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Characteristics of calcined natural zeolites for use in high-performance pozzolan blended cements

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HIGHLIGHTS

- Effects of calcination on properties of natural zeolites were investigated.
- Physical, mineralogical and pozzolanic properties were determined.
- Calcined forms showed less water demand and higher strength activity in blended cements.
- Strength performance was attributed to the porosity and pore size distribution.

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ABSTRACT

Two natural zeolites with different characteristics were calcined at various temperatures in order to improve the benefits provided by their use in blended cements as cement replacement material. Natural zeolites were firstly characterized for their crystallinity by X-ray diffraction analysis, specific surface area by nitrogen absorption, and pozzolanic activity by electrical conductivity method, before and after the calcination. In order to assess the performance of calcined natural zeolite as cement replacement material, blended Portland cement pastes and mortars with raw and calcined zeolites were tested for their water requirement, free lime content, pore size distribution and compressive strength. The experimental results indicated that calcined zeolites are more desirable with lower water requirement and higher strength performance as cement replacement material than the raw zeolites. Blended cement with calcined natural zeolite showed higher compressive strength performance, when compared to that with the raw zeolite due to decreased porosity and refined pore structure of the hardened cementitious system.

1. Introduction

Use of supplementary cementing materials (SCMs) in concrete mixtures or blended cements provides many benefits in the fresh and hardened properties of concrete, such as improved workability, reduced heat of hydration, increased ultimate strength and enhanced durability. Fly ash, finely-ground slag, silica fume and natural pozzolans are commonly used SCMs in blended cements and concrete mixtures.

Natural pozzolans (e.g. volcanic ash, volcanic tuff, diatomaceous earth, and calcined clays and shales) are the wide range of raw or calcined materials having pozzolanic property. Calcination (thermal treatment) is applied on clays and shales with little or no pozzolanic reactivity in order to provide pozzolanic property by altering crystal structure. Metakaolin as a highly reactive SCM, for instance, is produced by calcination of kaolin clay at a temperature in the range of 650–800 °C [1].

Natural zeolites are crystalline aluminosilicate minerals having similar chemical composition to clay minerals; however they have a three-dimensional structured framework in contrast to flat layered structure of clay minerals. Natural zeolites are known as possessing considerable pozzolanic activity, and used in blended cements and concrete mixtures as an SCM [2–12]. Uzal et al. [13] showed that the clinoptilolite-type zeolites have pozzolanic activity level between fly ash and silica fume, and higher activity than non-zeolitic natural pozzolans when compared the materials used in the study.

Published literature contains limited data on the effect of calcination on the efficiency of heulandite- and mordenite types

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of zeolites as cement additive materials [14,15]. In addition, the literature contains very limited information on the properties and performance of calcined clinoptilolite in cementitious systems as one of the most abundant types of natural zeolites over the earth [16]. One of the objectives of this study is to contribute the literature for better understanding the effect of calcination at various temperatures on the major properties of clinoptilolite type natural zeolites as a supplementary cementing material.

This paper presents the results of an investigation on the calcined natural zeolites as alternative pozzolan for use in blended cements. Two clinoptilolite-type zeolites with different characteristics were calcined in a laboratory furnace at 200 °C, 400 °C, and 600 °C for 2 h after they were finely ground by using a laboratory ball mill. The typical properties of raw and the calcined zeolites such as mineralogical composition, specific surface area, pozzolanic activity and water requirement were determined and evaluated comparatively. The performance of calcined zeolites in pozzolan blended cements was also evaluated by determining free lime content and pore size distribution of the cement pastes as well as compressive strength of mortars.

2. Experimental

2.1. Materials

Natural zeolites used in the study were obtained in bulk form from two different commercial deposits in western Turkey, Gordes and Bigadic, and they notated as ZA and ZB henceforth. They were crushed and ground to a fineness of 80% passing from the 45-μm sieve. Oxide compositions of the finely ground raw zeolites are shown in Table 1.

An ordinary Portland cement (type CEM I 42.5 R in accordance with EN 197-1) was used in the preparation of blended Portland cement pastes and mortars. Chemical composition and physical properties of the Portland cement (PC) used in the study are shown in Table 1. An analytical grade $Ca(OH)_2$ was also used in pozzolanic activity tests conducted with electrical conductivity measurements on lime–zeolite–water suspensions.

