical process with many unclarified points. In general, calcium silicates react with water to mainly amorphous products (C–S–H), having CaO/SiO_2 ratio less than 3, and calcium hydroxide. Calcium aluminate compounds react with gypsum and water producing, gradually, calcium tri-sulfate hydrate (ettringite or AFt), calcium monosulfate hydrate (AFm) and calcium aluminate hydrates with a variety of compositions. X-ray diffraction has long been used for the recording of hydration progress and the identification of the hydrated products. Measurements are preferably made in pastes (cement + water) which are stored in water for specific periods of time [1].

The hydration rate of cement can be evaluated by measuring the mass loss of hydrated samples up to 800 °C by means of a Thermobalance [2–8]. The amount of calcium hydroxide (dehydroxylation peak ∼500 °C) is directly related to the amount of calcium silicates that have reacted with water. Calcium hydroxide is easily carbonated and transformed to calcium carbonate, therefore the amount of calcium hydroxide which is equivalent to calcium carbonate (decomposition peak ∼700 °C) must be counted in. The water bound in the hydrated products is removed in the temperature range 100–350 °C. The dehydration of pore water takes place at ∼100 °C, while water chemically bound in the hydration products is removed at higher temperatures according to the bond energy. There is a strong overlapping of DTA and DTG peaks in this area, however the total mass loss is a measure of the rate of hydration, while any changes of the number and shape of peaks indicate changes of the stoichiometry in the hydrated products.

Zeolitic tuffs have been widely used, as mixtures with lime, in construction since Roman times. Nowadays, there is a lot of discussion concerning the pozzolanic activity of natural zeolites and their incorporation in blended cements [9–13]. 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

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properties. 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 [9, 14, 15].

Large zeolite deposits of potential economic interest, are present in 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 [16].

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

Experimental

Materials

The zeolite, used in this work, comes from natural deposits at 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.

Blended cements were produced by replacing the Portland Cement with 10 mass/mass% and 20 mass/mass% 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

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

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
LOI	12.31	4.57	3.67

Table 2 Fineness characteristics of zeolite

d_{20}* (μm)	d_{50} (μm)	d_{80} (μm)
1.7	8.9	31.0

* d_i: diameter where i% of the powder (mass/mass) have size less than d_i

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.

Techniques

Thermoanalytical methods (TG/DTG and DTA) were applied in order to evaluate the hydration rate of blended cements, while X-ray diffraction and FTIR spectroscopy were used in order to identify the hydrated products.

Differential thermal analysis (DTA) and thermogravimetric analysis (TG/DTG) was obtained simultaneously using a Mettler Toledo 851 instrument. The samples were heated from 20 to 1,200 °C at a constant rate of 10 °C/min in an atmosphere of carbon dioxide free nitrogen, flowing in 50 cm^3/min.

X-ray powder diffraction patterns were obtained using a Siemens D-5000 diffractometer, with Ni-filtered, CuKa$_1$ radiation ($\lambda = 1.5405$ 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 4,000 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.

Results and discussion

Hydration rate

A complete mineralogical characterization of zeolites can be performed, based on XRD, TG/DTG and FTIR measurements [12]. As it was found, the zeolite, used in this work, consists mainly of "heulandite type II", while feldspars, cristobalite and quartz contribute in minor amounts.

Figure 1 presents the TG and DTG curves of the pure cement (CEM I 42.5 N) after 1 and 28 days of hydration. The evaluation of the hydration rate, on the basis of the TG-DTG curves, consists of the following steps:

i. Determination of the total combined water: this is the total water incorporated in the cement paste. It corresponds directly to the mass loss up to 550 °C. The mass loss in the range 600–700 °C, if any,

corresponds to the CO_2 of $CaCO_3$ and must be converted to the equivalent $Ca(OH)_2$.

ii.   Determination of the $Ca(OH)_2$: it is found by the mass loss, due to the dehydroilation of $Ca(OH)_2$, in the range 400–550 °C.

