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Blended cements containing high volume of natural zeolites: Properties, hydration and paste microstructure

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ABSTRACT

In this study, properties and hydration characteristics as well as paste microstructure of blended cements containing 55% by weight zeolitic tuff composed mainly of clinoptilolite mineral were investigated. Free $Ca(OH)_2$ content, crystalline hydration products and decomposition of zeolite crystal structure, pore size distribution and microstructural architecture of hydrated cement pastes were examined. Superplasticizer requirement and compressive strength development of blended cement mortars were also determined. The blended cements containing high volume of natural zeolites were characterized with the following properties; (i) no free $Ca(OH)_2$ in hardened pastes at the end of 28 days of hydration, (ii) less proportion of the pores larger than 50 nm when compared to portland cement paste, (iii) complete decomposition of crystal structure of zeolite at the end of 28 days of hydration, (iv) presence of tetra calcium aluminate hydrate as a crystalline product of pozzolanic reaction, (v) more compatibility with the melamine-based superplasticizer when compared to the naphthalene based product, and (vi) similar 28 days compressive strength of mortars to that of reference portland cement.

1. Introduction

Portland cement industry is responsible for approximately 7% of global CO_2 emission [1]. Partial replacement of portland cements by one or more additives to obtain blended cements not only provides reduction in CO_2 emission and energy saving in cement production but also supplies more durable cementitious systems to construction industry.

The extent of the benefits provided by use of blended cements increases with increasing content of additives in blended portland cements. However, the content of additives in blended portland cements, especially for natural pozzolans, is limited by some factors such as increase in water requirement and decrease in rate of strength development of the cementitious systems. It has been found that the blended cements containing high volume (55% by weight) of natural pozzolans (volcanic tuff) posses lower 28-day compressive strength when compared to the reference portland cement, although they show similar strength values at 91 days of age [2,3]. Therefore production of high-volume natural pozzolan blended cements which are able to compete against ordinary portland cement requires natural pozzolans exhibiting significantly high strength activity.

Natural zeolites are crystalline aluminosilicates composed of a three dimensional arrangement of silicon–oxygen (SiO_4) and aluminum–oxygen (AlO_4) tetrahedra [4]. Zeolite group of minerals currently include more than forty naturally occurring species, and is the largest group of silicate minerals [4]. Clinoptilolite, heulandite, analcime, chabazite, and mordenite are the most common types of natural zeolite minerals on the earth. It is known that they show considerable pozzolanic activity despite their distinct crystalline structure. Pozzolanic activity of natural zeolites has been principally attributed to dissolution of zeolitic crystals of three-dimensional framework structure under the attack of OH^- ions available in hydrating cementitious system [5–10]. In a recent study, Uzal et al. [11] reported that the clinoptilolite zeolite possesses a lime reactivity which is comparable to silica fume, and higher than fly ash and a non-zeolitic natural pozzolan. They also concluded that the high reactivity of the clinoptilolite is attributable to its specific surface area for certain grinding method and duration as well as its reactive SiO_2 content.

It is known that zeolitic tuffs are used in some countries as a blending component during cement production and as a mineral admixture in concrete mixtures. However the knowledge on the properties and hydration characteristics of blended cements containing natural zeolites is limited. Published the literature contains no report on properties and hydration of blended portland cements

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containing high volume of natural zeolites, more than 50% by weight. One of the objectives of this study is to fulfill this need.

This paper presents the results of an investigation on blended cements containing 55% by weight clinoptilolite-rich zeolitic tuffs. Zeolitic tuffs obtained from two major deposits in Turkey, Gordes and Bigadic, were finely ground so as to blend with portland cement separately. Blended cements containing 55% zeolitic tuff were obtained, and tested for setting time; $Ca(OH)_2$ content and pore size distributions of the pastes; superplasticizer requirement and compressive strength development of mortars in comparison with the reference portland cement. In addition, the hardened blended cement pastes were examined for the crystalline products of hydration via X-ray diffraction (XRD) analysis and for the microstructural architecture using back-scattered scanning electron microscopy (BS-SEM).

2. Experimental

2.1. Materials

Chemical composition and physical properties of the ordinary portland cement (PC) used in the study are shown in Table 1.

2.1.1. Zeolitic tuffs

Zeolitic tuffs from two different deposits in west of Turkey, Gordes (notated as GZ) and Bigadic (notated as BZ), were used in the study. Zeolitic tuffs were crushed to pass No.12 sieve (170 mm) and then finely ground by using a ball mill so as to provide approximately 80% passing value through 45 μm sieve. For this purpose, GZ and BZ were ground for 90 min and 120 min, respectively, which indicate that GZ is more easily grindable when compared to BZ. Chemical composition and physical properties of the finely-ground zeolitic tuffs are given in Table 2, whereas their particle size distributions determined by using Malvern Mastersizer 2000 laser particle size analyzer are shown in Fig. 1. Reactive SiO_2 content of the zeolitic tuffs was also determined in accordance with EN 196-2 [12] and given in Table 2.

