Computers and Concrete, *Vol. 22, No. 5 (2018) 449-459*
DOI: https://doi.org/10.12989/cac.2018.22.5.449

Mechanical, durability and microstructure properties of concrete containing natural zeolite

Memduh Nas* and Şirin Kurbetci[a]

Department of Civil Engineering, Karadeniz Technical University, 61080, Trabzon, Turkey

(Received July 16, 2018, Revised November 14, 2018, Accepted November 15, 2018)

Abstract. Concrete is one of the most widely used construction materials in the world. Producing economical and durable concrete is possible by employing pozzolanic materials. The aim of this study is to underline the possibility of the utilization of natural zeolite in producing concrete and investigate its effects basically on the strength and durability of concrete. In the production of concrete mixes, Portland cement was replaced by the natural zeolite at ratios of 0%, 10%, 15%, and 20% by weight. Concretes were produced with total binder contents of 300 kg/m^3 and 400 kg/m^3, but with a constant water to cement ratio of 0.60. In addition to compressive and flexural strength measurements, freeze-thaw and high temperature resistance measurements, rapid chloride permeability, and capillary water absorption tests were performed on the concrete mixes. Compared to the rest mixes, concrete mixes containing 10% zeolite yielded in with the highest compressive and flexural strengths. The rapid chloride permeability and the capillary measurements were decreased as the natural zeolite replacement was increased. Freeze-thaw resistance also improved significantly as the replacement ratio of zeolite was increased. Under the effect of elevated temperature, natural zeolite incorporated concretes with lower binder content yielded higher compressive strength. However, the compressive strengths of concretes with higher binder content after elevated temperature effect were found to be lower than the reference concrete.

Keywords: natural zeolite; strength; durability; freeze-thaw; elevated temperature; rapid chloride permeability; capillary water absorption; microstructure

1. Introduction

Concrete is a cheap and durable construction material compared to its competitors, and it has many enemies around its environment. Under such deteriorating conditions, concrete continually losses its strength and durability depending on the exposure time, and these effects drastically shorten its expected service life.

As known, durability is a major property of concrete needs to be supplied. One of the most important components for durability is assumed to be the type and the amount of binder used in the production stage. For aggressive environments, it is possible to produce more durable and economical concrete by using pozzolanic materials.

Incorporation of natural pozzolans in concrete has been investigated for more than a half century. Pozzolans used in the production of the concrete result in producing additional binding gels by reacting with $Ca(OH)_2$ and therefore make concrete impermeable against aggressive agents of the environment. Pozzolanic materials which are frequently used in the production of concrete are silica fume (SF), fly ash (FA), blast furnace slag (BFS), pumice, rice husk ash, diatomite and metakaolin (Chore and Joshi 2015, Sadrmomtazi *et al.* 2017, Hwang *et al.* 2012, Panda and Prusty 2015, Kocak and Savas 2016, Lenka and Panda 2017, Joshaghani *et al.* 2017).

However, as it is more abundant and available in some geographical regions, zeolite has been used as a pozzolanic material as well (Feng and Peng 2005). The use of zeolites containing tuffs and limestone as hydraulic binder dates back to ancient times (Stanislao *et al.* 2011). Natural zeolite (NZ) contains clinoptilolite. The basic substance of clinoptilolite is aluminous silicate which has micro-porous crystalline framework structure. Zeolites generally consist of approximately 70% silicon dioxide and 12% aluminum oxide. Due to their very high specific surface area, zeolites are used as a catalyst support and sorbent; and they are also used as molecular sieve due to their crystal structure (Mishra *et al.* 2013, Lin *et al.* 2013, Xie *et al.* 2013). The use of zeolites in the production of concrete as a supplementary cementing material and its pozzolanic reaction have been a basic research topic in a great variety of studies. Although NZ is not as reactive as SF, it gives satisfactory results in concrete. With the increasing NZ replacement, the requirement of superplasticizer addition for concrete also increases. Water absorption and chloride permeability of concrete decreases up to a NZ replacement ratio of 20% (Ahmadi and Shekarchi 2010). Uzal *et al.* reported that the pozzolanic activity of clinoptilolite is comparable with SF and it is higher than FA (Uzal *et al.* 2010). This activity is assumed to be related to the size of the specific surface area and reactive SiO_2 content of

*Corresponding author, Ph.D. Student
E-mail: memduhnas@ktu.edu.tr
[a]Assistant Professor
E-mail: skurbetci@ktu.edu.tr

http://www.techno-press.org/?journal=cac&subpage=8
ISSN: 1598-8198 (Print), 1598-818X (Online)

clinoptilolite. Kocak *et al.* stated out that as the water demand of cement paste increases, the replacement ratio of zeolite increases. The reason for this increment is explained by the micro gaps in NZ and its high specific surface area (Kocak *et al.* 2013). Perraki *et al.* pointed out that NZ shows fairly good pozzolanic activity and one gram of NZ chemically bonds 0.555 grams of $CaOH_2$ (Perraki *et al.* 2003).

There are number of studies showing that the optimum amount of natural zeolite replacement ratio is approximately between 10-20% (Valipour *et al.* 2013a, Valipour *et al.* 2013b, Ahmadi and Shekarchi 2010, Canpolat *et al.* 2004, Najimi *et al.* 2012, Yilmaz *et al.* 2007, Vejmelková *et al.* 2015, Kocak and Savas 2016). Greater amount of natural zeolite replacement leads to decrease of compressive strength.

Sabet *et al.* stated that the 28-day compressive strength of self-compacting concrete with 10% NZ replacement is close to the values of the control mixture and the water absorption percentage is found to be reduced by approximately 20% (Sabet *et al.* 2013).

In a study it is reported that concretes containing NZ showed good mechanical properties, albeit unsatisfied permeability properties when it is not replaced more than 10% by wt. with cement (Vejmelkova *et al.* 2013). Effect of NZ, metakaolin and silica fume on concrete properties are compared in a study and it is reported that NZ decreases chloride ion permeability of concrete like metakaolin and silica fume (Valipour *et al.* 2013b).

Akçaozoğlu *et al.* reported that a decrease in unit weight, water absorption and porosity of concretes incorporated with NZ amount up to 20%. The effect of elevated temperature on the concrete containing NZ was also investigated by microscopic analyses in the same study. They stated that the residual compressive strength of concretes containing NZ is higher than the reference concrete, and the aggregates are less affected by the elevated temperature (Akcaozoglu *et al.* 2014).

Some researchers demonstrated that concrete containing NZ up to 10% yields higher compressive strength, freeze-thaw durability, and ultrasonic pulse velocity (UPV) measurements compared to the other mixtures (Nagrockiene and Girskas 2016, Markiv *et al.* 2016).

The durability of mortars containing NZ, FA and BFS at elevated temperatures was investigated by Karakurt and Topçu (Karakurt and Topçu 2012). It is noted that as the exposed temperature increases, the weight loss of mortars containing NZ is greater than those of without NZ. They obtained similar changes in the flexural strength and UPV measurements.

Bilim investigated the performance of mortars including NZ under extreme temperature and 50 freeze-thaw cycles (Bilim 2011). He found that 5% clinoptilolite replacement shows better freeze-thaw performance compared to the other mixtures. It is also reported that the effect of clinoptilolite incorporation on the resistance of elevated temperature seems to be related to the amount of clinoptilolite, temperature level, and the cooling method. Vejmelkova *et al.* stated that the frost resistance of mixtures containing NZ up to 20% is better than the reference mix (Vejmelkova *et al.* 2015).