iii. Determination of water combined in the hydration products (other than calcium hydroxide): it corresponds directly to the mass loss up to 350 °C. Any changes of the water content in the hydration products, when calculated on cement calcined mass basis, indicate that the kind and/or the stoichiometry of these compounds have changed.

iv.   Determination of carbonation: The mass loss in the range 600–700 °C, if any, corresponds to the CO_2 from the decomposition of $CaCO_3$, that was formed through the carbonation of $Ca(OH)_2$. The mass loss in this stage must be converted to the equivalent $Ca(OH)_2$ and must be taken into account in step ii.

v.   Tracing of modifications in hydrated products: Hydrated Portland cement is a complex mineral comprised mainly of calcium silicate hydrates (C–S–H). C–S–H is nearly an amorphous material, containing water of various energy levels which is removed in various stages. These stages cannot be traced on the thermogravimetric curve, due to extensive overlapping, but they are shown on the differential thermogravimetric curve.

As it is seen in Fig. 1, only one of the samples (the sample hydrated for 28 days), was carbonated. The carbonation of the paste is an accidental event that may take place during the curing of the paste or during the grinding of the paste previously to the TG measurement. The DTG
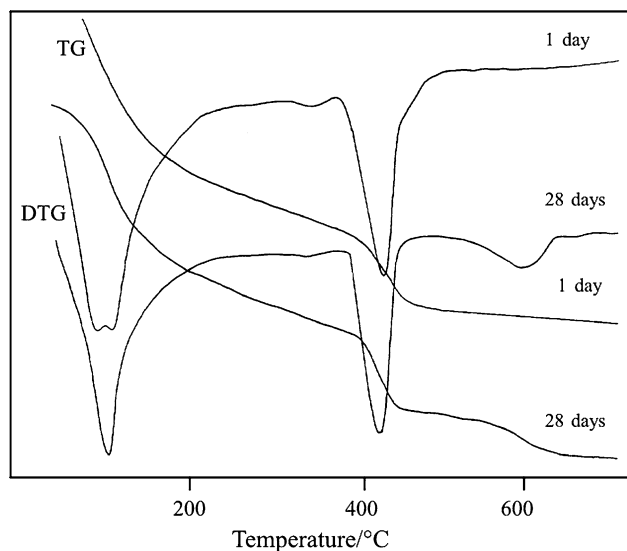
curves (up to 200 °C) indicate the difference of the hydration products which is due to the different age of hydration.

In zeolite-cement pastes the $Ca(OH)_2$ content is expected to be lower than in the pure cement pastes, due either to the dilution effect (10% and 20% respectively) or to the pozzolanic reaction. In order to clarify whether this decrease is due to the pozzolanic reaction or to the decrease of clinker content in the zeolite cements, the results from the TG measurements were expressed on cement oxide mass basis, present in the calcined mass of each sample. The equation used for the calculation of g of $Ca(OH)_2$ per g of pure cement (CEM I 42.5 or CEM I 52.5) is the following: $a = b \times (100 - c)]/((100 - d) \times e)$ where

a: the content of lime on the basis of clinker oxides mass
b: the lime content (mass/mass%) in the paste as taken from the TG measurement
c: the mass loss of anhydrous blended cement at 1,100 °C (mass/mass%)
d: the mass loss of the paste at 1,100 °C (mass/mass%)
e: the cement content in the zeolite blended cement (100, 90, 80%) Similar equations were applied for the calculation of total combined water and water in hydrated products. The results are presented in Figs. 2, 3, 4, 5, 6, 7, 8.