2.2. Methods

Finely-ground zeolites were calcined in an electrical muffle furnace as a single batch of 5 kg at various temperatures of 200 °C, 400 °C, and 600 °C for 2 h, and then allowed to cool in desiccators. The calcined zeolites were held at sealed containers up to test days in order to minimize contact with air. The calcined zeolites were notated with the suffix referring to the treatment temperature (e.g., ZA-400 refers to the ZA calcined at 400 °C) whereas the raw zeolites notated as ZA-raw and ZB-raw.

Table 1
Chemical composition and physical properties of the ordinary Portland cement.

	PC	ZA	ZB
Chemical compositions (%)			
SiO_2	18.85	69.08	67.65
Al_2O_3	5.14	11.41	10.97
Fe_2O_3	2.74	0.98	1.02
CaO	62.74	1.91	3.24
MgO	2.36	0.68	1.01
SO_3	3.52	n.a	n.a
Na_2O	0.31	0.66	0.17
K_2O	0.70	4.05	2.40
Loss on ignition	3.43	11.00	12.90
Compound compositions[a] *(%)*			
C_3S	59.09	–	–
C_2S	9.47	–	–
C_3A	8.98	–	–
C_4AF	8.34	–	–
Physical properties[b]			
Specific gravity	3.08	2.17	2.22
Blaine fineness, m^2/kg	331	875	1115
Initial setting time, min	160	–	–
Final setting time, min	225	–	–
Compressive strength, MPa			
2 days	24.7	–	–
7 days	39.7	–	–
28 days	51.6	–	–

[a] Calculated by using Bogue formulations.
[b] In accordance with EN standard test methods.

XRD analyses of the raw and the calcined zeolites in the form of finely ground powder were conducted by using Cu-∝1 radiation/40 kV X-ray diffractometer. Their specific surface areas were determined by nitrogen absorption (BET) technique. Pozzolanic activity of the zeolites was evaluated by using electrical conductivity method which is proposed by Paya et al. [17] for fly ashes and then applied by Uzal et al. [13] for raw zeolites with some modifications in the experimental set-up. Electrical conductivity of a solution prepared with 200 mg of analytical-grade $Ca(OH)_2$ and 250 ml of deionized water at 40 ± 1 °C was recorded before and after 5 mg zeolite addition, and time evolution of the conductivity was determined. The same procedure was repeated for the zeolite–water system prepared with 5 g of zeolite and 250 ml of deionized water. The net loss in electrical conductivity was calculated by subtracting conductivity of the zeolite–water system from that of the lime–zeolite–water system, and considered as a measure of pozzolanic activity.

The water requirement and compressive strength performance of the raw and calcined zeolites were determined for blended cement mortars prepared with 20% replacement of Portland cement by zeolite in accordance with ASTM C 311 [18]. The pozzolanic reactivity and pore refining performance of the calcined zeolite were evaluated on hardened pastes of 20% zeolite blended Portland cements by determining their free $Ca(OH)_2$ (portlandite) content and pore size distribution. The pastes were prepared with 0.5 water-to-cementitious materials ratio by using deionized water, and then immediately filled into plastic syringes, and the lids were sealed to prevent moisture loss and carbonation. The samples were cured in a temperature of 23 ± 1 °C till the test ages. The free $Ca(OH)_2$ content of the hardened pastes based on the ignited weight of the hardened cement pastes was determined at 7 days and 28 days of age by thermogravimetric analysis (TGA). At the test ages, the hardened pastes were crushed and sieved to particles smaller than 800-μm, and then analyzed between room temperature and 950 °C at a heating rate of 10 °C/min.

Pore size distribution of hardened blended cement pastes was determined by mercury intrusion porosimetry (MIP) at 28 days of age. The hardened pastes were crushed to a particle size range of approximately 3–5 mm and then immersed in acetone for 24 h to replace free water present in samples. The samples were then dried at 55 °C under vacuum condition for 24 h and analyzed by mercury intrusion porosimeter with a maximum 55,000 psi injection pressure for pore size range between 3 and 10,000 nm.