Table 1 Chemical composition and physical properties of Portland cement and NZ

Chemical Components	Content (% by mass)	
	Cement	NZ
SiO_2	19.46	64.7
Al_2O_3	5.11	11.21
Fe_2O_3	3.31	1.38
CaO	60.23	2.08
MgO	2.08	0.79
SO_3	3.05	0.03
Na_2O	0.27	-
K_2O	0.69	3.78
Cl^-	0.02	-
Physical properties		
Specific surface (m^2/kg)	413	23.965
Specific gravity (kg/m^3)	3.12	2
Loss on ignition (%)	3.00	8

The main aim of this study is to investigate the effects of NZ (which was obtained from Gordes/Manisa) on the properties of concrete including compressive and flexural strengths, elevated temperature and freeze-thaw resistance, rapid chloride permeability and capillary. In addition, the microstructures of NZ-containing concretes exposed to high temperature effect were examined by SEM (scanning electron microscopy). NZ was replaced at different rates with cement in concrete mixtures. Two different concrete mixtures with 2 binder dosages were also produced.

2. Experimental program

2.1 Materials

Ordinary Portland Cement CEM I 42.5 R (OPC) conforming to ASTM C-150 Type I which corresponds to TS EN 197-1 and natural zeolite (NZ) conforming to ASTM C618 were used as binder materials for concrete mixtures. OPC and NZ were provided from Trabzon Aşkale Cement Factory and Gordes Zeolite Mining Corporation, Turkey, respectively. The chemical composition and the physical properties of OPC and NZ are given in Table 1.

Mineralogical composition of the clinoptilolite-rich NZ was identified by X-ray diffraction (XRD) method using Rigaku D MAX 3C instrument with CuKα radiation and Ni filter under 2θ: 3-70° interval range, at the 6°/min/cm scanning speed. Datas were taken from every 0.05 degrees. XRD patterns of the NZ showed that clinoptilolite is the major crystalline phase. The other crystalline components of the natural zeolite are identified as cristobalite and quartz. No amorphous phase was seen the patten.

Aggregates used in the mixtures were lime based crushed stone and angular sand. The mixing ratios of coarse aggregate and sand were 35% and 65%, respectively. Physical properties of the aggregates used are given in Table 2. In order to achieve the desired workability for concrete mixtures, a polycarboxylic ether-based superplasticizer chemical additive was used.

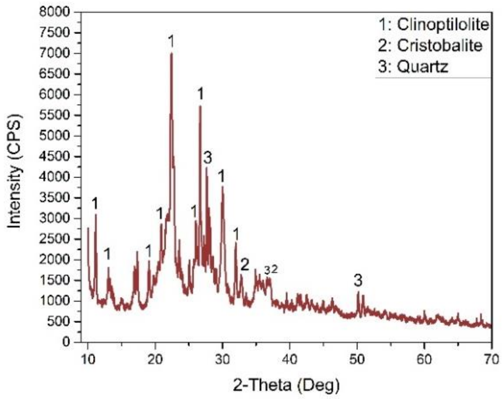

Fig. 1 XRD analyses of NZ

Table 2 Physical properties of the aggregate used

Properties	Coarse Aggregate	Fine Aggregate
Specific gravity (kg/m^3)	2730	2590
Water absorption (%)	1.13	3.23
Moisture content (%)	0.155	1.306

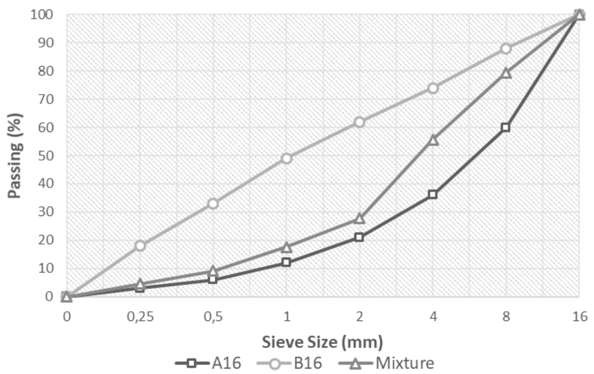

Fig. 2 Granulometric curve and boundary curves of the aggregate mixture

2.2 Methods

2.2.1 Mix design

The total cementitious materials for mixtures produced were adopted as 300 and 400 kg/m^3. The replacement ratios of NZ were adopted as 10%, 15% and 20 % by weight of cement. Reference mixtures without NZ were also produced for comparison. Since the use of NZ significantly increased the water requirement and reduced the workability of concrete according to the literature, the water/total binder ratio in all mixtures was determined as 0.6. The slump values of mixtures were tried to be kept in the range of 10-15 cm. All specimens were de-molded after the production day and then they were kept in lime saturated water at 20±2°C for 28 days. All experiments were conducted on concretes cured for 28 days in standard curing condition. Each experimental results were obtained by taking the mean values of samples. The mix proportions used for concrete mixtures are given in Table 3.

2.3 Test methods

2.3.1 Compressive strength

Table 3 Composition of the concrete mixtures

Total Binder Material (kg/m^3)	Mixture ID (kg/m^3)	Cement (kg/m^3)	NZ (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	Plasticizer (kg/m^3)
300	300-R	300	-	180	1200.99	646.89	8.11
	300-5M	290	30		1198.8	645.51	12.04
	300-10M	255	45		1195.04	643.48	12.38
	300-20M	240	60		1191.19	641.41	12.89
400	400-R	400	-	240	1050.71	565.79	7.27
	400-5M	360	40		1040.24	560.13	8.40
	400-10M	3340	60		1035.04	557.33	9.37
	400-20M	320	80		1029.85	554.53	10.96

Table 4 Chloride ion permeability classification according to ASTM C1202

Electrical Charge Passing (Coulomb)	Chloride Ion Permeability
>4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very low
<100	Negligible

For each mixture, 3 pieces of 15 cm cubic specimens were used for compressive strength measurements. The compressive strength was calculated by taking mean values of these three specimens. The test was performed according to TS 196-1.

2.3.2 Flexural strength

Flexural strength tests were performed on 10×10×40 cm prisms by subjecting the prisms to three-point loading with a span of 35 cm. The flexural strength was calculated by taking the mean values of two prisms.

2.3.3 Capillary

Capillary coefficients were determined according to ASTM C 1585. For this test, two pieces of 10-cm cube samples were used and the mean values of these samples are taken.

2.3.4 Rapid Chloride Permeability Test (RCPT)

RCPT was carried out according to ASTM C 1202 and the test setup is shown in Fig. 3. 50 mm-thick specimens cut from 100 mm-diameter cylinders had been previously saturated with water then placed on the test apparatus in order to make two surfaces of the samples contact with 3% NaCl and 0.3 M NaOH solutions. To prevent the leakage of the solutions around the specimen, the cylindrical faces of the specimen which was not in contact with the solutions were insulated with a water-resistant silicone agent. The electrical charge passed through the specimen for 6 hours under 60 V potential difference was measured in Coulombs (C). The permeability classification according to the relevant standard is given in Table 4.

Fig. 3 Set up for rapid chloride permeability test

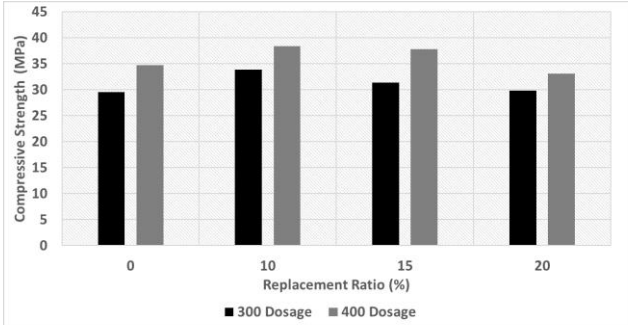

Fig. 4 28 days compressive strengths of the mixtures

2.3.5 Ultrasonic Pulse Velocity (UPV)

The ultrasonic pulse velocity (UPV) values of the cube samples were measured before and after the tests to determine the freeze-thaw effect and the deterioration degree of the inner structure of the concrete mixtures.

