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CHARACTERIZATION AND POZZOLANIC ACTIVITY OF THERMALLY TREATED ZEOLITE

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The pozzolanic reactivity of thermally treated zeolites was studied on the basis of the Chapelle test combined with X-ray diffraction (XRD) and Fourier Transform (FTIR) spectroscopy, as well as thermogravimetric analysis (TG/DTG) and differential thermal analysis (DTA). The raw zeolite samples are from the Pentalofos area, Thrace, NE Greece. Their main mineral constituent is 'heulandite type-II', an intermediate type of the heulandite-clinoptilolite isomorphous series. Calcination of the samples was carried out up to 400, 500, 600, 700 and 1000°C for 15 h. The changes were recorded using the above methods. The deformation of the zeolite crystal lattice starts at about 400°C and proceeds as the temperature of thermal treatment rises. The thermal treatment of zeolite at 400°C improves its pozzolanic reactivity and accelerates the reaction with $Ca(OH)_2$.

Keywords: *calcination, pozzolanic activity, zeolite*

Introduction

Zeolites, a type of natural pozzolanic material, have been used in producing blended cement and concrete. They are framework aluminosilicate minerals with a cage-like structure that offers large (internal and external) surface areas. The high surface area is the base of high reactivity. Both clinoptilolite and heulandite are monoclinic zeolites (C2/*m* group) with the following unit cell parameters: a=17.70 Å, b=17.94 Å, c=7.42 Å, β=116° 24 and a=17.62 Å, b=17.91 Å, c=7.39 Å, β=116° 18, respectively [1, 2], characterized by large intersecting open channels of ten- and eight-membered rings of tetrahedra. Clinoptilolite and heulandite are distinguished on the basis of the Si/Al ratio. Si/Al >4 characterizes clinoptilolite while Si/Al<4 characterizes heulandite.

Zeolitic tuffs, mixed with lime, have been widely used 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. It is generally considered that zeolite contributes to concrete strength mainly through the pozzolanic reaction with $Ca(OH)_2$ [3–8]. According to ASTM C595, a pozzolan is defined as 'a siliceous and aluminous material which in itself possesses little or no cementitious value but in presence of moisture chemically reacts with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties' [9]. The pozzolanic properties of zeolites are due to the reactive SiO_2 and Al_2O_3, which can react with $Ca(OH)_2$ and be converted into C–S–H-gel and hydrated aluminate phases. The pozzolanic activity is an index of the extent of the pozzolan–$Ca(OH)_2$ reaction, and it is a primary factor in assessing the suitability of the different materials as pozzolans [10].

Thermoanalytical methods (TG/DTG, DTA and DSC) have been widely used for the evaluation of the pozzolanic activity of various materials [11–15].

Cement is a system composed of numerous minerals that react with water at different rates giving hydration products of different composition and crystallinity. Calcium hydroxide is one of the hydration products and precipitates from the saturated, high pH, pore solution. When a cement-water mixture comes in contact with a zeolite the aluminosilicate network of the last starts decomposing under the attack of OH^- in a high pH solution according to the following Eqs (1), (2).

$$\equiv Si{-}O{-}Si\equiv + 6OH^- \rightarrow 2[SiO(OH)_3]^- \qquad (1)$$

$$\equiv Si{-}O{-}Al\equiv + 7OH^- \rightarrow [SiO(OH)_3]^- + [Al(OH)_4]^- \qquad (2)$$

The depolymerised species, such as $[SiO(OH)_3]^-$ and $[Al(OH)_4]^-$, enter the solution and react with Ca^{2+}, forming hydrated calcium aluminosilicate compounds, very similar to those formed during the hydration of cement [16]. As a result of the pozzolanic reaction in the presence of zeolite the amount of C–S–H increases, the

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micro-structure of hardened paste is significantly improved and the performance of the cement and concrete is positively affected.

Upon heating, zeolites undergo a series of chemical and structural changes (loss of water, modification of cage dimensions etc.) until they are largely converted to an X-ray amorphous material. It was suggested that the thermal behaviour of the zeolite framework is related to the Al concentration. Clinoptilolite (Si/Al>4) is thermally stable at temperature in excess of 450°C, while heulandite (Si/Al<4) undergoes structure collapse below 450°C.