3. Results and discussion

3.1. Thermal characterization of the raw zeolites

Thermogravimetric analyses of the raw zeolites were made up to 950 °C at a heating rate of 10 °C/min, and the results are shown in Fig. 1. According to Knowlton et al. [19], there are three different types of water associated with clinoptilolite as externally adsorbed water, loosely bound zeolitic water and tightly bound zeolitic water, and they can be differentiated by inflection points on TGA curves. For the clinoptilolite-rich zeolitic tuffs, the part of the TGA curves corresponding to temperatures <50 °C represents desorption of water from the surface of zeolitic particles, whereas the middle portion approximately between 50 °C and 200 °C represents the loosely bound zeolitic water. The part of TGA curves

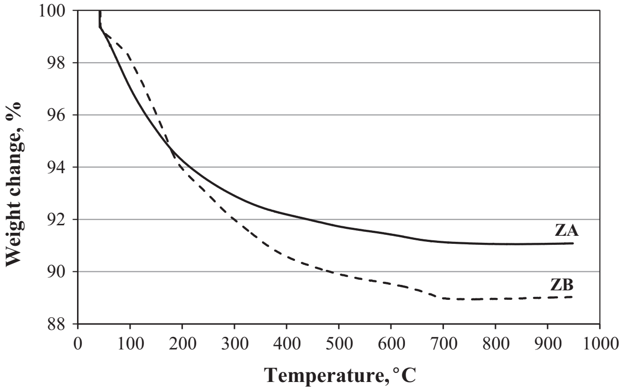


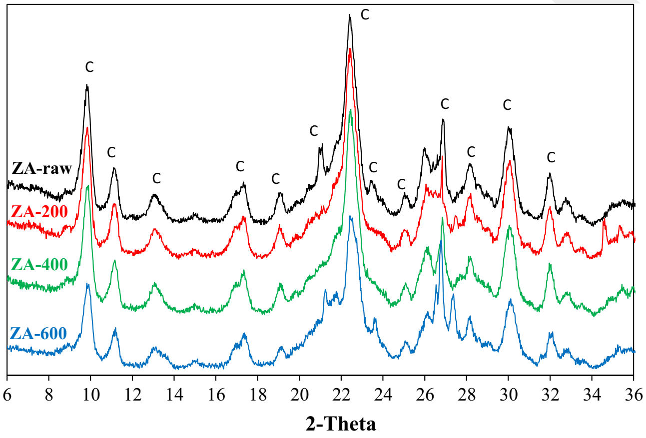
Fig. 1. TG curves of the natural zeolites.

approximately from 200 °C to 700 °C denotes the slow desorption of water that is tightly bound to zeolitic structure [19].

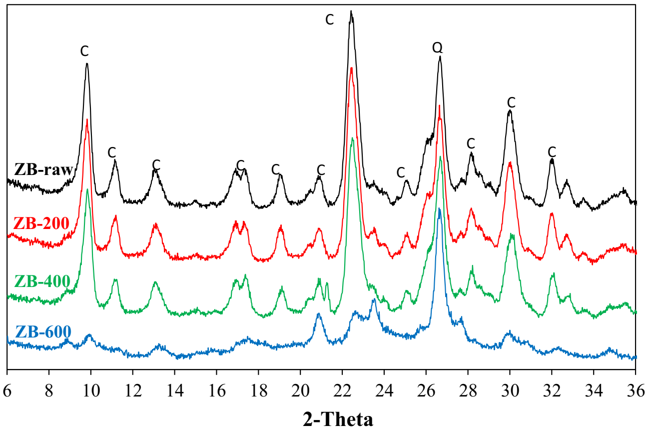
As can be seen from Fig. 1, the samples exhibited a continuous weight loss at different rates up to approximately 700 °C due to desorption of the three types of water indicated above. Considering the types of water present in clinoptilolite as defined above, it was observed that ZA and ZB contains similar amounts of externally absorbed and loosely bound water. On the other hand, their tightly bound water contents, e.g. the weight loss between 200 °C and 700 °C, were calculated from the curves as approximately 3% and 5% for ZA and ZB, respectively. In addition, the total amount of water present in zeolites, e.g. the total weight loss at the end of 950 °C, was found to be approximately 9% and 11% for ZA and ZB, respectively. Thus, it can be concluded that the ZA and ZB have different characteristics not only on their major cation contents but also on nature and amount of the water present in their structure.