2.3.6 Elevated temperature resistance

To investigate the effect of high temperature on the concrete, 3 pieces of 10 cm cube specimens were placed in an oven at 70℃ for 48 hours and then placed in a furnace with 6-10℃/min heating rate and kept under the desired temperature for 1 hour according to TS EN 1363-1. At the end of an hour, the samples were removed from the furnace and left to cool down in the laboratory. The temperatures employed were 200℃, 500℃, and 800℃. The microstructure of selected samples was examined by scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS) detector by using a zeiss evo ls 10 electron microscope.

2.3.7 Freeze-thaw resistance

Freeze-thaw test was performed according to the procedures prescribed in ASTM C 666. Three pieces of 15 cm cubes were used for the freeze-thaw test. Prior to freeze-thaw testing, the weights and the UPV values of samples were determined. The weight change is an indicator of the damages magnitude due to scaling while the UPV values are indicator of the internal damage of the concrete due to freeze-thaw. Compressive strengths measurements were performed on cubic samples before and after the freeze-thaw cycles. The specimens in the tank were cooled down from +20℃ to -20℃ for 4 hours with a cooling rate of 10℃/h. After keeping the specimens in the tank at -20℃ for 4 hours, the temperature was risen to +20℃. Each freeze-thaw cycle lasted for 12 hours. A total number of 100 cycles were performed.

3. Results and discussion

3.1 Slump test

A superplasticizer admixture was used to keep the slumps of all mixes in the range of 10-15 cm. The amounts of superplasticizer used for each mix are given in Table 3.

The amount of superplasticizer used for the reference mixture with total binders of 300 and 400 kg/m^3 were 8.11 kg/m^3 and 7.27 kg/m^3 respectively, while for those containing 20% NZ were 12.89 kg/m^3 and 10.96 kg/m^3 respectively. This indicates that the amount of superplasticizer necessary for the aimed slump increases as the replacement ratio of NZ increases in the mix. Feng *et al.* have attributed this to the large number of pores present in the NZ as such pores are able to absorb much mixing water (Feng *et al.* 1990). Vejmelkova *et al.* stated that water demand of mixtures for the same slump increased as the replacement ratio of NZ increased (Vejmelkova *et al.* 2015). It has been explained elsewhere that the reason for this water was imbibed by the zeolite due to the tiny gaps in its structure (Vejmelková *et al.* 2013).

3.2 Compressive strength

The average 28day compressive strengths measured on 15cm cubes are given in Table 4. The change in the compressive strength depending on the replacement ratio of NZ is presented in Fig. 4. As can be seen from the figure, the compressive strength is the highest for the concretes containing 10% NZ irrespective of the total binder. The increase in the compressive strength is about 15% for concretes with a binder content of 300 kg/m^3, while it is about 10% for concretes containing 400 kg/m^3 binder. Concerning concretes containing 20% NZ, no change in strength was observed for those with a binder of 300 kg/m^3 cement; however, there was about 5% loss in the strength for concretes containing 400 kg/m^3 binder. These results seem to be parallel with some studies in the literature. Chan and Ji reported that a substitution ratio of NZ up to 15% provided an increase in compressive strength at a level of 14% approximately (Chan and Ji 1999). Canpolat *et al.* indicated that the compressive strength of concrete increased up to a replacement ratio of 15% NZ; however, Sabet *et al.* indicated that a replacement ratio of 20% NZ resulted in 8% decrease in the compressive strength (Canpolat *et al.* 2004, Sabet *et al.* 2013).

Table 5 shows the values of ANOVA test (analysis of variance test), indicating if the differences in the compressive strength of all specimens are statistically significant. According to the significance level (0.05), if the *p*-value of the NZ-containing specimens is equal or less than 0.05, it can be said that the increase in the compressive strength of the specimens containing NZ makes a meaningful difference compared to the control specimens. On the contrary, specimens with a *p*-value greater than 0.05 have an insignificant (negligible) differences compared to the control specimens (Tabatabaeian *et al.* 2017). Thus, the

Table 5 ANOVA results of compressive strength

Mixtures	300 Dosage				400 Dosage			
	OPC	NZ10	NZ15	NZ20	OPC	NZ10	NZ15	NZ20
Std. Dev.	1.902	1.695	1.399	1.635	1.715	1.315	1.825	1.470
Sig.*	-	0.050	0.572	0.997	-	0.088	0.152	0.608

*The mean difference is significant at the 0.05 level

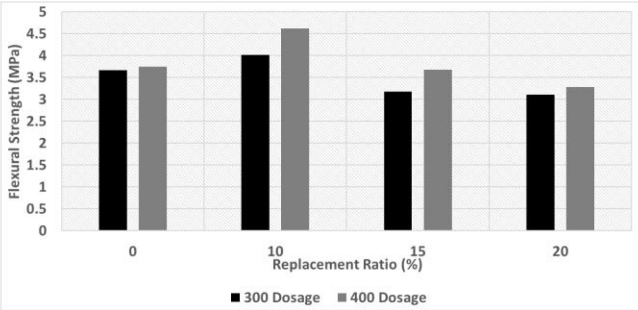

Fig. 5 28 days flexural strength values of the mixtures

compressive strengths of mixtures containing 5% NZ with a total binder amount of 300 kg/m^3 increased significantly. No statically significant increase was observed in any of the mixtures with total binder amount of 400 kg/m^3. But, the mixture containing 10% NZ with total binder amount of 400 kg/m^3 had a *p*-value of 0.088 which is close to 0.05.

3.3 Flexural strength

The 28-day three-point flexural strengths are shown in Table 5. 10% NZ replacement increased the flexural strengths by 9.56% and 23.2% for concretes containing total binder contents of 300 and 400 kg/m^3, respectively. Considerable decreases in the flexural strength were observed as the replacement ratio of NZ increased. The strength loses were 15% and 12.5% for concretes containing binder contents of 300 and 400 kg/m^3 with a replacement ratio of 20% NZ, respectively. It can be seen that as the replacement ratio of NZ increased beyond 10%, the flexural strengths started to decrease compared to those without NZ. Sreeharsha and Ramana observed increases of 2.05% and 5.64% in the flexural strength of concretes with 10% and 15% NZ substitution (Sreeharsha and Ramana 2016). Reduction in flexural strength was reported in substitutions above 15%. These results are similar to our study.

