Properties of cement mortars containing clinoptilolite as a supplementary cementitious material

Cahit Bilim

Mersin University, Engineering Faculty, Department of Civil Engineering, Mersin, Turkey

ARTICLE INFO

ABSTRACT

This paper presents a study of the properties and behavior of cement mortar with clinoptilolite which is one of the most common zeolite minerals found in nature. Six mortar mixtures were prepared by replacing the Portland cement with 0%, 5%, 10%, 15%, 20% and 30% clinoptilolite by weight. Test results showed that water demand, soundness and setting times of the cement pastes increased with the increase of clinoptilolite content. Compressive and flexural strength of the mortars containing clinoptilolite were higher than the control mixture. Dry unit weight of the mortars with clinoptilolite was lower than the control mortar. Clinoptilolite replacement decreased water absorption and porosity of the mortars. The control mortar showed less durability to carbonation compared to the mortars made with clinoptilolite at the end of carbonation tests. Freeze–thaw resistance of the mortars containing 5% clinoptilolite was higher than control mortar. The effect of clinoptilolite incorporation on high-temperature resistance seemed to be dependent on amount of clinoptilolite, temperature level, and the cooling method.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Cement is the most produced and used binding material in the world with its 1.6 billion tons of annual production [1]. Most cement plants consume large amounts of energy and produce a number of undesirable products which negatively affect the environment [2]. The world cement industry is responsible for 7% of the total CO_2 emission [3]. Thus, the cement industry has a crucial role in the global warming. In order to reduce energy consumption, CO_2 emission and increase production, cement manufacturers are blending or intergrinding mineral additives such as natural and artificial pozzolans into the cement.

Zeolite tuffs are substances containing alumina silicate just as pozzolans which are being used as blend materials in cements [4,5]. They have unique characteristics such as high specific surface area and cation exchange capacity as well as ability to store heat between hydration and dehydration cycles [6]. They play a significant role among industrial raw materials used in such fields as pollution management, energy, agriculture, stock farming and mine metallurgy due to their physical structures and chemical properties. Similar to other pozzolanic materials such as silica fume and fly ash, natural zeolite combines with $Ca(OH)_2$, a byproduct of cement hydration to form further calcium silicate. This reaction called pozzolanic reaction is responsible for increasing the long term strength and refining the pore structure of blended concrete [7]. In scientific studies performed on the usability of natural zeolite as cement blend material, strength development and other properties of cements depending on the percentage of zeolite blend ratios were examined and results were found positive [8]. In general, natural zeolite, like other pozzolanic materials, contributes to the strength of concrete better than the strength of cement [9]. Natural zeolite also prevents the undesirable expansion due to alkali aggregate reaction and sulfate attack [10]. Moreover, zeolite, which is a softer material than the Portland cement clinker, increases the fineness of the ground material and reduces the grinding time [9]. Zeolitic tuffs need more water to produce paste of the same consistency. When zeolitic cement is used for concrete production, it is likely that a superplasticizer has to be added to control the rheological properties of the mixture [11,12]. No segregation or bleeding was observed in the flowing fresh concrete because the viscosity of fresh concrete increases by the added zeolite [13].

Generally, despite the good performance of zeolite as pozzolanic material, limited researches are performed and published especially about the durability aspects of mortar. Natural zeolite is abundantly deposited in Turkey and it can be easily quarried and processed. The exploitation of natural zeolite, when used as a partial replacement for cement, can lead to a considerable economic benefit and durability. Therefore, the objective of this study is to evaluate the effect of clinoptilolite (natural zeolite), coming from Gördes region of Manisa, on some properties of mortar using various testing methods.

Table 1
Physical, chemical and mechanical properties of cement and clinoptilolite.