3.2. XRD analysis and BET surface area of the zeolites

XRD pattern of the raw and calcined zeolites are shown in Fig. 2. Calcination at temperatures of 200 °C and 400 °C did not substantially change the XRD patterns of the zeolites; however intensity of the clinoptilolite peaks decreased at about 40% on XRD pattern of ZA-600 when compared to that of the original ZA (Fig. 2a). On the other hand, calcination at 600 °C resulted in complete disappearance of zeolite peaks on XRD pattern of ZB indicating a transformation into an amorphous structure, and only the peak corresponding to quartz phase remained unchanged as seen from Fig. 2b. These observations suggest that zeolite crystal structure of ZA be more stable against calcination at temperatures studied when compared to that of ZB. A possible reason for the dissimilarity between thermal stability of ZA and ZB can be associated with the dissimilar amount and nature of water present in their crystal structures as discussed above (Fig. 1).



(a) ZA



(b) ZB

Fig. 2. XRD patterns of the raw and calcined natural zeolites (C: clinoptilolite, Q: quartz).

Surface area of the raw and the calcined zeolites were determined by BET nitrogen adsorption technique, and the results are shown in Table 2. It is observed that the surface area of ZA is considerably higher than that of ZB for their raw and calcined forms. The lower specific surface of ZB, when compared to ZA, can be associated with the presence of quartz in its mineralogical composition as an impurity. Calcination of the raw zeolites decreased their BET surface area, except calcination of ZB at 200 °C which showed similar specific surface to the raw ZB. According to Christidis et al. [20], the decreases in specific surface area of the zeolites after calcination causes from decreased microporosity on zeolite crystal surfaces due to slight decompositions in the crystal structure.

3.3. Pozzolanic activity of the zeolites

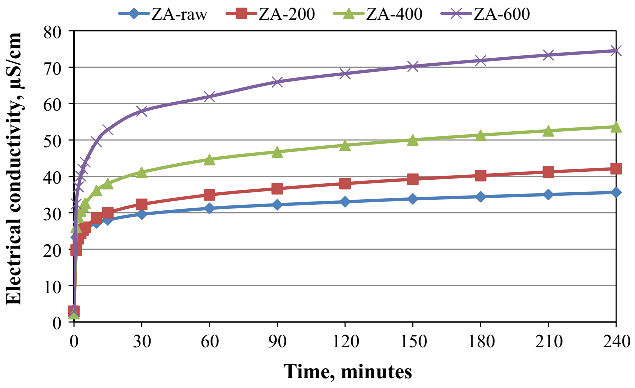
Time evolution of electrical conductivity of the zeolite–water suspensions at 40 ± 1 °C was determined for the raw and the calcined zeolites in order to assess the availability of water soluble ions present in their structure. It is known that water soluble ions, particularly Na^+ and K^+, have an exaggerating effect on pozzolanic reaction by enhancing the protonic attack of water to pozzolanic material grains [21,22]. Therefore potential changes in the solubility of ions may also affect the pozzolanic reactivity indirectly.

Time evolution of electrical conductivity of the zeolite–water suspensions are presented in Fig. 3. As can be seen from Fig. 3, the conductivity of the aqueous mediums increased after the addition of the raw and calcined zeolites probably due to the release of some soluble cations (sodium, potassium and calcium) from zeolite structure. Electrical conductivity of zeolite–water suspensions of calcined ZA was higher than that of the raw ZA, and the conductivity increased with increasing calcination temperature (Fig. 3a). However, it was observed that calcination of ZB slightly decreased the conductivity of the suspensions when compared to raw ZB (Fig. 3b). Time evolution of the electrical conductivity of zeolite–water systems have been associated in published literature with the cation exchange phenomenon consisting of releasing some cations from zeolite structure and taking hydrogen ions from water [23]. Thus, it can be concluded that the calcination increased the solubility of ions in ZA, but decreased in ZB. Considering the exaggerating effect of soluble ions in pozzolanic materials, it could be expected that ZA has a more potential for an increase in pozzolanic reactivity after calcination when compared to ZB.