3.4 Capillary

The capillary coefficients obtained on concretes at the end of 28 days are presented in Fig. 6. The capillary coefficients showed a trend just like the compressive strength test. The capillary coefficients of all mixtures containing NZ were lower than the reference mixtures for both binder dosages. The lowest capillary coefficients were obtained with 10% and 15% NZ substitution ratios for the mixtures with total binder amount of 300 and 400 kg/m^3, respectively. Capillary coefficients of the mixtures containing 20% NZ were slightly higher than the other NZ-

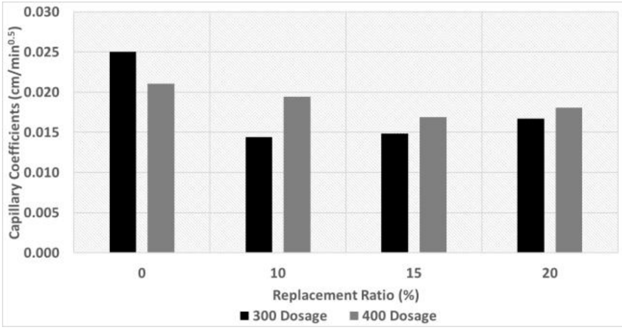

Fig. 6 Capillary coefficients of the mixtures

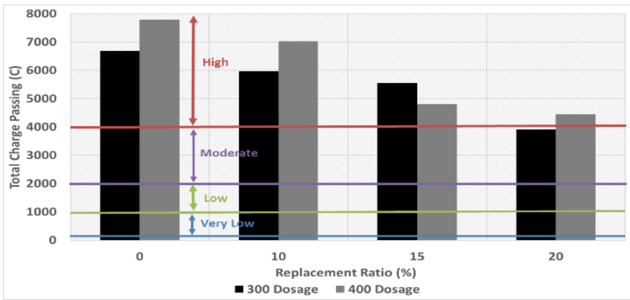

Fig. 7 Total charge passing from the mixtures

containing mixtures, but still lower than the reference mixtures. The reduction in capillary coefficient was more pronounced for concrete with 300 kg/m^3 binder. NZ replacement of 10-15% seemed to be more efficient in reducing water absorption due to capillary. Reduction of the capillary coefficients by the use of NZ is an indication of the improvement of the pore structure of the cement paste phase and the reduction of the pore diameters (Bai *et al.* 2002). Valipour *et al.* reported in their study that the lower capillary coefficient was obtained in 10% NZ substitution compared to the reference concrete. The capillary coefficient was higher than the reference concrete for higher NZ substitution ratios over 10% (Valipour *et al.* 2013a).

3.5 Rapid Chloride Permeability Test (RCPT)

The total charge passing through the concrete specimens measurements according to ASTM C 1202 are presented in Fig. 7. The RCPT classification limit values according to the relevant standard are also shown in the same figure. As can be seen from the figure, NZ replacement improved chloride ion permeability resistance for concretes containing total binder amount of 300 kg/m^3 and 400 kg/m^3 both. While the reference concrete mixture with total binder amount of 300 kg/m^3 were at high permeability class according to ASTM C 1202, it switched to medium class with the 20% NZ replacement. Replacement ratio of 20% NZ resulted in an average of 42% reduction in the total chloride ion permeability compared to the reference concretes. There are some studies which are quite compatible to our results. It has been reported in a study that the chloride permeability of 5% and 10% zeolite-substituted concretes reduced by 30%-49% (Eskandari *et al.* 2015). Similarly, Jana, Uzal *et al.* and Feng *et al.* stated that as the NZ substitution increased, the chloride permeability

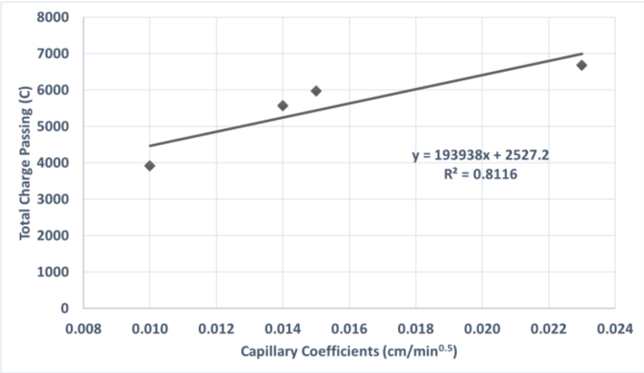

Fig. 8 Relationship between capillary coefficients and charge passing values of 300 dosage mixtures

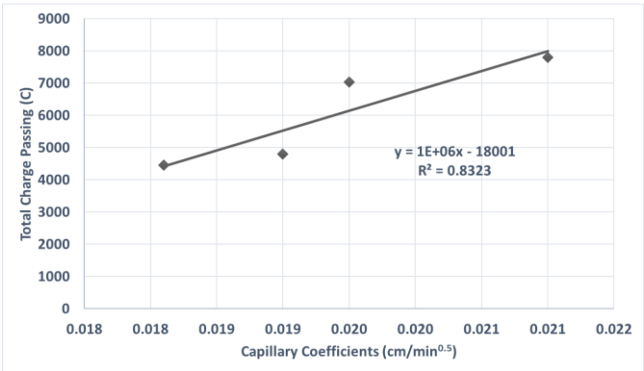

Fig. 9 Relationship between capillary coefficients and charge passing values of 400 dosage mixtures

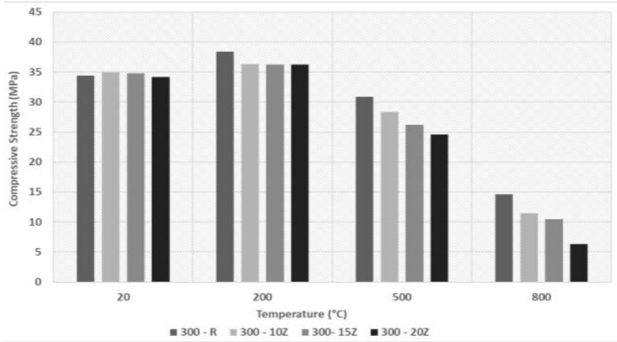

Fig. 10 Compressive strength-temperature relation of 300 dosage mixtures

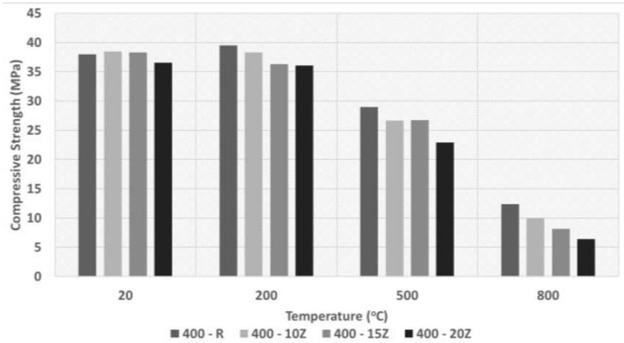

Fig. 11 Compressive strength-temperature relation of 400 dosage mixtures

decreased (Jana 2007, Uzal *et al.* 2007, Feng *et al.* 2002).

The relationship between rapid chloride ion permeability and capillary coefficients of the concrete mixtures are plotted in Figs. 8 and 9, indicating that there is a strong relationship between chloride permeability and capillary values of the concrete mixtures. The coefficient of determination (R^2) values are found to be close to 0.85

3.6 Elevated temperature resistance

3.6.1 Effect of high temperature on compressive strength

The compressive strengths of concrete mixtures exposed to high temperature are given in Figs. 10 and 11 for total binder amounts of 300 kg/m^3 and 400 kg/m^3, respectively. It can be seen that the compressive strength of all concrete mixtures with NZ and containing 300 kg/m^3 binder indicate a considerable increase at 200°C. This is what actually accentuated in the literature. Unhydrated cement particles at 200°C can hydrate due to the effect of pressurized vapor at capillary pores and this may result in an increase in compressive strength (Baradan *et al.* 2002, Saad *et al.* 1996). Likewise, the capillary water is entirely disappeared at 200°C (Hager 2013). A remarkable decrease in compressive strength was noticed and cracks were observed at temperatures above 200°C. Above 500°C, evident decline in compressive strength and cracks were observed in samples. The strength loss of concrete can be attributed to decomposition of $Ca(OH)_2$ into CaO and disappearance of water from the micropores of hydrates (Fares *et al.* 2010). Moreover, the most essential binding gel of concrete, CSH, starts to decompose at around 560°C (Peng and Huang 2008). In this study, at 500°C the best compressive strength results were obtained in the reference mixtures. For both dosages, compressive strength of the mixtures decreased as the NZ replacement ratio increased. The scenario did not change at 800°C. Additionally; at this temperature the compressive strength of the concrete mixtures fell to a very low level of 5-10 MPa. The compressive strengths of the mixtures with total binder amount of 300 kg/m^3 containing 0, 10, 15 and 20% NZ were reduced by 58, 67, 70 and 82%, respectively to ones not subjected to elevated temperature impact. The compressive strengths of the mixtures with total binder amount of 400 kg/m^3 containing 0, 10, 15 and 20% NZ were reduced by 67, 74, 79 and 83%, respectively.