Powder X-ray diffraction patterns of the zeolitic tuffs showed that clinoptilolite, a common zeolite mineral, is the major crystalline phase in both tuff samples, and they also contains quartz as a minor impurity (Fig. 2). Petrographical analysis of the tuffs indicated that clinoptilolite content of GZ and BZ are approximately 75% and 80%, respectively. Clinoptilolite crystals were clearly observed in scanning electron micrographs of the bulk tuff samples as shown in Fig. 3.

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

Chemical compositions (%)	
SiO_2	19.94
Al_2O_3	5.34
Fe_2O_3	3.72
CaO	63.02
MgO	2.44
SO_3	2.95
Na_2O	0.52
K_2O	0.81
Loss on ignition	1.02
Insoluble residue	0.51
Physical properties*	
Specific gravity	3.03
Blaine fineness, (m^2/kg)	313
Initial setting time, (min)	140
Final setting time, (min)	205
Compressive strength, (MPa)	
3 days	35.3
7 days	39.5
28 days	54.6

* In accordance with ASTM standard test methods.

Table 2
Chemical composition and physical properties of the finely-ground zeolitic tuffs.

Definition	Gordes zeolite	Bigadic zeolite
Notation	GZ	BZ
Chemical compositions (%)		
SiO_2	69.32	66.05
Al_2O_3	11.35	11.04
Fe_2O_3	1.28	1.08
CaO	1.72	3.71
MgO	0.82	0.96
Na_2O	0.95	0.19
K_2O	3.96	1.75
Loss on ignition (105–750 °C)	6.15	9.35
Reactive SiO_2	51.29	54.93
Physical properties		
Specific gravity	2.16	2.19
Fineness		
Passing 45 μm (%)	80	80
Median particle size, (μm)	13.9	8.2
Blaine fineness, (m^2/kg)	995	1287
BET surface area, (m^2/kg)	35,500	26,870
Strength Activity Index, (%)		
7-days	71	79
28-days	84	98

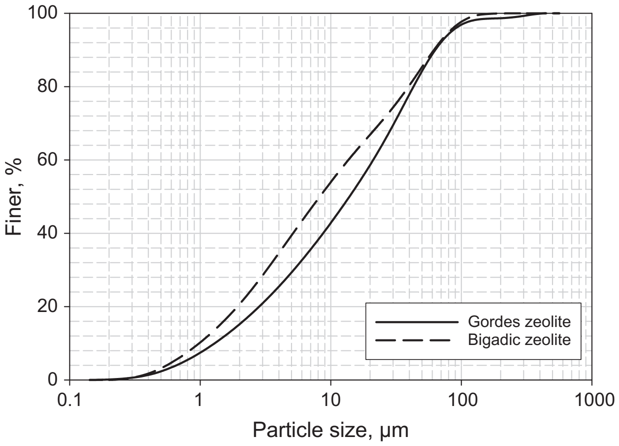


Fig. 1. Particle size distribution curves of the natural zeolites.

2.1.2. Superplasticizers

Two kinds of superplasticizers in dry powder form, a sulfonated melamine condensate and a sulfonated naphthalene condensate, were used in blended cement mortars to provide a flow value which is similar to that of the reference PC mortar. Two kinds of superplasticizers were compared for their relative efficacy with the zeolite blended cements.

Blended cements were obtained with direct replacement of portland cement by the zeolitic tuff and their efficient mixing for homogenization, and notated in accordance with the origin and content of the zeolitic tuff incorporated. GZ55 and BZ55 refer to the blended cements containing 55% Gordes zeolitic tuff (GZ) and Bigadic zeolitic tuff (BZ), respectively.

2.2. Methods

2.2.1. Normal consistency and setting time

The blended cements and the reference portland cement (PC) were tested for normal consistency and setting time in accordance with ASTM C 187 [13] and C 191 [14], respectively.