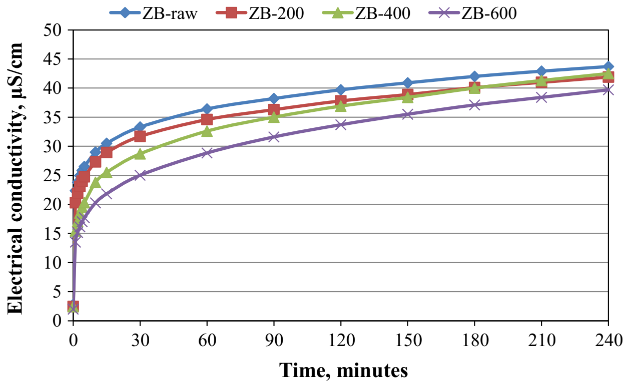
Fig. 4 shows the data for the net loss in electrical conductivity of lime–zeolite–water systems as a measure for the pozzolanic reactivity. Calcined zeolites exhibited comparable pozzolanic activity to the raw zeolites. It can be observed that the calcination up to 400 °C is not considerably influential on the pozzolanic activity of ZA. However, ZA-600 showed slightly higher pozzolanic activity than ZA-raw. On the other hand, calcined ZB samples exhibited similar activity to the each other for all the calcination temperatures, and they showed slightly reduced activity when compared to the raw ZB. By considering the disappearance of zeolite peaks on XRD pattern of ZB after the calcination at 600 °C (Fig. 2b), it can be concluded that the destruction of zeolite crystal structure is not influential on its pozzolanic reactivity. Based on these results, it can also be concluded that calcination of the clinoptilolite zeolites up to 600 °C is not so useful to improve their pozzolanic reactivity with lime, and the lime reactivity could be negatively

Table 2
BET specific surface area and water requirement of the raw and calcined natural zeolites.

Calcination temperature	Specific surface area (m^2/g)		w/cm Required for a standard flow value		Water requirement (%)	
	ZA	ZB	ZA	ZB	ZA	ZB
Raw	41.3	14.3	0.58	0.53	120	110
200 °C	35.5	14.8	0.55	0.51	113	105
400 °C	35.7	13.8	0.53	0.53	110	110
600 °C	32.6	12.9	0.54	0.52	112	107



(a) ZA



(b) ZB

Fig. 3. Water solubility of the zeolites as determined by electrical conductivity of zeolite–water suspensions.

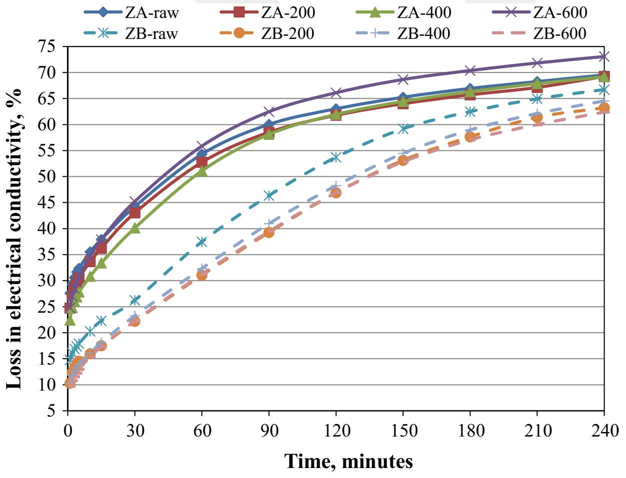


Fig. 4. Pozzolanic activity of the zeolites.

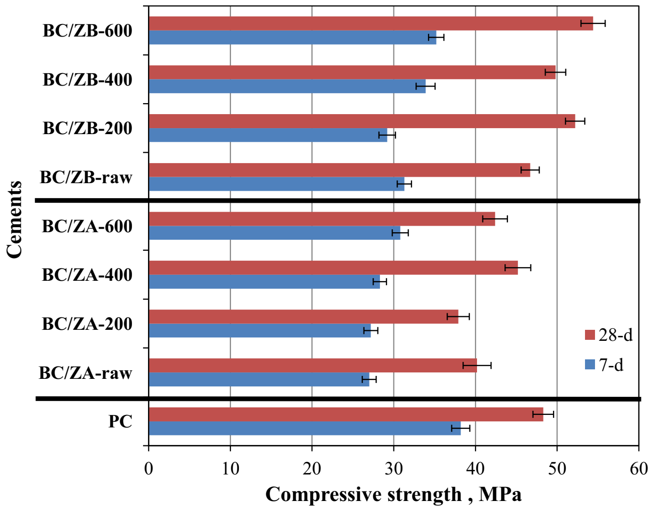


Fig. 5. Compressive strength of the cement mortars with raw and calcined natural zeolites at 7 days and 28 days of age.

affected by calcination depending on the decomposition of zeolite structure and reduction on specific surface area. The slight increase in pozzolanic reactivity of ZA after calcination particularly at 600 °C could be associated with the increased solubility of ions in ZA after calcination as indicated by electrical conductivity of zeolite–water suspensions shown in Fig. 3a.