The lowest loss in compressive strength was noticed in concretes with 10% NZ and containing 300 kg/m^3 binder. The strength losses were more pronounced for concretes containing 400 kg/m^3 binder. These results are similar to the work of Bilim which is on cement mortars containing NZ (Bilim 2011).

3.6.2 Effect of High Temperature on Ultrasonic Pulse Velocity (UPV)

The UPV measurements for concretes incorporating NZ subjected to elevated temperatures are illustrated in Fig. 12 and Fig. 13. As can be seen from the figures, all UPV values obtained decreased noticeably as the temperature increased. Similar changes were observed for both concretes containing total binder material of 300 kg/m^3 and

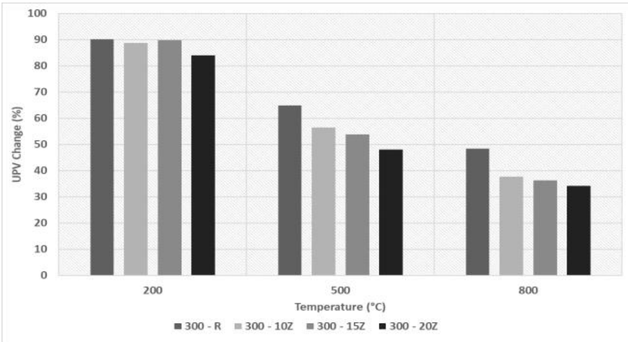

Fig. 12 The UPV-temperature relation of 300 dosage mixtures

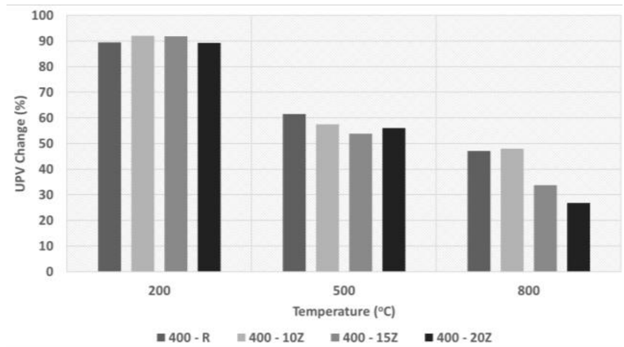

Fig. 13 The UPV temperature change of 400 dosage mixtures

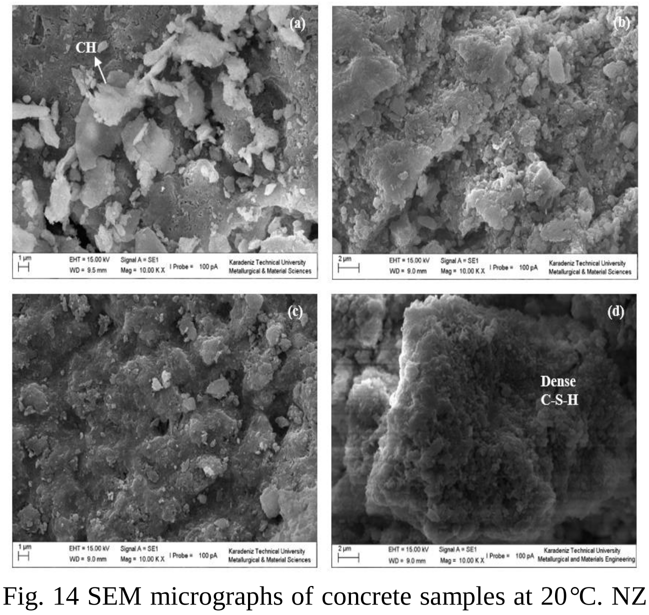

Fig. 14 SEM micrographs of concrete samples at 20℃. NZ replacement of 0, 10, 15, 20 wt.% (a,b,c,d)

400 kg/m^3 binder at 200℃ like compressive strength. It is quite obvious that as temperature increased the internal damage is increased; the structure of binding paste deteriorated and concrete become porous. In the end, as the sound waves are transmitted harder in porous concrete, the UPV values of concrete decreased.

3.6.3 Effect of high temperature on the microstructure

Figs. 14-16 show SEM micrographs demonstrating the

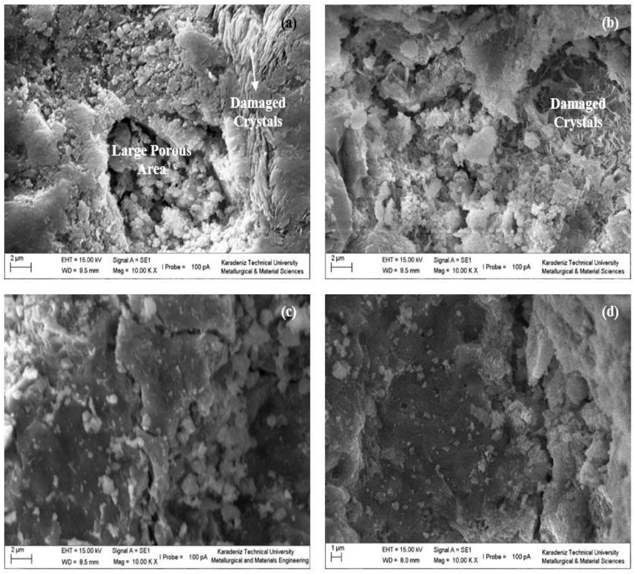

Fig. 15 SEM micrographs of concrete samples at 500^{o}C. NZ replacement of 0, 10, 15, 20 wt.% (a,b,c,d)

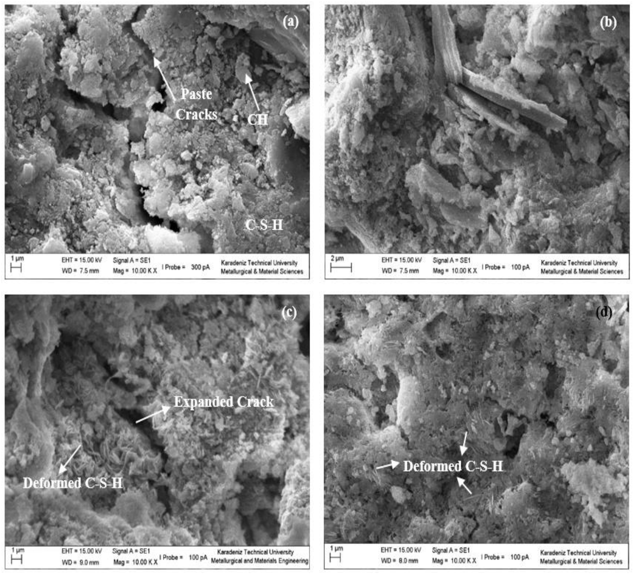

Fig. 16 SEM micrographs of concrete samples at 800^{o}C. NZ replacement of 0, 10, 15, 20 wt.% (a,b,c,d)

microstructure properties of concrete at 20, 500 and 800℃, respectively.