In this paper, we study the pozzolanic activity of thermally treated zeolites in order to find out if the structural deformation of the mineral affects its reactivity. The positive effect of structural deformation on the pozzolanic activity has been recorded in the case of other aluminosilicate materials, the most known of which is kaolinite. Kaolinite, although not a pozzolanic material as it is, turns out to be one of the most reactive pozzolans after thermal treatment. Zeolites were chosen because their thermal treatment is accompanied by a structure collapse which is expected to improve their reactivity.

Experimental

Materials

Zeolites from the Pentalofos area, Thrace, NE Greece, are examined in order to study their pozzolanic activity after their thermal treatment up to 400, 500, 600, 700 and 1000°C, for 15 h. The chemical composition of the zeolite is shown in Table 1.

Mixtures of zeolite and chemical grade $Ca(OH)_2$ (mass ratio 1:1) were mixed with water in order to prepare pastes. A water-to-solid ratio (W/C) of 0.6 was retained for all pastes and deionised water was used. The pastes were put in plastic containers, sealed hermetically and wet-cured at 20°C. Samples hydrated for periods of 2, 7, 28 and 90 days were subjected to acetone and isopropyl ether treatment and then dried for 24 h in vacuum. The hydrated samples were ground to pass through a 54 μm sieve.

Techniques

The zeolites used were studied by means of X-ray diffraction (XRD), Fourier Transform (FTIR) spectroscopy, thermogravimetric analysis (TG/DTG) and differential thermal analysis (DTA). These techniques were also applied in order to identify the products of the pozzolanic reactions.

X-ray powder diffraction patterns were obtained using a Siemens D-5000 diffractometer, $CuK_{\alpha 1}$ radiation (λ=1.5405 Å), operating at 40 kV, 30 mA. The IR measurements were carried out using a Fourier Transform IR (FT-IR) spectrophotometer (PerkinElmer 880). The FTIR spectra in the wavenumber range from 400 to 4000 cm^{-1} were obtained in air atmosphere 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) were obtained simultaneously using a Mettler Toledo 851 instrument. The samples were heated from 20 to 1200°C at a constant rate of 10°C min^{-1} in an atmosphere nitrogen (free of carbon dioxide), flowing in 50 cm^3 min^{-1}.

Chapelle test is a quick test for the evaluation of the pozzolanic activity of a material. 1 g 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 and the free $Ca(OH)_2$ is determined by means of sucrose extraction and titration with a HCl solution. Free $Ca(OH)_2$ was also measured in the $Ca(OH)_2$–zeolite pastes after varying time of curing.

Results and discussion

Characterization of the raw and thermally treated zeolites

From the combined study of the raw and thermally treated zeolites by XRD, DTA, TG, DTG and FTIR it is concluded that:

- According to the XRD study, the main mineral constituent is 'heulandite type-II', based on the intensities of the d=8.99 Å (020) and d=3.98 Å (004) reflections. Furthermore, after heating of the raw material up to 400°C for 15 h, these characteristic reflections became weaker, while after heating up to 500°C for the same time, they entirely disappeared (Fig. 1), indicating that deformation of the crystal lattice starts before 400°C and is completed at ~500°C. Feldspars, micas, quartz, cristobalite and smectites contribute in minor amounts. After the calcination of the raw zeolites up to 1000°C for 15 h, the only reflections remained are those of cristobalite (d=4.09, 2.51 Å) and feldspars (d=3.20 Å). The TG/DTG curves (Fig. 2)

Table 1 Chemical composition of zeolite (% mass/mass)

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
67.24	12.66	0.15	0.49	3.01	0.48	1.62

Table 2 Mass loss of zeolite at different temperature ranges (% mass/mass)

25–100°C	100–200°C	200–300°C	300–400°C	400–500°C	500–600°C	600–1000°C
3.96	4.01	2.32	1.72	0.95	0.62	0.52

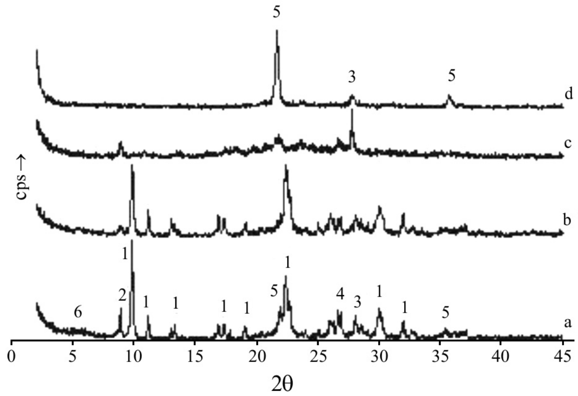

Fig. 1 XRD patterns of raw and thermal treated samples a – raw, b – 400°C, c – 500°C and d – 1000°C 1 – Zeolite, 2 – Muscovite, 3 – Feldspars, 4 – Quartz, 5 – Cristobalite, 6 – Smectite