3.4. Water requirement and compressive strength of the mortars

In order to evaluate the effect of calcination of the natural zeolites on the water requirement of 20% zeolite blended cements, water requirements for 20% zeolite blended cementitious mortars were determined in accordance with ASTM C 311 [18]. The water requirement values of the raw and the calcined natural zeolites are shown in Table 2. It was observed that calcination decreased the water requirement of ZA for all the temperatures applied whereas calcined ZBs exhibited comparable water requirements to the raw ZB. The decreases in water requirement of ZA after calcinations could be associated with more intense decreases in BET surface area of ZA when compared to ZB (Table 2). The decreases in BET surface of ZA and ZB after calcination at 600 °C are 21.1% and 9.7%, respectively. Although there is no any linear or direct relationship between BET surface area and water requirement of the zeolites, BET surface area could be designated as the major parameter explaining the difference between ZA and ZB in terms of effect of calcination on their water requirements. These outcomes demonstrated that calcination may reduce the water requirement of natural zeolites and has the potential to eliminate their undesirable high water requirement as cement replacement material.

Compressive strengths of blended cement mortars prepared with 20% zeolite replacement and variable w/cm ratios depending on their water requirements given in Table 2 were shown in Fig. 5 for 7 days and 28 days of age. The compressive strength of the PC

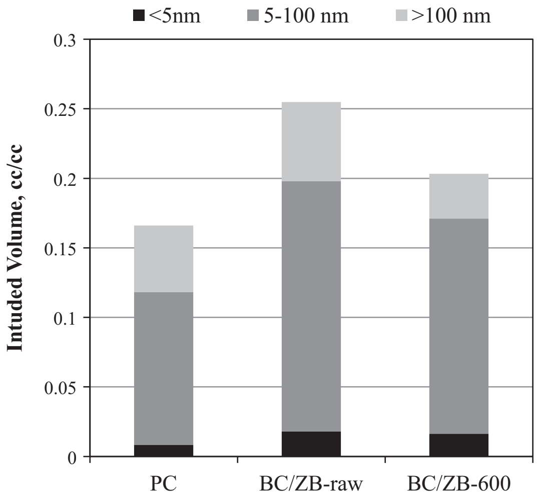


Fig. 6. Total porosity and pore size distribution of the hardened cement pastes at 28 days of age as determined by mercury intrusion porosimetry.

mortar without a zeolite replacement was also shown in Fig. 5 for comparison. Blended cements with raw zeolites exhibited lower compressive strength when compared to PC at both test ages. On the other hand, compressive strength of the blended cement mortars with calcined zeolites was similar or higher than that of the mortars with corresponding raw zeolite. Strength contribution of the zeolites increased or remained alike with increasing calcination temperature. It was observed that strength contribution of ZB was higher than that of ZA for their raw and calcined forms, and 28-day compressive strengths of blended cements mortars with calcined ZBs were higher than that of the PC mortar. Especially, blended cement mortar with ZB-600 exhibited 16% higher compressive strength when compared to raw ZB. From another point of view, 28-d relative strength of the mortar of raw ZB with respect to the strength of PC mortar (e.g. the strength activity index of ZB) increased from 97% to 113% after calcination at 600 °C. The relatively higher strength performance of ZB-600 can be attributed to the destruction on zeolite structure as indicated by its XRD pattern shown in Fig. 3. In addition, it should be noticed that improvements in strength contribution of the zeolites are caused by the mechanisms other than pozzolanic activity since the negative effects of calcination on the lime reactivity of ZB are demonstrated above (Fig. 4). Therefore, the loss of combined water in the zeolite structure due to calcination may be responsible for the increase in its strength contribution relating to porosity and pore structure of the hardened cementitious systems. In order to examine this hypothesis, pore size distributions and free $Ca(OH)_2$ contents of the hardened blended cement pastes with ZB-600 were discussed in comparison to ordinary Portland cement paste below.

