

## Effect of the PC, diatomite and zeolite on the performance of concrete composites

Yilmaz Kocak<sup>\*1</sup> and Muhsin Savas<sup>2</sup>

<sup>1</sup>*Department of Construction, Kutahya Vocational School of Technical Sciences,  
Dumlupinar University, Kutahya, Turkey*

<sup>2</sup>*Department of Construction, Institute of Sciences, Duzce University, Düzce, Turkey*

(Received May 12, 2015, Revised December 14, 2015, Accepted March 8, 2016)

**Abstract.** This study has been carried out to investigate the effect of the surface properties of Portland cement, diatomite and zeolite on the performance of concrete composites. In this context, to describe the materials used in this study and determine the properties of them, chemical, physical, mineralogical, molecular, thermal, and zeta potential analysis have been applied. In the study, reference (Portland cement), 10%–20% diatomite, 10%–20% zeolite, 5+5%–10+10% diatomite and zeolite were substituted for Portland cement, a total of 7 different cements were obtained. Ultrasonic pulse velocity, capillary water absorption and compressive strength tests were performed on the hardened concrete specimens. Hardened concrete tests have been done on seven different types of concrete, for 28, 56 and 90 days. As a result of experiments it has been identified that both the zeolite and diatomite substitution has a positive effect on the performance of concrete.

**Keywords:** concrete; diatomite; zeolite; zeta potential; strength

### 1. Introduction

Cement and pozzolans have become common principal construction materials in today's fast developing construction sector. Due to economic and ecological factors, natural pozzolanic materials like trass, zeolite, diatomite and pumice and artificial pozzolanic materials like fly ash, blast furnace slag, bottom ash and silica fume are intensely used in the cement and concrete technology. Some characteristics such as strength, durability and low permeability expected from good concrete are closely related not only to mix proportions but also to cement properties. Some pozzolans like fly ash, silica fume, blast furnace slag, rice husk ash, pumice, zeolite and diatomite are applied in the cement and concrete technology to develop these characteristics (Wang *et al.* 2011, Kocak *et al.* 2013, Gerengi *et al.* 2013, Gerengi *et al.* 2015, Goñi *et al.* 2013, Yildiz *et al.* 2010). Diatomite and zeolite are natural and among the most abundant minerals in Turkey.

Diatomite is a mineral described as consisting of the fossilized siliceous shell of the

---

<sup>\*</sup>Corresponding author, Ph.D., E-mail: [yilmaz.kocak@dpu.edu.tr](mailto:yilmaz.kocak@dpu.edu.tr)

microscopic single-celled alga and possessing the structural properties of amorphous silica. There are nearly fifteen thousand types of diatomite in the nature. Diatomites generally have the shape of a round tray or a long fish. The size of them are 2-200  $\mu\text{m}$ , when they are dry their specific gravity is 0.15-0.40, they contain 70-90% of  $\text{SiO}_2$  and are cellular materials with high water absorption rate (Aruntas and Tokyay 1996).

Zeolite is defined as allophones that consist of alkali and alkaline-earth cations and have the crystal structure. Zeolites have water molecules in their canals which is one of the most significant properties setting apart them from other mineral groups. When they are heated at 100-350°C, these water molecules leave the material continuingly without changing the structure of the zeolite. Another important property of zeolite is ring canals (oxygen windows). These canals are full with univalent and bivalent cations such as  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^+$  with water molecules clinging on them (Canpolat 2002, Serbest 1999).

The studies on surface and interface interactions between mineral additives like diatomite and zeolite and cement are rather limited. However, it is important to explore not only the physical and chemical but also the physico-chemical characteristics of the minerals. Because the surface characteristics and their reactions in the process of hydration are important in terms of stating consistency or inconsistency of the minerals with the cement. In this respect, it is very significant to determine XRD, FT-IR, zeta potential and thermal properties.

In this study, it is tried to state the chemical, physical and mechanic characteristics of the concrete produced with diatomite and zeolite substitution in which Turkey is quite rich. Besides, it is aimed to determine the influence of mineral characteristics and their consistence on the produced concrete via structural analysis techniques (XRD, DTA-TG, FT-IR, and Zeta Potential).

## 2. Materials and methods

### 2.1 Materials

In preparing the test samples, CEM I 42.5 R Portland cement (PC) diatomite and zeolite produced by Bolu Cement Factory is used as a connector in the concrete and diatomite from Kutahya region and zeolite from Balikesir–Bigadic region are used as a pozzolan. Diatomite is supplied from ASU Chemistry and Mining Firm and zeolite from a Turkish Zeolite Firm. The physical, chemical and mechanical properties of the cement, diatomite and zeolite used in the study are given at the Table 1.

0-5 mm crashed sand with 2.66 specific gravity and 0.615% water absorption rate, 5-19 mm crushed stone with 2.69 specific gravity and 0.666% water absorption rate and 19-30 mm with 2.70 specific gravity and 1% water absorption rate are used. These are Asar River aggregates in Duzce region.

In the study, well water from Doganli village in Duzce is used as mixing water. Moreover, the type of fluid 70 produced by AYDOS Construction Chemicals Factory and new generation hyper plasticizer with solid matter content of 34.32, intensity of 1.184 (20°C), pH value of 7.26 (20°C) are applied as admixture for concrete.

### 2.2 Methods

In the study as reference (PC) 10-20% diatomite, 10-20% zeolite, 5+5%–10+10% diatomite

Table 1 The chemical, physical and mechanical properties of of PC, diatomite and zeolite

Materials	PC	Diatomite	Zeolite	Materials	PC	Diatomite	Zeolite
Chemical composition, wt. %				Physical and mechanical properties			
SiO <sub>2</sub>	18.68	79.56	68.85	Blaine, cm <sup>2</sup> /g	4249	13640	5740
Al <sub>2</sub> O <sub>3</sub>	4.67	6.54	11.71	Specific gravity	3.17	2.28	2.18
Fe <sub>2</sub> O <sub>3</sub>	3.53	2.76	1.29	Setting time, minute			
CaO	64.56	2.45	3.97	Initial	118	-	-
MgO	0.98	0.79	1.06	Final	-	-	-
SO <sub>3</sub>	3.00	0.48	0.18	Compressive strength, MPa			
Na <sub>2</sub> O	0.14	2.63	0.29	7 days	29.6	-	-
K <sub>2</sub> O	0.73	0.69	2.19	28 days	52.8	-	-
S+A+F	-	88.86	81.85				
Loss on ignition	3.92	3.88	10.00				
Insoluble residue	0.50	75.98	37.32				
Free CaO	1.74	-	-				

and zeolite are substituted for Portland cement, so 7 different cements are used. The materials used in the experiments are analyzed chemically, physically, molecularly, thermally and electrokinetically (zeta potential).