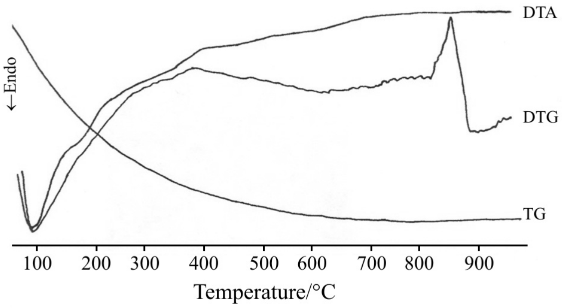

Fig. 2 TG/DTG and DTA curves of a representative zeolite sample from Pentalofos

show a continuous mass loss during heating up to 700°C, due to the loss of the hygroscopic water and the loss of the water residing in the channels and the cavities of the zeolite framework. The great endothermic reaction at ~100°C, as well as the dehydration rate of the zeolite, in the temperature range from 100 to 400°C (Table 2), are characteristic of the ‘heulandite type-II’, taking into consideration that the dehydration rate for the clinoptilolite type zeolites is much higher [17, 18]. On the other hand, as the temperature rises, amorphous or strongly disordered phases can be formed between the subsequent crystalline phases during their transformation at higher temperatures. These transformations are recognized by the exothermic effects at about 880°C.

- In the FTIR diagram of the raw sample (Fig. 3), the band at exactly 1045 cm^{-1} confirms that the zeolite is ‘heulandite type-II’ as it appears in a position between clinoptilolite (1059 cm^{-1}) and heulandite (1022 cm^{-1}). This band is due to the T–O stretching vibration, depends on the Al/Si ratio and is significant for estimating the Al^{III} content in the crystalline framework (determinative for the Al atoms per formula unit). Besides, the exact position of the vibration at 597 cm^{-1} indicates, also, the presence of ‘heulandite type-II’, considering that clinoptilolite gives a peak at 602 cm^{-1} and heulandite gives a peak at 594 cm^{-1} [19]. The vibrations in the region 1600–3700 cm^{-1} are assigned to the presence of zeolite water. The isolated OH stretching (~3620 cm^{-1}) is attributed to interaction of the water hydroxyl with the cations. The other bands are attributed to the hydrogen bonding of the water molecule to surface oxygen (~3440 cm^{-1}) and to the bending mode of the water (~1640 cm^{-1}).
- The FTIR spectra of the thermally treated samples (Fig. 3) shows the following changes: After heating up to 400°C, the 3447, 1638, 1045 and 466 cm^{-1} vibrations, significantly decrease while the vibration at 597 cm^{-1}, disappears. This is attributed to a heat-collapsed structure with an identical tetrahedral framework topology, but strongly altered T–O–T angles [20]. After heating up to 500, 600 and 700°C, the bands at 3447, 1638, 1045 and 466 cm^{-1}, further decrease. After heating up to 1000°C, further decrease of the bands at 1045 and 466 cm^{-1}, is observed.

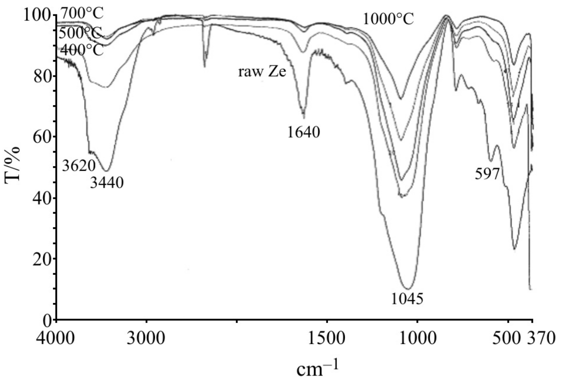

Fig. 3 FTIR spectra of raw and thermal treated zeolites

The above changes indicate that the deformation of the crystal lattice starts at about 400°C and proceeds as the temperature of thermal treatment rises.