In Fig. 14 well-developed $Ca(OH)_2$ and CSH crystals are formed in 28 days-concrete. The inner structures of the concretes which were not exposed to the high temperature effects are dense and CSH crystals are consisted in viscous blocks. In the zeolite-substituted concretes, the pozzolanic properties of natural zeolite resulted in a dense and low porosity microstructure with reduced CH content and intense CSH crystals.

As shown in Fig. 15, CH and CSH crystals began to deform at 500℃. $Ca(OH)_2$ turned into $CaCO_2$ and microcracks are intermingled, crack size, width and density increased. Porosity of microstructure began to increase due to developing of microcracks. Since the CH crystals were decomposed at 500℃ no CH crystals were found in the

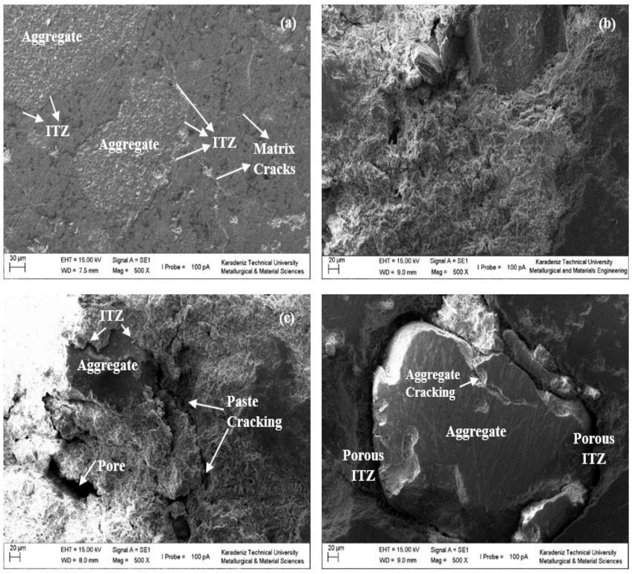

Fig. 17 SEM micrographs of interfacial transition zones of concrete samples. (a,b) 20^{o}C, (c) 500^{o}C, (d) 800^{o}C

figures.

As can be seen in Figure 16, large cracks and large voids can easily be seen due to the decomposition of the cement matrix (i.e., losing the physical and chemical integrity) at 800℃. The CH crystals were deformed, the dense structure of CSH gels were deteriorated and began to disintegrate, the microcracks expanded and porosity increased due to the high temperature. Due to the dehydration of CSH into calcium silicates and lime, needle-shaped bundles were formed. When concretes exposed to 800℃; cracks, voids and ITZ weakness in the microstructure of concrete were also increased. Similar results had been reported in the literature (Arıöz 2007, Demirel and Keleştemur 2010, Akca and Zihnioğlu 2013).

In Fig. 17 the micrographs of aggregate-cement matrix interface taken from concrete samples which were exposed to 20, 500, 800℃, respectively are illustrated. In Fig. 17(a), sand particles and tightly wrapped cement matrix around them can be seen. In Fig. 17(b), it can be seen that the aggregate-cement matrix is stronger as a result of the hydration reaction proceed with NZ substitution. Microcracks and pores can be seen along the ITZ between aggregate-cement matrix at 500℃ (Fig. 17(c)). When the temperature rised to 800℃, it can be seen that ITZ between aggregate-cement matrix was weakened and very large cracks were formed.

In Fig. 18, EDS profiles of CH and CSH phases are illustrated.

3.7 Freeze-thaw resistance

3.7.1 Effect of freeze-thaw on compressive strength

Prior to and after freeze-thaw exposure, the compressive strengths, weights and UPV values of concretes measured are given in Table 5. As an outcome of this test, spalling and honeycomb-like gaps were observed on the concrete samples. The change in the compressive strength of concretes subjected to 100 freeze-thaw cycles compared to

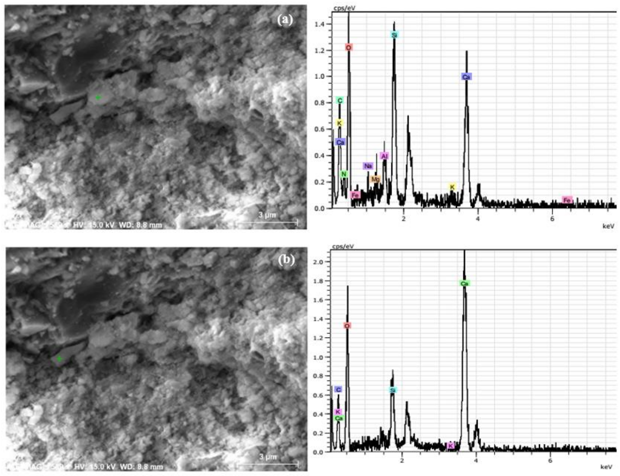

Fig. 18 SEM micrographs and EDS of CSH (a) and CH (b)

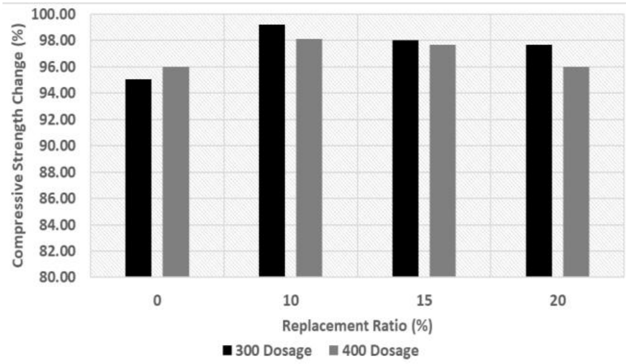

Fig. 19 Compressive strength change of the mixtures due to freeze-thaw

concretes without NZ is illustrated in Fig. 18. At the end of 100 freeze-thaw cycles, the compressive strengths loss of reference concretes with 300 kg/m^3 and 400 kg/m^3 binder were about 5% and 16% compared to their initial strengths, respectively. The change in the compressive strengths of concretes containing 10% NZ were 99.7% and 97% for concretes of 300 kg/m^3 and 400 kg/m^3, respectively. This was the lowest strength loss obtained at this replacement ratio. It can be seen that the strength loss increased as the NZ replacement ratio increased; however, none of the concretes containing NZ had strength loss greater than observed for those of without NZ. In a study on clinoptilolite-substituted mortars at different ratios, the compressive strength of the mortars containing 5% clinoptilolite at the end of the 50 freeze-thaw cycles was higher than the reference mixture; the clinoptilolite substitution ratio of more than 5% was reported to decrease the compressive strength (Bilim 2011). Similarly, some researchers reported that at the end of 100 freeze-thaw cycles concretes containing 10% clinoptilolite suffered less than the reference concrete in terms of compressive strength (Markiv *et al.* 2016, Vejmelková *et al.* 2015).