The chemical analyses of PC, diatomite and zeolite are carried out with ARL 8680 S model X-Ray spectrometer (XRF). Malvern Hydro 2000 G is used in the particle size analyses. Surface area is determined with Toni Technik 6565 model Blaine device and specific gravity with Quantachrome MVP-3 model. Mineralogical properties are stated with Rikagu miniflex model XRD using Cu K<sub>α</sub> ( $\lambda=1.54 \text{ \AA}$ ) radiation. FT-IR analyses are carried out with Bruker Vertex 70 model. The materials are measured 400–4000 cm<sup>-1</sup> in wave number spectrum with ATR device.

Zeta potential is measured via Zeta-Meter System 3.0 + device that works according to electrophoresis method. 0.5 g samples from all materials are put in 50 ml pure water in different beakers and mixed for 10 minutes to adjust their HCl, NaOH and pH values. After they have been retained for 5 minutes for the big particles to settle in the water, their zeta potential is calculated. In all pH values sufficient numbers of particles (at least 10) are calculated according to their movement speed via microprocessor of the device and these findings are converted to zeta potential values, so their average zeta potential values are determined.

Simultaneous Thermal Analyses of the samples (STA) are carried out at a heating rate of 20 °C/minute, so they reach 1000 °C maximum temperature. Nitrogen gas and samples of nearly 50 mg are used in the analyses. STAs are determined via Perkin Elmer S II device at the laboratory in the department of Chemical Engineering in Dumlupınar University.

For concrete mixture design, materials' amounts to be put into the mixture are determined within the framework of the method stated in TS 802 standards. According to the type and rate of mineral additive, which is substituted for the concrete, seven types of concrete are produced. They are encoded as R, 10D, 20D, 10Z, 20Z 5D5Z and 10D10Z according to the addition rate and the used mineral additive. According to TS EN 12350-2, consistency of concrete in fresh concrete is stated for each mixing group individually. The materials amounts of the samples in concrete mixture of 1m<sup>3</sup> and the characteristics of fresh concrete are given in the Table 2.

Table 2 Material quantity in the 1 m<sup>3</sup> for each concrete group

Materials	Specific gravity	R, kg	10D, kg	20D, kg	10Z, kg	20Z, kg	5D+5Z, kg	10D+10Z, kg
Aggregate	0-5	2.66	822	831	822	843	855	855
	5-19	2.69	586	593	586	602	611	611
	19-30	2.70	428	433	428	439	446	445
	Total		1836	1857	1836	1884	1912	1911
PC	3.17	400	360	320	360	320	360	320
Diatomite	2.28	-	40	80	-	-	20	40
Zeolite	2.18	-	-	-	40	80	20	40
Hyper plasticizer	1.184	4.800	4.320	4.800	4.320	4.800	4.320	3.840
Water	1	139.7	139.7	123.3	139.7	123.2	139.7	124.2

The produced concrete is poured into 15x15x15 cm cubic molds without segregation. These concretes are retained for 24 hours in the molds and harden, then, they are cured in 23±2°C water for 28, 56 and 90 days. After the curing periods ultrasonic pulse velocity and capillary water absorption tests are carried out on the hardened concrete samples. Compressive strength tests of concrete are carried out up to the Standard of TS EN 12390-3.

### 3. Findings and discussion

Chemical, physical, mineralogical, molecular, thermal and zeta potential analyses are carried out to state the characteristics of the materials used in the study. Moreover, slump value, ultrasonic pulse velocity, capillarity coefficient and compressive strength tests are carried out during pouring of concrete. The findings of these experiments are given below.

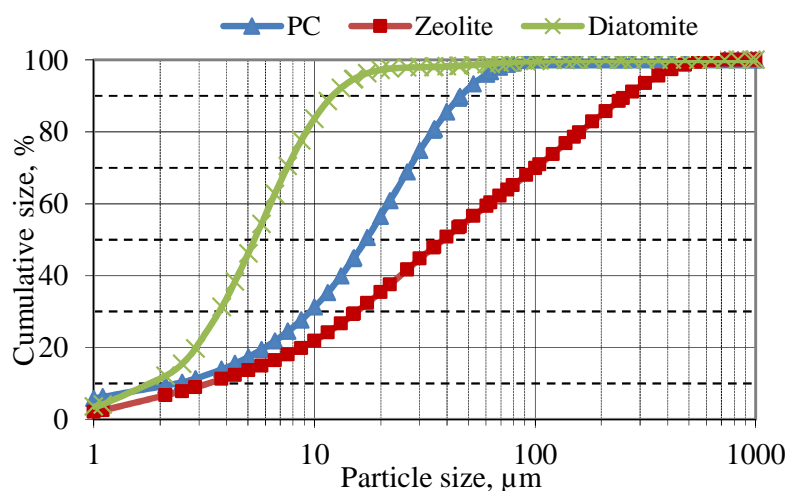


Fig. 1 Particle size distributions of PC, zeolite and diatomite

### 3.1 Chemical analysis

PC includes a high rate of CaO, but a low rate of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SO}_3$  components. The main component of diatomite is  $\text{SiO}_2$  and its  $\text{SiO}_2/\text{Al}_2\text{O}_3$  percentage by weight (S/A) is 12.17. The main component of zeolite is also  $\text{SiO}_2$  and its S/A rate is 5.88. The fact that the rate of  $\text{Na}_2\text{O}$  is higher than the rate of  $\text{K}_2\text{O}$  in diatomite shows that it is rich in  $\text{Na}^+$  ions. The fact that the rate of  $\text{K}_2\text{O}$  is higher than the rate of  $\text{Na}_2\text{O}$  in zeolite shows that it is rich in  $\text{K}^+$  ions. Beside, according to ASTM C 618, total of S+A+F which is supposed to be minimum 70%, is almost 89% in diatomite and 82% in zeolite. Their pozzolanic properties are chemically observed affirmative (Table 1) (ASTM C 618-85 1985).

### 3.2 Physical analysis

Particle size distribution, Blaine values (specific surface areas) and specific gravities are determined in physical analyses. The particle size distribution of PC, diatomite and zeolite are given in the Fig. 1.

The figures of the particle size analysis prove that diatomite has finer particle size. According to their 90% subsieve fractions, the particle size of PC, diatomite and zeolite are 50, 13 and 280  $\mu\text{m}$  respectively. Considering the particle size analysis the finest material is diatomite followed by PC and zeolite (Fig. 1). According to Blaine values, diatomite is the smallest material followed by zeolite and PC (Table 1).