Pozzolanic activity (Chapelle test)

Table 3 presents the amount of $Ca(OH)_2$ consumed per gram of raw and thermally treated zeolite, during the pozzolanic reaction (Chapelle test). According to

Table 3 Reacted Cs$(OH)_2$ g/g zeolite (Chapelle test)

Sample	$Ca(OH)_2$ (g/g zeolite)
Raw zeolite	0.5550±0.005
Zeolite treated at 400°C	0.6075±0.005
Zeolite treated at 500°C	0.5793±0.005
Zeolite treated at 600°C	0.5604±0.005

Chapelle test, 0.555 g of $Ca(OH)_2$ are consumed per g of raw zeolite. The thermal treatment of zeolite seems to improve its reactivity, as the amount of reacted $Ca(OH)_2$ increases as the temperature rises. The zeolite treated at 400°C has the higher reactivity (0.61 g $Ca(OH)_2$ per g of zeolite).

Hydration of zeolite–$Ca(OH)_2$ mixtures

The hydrated zeolite-$Ca(OH)_2$ pastes were examined by means of XRD, FTIR and TG-DTG, after curing for 2, 7, 28 and 90 days. The first two techniques were applied in order to identify the hydrated compounds while the third one was applied to evaluate the reaction rate between $Ca(OH)_2$ and zeolite. Figure 4, presents some representative TG and DTG curves of zeolite–$Ca(OH)_2$. The following three peaks are observed:

- An endothermic peak in the temperature range 100–300°C related to the dehydration of calcium aluminosilicate hydrates. It clearly increases with hydration time.
- An endothermic peak in the temperature range 400–550°C, attributed to the $Ca(OH)_2$ decomposition. This peak decreases with increasing hydration time, indicating the progress of pozzolanic reaction (consumption of $Ca(OH)_2$ by zeolite).
- An endothermic peak at the temperature 680–750°C attributed to the $CaCO_3$ decomposition. The carbonation of the paste is an accidental event that may take place during the preparation of the paste or during the grinding of the paste previous to the TG measurement. 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 $Ca(OH)_2$.

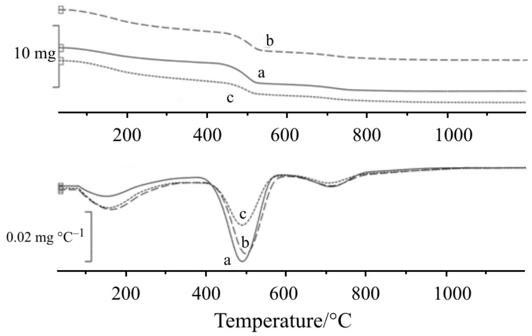

Fig. 4 TG-DTG curves of zeolite–$Ca(OH)_2$ pastes after a – 2, b – 7 and c – 28 days hydration

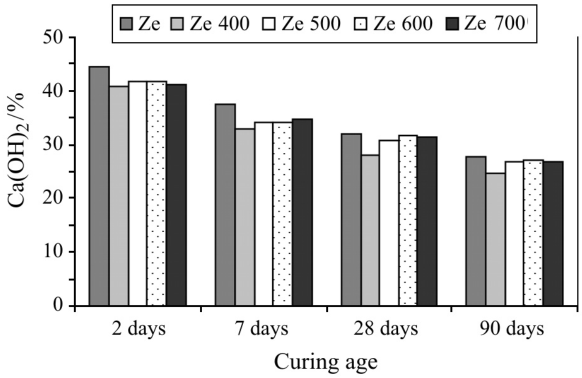

Fig. 5 $Ca(OH)_2$ content in the zeolite–$Ca(OH)_2$ pastes in relation to the temperature of thermal treatment and the curing time

Figure 5, presents the amount of the $Ca(OH)_2$ that has remained in the paste, in relation to the temperature of thermal treatment of zeolite and the curing time of the pastes. For all the pastes, it is obvious that the consumption of $Ca(OH)_2$ increases with the time. As it is shown, the zeolite treated at 400°C shows the higher reactivity. These results are in good agreement with the results of the Chapelle test.