Figures 2, 3, 4 present the content of the water in hydrated products, the $Ca(OH)_2$ and the total combined

Fig. 1 TG and DTG curves of the pure cement (CEM I 42.5 N) after 1 and 28 days of hydration
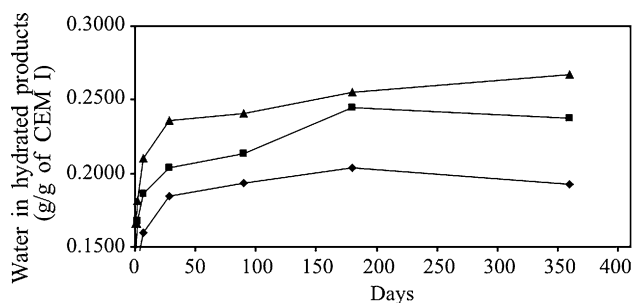

Fig. 2 Water of hydrated products in the zeolite-CEM I 42.5 N pastes, in relation to the hydration age and the zeolite content
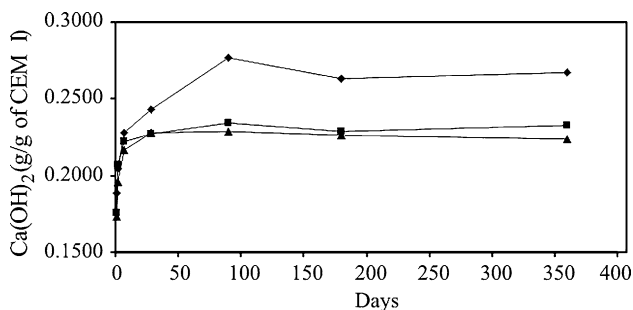

Fig. 3 $Ca(OH)_2$ content in the zeolite-CEM I 42.5 N pastes, in relation to the hydration age and the zeolite content

water per gram of clinker, in the zeolite-CEM I 42.5 N pastes, in relation to the hydration age and the zeolite content. The water in hydration products is higher in zeolite pastes, indicating that the presence of zeolite affects the amount and/or the kind of hydration compounds (Fig. 2). This is in agreement with XRD studies which indicated the formation of calcium aluminosilicate compounds in cement-zeolite pastes. Besides, the consumption of portlandite by pozzolanic materials shifts the hydration reactions of calcium silicates to the right, causing, in this way, the increase of hydration rate and therefore of the hydrated products.

The reduction of the portlandite content per gram of clinker (Fig. 3) proves the pozzolanic activity of the zeolite. As it is seen, the pozzolanic reaction of the zeolite is rather slow during the first days of hydration and is accelerated later. The increase of the zeolite content in the blended cement does not seem to increase further the consumption of portlandite. The $Ca(OH)_2$ content in all samples, remains practically constant after 90 days, indicating that most of the calcium silicate compounds have already reacted with water (in cement pastes) and that the pozzolanic reaction has been almost completed (in zeolite-cement pastes). According to Fig. 3, 6–7% of the produced portlandite takes part in the pozzolanic reaction. On the basis of hydrated cements, the $Ca(OH)_2$ content in cements containing 10–20% of zeolite, is 14–23% lower than in pure cement pastes, at 28 days and 19–34% lower at 360 days (TG measurements). This is very important, from the practical point of view, since portlandite is a reactive compound which may cause durability problems through carbonation, leaching etc. As it is expected, the total combined water (Fig. 4) in zeolite blended pastes is generally higher than in pure cement since the decrease of the $Ca(OH)_2$ content is overbalanced by the increase of the water content in the hydration products.

Figures 5, 6, 7 present the content of the water in hydrated products, the $Ca(OH)_2$ and the total combined water in the zeolite-CEM I 52.5 N pastes, in relation to the hydration age and the zeolite content. As it is seen the zeolite-CEM I 52.5 N pastes have a similar behavior as the zeolite-CEM I 42.5 N pastes, indicating that the type of cement does not affect the pozzolanic activity of zeolite.