Considering specific gravity values, PC is 3.17, diatomite 2.28 and zeolite 2.18, thus, zeolite has the lowest specific gravity (Table 1).

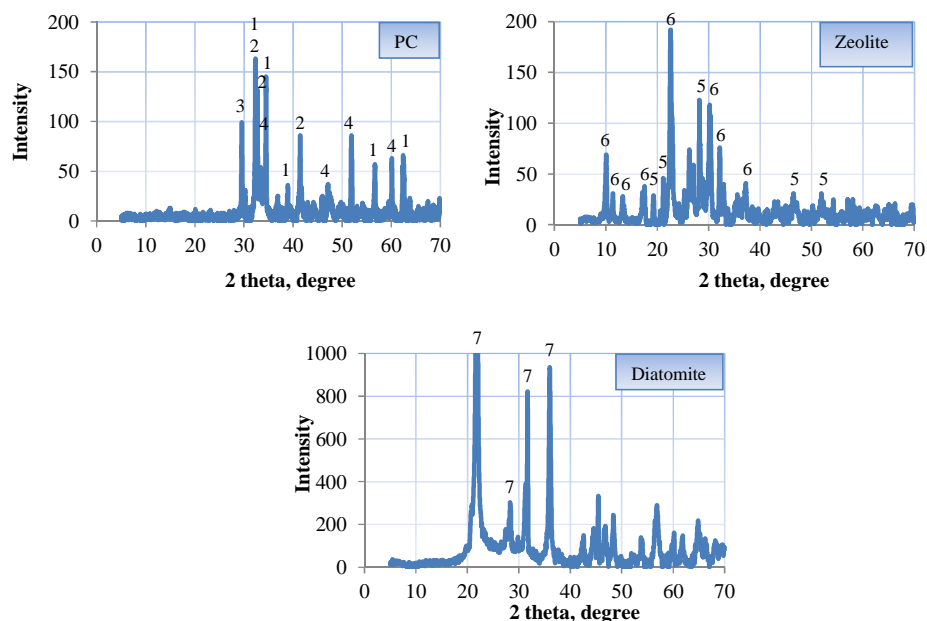


Fig. 2 XRD analysis of PC, zeolite and diatomite [1: Alite ( $3\text{CaOSiO}_2$ ), 2: Belite ( $2\text{CaOSiO}_2$ ), 3: Tricalcium aluminate ( $3\text{CaOAl}_2\text{O}_3$ ), 4: Brownmillerite ( $\text{Ca}_2(\text{Al,Fe}^{3+})_2\text{O}_5$ ), 5: Quartz ( $\text{SiO}_2$ ), 6: Clinoptilolite,  $(\text{Na,K})_6[\text{Al}_6\text{Si}_{30}\text{O}_{72}]\cdot 20\text{H}_2\text{O}$ ), 7: Cristobalite]

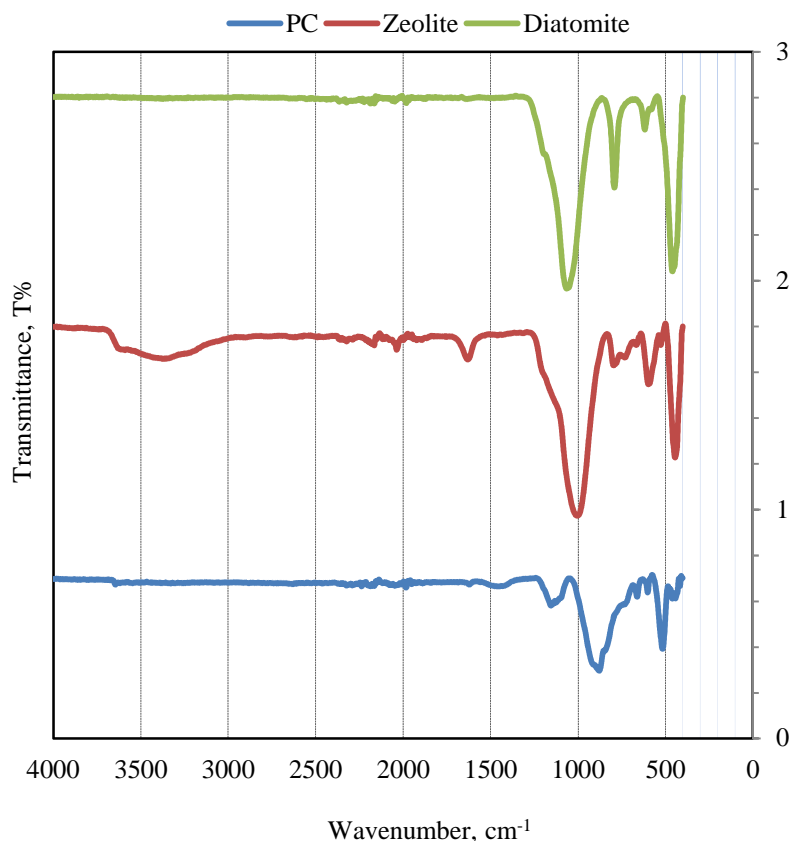


Fig. 3 FT-IR spectrum analysis of PC, zeolite and diatomite

### 3.3 XRD analysis

XRD analyses are carried out to determine the mineralogical structure of PC, zeolite and diatomite used in the study (Fig. 2).

PC is crystal and composed of alite–tricalcium silicate ( $3\text{CaOSiO}_2$ ), belite–dicalcium silicate ( $2\text{CaOSiO}_2$ ), tricalcium aluminate ( $3\text{CaOAl}_2\text{O}_3$ ) and brownmillerite ( $\text{Ca}_2(\text{Al,Fe}^{3+})_2\text{O}_5$ ). XRD of zeolite's mineralogical composition shows that it has a crystal structure of quartz ( $\text{SiO}_2$ ) and clinoptilolite ( $(\text{Na,K})_6[\text{Al}_6\text{Si}_{30}\text{O}_{72}]20\text{H}_2\text{O}$ ) (Blanco *et al.* 2006). With its form of silica, diatomite is composed of cristobalite (Fig. 2) (Jia *et al.* 2008).

### 3.4 FT-IR analysis

Thanks to the results of FT-IR of PC, zeolite and diatomite, the surface structures of the molecules are stated and given in the Fig. 3.