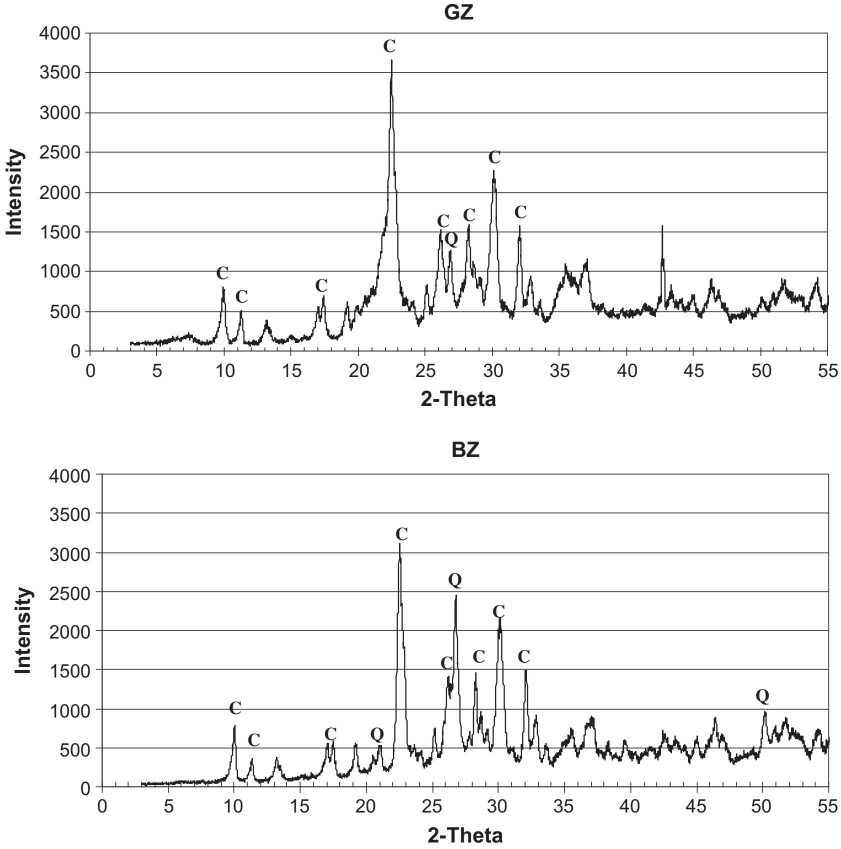
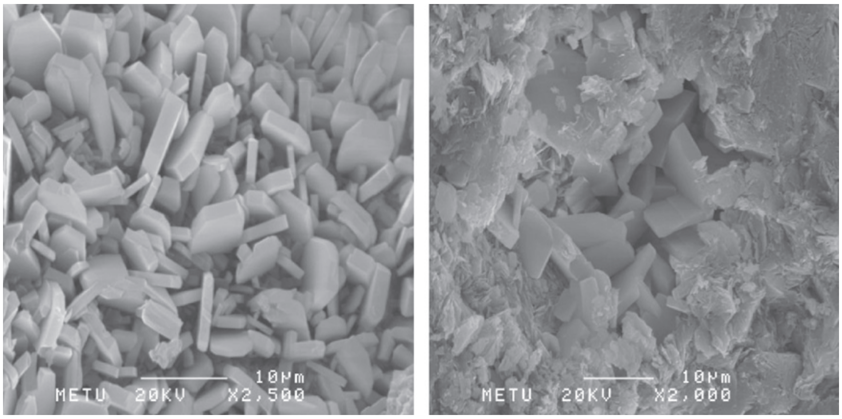


Fig. 2. XRD patterns and identified phases of the natural zeolites (C: clinoptilolite and Q: quartz).



(a) Gordes zeolite (GZ) (b) Bigadic zeolite (BZ)

Fig. 3. SEM micrographs of bulk samples of the natural zeolites.

2.2.2. Preparation of cement paste samples

Cement paste samples to be used for thermal analysis, mercury intrusion porosimetry (MIP), XRD analyses and SEM observations were prepared with 0.5 water-to-cement ratio using deionized water. Fresh pastes were immediately filled into plastic syringes and the lids were sealed to prevent moisture loss and carbonation, then the samples were cured in temperature of 23 ± 1 °C till the test ages.

2.2.3. Free $Ca(OH)_2$ content of the hardened pastes

The free $Ca(OH)_2$ (abbreviated as CH) content referred to the ignited weight of the hardened cement pastes were determined at 3, 7, 28, and 91 days of age by thermo-gravimetric analysis using Perkin Elmer Pyris 1 TGA device. At specified test ages, the hardened pastes were crushed and sieved to obtain particles smaller than 800 μm, and then immediately analyzed between room temperature and 1000 °C at a heating rate of 10 °C/min.

2.2.4. Pore size distribution of the hardened pastes

Mercury intrusion porosimetry (MIP) was utilized to determine the pore size distribution of the hardened cement pastes at 28 and 91 days of age.

Determination of pore size distribution of hardened cementitious systems requires the complete removal of free water in specimens. Since oven-drying at 100–105 °C may cause damage to microstructure and pore system of the hardened pastes, some special drying procedures are commonly applied before mercury intrusion porosimetry such as vacuum drying at relatively low temperatures, freeze drying, and methanol replacement [15]. A drying procedure consisting of methanol replacement followed by vacuum drying at 55 °C was applied in the study.

The hardened pastes were crushed to 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 subjected to vacuum drying at 55 °C in a vacuum oven for 24 h. The pretreated samples were analyzed by Quantachrome Corporation Poremaster 60 mercury intrusion porosimeter with a maximum 55,000 psi injection pressure for pore size range between 3 and 10,000 nm. In calculations for pore size distribution from mercury intrusion data, the contact angle was taken as 142°. For all the samples, the completely identical preparation procedure was applied.

2.2.5. XRD and BS-SEM examinations on hardened pastes

In order to examine crystalline hydration products qualitatively and to observe a possible decomposition of zeolite crystal structure in blended system, the hardened pastes were analyzed with XRD technique after crushing and sieving to obtain particles smaller than 800 μm. XRD patterns of the hardened pastes were obtained by using a Cu $\alpha 1$ radiation/40 kV X-ray diffractometer between 2-theta angles of 5° and 65°.