3.7.2 Effect of freeze-thaw on weight change

As it is known, due to scaling and spalling, mass of concrete decrease because of freeze-thaw effects. Hence, mass loss is a factor in evaluating the damage that occurs in

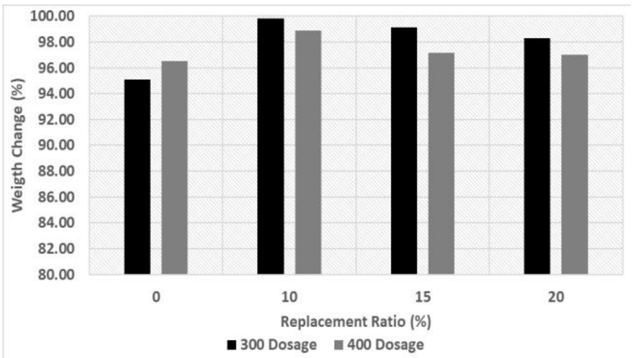

Fig. 20 The weight changes of the mixtures due to freeze-thaw effect

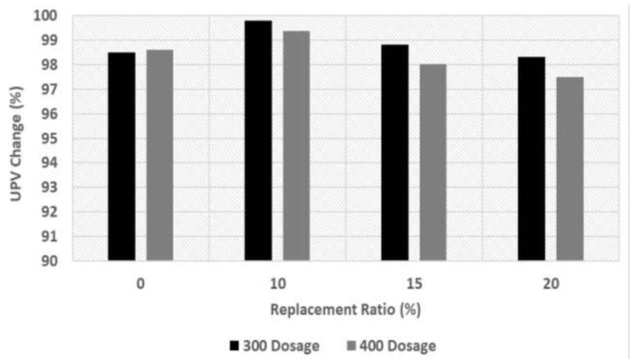

Fig. 21 The UPV changes of the mixtures due to freeze-thaw effect

concrete samples due to freeze-thaw effects. Compared to reference specimens, the change in the weights of the specimens measured at the end of 100 freeze-thaw cycles is given in Fig. 19. The highest loss was noticed for concretes without NZ. Incorporation of NZ at any ratio has resulted in less weight loss in concrete. While a weight loss of 5% was noticed in reference concrete of 300 kg/m^3 cement, it was only 1% for concretes containing 10% NZ, which was the lowest weight loss. During freezing, internal stresses occur when the water in the pores of the concrete is frozen. If the stresses are high enough to form cracks, the cracks develop from the concrete surface to the deeper zones and cause a flake to break and come off. These broken parts cause a decrease in the mass of concrete (Sun and Scherer 2010).

3.7.3 Effect of freeze-thaw on UPV

UPV measurements obtained on concretes subjected to 100 freeze-thaw cycles are illustrated in Fig. 20. As can be seen from the figure, the UPV values of reference concretes decreased approximately 1.5% at the end of 100 freeze-thaw cycles. Limited change in UPV values of concretes with NZ were noticed.

4. Conclusions

The effects of natural zeolite (NZ) on the compressive and flexural strength, capillary water absorption, rapid chloride permeability, high temperature and freeze-thaw resistance of concrete were investigated in this study. The main conclusions obtained are given below:

- The 28-day compressive strength of concretes of 300 kg/m^3 and 400 kg/m^3 binder containing 10% and 15% NZ increased. Concrete with a 10% NZ replacement yielded the highest compressive strength.
- Concretes containing 10% NZ with 300 kg/m^3 and 400 kg/m^3 binder contents yielded higher flexural strength compared to reference concretes. Loss in flexural strengths were noticed as the replacement ratio of NZ increased.
- NZ replacement resulted in reduction in capillary coefficient of concrete for both binder contents. 10% and 15% NZ replacement ratios were considered as the most appropriate ratios in relation with decreasing in capillary of concrete mixtures.
- At the end of 100 freeze-thaw cycles, considerable decreases in the weight loss of concretes were noticed regardless of NZ replacement ratio compared to reference concretes.
- At the end of 100 freeze-thaw cycles, the strength loss was less in concretes containing natural NZ compared to reference concretes. The minimum strength loss was noticed in concretes containing 10% NZ.
- 10%NZ substitution was found to be the best replacement ratio against high temperature effect regardless of the binder content.
- The decrease in the UPV and strength values of concretes were crucial when the temperatures higher than 500℃. The reason for this decrease was the deterioration of the CH and CSH gels, the voids in the cement matrix and the weakening of the aggregate-cement matrix interface.
- SEM analysis showed that the CH and CSH gels deteriorated and the microcracks were expanded as temperature increased.
- According to the results of this study, it can be said that the optimum replacement ratio for NZ obtained from Gordes/Manisa region is 10% with respect to the durability of concrete.

Acknowledgments

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

Ahmadi, B. and Shekarchi, M. (2010), "Use of natural zeolite as a supplementary cementitious material", *Cement Concrete Compos.*, **32**, 134-141.

Akca, A.H. and Zihnioğlu, N.Ö. (2013), "High performance concrete under elevated temperatures", *Constr. Build. Mater.*, **44**, 317-328.

Akcaozoglu, K., Fener, M., Akcaozoglu, S. and Öcal R. (2014), "Microstructural examination of the effect of elevated temperature on the concrete containing clinoptilolite", *Constr. Build. Mater.*, **72**, 316-325.

Arıöz, O. (2007), "Effects of elevated temperatures on properties of concrete", *Fire Saf. J.*, **42**, 516-522.

ASTM C1202 (2012), Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration, American Society of Testing and Materials; Philadelphia, U.S.A.

ASTM C1585 (2013), Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic Cement Concretes, American Society of Testing and Materials; Philadelphia, U.S.A.

ASTM C666 (2015), Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing, American Society of Testing and Materials; Philadelphia, U.S.A.

ASTMC 618-17 (2017), Standard Specifications for Fly Ash and Raw or Calcined Natural Pozzolan for Use as Mineral Admixture in Portland Cement Concrete, ASTM, Philadelphia, USA.

Bai, J., Wild, S. and Sabir, B.B. (2002), "Sorptivity and strength of air-cured and water-cured PC-PFA-MK concrete and the influence of binder composition on carbonation depth", *Cement Concrete. Res.*, **32**, 1813-1821.

Baradan, B., Yazıcı, H. and Un, H. (2002), *Durability of Reinforced Concrete Structures*, 1st Edition, DEU Press, Izmir.

Bilim, C. (2011), "Properties of cement mortars containing clinoptilolite as a supplementary cementitious material", *Constr. Build. Mater.*, **25**, 3175-3180.

Canpolat, F., Yilmaz, K., Kose, M.M., Sumer, M. and Yurdusev, M.A. (2004), "Use of zeolite, coal bottom ash and fly ash as replacement materials in cement production", *Cement Concrete Res.*, **34**, 731-735.

Chan, S.Y.N. and Ji, X. (1999), "Comparative study of the initial surface absorption and chloride diffusion of high performance zeolite, silica fume and PFA concretes", *Cement Concrete Compos.*, **21**, 293-300.

Chore, H.S. and Joshi, M.P. (2015), "Strength evaluation of cocnrete with fly ash and GGBFS as cement replacing materials", *Adv. Concrete Constr.*, **3**(3), 223-236.

Demirel, B. and Keleştemur, O. (2010), "Effect of elevated temperature on the mechanical properties of concrete produced with finely ground pumice and silica fume", *Fire Saf. J.*, **45**, 385-391.

Eskandari, H., Vaghefi, M. and Kowsari, K. (2015), "Investigation of mechanical and durability properties of concrete influenced by hybrid nano silica and micro zeolite", *Procedia Mater. Sci.*, **11**, 594-599.

Fares, H., Remond, S., Noumowe, A. and Cousture, A. (2010), "High temperature behaviour of self- consolidating concrete microstructure and physicochemical properties", *Cement Concrete Res.*, **40**, 488-96

Feng, N., Feng, X., Hao, T. and Xing, F. (2002), "Effect of ultrafine mineral powder on the charge passed of the concrete", *Cement Concrete Res.*, **32**(4), 623-627.

Feng, N.Q. and Peng, G.F. (2005), "Applications of natural zeolite to construction and building materials in China", *Constr. Build. Mater.*, **19**, 579-584.