In FT-IR spectroscopy the atomic vibrations forming solid cages are observed in  $400\text{--}1600\text{ cm}^{-1}$  region, the molecular vibrations in  $1600\text{--}4000\text{ cm}^{-1}$  region. The result of the FT-IR analysis of PC proves that there are vibrations in the wave numbers 459, 500, 600, 660, 892, 1150, 1446, 1689, 3400 and  $3640\text{ cm}^{-1}$ . Al–O bonds accompanying Si–O produce 459 and  $500\text{ cm}^{-1}$

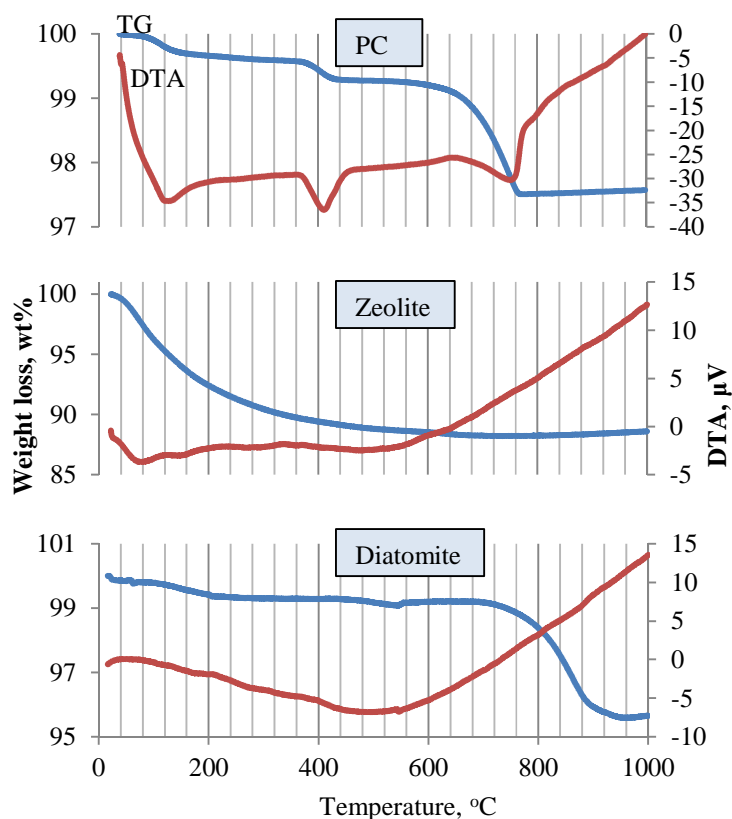


Fig. 4 DTA and TG analysis of PC, zeolite and diatomite

symmetrical vibrations. Si–O bonds in solid cages are in the form of symmetrical vibrations in the wave number  $892\text{ cm}^{-1}$ . Sulphur–Oxygen bonds (S–O) showing the plaster work in CEM I 42.5 R cement are observed in  $600, 660, 1150$  and  $1689\text{ cm}^{-1}$ .  $\text{CO}_3^{2-}$  is seen in  $1446\text{ cm}^{-1}$ . Water ions and molecules in its structure are found in the wave numbers  $3400$  and  $3640\text{ cm}^{-1}$  (Fig. 3) (Gomes *et al.* 2005, Govin *et al.* 2006).

The results of FT–IR analysis of diatomite show that there are vibrations in the wave numbers  $468, 619, 798$  and  $1080\text{ cm}^{-1}$ . Si–O–Si bonds produce asymmetrical vibrations in the wave numbers  $468$  and  $1080\text{ cm}^{-1}$ . In the structures Al–O–Si bonds are in the form of vibration in the wave numbers  $619$  and  $798\text{ cm}^{-1}$  (Fig. 3) (Skripkiunas *et al.* 2007, Sprynsky *et al.* 2010).

Finally, the results of FT–IR analysis of zeolite shows that there are vibrations in the wave numbers  $452, 600, 800, 1000, 1639, 3390$  and  $3600\text{ cm}^{-1}$ . Si–O–Si and Si–O–Al bonds produce vibrations in the wave numbers  $452$  and  $1000\text{ cm}^{-1}$ . In the structure Al–O–Al bonds are in the form of vibration in the wave number  $600\text{ cm}^{-1}$ . Si–O–Si bond is in the form of symmetrical vibrations in the wave number  $800\text{ cm}^{-1}$ . Zeolite water (H–OH) is stated in the wave number  $1639\text{ cm}^{-1}$  and the vibrations attaching to the water with hydrogen bridges (OH) in the wave numbers  $3390$  and  $3600\text{ cm}^{-1}$ . According to the studies, while interpreting the wave numbers  $500\text{--}800\text{ cm}^{-1}$  of FT–IR spectrums, it is emphasized that there are clinoptilolite peaks in the wave number  $602\text{ cm}^{-1}$  and heulandite peaks in the wave number  $594\text{ cm}^{-1}$ . In this study, the group in the wave number  $600$

Table 3 % Weight loss in the various temperature ranges of PC, diatomite and zeolite

Materials	0-200°C	200-400°C	400-600°C	600-800°C	Total
PC	0.341	0.216	0.240	1.689	2.432
Diatomite	0.582	0.135	0.087	0.811	4.343
Zeolite	7.582	2.997	0.890	0.269	11.385