Hydration products

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 as those in pure Portland cement. Of course, in blended cement pastes, $Ca(OH)_2$ content is lowered, due to the dilution of clinker and the pozzolanic
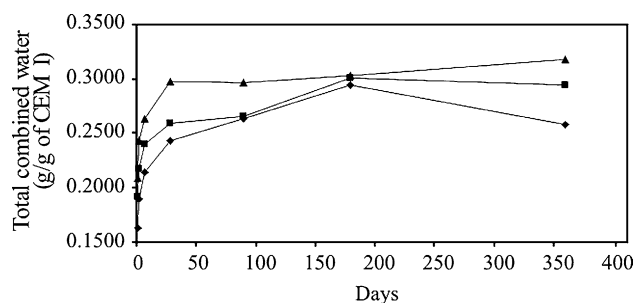

Fig. 4 Total combined water in the zeolite-CEM I 42.5 N pastes, in relation to the hydration age and the zeolite content
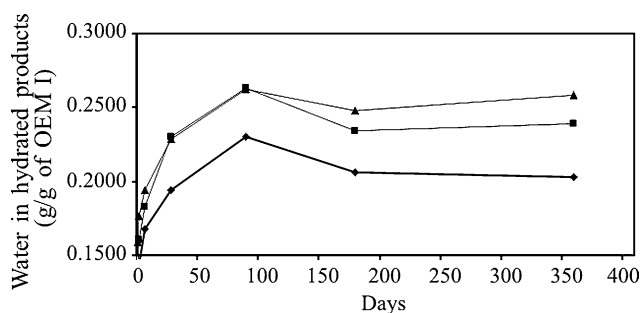

Fig. 5 Water of hydrated products in the zeolite-CEM I 52.5 N pastes, in relation to the hydration age and the zeolite content
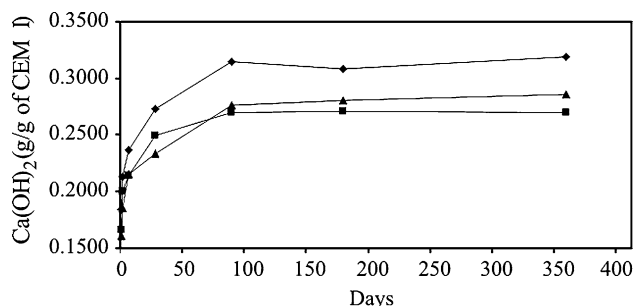

Fig. 6 $Ca(OH)_2$ content in the zeolite-CEM I 52.5 N pastes, in relation to the hydration age and the zeolite content
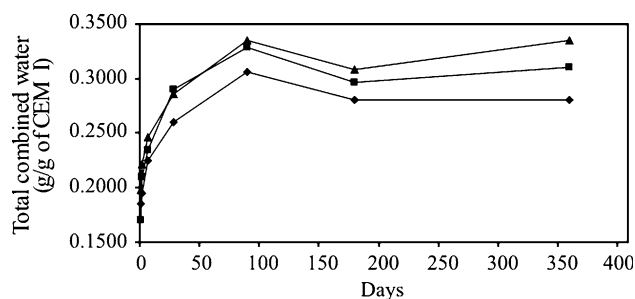

Fig. 7 Total combined water in the zeolite-CEM I 52.5 N pastes, in relation to the hydration age and the zeolite content
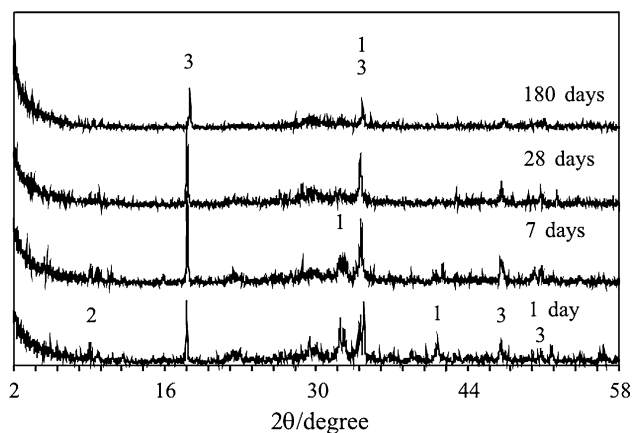
Fig. 8 XRD patterns of zeolite cement pastes in relation to hydration age (sample: CEM I 52.5 N + 20% zeolite)

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.