Microstructure and hydration products of the hardened cement pastes were examined with backscattered-mode of scanning electron microscopy (BS-SEM by JEOL JSM-6400 scanning electron microscope equipped with NORAN System six energy dispersive X-ray analysis (EDX) system. Hardened cement pastes at 28 days of age were crushed to size of approximately 15–20 mm and immersed in methanol for 48 h in order to remove free water and to stop hydration. Since backscattered-mode SEM requires polished samples, hardened cement paste specimens were then immersed in epoxy resin under vacuum condition and finally the polished surfaces were prepared. The polished surfaces were coated with gold–palladium alloy to provide conductive surface before SEM examination. The polished surfaces of pastes were qualitatively examined for the microstructural architecture of the pastes as seen in backscattered SEM.

2.2.6. Superplasticizer requirement and compressive strength of mortars

Compressive strength development of blended cements and the reference portland cement were determined on mortar specimens prepared with 0.5 water-to-cementitious materials ratio (w/cm) and 2.75 sand-to-cement ratio. The CEN (the European Committee for Standardization) standard sand in accordance with EN 196-1 [16] was used in mortar mixtures.

Two different types of superplasticizers in a dry powder form, the products of a naphthalene-based and a melamine-based, were used to obtain a flow value similar to that of the reference portland cement mortar. Flow value of fresh mortars was determined in accordance with ASTM C 109 [17] as a measure of workability. Thus superplasticizer requirement was also determined for both types of superplasticizers.

Mortar mixtures were prepared by applying the standard mixing, molding and curing procedures stated in ASTM C 109 [17]. Compressive strength of 50 mm cube mortar specimens was determined at 3, 7, 28, 91, 180 and 360 days of age, with a constant loading rate of 90 kgf/s.

3. Results and discussion

3.1. Normal consistency and setting time

Water-to-cement ratios required for normal consistency and setting time of cements are shown in Table 3. Water demand of GZ55 and BZ55 blended cements for normal consistency was approximately 60% and 40% higher than that of reference PC, respectively. Significantly increased water demand of blended cements when compared to PC is probably due to high capacity of zeolite particles to absorb water. Lower water demand of BZ55 could be attributed to lower BET surface area of BZ when compared to GZ.

Table 3
Normal consistency water content and setting time of the cements.

Cement	w/cm for normal consistency	Setting time, minutes	
		Initial	Final
PC	0.27	218	245
GZ55	0.43	112	185
BZ55	0.38	54	164

Blended cements containing high volume of zeolites exhibited a different behavior when compared to blended cements containing low amount of zeolite replacement reported in literature [18]. Initial and final setting times of the blended cements containing high volume of natural zeolites were shorter than that of reference PC. It is usually expected that replacing portland cement by mineral additives results in a delay in setting time of cementitious system due primary to lower proportion of portland cement in blended system. The reverse case observed is probably due to rapid decrease in consistency of the blended cement pastes, caused from continuously absorption of water by zeolitic tuff particles after preparation of cement pastes in normal consistency. The extent of shortening in setting time is less for initial setting time than the final, and this case supports the proposed cause of shortening in setting times. Because the absorption process gets slower with time while the zeolite particles come near to saturation.

3.2. Free CH content of the hardened pastes

The CH content in hardened cement pastes was determined by TGA at various ages, and the results are given in Table 4. The CH contents normalized with respect to the proportion of portland cement present in the blended cements is also shown in Table 4.

Free CH content of blended cement pastes was lower than that of PC paste at all test ages due to lower amount of CH production as well as its consumption by pozzolanic activity of natural zeolite.

The normalized values of CH content of blended cement and PC pastes indicated that little amount of CH was consumed at early ages by pozzolanic reaction, indicating that pozzolanic action of zeolite particles slowly develops at initial stages of hydration. Pozzolanic activity of clinoptilolite crystals in cementitious systems is generally associated with decomposition/dissolution of the crystal structure at a high-pH medium resulted from presence of CH [5,7,19]. This explanation is supported by some reports focused on the morphological and structural changes of zeolite crystals in alkaline or acidic aqueous solutions [20–22]. Consequently, slow pozzolanic action in pastes of blended cement containing large amounts of zeolitic tuff at early ages is attributable to relatively low pH of pore solution which is inadequate for decomposition of the crystal structure of zeolite.

The content of free CH was 0.8% and 2.8% for GZ55 and BZ55 pastes, respectively, at the end of 28 days whereas it is under detectable limit at 91 days for the both, which means that available CH was almost completely consumed as a result of pozzolanic reaction. In a previous study of the authors [23], CH content of the pastes of blended cements containing 55% of non-zeolitic natural pozzolan had been found to be approximately 2.4% at the end of 90 days of age. Therefore it seems that lime reactivity of clinoptilolite zeolites in hydration period before 28 days of age is

Table 4
$Ca(OH)_2$ content of the hardened cement pastes (referred to ignited weight).

Cement	(%) $Ca(OH)_2$				(%) $Ca(OH)_2$ (normalized to portland cement content)			
	3-day	7-day	28-day	91-day	3-day	7-day	28-day	91-day
PC	18.1	18.9	21.6	21.9	18.1	18.9	21.6	21.9
GZ55	4.2	5.3	0.8	n.d*	9.3	11.8	1.7	n.d*
BZ55	6.9	7.1	2.8	n.d*	15.3	15.8	6.2	n.d*

n.d: not detected.

dramatically higher than non-zeolitic natural pozzolans studied by the authors previously [23]. The results indicating high rate and capacity of zeolite particles to fix lime are in line with the conclusions reported by some authors in the literature about zeolite blended portland cement systems [18,24].