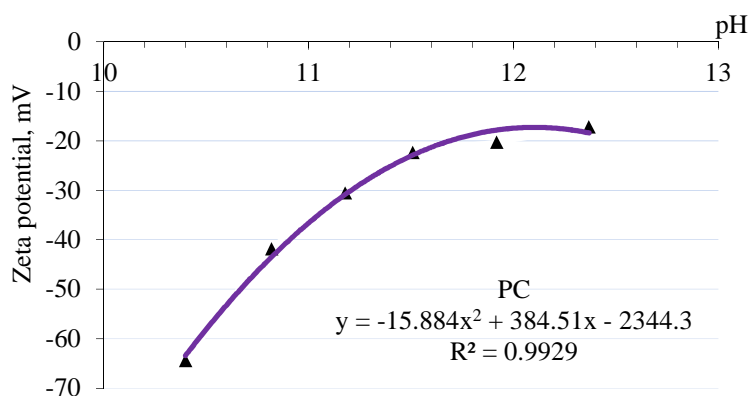


Fig. 5 Zeta potential of PC

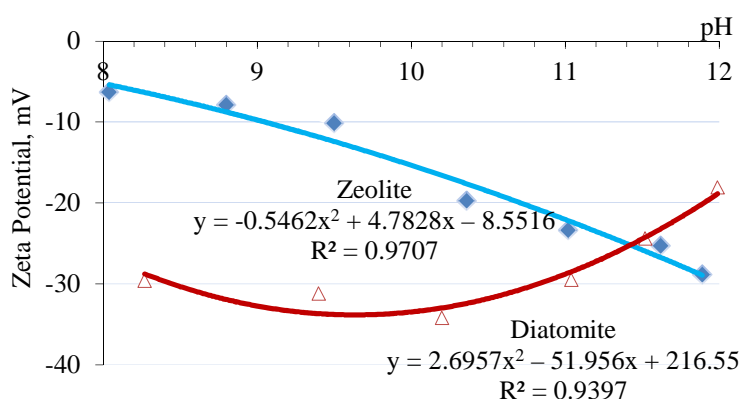


Fig. 6 Zeta potentials of zeolite and diatomite

$\text{cm}^{-1}$  proves the existence of silica-rich clinoptilolite (Fig. 3) (Karakaya 2006, Blanco *et al.* 2006, Mozgawa 2001, Perraki and Orfanoudaki 2004).

### 3.5 Thermal analysis

Differential Thermal Analysis (DTA) and Thermal Gravimetry (TG) curves of PC, zeolite and diatomite are given in the Fig. 4. Weight loss in various temperature ranges is calculated through the data of the curves in the Fig. 4 and they are shown in the Table 3.

As it is seen from the DTA curves, while endothermic peaks appear at 127, 410 and 753 °C in PC and at 75 and 152 °C in zeolite, there are no obvious peaks in diatomite (Fig. 4). When



examined the weight loss at various temperatures, zeolite has the most abundant stoma and biggest dehydration of the physical and chemical water in its structure, followed by diatomite and PC. While the obvious peak showing decarbonization of carbonate phases ( $\text{CaCO}_3$ ) is observed at  $753^\circ\text{C}$  in the cement, there is no obvious peak in diatomite and zeolite (Fig. 4). In terms total weight loss, zeolite is ranked as the 1st (11.385%), diatomite the 2nd (4.343%) and PC the 3rd (2.432%) (Table 3).

### 3.6 Zeta potential

Zeta potential measurements for PC are given in the Fig. 5, the ones for diatomite and zeolite in the Fig. 6.

The researches show that the surface charge of the cement is generally negative (Yildiz *et al.* 2010, Viallis *et al.* 2001, Yoshioka *et al.* 2002), but may be positive (Nachbaur *et al.* 1998, Termkhajornkit and Nawa 2004) depending on its structure. According to the results of experimental studies, it is seen that PC (Fig. 5), diatomite and zeolite (Fig. 6) hold negative ions. At the same time,  $\text{Ca}^{2+}$  ions in PC approach PC towards positive ions depending on pH increase. The reason why PC has negative ions is because of  $\text{SO}_4^{2-}$  ions coming from gypsum ( $\text{CaSO}_4$ ) and  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$  and Si-O bonds in its structure (Fig. 3). Therefore,  $\text{Ca}^{2+}$ ,  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{SO}_4^{2-}$  are the ions determining the potential of PC.

When the zeta potential of the pozzolanic materials are examined, both diatomite and zeolite have negative ions in all pH values. While the surface charge of diatomite decreases from  $-29$  in pH 8 to  $-18\text{mV}$  in pH 12, zeolite increases from  $-6$  in Ph 8 to  $-29$  mV in pH 12 in terms of absolute value (Fig. 6).

According to DLVO theory (Skripkiunas *et al.* 2007, Gabrovsek *et al.* 2006), interactions of the particles with each other depend on their surface charge and the distance between them. Due to electrical double layer and Van der Waals forces the particles that have surface charge of between  $-25$  and  $+25$  mV are magnetized to each other as they approach to each other (Gabrovsek *et al.* 2006, Drazan and Zelic 2006). In the exact opposite situation, they disperse. However, when the particles with different surface charge show up, opposite or equal charges emerge in addition to the events mentioned above. In other words, while the particles electrostatically charged opposite pull towards each other, the particles charged equally push away from each other. Here, PC whose media-pH is about 12, diatomite and zeolite in the same media but individually are supposed to

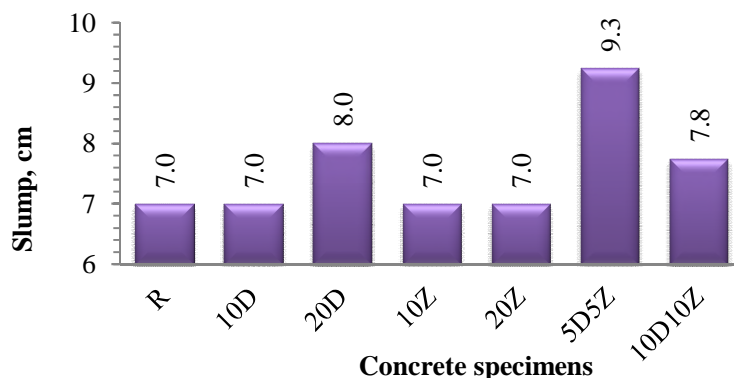


Fig. 7 Slump test results of concrete specimens

push away from each other. However, because the surface charges of the pozzolans are  $-25$  mV, so very close to  $-25$  and  $+25$  mV values, electrical double layer forces and Van der Waals forces with minor effect come into play (Nachbaur *et al.* 1998, Gabrovsek *et al.* 2006, Pan *et al.* 2002). Thus, it can be said that pozzolans are consistent with PC. But, if zeolite and diatomite are used together, the influence of its negative surface charge is considered to be a bit more inverse.

### 3.7 Slump test

While the samples are being prepared for the study, it is aimed to make a mixture design with a slump between 7 cm and 10 cm. Slump test results belonging to the produced concretes are given in the Fig. 7.

In the light of the data, the slump amount is 7 cm in the concretes with PC, 10D, 10Z and 20 Z codes, 7.8 cm in the concrete with 10D10Z code, 8 cm in the concrete with 20D code and 9.3 cm in the concrete 5D5Z code (Fig. 7).

### 3.8 Capillary water absorption

A graphic is drawn between the averages of water amount absorbed per unit area ( $Q/A$ ) and the square root of capillary water absorption durations ( $t^{0.5}$ ). Capillarity coefficients are obtained from the curves of the graphs and the average capillarity coefficients of capillary water absorption test results are given in the Fig. 8.