3.5. Free $Ca(OH)_2$ content and pore size distribution of the hardened cement pastes

Table 3
Free $Ca(OH)_2$ content of the hardened cement pastes.

Cement	% $Ca(OH)_2$		% $Ca(OH)_2$ normalized to PC content	
	7-day	28-day	7-day	28-day
PC	19.8	24.8	19.8	24.8
BC/ZB-raw	15.9	16.7	19.9	20.9
BC/ZB-600	15.6	17.8	19.5	22.3

Table 3 shows the free $Ca(OH)_2$ content of the hardened pastes prepared with the ordinary Portland cement (PC) as well as pastes prepared with 20% replacement of PC by ZB-raw and ZB-600. Comparing the free $Ca(OH)_2$ content of the hardened paste with raw and calcined ZB; it was observed that they have similar content of $Ca(OH)_2$ at 7 days of age; however $Ca(OH)_2$ content of the paste with ZB-600, at 28 days, was slightly higher than that of the paste with ZB-raw. These outcomes are in line with pozzolanic activity test results indicated that the lime reactivity of ZB-600 is slightly lower than that of ZB-raw (Fig. 4). On the other hand, slightly higher $Ca(OH)_2$ content of the paste with ZB-600 at 28 days of age can be attributed to an enhanced hydration of Portland cement phase in the blended system. However, this minor increment in $Ca(OH)_2$ content indicating an improved degree of hydration of Portland cement phase is away from explaining the 16% increased 28-day strength contribution of ZB after calcination at 600 °C.

Pore size distributions of hardened pastes at 28 days of age are shown in Fig. 6. Zeolite replacement increased the total porosity of the paste when compared to PC paste as expected from the blended cements containing replacement materials. It was also observed that the total porosity of the blended cement paste with ZB-600 is considerably lower than that of the paste with ZB-raw, which is directly caused from the lower amount of pores larger than 5 nm. It is known that the amount of relatively larger pores is inversely proportional to the strength of cementitious systems. Therefore, the higher strength contribution of ZB-600 than that of ZB-raw can be explained with a lower amount of relatively larger pores (>100 nm) present in its porous system.

Calcination at 600 °C significantly enhanced the strength contribution of ZB without an improvement in its pozzolanic activity. Therefore, it is proposed that the strength enhancement is related to the decreased total porosity of the paste that results from mechanisms other than pozzolanic activity such as filler effect and nucleation effect of cement replacement materials.

4. Conclusions

Based on the experimental results above, the following conclusions can be drawn about properties and performance of calcined natural zeolites as alternative cement replacement material:

1. Crystal structures of the zeolites altered in various levels after calcination depending on the amount and nature of water present in their structures. Zeolite structure of ZB containing relatively higher crystal water in its raw form completely destructed after calcination at 600 °C.
2. Specific surface area and water requirement of the calcined natural zeolites are principally lower than that of the raw forms, which makes them more desirable cement replacement material in terms of water requirement or workability of fresh cementitious systems.
3. Calcination is positively or negatively influential on the ion solubility of zeolites in water mainly related to availability of exchangeable cations. Therefore the cementitious systems with calcined zeolites should be evaluated in terms of alkali–aggregate reactions in further research studies.
4. Calcined natural zeolites showed slightly higher or lower pozzolanic activity depending on the nature of the zeolite and calcination temperature. On the other hand, blended cements with calcined zeolites showed higher compressive strengths up to approximately 15% when compared to the blended cements with raw zeolites.
5. Consequently, it is demonstrated that the calcined natural zeolites have more desirable properties and higher performance as cement replacement material than the raw zeolites, especially in terms of water requirement and compressive strength of blended cements.

6. The energy and cost efficiency are the concerns that should be considered for calcined natural pozzolans. Some innovative calcination technologies such as flash calciners, instead of traditional rotary kiln calciners, provide more energy efficient ways for calcination of raw materials. Therefore calcined natural zeolites should be evaluated in terms of their energy and cost efficiency in further studies by considering recent advances in calcination technologies.

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