Figure 8 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 ∼ 4.9, 2.6, 1.9, 1.8 Å) content, accompanied by a corresponding decrease of the anhydrous calcium silicate compounds (d ∼ 2.8, 2.7, 2.6, 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 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.

Figure 9 presents the FTIR spectra of the zeolite cement (CEM I 42.5 +20% zeolite) in relation to the hydration age. The vibration intensities at 1,640 and 3,450 cm^{-1} indicates the formation of calcium silicate hydrates. Any peaks in the region 630–760 cm^{-1} generally correspond to units such as the aluminosilicate ring and cage structures and indicate the presence of crystalline zeolitic phases. The disappearance of these peaks and the shift of the peak at 1,045 cm^{-1} towards lower wavenumber, indicate the deformation of the zeolitic lattice, due to the pozzolanic reaction. The O–H vibration at 3,644 cm^{-1} is associated with the presence of $Ca(OH)_2$ and, in the case of pure
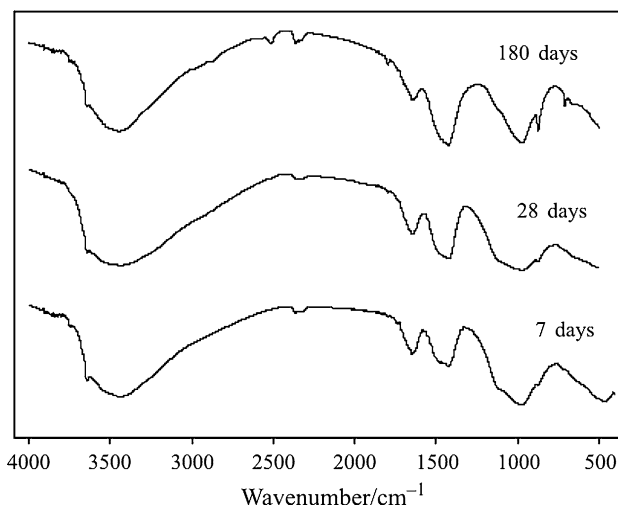

Fig. 9 FTIR spectra of the zeolite cement pastes in relation to the hydration age (sample:CEM I 42.5 + 20% zeolite)

cements, it increases proportionally with the hydration age. However, in the zeolite cement, this vibration remains constant indicating that most of the $Ca(OH)_2$ produced after the first 7 days of hydration, is consumed in the pozzolanic reaction of zeolite. The TG measurements, also, show that the $Ca(OH)_2$ in the zeolite cement remains practically constant after the first days of hydration (Fig. 3).

All the above measurements show that the zeolite coming from Metaxades area, is a pozzolanic material that participates in the hydration process of Portland cement. Most natural pozzolanas are of volcanic origin and their usual active constituents are amorphous phases rich in silica. Zeolites show a high reactivity, although they have an almost perfect crystalline structure. This may be due to the correlation between the reactivity and the capability of cation exchange. Materials, capable of cation exchange, are found to be, in some cases, more reactive than those containing vitreous constituents [17]. In any case, the efficiency of zeolites, as cement main constituents, is to be evaluated on the basis of physical and mechanical properties of the zeolite blended cements. Our measurements, that will be published soon, have shown that the addition of zeolite up to 20 mass/mass%, increases the water demand but does not affect the setting time and the 1 year compressive strength of the blended cement. More work must be done on the durability of these cements and concrete made from zeolite blended cements.

Conclusions

Thermal analysis, and especially TG/DTG, is a very useful technique for the study of the hydration in blended

cements. The calculation of TG raw data on clinker oxide mass basis provides a quantitative evaluation of hydration rate and pozzolanic reactivity in cements, with or without substitution by other main constituents. The application of this calculation mode, in the case of a zeolite-cements, confirms that zeolite is a pozzolanic material that contributes to the consumption of $Ca(OH)_2$ formed during the cement hydration and the formation of cement-like hydrated products. The pozzolanic reaction of the zeolite is rather slow during the first days of hydration but it is accelerated after the 28 days. The hydration products in the zeolite blended cements are similar to those in pure cement.

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