As a result of the experiments conducted, it is found out that at the end of 28 days the concrete sample with 10D10Z code has the highest average capillarity coefficient ( $4.8 \times 10^{-4}$  cm/s<sup>0.5</sup>) and the concrete sample with 10D code has the lowest average capillarity coefficient ( $3.6 \times 10^{-4}$  cm/s<sup>0.5</sup>), at the end of 56 days, the concrete sample with 10D10Z code has the highest value ( $4.5 \times 10^{-4}$  cm/s<sup>0.5</sup>) and the concrete sample with 10Z code has the lowest value ( $2.6 \times 10^{-4}$  cm/s<sup>0.5</sup>), at the end of 90 days, the concrete sample with 20Z code has the highest value ( $3.9 \times 10^{-4}$  cm/s<sup>0.5</sup>) and the concrete sample with 10Z code has the lowest value ( $2.6 \times 10^{-4}$  cm/s<sup>0.5</sup>) (Fig. 8). According to the findings, there is an inverse relationship between the increase of hydration period and capillarity coefficient.

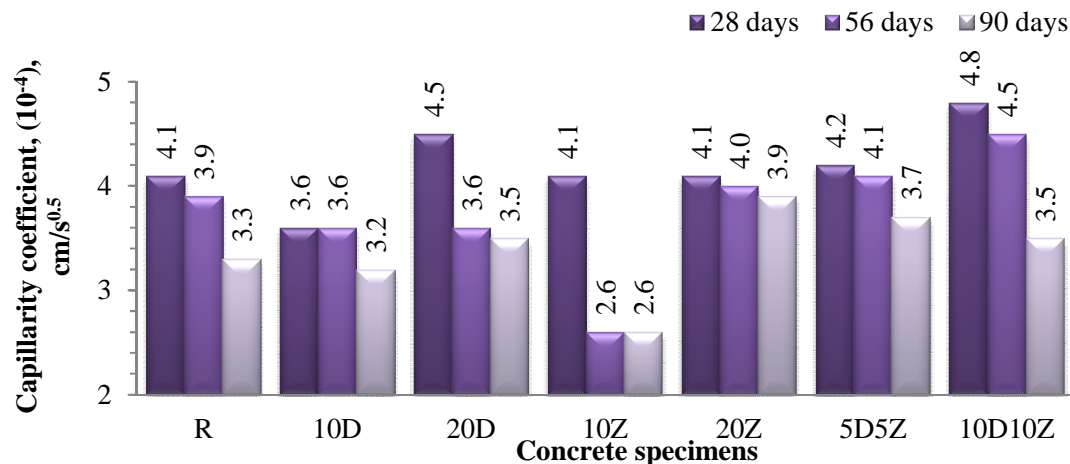


Fig. 8 Capillarity coefficients of concrete specimens

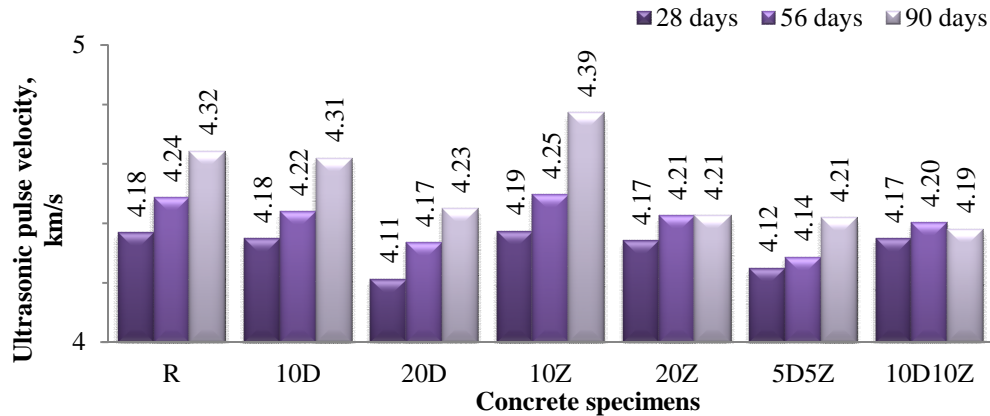


Fig. 9 Ultrasonic pulse velocity of concrete specimens

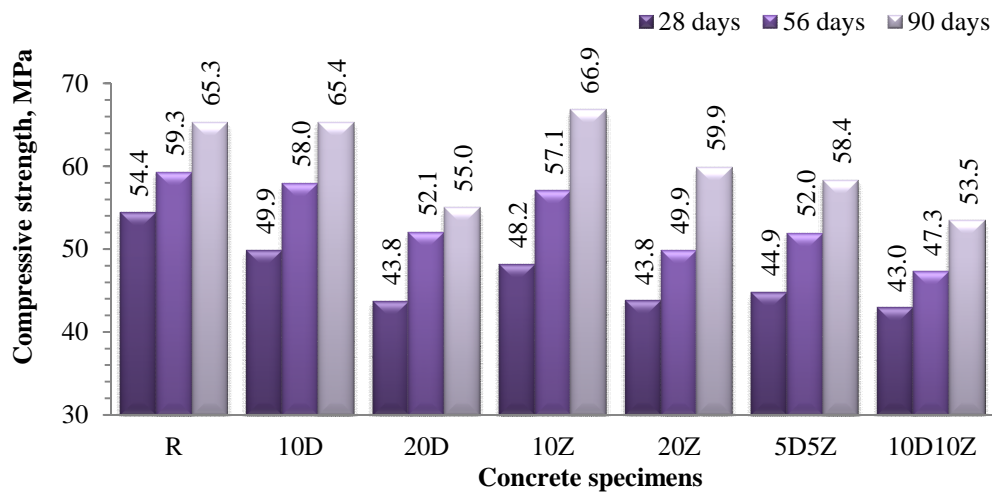


Fig. 10 Compressive strength of concrete specimens

The researches show that the produced concretes have a low capillary spaces and their quality is good (Ghrici *et al.* 2007, Siddique and Kadri 2011, Topcu *et al.* 2009, Kelestemur and Demirel 2010, Kelestemur 2010).

### 3.9 Ultrasonic pulse velocity

Ultrasonic pulse velocity test results of the produced concretes are shown in the Fig. 9.

As a result of the experiments conducted, it is found out that at the end of 28 days the concrete sample with 10Z code has the highest ultrasonic pulse velocity (4.19 km/s) and the concrete sample with 5D5Z code has the lowest ultrasonic pulse velocity (4.12 km/s), at the end of 56 days, the concrete sample with 10Z code has the highest value (4.25 km/s) and the concrete sample with 5D5Z code has the lowest value (4.14 km/s), finally, at the end of 90 days, the concrete sample

with 10Z code has the highest value (4.39 km/s) and the concrete sample with 10D10Z code has the lowest value (4.19 km/s) (Fig. 9). According to the assessment of the quality of all concrete samples produced up to the ultrasonic pulse velocity values by Whitehurst (3.5–4.5 km/s), they belong to the good category of concrete (Erdogan 2010).