It was also observed that free CH content of GZ55 paste is lower than that of BZ55 paste at all test ages, revealing that lime reactivity of GZ is higher than that of BZ. The difference between lime reactivity of GZ and BZ could be attributed to the major cation present in their compositions. Although the common major cation in clinoptilolite is Na^+, some clinoptilolite occurrences can be rich in K^+ or Ca^{++} content. BZ is a Ca-rich zeolitic tuff whereas GZ is rich in K^+ as seen in their chemical compositions (Table 2). The published reports on solubility and stability of zeolites in aqueous solutions have experimentally shown that Ca-rich clinoptilolite is more stable (less soluble) than K-rich clinoptilolite in alkaline mediums [25,26]. Therefore less pozzolanic activity of BZ, when compared to that of GZ, is probably due to Ca-rich composition of BZ.

3.3. Pore size distribution of the hardened pastes

Pore size distribution of the hardened cement pastes was determined at 28 days and 91 days of age by mercury intrusion porosimetry (MIP) and shown in Fig. 4.

It was observed that total porosity of the blended cement pastes at 28 days was significantly higher than that of the reference portland cement paste, and the difference mainly originates from the pores smaller than 50 nm. It is known that the pore size distribution, not the total porosity, actually controls the strength, permeability and volume changes of hardened cementitious systems. It is believed that pores larger than 50 nm are probably more influential on strength and impermeability characteristics whereas pores smaller than 50 nm play an important role in drying shrinkage and creep [27,28]. Therefore increased total porosity in hardened cement pastes would not be detrimental on their strength and impermeability.

No drastic change was observed in pore size distribution and total porosity of BZ55 blended cement paste between 28 days and 91 days of age. However, a considerable decrease in total porosity of GZ55 paste occurred after 28 days mainly due to decrease in volume of 5–50 nm pores, which could be associated with becoming denser of pore system as a result of further formation and growth of pozzolanic reaction products. This kind of process was not observed for BZ55 paste since pozzolanic activity in BZ55 paste is relatively lower, when compared to GZ55, as indicated by higher amount of free $Ca(OH)_2$ present in BZ55 paste at the specified ages. At the end of 91 days, it was observed that zeolite blended cement pastes contain lower volumes of pores >50 nm than PC paste, which could be adopted as a precursor for better strength and impermeability performance of blended cements containing high volume of natural zeolite.

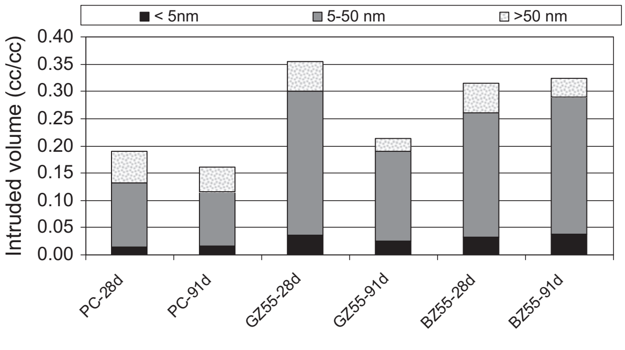


Fig. 4. Pore size distribution of the hardened cement pastes.

3.4. XRD analysis of the hardened pastes

XRD patterns of the hardened cement pastes are given in Fig. 5 with identified phases.

As seen from Fig. 5, tetra calcium aluminate hydrate ($4CaO.Al_2O_3.13\ H_2O$) was detected as a crystalline hydration product formed in natural zeolite blended cement pastes. The peaks corresponding to CH were observed with low intensities on 7-day XRD pattern of blended cement pastes, however no CH peak was detected in 28-day patterns, conforming the results of thermal analyses. The peaks corresponding to clinoptilolite got smaller in intensity and reduced in sharpness on 28-day XRD pattern of the blended cements, when compared to the 7-day patterns. This observation is associated with decomposition of zeolite phase in alkaline media. On the other hand, it was observed that no reduction in intensity of the peaks corresponding to quartz phase in zeolite blended cements between 7 days and 28 days of hydration since the quartz is an inert mineral in terms of pozzolanic reaction. In addition, it should be noted that the peaks corresponding to clinoptilolite were more evident on the patterns of BZ55 paste when compared to those of GZ55 paste, which also confirms relatively less decomposition (more stability) of Ca-rich clinoptilolite present in BZ tuff.

3.5. BS-SEM observations on the hardened pastes

28-day old hardened cement pastes were examined with backscattered-scanning electron microscopy (BS-SEM) equipped with EDX (energy dispersive X-ray spectroscopy) system.

Backscattered electron image (BEI) shown in Fig. 6 was taken from PC paste at a relatively low magnification (×500), and it exhibited the general microstructural architecture of hardened PC paste. Partially hydrated individual cement grains were clearly observed with a relatively brighter unhydrated core and surrounding shell of hydration products in a relatively darker color. Micro pores appeared as black areas as well as some micro cracks which are probably induced by drying shrinkage and mechanical stresses occurred during sample preparation were also observed.