Feng, N.Q., Li, G.Z. and Zang, X.W. (1990), "High-strength and flowing concrete with a zeolitic mineral admixture", *Cement Concrete Aggreg.*, **12**(2), 61-69.

Hager, I. (2013), "Behaviour of cement concrete at high temperature", *Bull. Pol. Acad. Sci.-Tech.*, **61**(1), 145-154.

Hwang, C.L., Bui, L.A.T. and Chen, C.T. (2012), "Application of Fuller's ideal curve and error function to making high performance concrete using rice husk", *Comput. Concrete*, **10**(6), 631-647.

Jana, D. (2007), "A new look to an old pozzolan, clinoptilolite - a promising pozzolan in concrete", *Proceedings of the 29th ICMA Conference on Cement Microscopy*, Quebec City.

Joshaghani, A., Moeini, M.A. and Balapour, M. (2017), "Evaluation of incorporating metakaolin to evaluate durability and mechanical properties of concrete", *Adv. Concrete Constr.*, **5**(3), 241-255.

Karakurt, C. and Topcu, I.B. (2012), "Effect of blended cements with natural zeolite and industrial by-products on rebar corrosion and high temperature resistance of concrete", *Constr. Build. Mater.*, **35**, 906-911.

Kocak, Y. and Savas, M. (2016), "Effect of the PC, diatomite and zeolite on the performance of concrete composites", *Comput. Concrete*, **17**(6), 815-829.

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.

Lenka, S. and Panda, K.C. (2017), "Effect of metakaolin on the properties of conventional and self compacting concrete", *Adv. Concrete Constr.*, **5**(1), 31-48

Lin, W.G., Zhou, Y., Cao, Y., Zhou, S.L., Wan, M.M. and Wan, Y. (2013), "Applying heterogeneous catalysis to health care: in situ elimination of tobacco specific nitrosamine", *Catalysis Today*, **212**, 52-61.

Markiv, T., Sobol, K., Franus, M. and Franus, W. (2016), "Mechanical and durability properties of concretes incorporating natural zeolite", *Arch. Civil Mech. Eng.*, **16**, 554-562.

Mishra, D.K., Dabbawala, A.A. and Hwang, J.S. (2013), "Ruthenium nano particles supported on zeolite Y as an efficient catalyst for selective hydrogenation of xylose to xylitol-", *J. Mol. Catal A-Chem.*, **376**, 63-70.

Nagrockiene, D. and Girskas, G. (2016), "Research into the properties of concrete modified with natural zeolite addition", *Constr. Build.Mater.*, **113**, 964-969.

Najimi, M., Sobhani, J., Ahmadi, B. and Shekarchi, M. (2012), "An experimental study on durability properties of concrete containing zeolite as a highly reactive natural pozzolan", *Constr. Build. Mater.*, **35**, 1023-1033.

Panda, K.C. and Prusty, S.D. (2015), "Influence of sipnozz and rice hust ash on enhancement of concrete strength", *Adv. Concrete Constr.*, **3**(3), 203-221.

Peng, G. and Huang, Z. (2008), "Change in microstructure of hardened cement paste subjected to elevated temperatures", *Constr. Build. Mater.*, **22**(4), 593-599.

Perraki, Th., Kakali, G. and Kontoleon, F. (2003), "The effect of natural zeolites on the early hydration of Portland cement", *Microporous Mesoporous Mater.*, **61**, 205-212.

Saad, M., Abo-El-Enein, S.A., Hanna, G.B. and Kotkata, M.F. (1996), "Effect of temperature on physical and mechanical properties of concrete containing silica fume", *Cement Concrete Res.*, 26(5), 669-675.

Sabet, F.A., Libre, N.A. and Shekarchi, M. (2013), "Mechanical and durability properties of self consolidating high performance concrete incorporating natural zeolite, silica fume and fly ash", *Constr. Build. Mater.*, **44**, 175-184.

Sadrmomtazi, A., Tahmouresi, B. and Amooie, M. (2017), "Permeability and mechanical properties of binary and ternary cementitious mixtures", *Adv. Concrete Constr.*, **5**(5), 423-436.

Sreeharsha, N. and Ramana, K.V. (2016), "Study on the strength characteristics of concrete with partial replacement of cement by zeolite and metakaolin", *Int. J. Innovat. Res. Sci. Eng. Tech.*, **5**(12), 20363-20371.

Stanislao, C., Rispoli, C., Vola, G., Cappelletti, P., Morra, V. and Gennaro, M.D. (2011) "Contribution to the knowledge of ancient Roman seawater concretes: Phlegrean pozzolan adopted in the construction of the harbour at Soli-Pompeiopolis (Mersin. Turkey)", *Period. Miner.*, **80**, 471-88.

Sun, Z. and Scherer, G.W. (2010), "Effect of air voids on salt scaling and internal freezing", *Cement Concrete Res.*, **40**(2), 260-270.

Tabatabaeian, M., Khaloo, A., Joshaghani, A. and Hajibandeh, E. (2017), "Experimental investigation on effects of hybrid fibers on rheological, mechanical, and durability properties of high-strength SCC", *Constr. Build. Mater.*, **147**, 497-509.

TS EN-197-1 (2012), Cements-Part 1: Compositions and Conformity Criteria for Common Cements, Turkish Standards Institute, TSE, Ankara, Turkey.

TS EN 196-1 (2009), Methods of Testing Cement. Part 1. Determination of Strength, Turkish Standard Institute, TSE, Ankara, Turkey.

Uzal, B., Turanli, L. and Mehta, P.K. (2007), "High-volume natural pozzolan concrete for structural applications", *ACI Mater. J.*, **104**(5), 535-8.

Uzal, B., Turanli, L., Yucel, H., Goncuoglu, M.C. and Culfaz, A. (2010), "Pozzolanic activity of clinoptilolite: A comparative study with silica fume, fly ash and a non-zeolitic natural pozzolan", *Cement Concrete Res.*, **40**, 398-404.

Valipour, M., Pargar, F., Shekarchi, M. and Khani, S. (2013a), "Comparing a natural pozzolan, zeolite, to metakaolin and silica fume in terms of their effect on the durability characteristics of concrete: A laboratory study", *Constr. Build. Mater.*, **41**, 879-888.

Valipour, M., Pargar, F., Shekarchi, M., Khani, S. and Moradian, M. (2013b), "In situ study of chloride ingress in concretes containing natural zeolite, metakaolin and silica fume exposed to various exposure conditions in a harsh marine environment", *Constr. Build. Mater.*, **46**, 63-70.

Vejmelková, E., Keppert, M., Ondrácek, M. and Cerny, R. (2013), "Effect of natural zeolite on the properties of high performance concrete", *Cement Wapno Beton*, **18**(3), 150-159.

Vejmelková, E., Konáková, D., Kulovaná, T., Keppert, M., Zumár, J., Rovnaníková, Pavla, Keršner, Z., Sedlmajer, M. and Cerný, R. (2015), "Engineering properties of concrete containing natural zeolite as supplementary cementitious material: Strength, toughness, durability, and hygrothermal performance", *Cement Concrete Compos.*, **55**, 259-267.

Xie, Q., Xie, J., Chi, L.N., Li, C.J., Wu, D.Y., Zhang, Z.J. and Kong, H. (2013), "A new sorbent that simultaneously sequesters multiple classes of pollutants from water: surfactant modified zeolite", *China Technol. Sci*, **56**, 1749-1757.

Yilmaz, B., Ucar, A., Oteyaka, B. and Uz, V. (2007), "Properties of zeolitic tuff (clinoptilolite) blended portland cement", *Build. Environ.*, **42**, 3808-3815.

CC