### 3.10 Compressive strength

Compressive strength test results of the produced concrete samples are given in the Fig. 10.

When the test results are examined, it is obvious that compressive strength of the concrete samples depend on type of mineral additives, substitution rate, particle size, specific surface areas and hydration duration.

According to the compressive strength test results, it is stated that at the end of 28 and 56 days the concrete samples with 10D10Z code have the lowest compressive strength and reference concretes have the highest compressive strength. It is found out that at the end of 90 days the concrete samples with 10D10Z code still have the lowest value but the concrete sample with 10Z code has the highest value. When the compressive strength tests carried out at the end of 28 days are taken as basis, according to mortar samples carried out with reference cement, the concrete samples with 10D, 20D, 10Z, 20Z, 5D5Z and 10D10Z exhibit a strength decrease of 8.4%, 19.6%, 11.4%, 19.5%, 17.6%, and 21.1% respectively. When the compressive strength tests carried out at the end of 56 days are taken as basis, according to mortar samples carried out with reference cement, the concrete samples with 10D, 20D, 10Z, 20Z, 5D5Z and 10D10Z exhibit a strength decrease of 2.2%, 12.2%, 3.7%, 15.8%, 12.4%, and 20.2% respectively. When the compressive strength tests carried out at the end of 90 days are taken as basis, according to mortar samples carried out with reference cement, while the concrete samples with 20D, 20Z, 5D5Z and 10D10Z exhibit a strength decrease of 15.8%, 8.3%, 10.7%, and 18.1%, the concrete samples with 10D and 10Z code exhibit a strength increase of 0.1% and 2.4% (Fig. 8). When the rate of 10% is taken as basis, this fact proves that both diatomite and zeolite substitution increase compressive strength in the future hydration phases due to their pozzolanic properties, the concrete samples with diatomite and zeolite substitution acquire strength more slowly compared to the reference concrete. Besides, it is obvious that the compressive strength of the concretes in which diatomite and zeolite substitutions are used together is much lower compared to the compressive strength of the concretes in which diatomite or zeolite substitutions are used separately. It is because of the fact that due to diatomite and zeolite potentials have negative values; these pozzolans cannot show enough positive surface property (Fig. 6).

According to the compressive strength test results, it develops in consistency with both ultrasonic pulse velocity and capillary coefficients at the end of 90 days, it is determined that the compressive strength of diatomite and zeolite for 10% substitution leaves the reference concrete behind even a little. Moreover, it is thought that more durable concretes can be produced by making no concessions to strength due to the fact that there are just a few capillary spaces (Fig. 8).

## 4. Results and recommendations

To sum up the results of chemical, physical, mechanical, mineralogical, molecular, thermal and zeta potential analyses relating to using diatomite, zeolite or various combinations of both in a high strength concrete;

- As a result of the chemical analyses, it is stated that diatomite and zeolite are positive in terms of pozzolanic characteristics ( $S+A+F \geq 70\%$ ),
- As a result of the XRD analyses, zeolite has a crystal structure composed of quartz and clinoptilolite and cristobalite consistent with the silica form of diatomite, Portland Cement has a crystal structure of the main components such as alite, belite, tricalcium aluminate and brownmillerite,
- As a result of the particle size analysis, the particles of zeolite are coarse, the ones of PC are medium and the ones of diatomite are fine,
- According to their specific gravities, PC weighs 3.17, diatomite 2.28 and zeolite 2.18, thus, zeolite has the lowest specific gravity,
- According to the zeta potential of the materials, PC, diatomite and zeolite have negative surface charge in all pH values,
- The slump amount in the concrete mixture prepared with the reference and pozzolan substituted cements is about 7 cm, thus, the concrete of plastic consistency is produced and the cohesion in all types of concrete is fine, no disintegration is observed,
- Ultrasonic pulse velocity values depend on concrete type and age, as hydration day increases, ultrasonic value increases accordingly in the concrete samples,
- In all media, as hydration age gets along, water amount absorbed via capillary channels decreases and develops in consistency with ultrasonic pulse velocity values,
- The compressive strength values of the concrete samples depend on material type, substitution rate and concrete age; the speed of strength acquisition of the diatomite and zeolite substituted concrete samples is slower than the one of reference concrete; compressive strength values develop in consistency with ultrasonic pulse velocity and capillary water absorption values.

As the results of the tests, it is stated that both diatomite and zeolite substitutions have a positive influence on the produced concrete samples and the most proper substitution rate is determined to be 10%. In the concrete samples produced up to this rate, especially a 90-days compressive strength results turn out to be better than the ones of reference concrete. Besides, the fact that capillary water absorption rates turn out to be very low in these substitution rate makes us think that it is possible to produce not only high-strength concrete but also highly durable one. Although Turkey is rich in diatomite and zeolite, their use is very limited. It is thought that both diatomite and zeolite may be an alternative to the materials in the artificial pozzolan category like blast furnace slag, fly ash and silica fume which are widely used in the concrete sector.

## Acknowledgement

In this study, the authors thank Duzce University Presidency of Scientific Research Projects that provided financial support with the project code number 2011.03.HD.009 and Duzce Yigitler Beton that enabled the tests to be carried out.

## References

- Aruntas, H.Y. and Tokyay, M. (1996), "The use of diatomite as pozzolanic material in blended cement production", *Cement Concrete World*, **1**(4), 3-41.
- ASTM C 618-85. (1985), *Standard specifications for fly ash and raw or calcined natural pozzolan for use as mineral admixture in Portland cement concrete*, ASTM, Philadelphia, USA.