BS-SEM image taken from GZ55 paste at 500 × magnification, shown in Fig. 7, displayed a completely different microstructural architecture when compared to the reference PC paste. Zeolitic tuff grains in a wide range of particle sizes were clearly observed in a

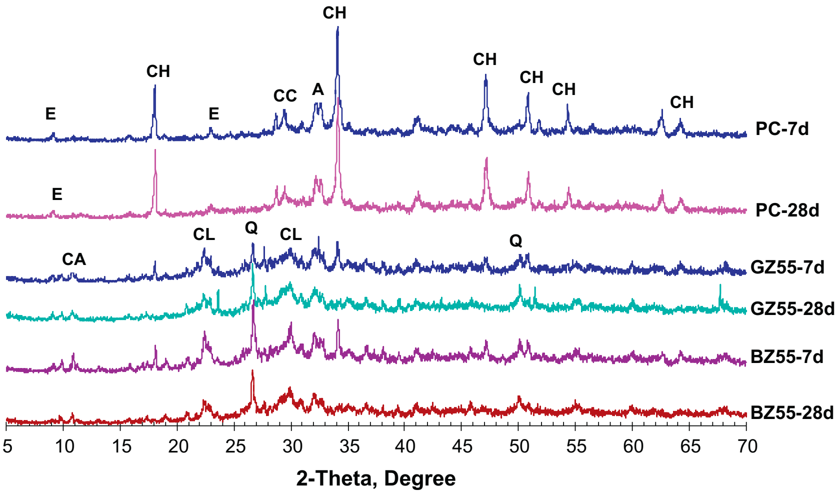


Fig. 5. XRD patterns of hardened cement pastes at 7 days and 28 days (A: alite, CA: tetra calcium aluminate hydrate, CC: calcite, CH: calcium hydroxide, CL: clinoptilolite, E: ettringite and Q: quartz).

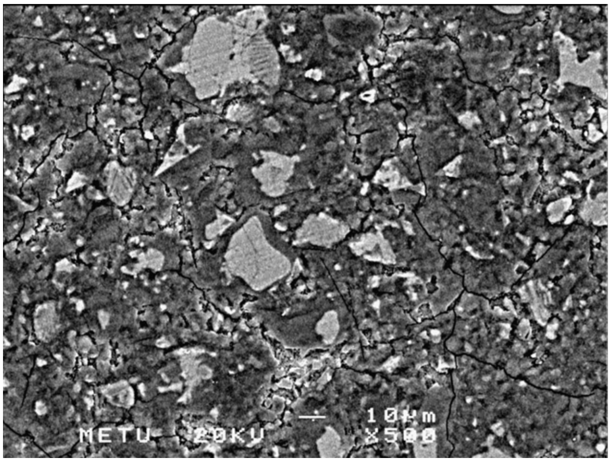


Fig. 6. BS-SEM image taken from 28-day PC paste.

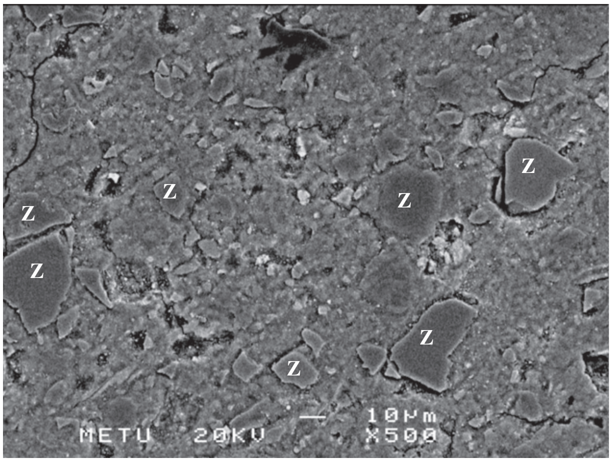


Fig. 7. BEI of 28-day old GZ55 paste at 500× magnification (Z: zeolitic tuff grains).

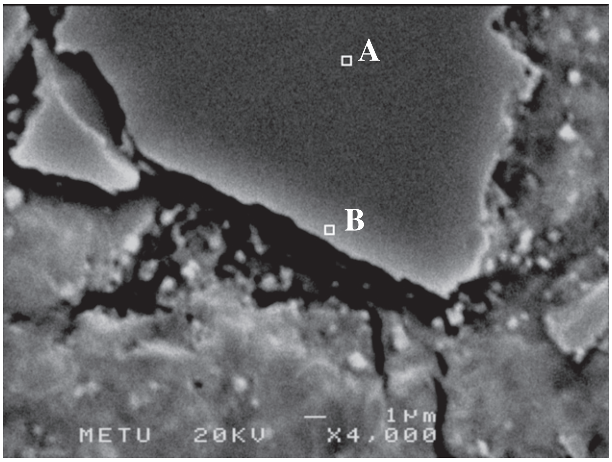


Fig. 8. BEI of a zeolitic tuff grain in 28-day old GZ55 paste at 4000× magnification.

granular matrix containing some pores. It should be noted that no distinctly unreacted cement particles was observed on general microstructural architecture of GZ55 paste.