The products of the pozzolanic reaction

Usually, the products of the pozzolanic reaction belong to the heulandite group ($CaAlSi_7O_{18}\cdot 6H_2O$) and it is difficult to be distinguished from the compounds of the unreacted zeolite. However, the increased background in the 2θ range 25–35° and the small peaks at *d*:2.283 Å and *d*:3.110 Å, in the XRD pattern of zeolite–$Ca(OH)_2$ mixture, indicate the formation of calcium silicate hydrates (probably $Ca_6Si_3O_{12}\cdot H_2O$) and prove the decomposition of the zeolitic structure and the participation of the zeolite in the pozzolanic reaction [21].

The above remarks are also confirmed by the FTIR spectra of the zeolite–$Ca(OH)_2$ pastes (Fig. 6). The increase of the vibration intensities at 1640 and 3450 cm^{-1} indicates the formation of calcium silicate hydrates, while the disappearance of the peak at 525 cm^{-1} and the shift of the peak at 1045 cm^{-1} towards lower wavenumber, indicate the deformation of the zeolitic lattice due to the pozzolanic reaction. It must be noted that the same hydration products have been found in the mixtures of raw zeolites and cement [21]. It seems that thermal treatment of zeolite does not alter the kind of the products of the pozzolanic reaction. The above remarks were also confirmed by the XRD and FTIR measurements in the solid residue of Chapelle test.

All the above measurements and observations lead to the conclusion that the thermal treatment of zeolite at 400°C improves its pozzolanic reactivity. This effect is attributed to a heat-collapsed structure with strongly al-

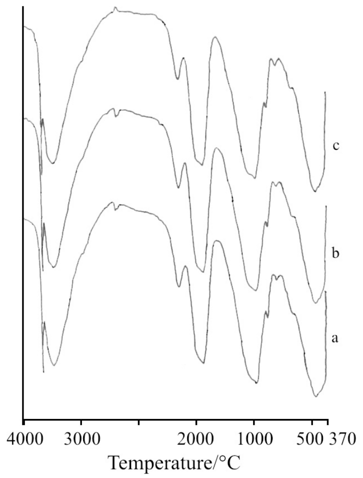

Fig. 6 FTIR spectra of hydrated zeolite–$Ca(OH)_2$ pastes after 28 days hydration. a – raw zeolite-$Ca(OH)_2$ paste, b – thermally treated at 400°C zeolite–$Ca(OH)_2$ paste, c – thermally treated at 500°C zeolite–$Ca(OH)_2$ paste

tered T–O–T angles. The high temperature dehydration results a heat-collapsed structure, characterized by a change in cell dimensions, because the dominant channel cations migrate to sites closer to the channel wall. These changes have been previously reported [20]. As a result, the structure is less stable and therefore more reactive. However this effect is not as strong as in the case of other aluminosilicate materials (e.g. kaolinite). It must be noted that the high reactivity of metakaolinite is also connected to the change of Al^{3+} coordination from octahedral in kaolinite to tetrahedral in metakaolinite (tetrahedral Al^{3+} is generally more reactive than octahedral Al^{3+}) [22]. The increase of the reactivity of zeolite at 400°C is due to the initial deformation of its structure. The deformation also proceeds at higher temperature but the reactivity does not further increase. This may be due to the correlation between the reactivity and the capability of cation exhange. As it is known, materials containing zeolites, capable of cation exchange, are more reactive than those containing vitreous constituents [10]. The thermal treatment of zeolite at high temperature increases the fraction of amorphous phase but also reduces the ion exchange capability of the material.

Conclusions

- A complete mineralogical characterization of raw and thermally treated zeolites, from the Pentalofos area, Thrace, NE Greece, was performed using a combination of techniques. The main constituent of the raw material is 'heulandite type II'. Feldspars, micas, quartz, cristobalite and smectites are minor constituents. All the changes recorded during the thermal treatment indicate that the deformation of the crystal lattice starts. The above changes indicate that the deformation of the crystal lattice starts at about 400°C, and proceeds as the temperature of thermal treatment rises.
- The thermal treatment of zeolite at 400°C, improves its pozzolanic reactivity and accelerates the reaction with $Ca(OH)_2$, but further calcination has a negative effect.
- Hydrated calcium aluminosilicate compounds were identified as the products of the reaction between calcined zeolite and $Ca(OH)_2$. There are no indications that the thermal treatment of zeolite alters the products of the above reaction.

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