- Canpolat, F. (2002), "Utilization of natural zeolite and industrial waste in improving cement performance in cement production", Doctorate Thesis, Suleyman Demirel University, Graduate School of Science, Engineering and Technology; Sakarya (in Turkey).
- Erdogan, T.Y. (2010), *Concrete*, Metu Press Publishing Company ; Ankara, Turkey.
- Gabrovšek, R., Vuk, T. and Kaučič, V. (2006), "Evaluation of the hydration of Portland cement containing various carbonates by means of thermal analysis", *Acta Chim. Slov.*, **53**, 159-165.
- Gerengi, H., Kocak, Y., Jazdzewska, A., Kurtay, M. and Durgun, H. (2013), "Electrochemical investigations on the corrosion behaviour of reinforcing steel in diatomite-and zeolite-containing concrete exposed to sulphuric acid", *Constr. Build. Mater.*, **49**, 471-477.
- Gerengi, H., Kurtay, M. and Durgun, H. (2015), "The effect of zeolite and diatomite on the corrosion of reinforcement steel in 1M HCl solution", *Result. Phys.*, **5**, 148-153.
- Ghrici, M., Kenai, S. and Said-Mansour, M. (2007), "Mechanical properties and durability of mortar and concrete containing natural pozzolana and limestone blended cements", *Cement Concrete Compos.*, **29**(7), 542-549.
- Gomes, C.E.M., Ferreira, O.P. and Fernandes, M.R. (2005), "Influence of vinyl acetate-versatic vinylester copolymer on the microstructural characteristics of cement pastes", *Mater. Res.*, **8**(1), 51-56.
- Göni, S., Frias, M., de la Villa, R.V. and García, R. (2013), "Sodium chloride effect on durability of ternary blended cement. Microstructural characterization and strength", *Compos. Part B: Eng.*, **54**, 163-168.
- Govin, A., Peschard, A. and Guyonnet, R. (2006), "Modification of cement hydration at early ages by natural and heated wood", *Cement Concrete Compos.*, **28**(1), 12-20.
- Jia, Y., Han, W., Xiong, G. and Yang, W. (2008), "A method for diatomite zeolitization through steam-assisted crystallization with in-situ seeding", *Mater. lett.*, **62**(16), 2400-2403.
- Jozic, D. and Zelic, J. (2006), "The effect of fly ash on cement hydration in aqueous suspensions", *Ceramics-Silikaty*, **50**(2), 98-105.
- Karakaya, M.C. (2006), *Properties of clay minerals and identification methods*, Bizim Buro Press Publishing Company; Ankara, Turkey.
- Keleştemur, O. (2010), "Utilization of waste vehicle tires in concrete and its effect on the corrosion behavior of reinforcing steels", *Int. J. Min., Metallurgy Mater.*, **17**(3), 363-370.
- Keleştemur, O. and Demirel, B. (2010), "Corrosion behavior of reinforcing steel embedded in concrete produced with finely ground pumice and silica fume", *Constr. Build. Mater.*, **24**, 1898-1905.
- Kocak, Y., Tasci, E. and Kaya, U. (2013), "The effect of using natural zeolite on the properties and hydration characteristics of blended cements", *Constr. Build. Mater.*, **47**, 720-727.
- Mozgawa, W. (2001), "The relation between structure and vibrational spectra of natural zeolites", *J. Mol. Struct.*, **596**(1), 129-137.
- Nachbaur, L., Nkinamubanzi, P.C., Nonat, A. and Mutin, J.C. (1998), "Electrokinetic properties which control the coagulation of silicate cement suspensions during early age hydration", *J. Colloid Interf. Sci.*, **202**(2), 261-268.
- Pan, Z., Cheng, L., Lu, Y. and Yang, N. (2002), "Hydration products of alkali-activated slag-red mud cementitious material", *Cement Concrete Res.*, **32**, 357-362.
- Perraki, T. and Orfanoudaki, A. (2004), "Mineralogical study of zeolites from Pentelofos area, Thrace, Greece", *Appl. Clay Sci.*, **25**(1), 9-16.
- Serbest, D. (1999), "The use of natural zeolites in the industry of the light construction", Master's Thesis, Anadolu University, Graduate School of Science, Engineering and Technology; Eskişehir (in Turkey).
- Siddique, R. and Kadri, E.H. (2011), "Effect of metakaolin and foundry sand on the near surface characteristics of concrete", *Constr. Build. Mater.*, **25**(8), 3257-3266.
- Skripkiūnas, G., Sasnauskas, V., Daukšys, M. and Palubinskaite, D. (2007), "Peculiarities of hydration of cement paste with addition of hydrosodalite", *Mater. Sci.-Poland*, **25**(3), 627-635.
- Sprynsky, M., Kovalchuk, I. and Buszewski, B. (2010), "The separation of uranium ions by natural and modified diatomite from aqueous solution", *J. Hazard. Mater.*, **181**(1), 700-707.
- Termkhajornkit, P. and Nawa, T. (2004), "The fluidity of fly ash-cement paste containing naphthalene sulfonate superplasticizer", *Cement Concrete Res.*, **34**(6), 1017-1024.

- Topcu, I.B., Bilir, T. and Uygunoğlu, T. (2009), "Effect of waste marble dust content as filler on properties of self-compacting concrete", *Constr. Build. Mater.*, **23**(5), 1947-1953.
- TS 802. (2009), *Design of concrete mixes*, Turkish Standards, Ankara (in Turkey).
- TS EN 12350-2 (2010), *Testing fresh concrete-Part 2: Slump test*, Turkish Standards, Ankara (in Turkey).
- TS EN 12390-3 (2003), *Testing hardened concrete-Part 3: Compressive strength of test specimens*, Turkish Standards, Ankara (in Turkey).
- Varela, M.B., Ramírez, S.M., Ereña, I., Gener, M. and Carmona, P. (2006), "Characterization and pozzolanicity of zeolitic rocks from two Cuban deposits", *Appl. Clay Sci.*, **33**(2), 149-159.
- Viallis-Terrisse, H., Nonat, A. and Petit, J.C. (2001), "Zeta-potential study of calcium silicate hydrates interacting with alkaline cations", *J. Colloid Interf. Sci.*, **244**(1), 58-65.
- Wang, X.Y., Cho, H.K. and Lee, H.S. (2011), "Prediction of temperature distribution in concrete incorporating fly ash or slag using a hydration model", *Compos. Part B: Eng.*, **42**(1), 27-40.
- Yildiz, K., Dorum, A. and Kocak, Y. (2010), "The investigation of the effect of minerological molecular electrokinetical and thermal compliance of pumice, zeolite and CEM I cement on high strength concrete", *Journal of the Faculty of Engineering and Architecture of Gazi University*, **25** (4), 867-879.
- Yildiz, K., Dorum, A. and Kocak, Y. (2010), "The investigation of the effect of minerological molecular electrokinetical and thermal compliance of pumice, zeolite and CEM I cement on high strength concrete", *J. Fac. Eng. Archit. Gazi Univ.*, **25**(4), 867-879.
- Yoshioka, K., Tazawa, E.I., Kawai, K. and Enohata, T. (2002), "Adsorption characteristics of superplasticizers on cement component minerals", *Cement Concrete Res.*, **32**(10), 1507-1513.