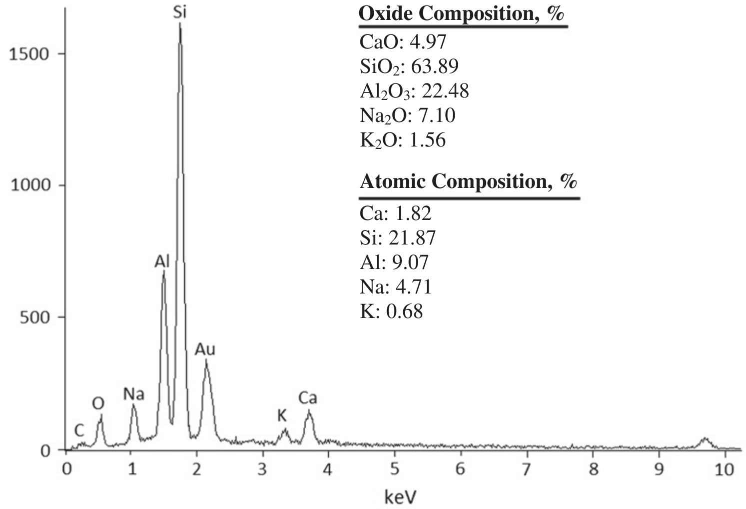
Relatively brighter rims surrounding zeolitic tuff grains were clearly observed in BS-SEM image of GZ55 paste (Fig. 7). This kind of a particle was imaged at 4000 × magnification and shown in Fig. 8. Chemical compositions of relatively darker center and brighter edge of the particle were determined by EDX analysis taken from the points marked with A and B in Fig. 8, and given in Fig. 9. EDX analyses indicated that the surrounding rim (Point B) contains more Ca and less Si when compared to the center of the particle (Point A), and this could be an indication of zeolite dissolution and pozzolanic reaction with Ca^{2+} ions on the surface of the particle.

BS-SEM image of BZ55 paste shown in Fig. 10 exhibited a similar architecture to GZ55 paste. Since BZ has a finer particle size distribution than GZ, relatively small zeolitic tuff grains were generally observed in the hardened BZ55 paste.

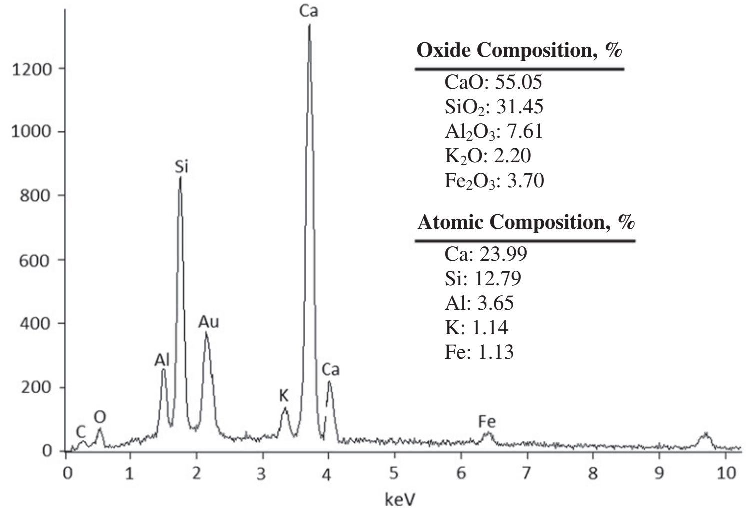
3.6. Superplasticizer requirement and compressive strength of mortars

Superplasticizer dosages used in blended cement mortars to provide a flow value which is similar to that of reference portland cement mortar are given in Table 5 for the naphthalene-based (N-SP) and the melamine-based (M-SP) products.

GZ55 blended cement required approximately three times and two times higher dosages of N-SP and M-SP, respectively, when compared to BZ55, which is probably due to higher BET surface area of GZ (Table 2). It was also observed that M-SP is more



(a) Point A



(b) Point B

Fig. 9. EDX spectrum and corresponding compositions of Point A and Point B shown in Fig. 8.

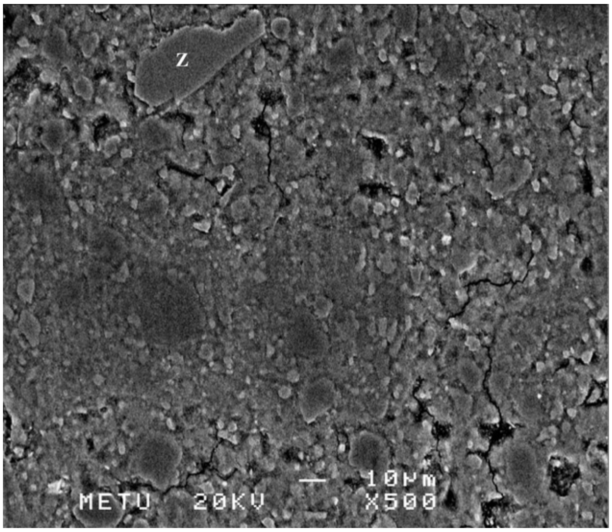


Fig. 10. BS-SEM image taken from 28-day old BZ55 paste at 500× magnification.

effective than N-SP for GZ55, i.e. fewer amounts of M-SP was adequate to provide the desired flow, whereas the reverse was true for BZ55.

Efficiency of superplasticizers in cementitious system depends not only on the active ingredients but also on specific compatibility between the product and the cementitious system. Therefore, without considering the probable causes, it can be stated that GZ55 is more compatible with the melamine-based product whereas BZ55 has a better compliance with the naphthalene-based superplasticizer used in the study in terms of plasticizing ability.

Compressive strength development of blended cement mortars made with N-SP and M-SP are shown in Fig. 11 together with the data belonging to the reference PC mortar without superplasticizer. Blended cement mortars exhibited lower compressive strengths, at

Table 5
Superplasticizer dosages of blended cement mortars.

Cement	w/c	NS		MS	
		Dosage (%)	Flow (%)	Dosage (%)	Flow (%)
GZ55	0.5	2.95	98	2.50	98
BZ55	0.5	1.00	97	1.20	97

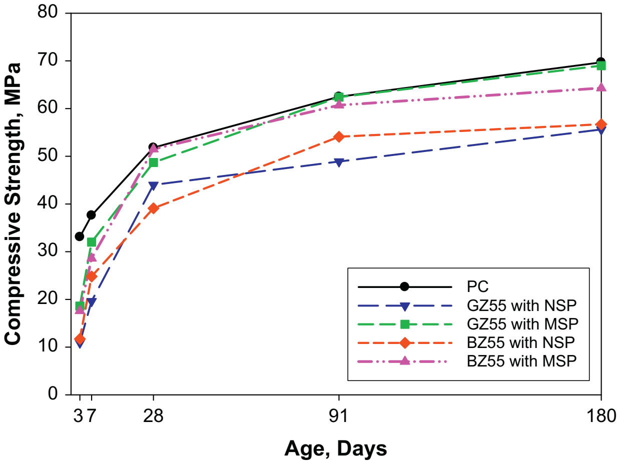


Fig. 11. Compressive strength development of the cement mortars prepared with superplasticizer.

3 days and 7 days of age, than the reference PC mortar. However, at 28 days, blended cement mortars showed similar compressive strength values to the reference PC mortar. It was also observed that the blended cement mortars prepared by using N-SP exhibited lower strength than the corresponding mortars prepared with M-SP.

Considering the strength performance of blended cement mortars together with their pore size distributions, it is clearly confirmed that the higher total porosity of the blended cement pastes mainly originated from pores smaller than 50 nm, when compared to PC paste, does not adversely affect their strength performance. Because the amounts of pores which may negatively affect the mechanical strength of hardened cementitious systems, namely pores larger than 50 nm, are similar for blended cement pastes and reference PC paste (Fig. 4).

4. Conclusions

Based on the experimental results, the following conclusions can be drawn;

1. Blended cements containing large amount of clinoptilolite tuff demonstrated faster initial and final setting time than the ordinary portland cement. This fact may be related to consistency loss resulted from high water absorption of zeolite particles indicated by high water demand of blended cements for normal consistency, rather than setting of the blended system.
2. In blended cement pastes, $Ca(OH)_2$ formed from hydration of PC phase was almost completely consumed at the end of 28 days of hydration. Accordingly blended cements containing large amounts of clinoptilolite tuff were found to be more reactive in terms of pozzolanicity when compared to similar blended systems with non-zeolitic natural pozzolans studied by the authors previously [3].
3. The type of major cation was found to be one of the probable factors governing the pozzolanic activity of clinoptilolite zeolites by affecting their degree of solubility in alkaline conditions.
4. It was experimentally demonstrated that pastes of blended cements containing large amount of clinoptilolite tuff contain less amount of pores >50 nm when compared to portland cement paste, which is beneficial in terms of mechanical strength and impermeability of the pastes.
5. Dissolution of clinoptilolite phase in blended cements pastes was demonstrated by reduced intensity and sharpness of X-ray diffraction peaks corresponding to clinoptilolite crystals between 7 days and 28 days of hydration. Tetra calcium aluminate hydrate ($4CaO.Al_2O_3.13\ H_2O$) was detected as a crystalline product of pozzolanic reaction in blended cement pastes.
6. BS-SEM observations on hardened pastes of blended cements containing 55% natural zeolites indicated that some part of zeolitic tuff particles, especially relatively coarser grains, remains unreacted at 28 days of age. EDX analyses of outer rim of unreacted zeolite particles indicated a possible decomposition and pozzolanic reaction of clinoptilolite on the surface with more calcium and less silicon content when compared to the inner parts.
7. It can be concluded that the natural zeolite of Bigadic source seems to be more viable for use in production of blended cements containing high volume of natural pozzolan since water or superplasticizer requirement of blended systems with Bigadic zeolite is lower than that of Gordes zeolite.
8. Blended cement consisting of 55% zeolitic tuff (BZ) and 45% portland cement exhibited an extraordinary strength performance because it showed similar 28-day compressive strength to that of 100% portland cement. Therefore it can be concluded that the use of zeolitic tuffs in high-volume natural pozzolan systems could eliminate the disadvantage of the lower 28-day strength of this kind of blended systems when compared to ordinary portland cements.

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