Chemical composition (%)	Cement	Clinoptilolite	Physical properties of Portland cement	
SiO_2	18.69	63.01	Specific gravity	3.12
Al_2O_3	5.61	10.72	Initial setting time (min)	190
Fe_2O_3	2.52	2.68	Final setting time (min)	225
CaO	62.68	3.87	Volume expansion (mm)	1.0
MgO	2.63	1.07	Specific surface (Blaine) (cm^2/g)	3200
Na_2O	0.13	0.23	Compressive strength (MPa) of cement	
K_2O	0.77	3.80	2 days	27.2
SO_3	2.73	0.22	7 days	41.0
LOI	2.88	14.00	28 days	51.2
Free CaO	0.93	–	Physical properties of clinoptilolite	
Insoluble residue	0.96	–	Specific gravity	2.17
Cl^-	0.012	–	Specific surface (Blaine) (cm^2/g)	9660
			Pozzolanic activity index (%) of clinoptilolite	
			7 days	58
			28 days	81

Table 2
Hyperplasticizer dosages and flow values of the mortars.

Mixture	Clinoptilolite (%)	Hyperplasticizer (%)	Flow (%)
Control	0	–	55
C5	5	1.1	45
C10	10	1.6	45
C15	15	2.8	50
C20	20	4.4	65
C30	30	7.0	50

2. Experimental study

The binding materials used for this study consisted of clinoptilolite and ordinary Portland cement CEM I 42.5 R. Ground clinoptilolite used in the mixtures was supplied by the Enli Mining Company, Gördes region, Turkey. Chemical composition and physical properties of Portland cement and clinoptilolite are presented in Table 1. The particle size distributions of these materials, which were obtained using a laser scattering technique, are given in Fig. 1.

Sand used in the experimental study was standard Rilem Cembureau type according to TS EN 196-1 [14]. Water used in the study was drinkable tap water provided from city waterworks.

The mortar mixture proportions were 1:3:0.5 by weight of cement, sand and water, respectively. Clinoptilolite was used at 0%, 5%, 10%, 15%, 20% and 30% replacement by weight of cement while sand and water quantities were kept constant. Water demand and setting time analyses of cement pastes were performed by using an automatic Vicat machine while soundness tests were carried out by using Le chatelier tool. These measurements were conducted according to TS EN 196-3 [15]. In the mortars containing clinoptilolite, hyperplasticizer chemical admixture was used. The flow tests were carried out in accordance with TS EN 1015-3 [16]. While determining hyperplasticizer dosages, the flow values of clinoptilolite incorporated mortars were maintained in the vicinity of ± 10% of the flow value obtained from control mortar. The dosages of chemical admixture used and flow values obtained from fresh mortar mixtures were given in Table 2.

Mixture preparation was conducted according to the TS EN 196-1 [14] procedure. For each mixture, 40 × 40 × 160 mm prisms were prepared and kept in the laboratory for 24 h. After demolding, the specimens were cured in two ways until the time of testing; One group of specimens were placed in a humidity chamber at 21 ± 1 °C with 50% RH for solely carbonation experiments while second group of specimens were cured in water at 21 ± 1 °C for the other tests.

The strength tests of the specimens were conducted at 2, 7, 28, 56 and 90 days of age according to TS EN 1015-11 [17]. For flexural strength test, three prismatic specimens from each mixture were prepared and tested by one-point loading con-
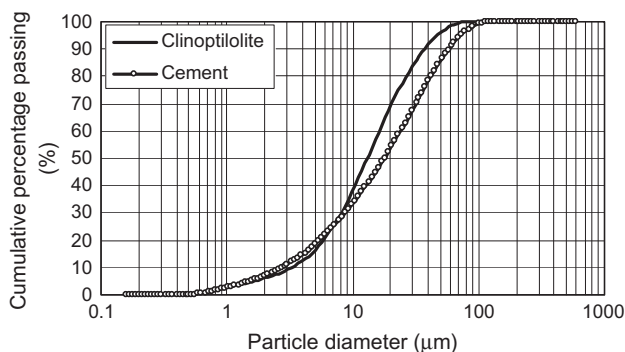
figuration with span of 10 cm. The compressive strength test was performed using six broken pieces of test prisms left flexural strength test. The flexural strengths were determined by taking the average of three test results whereas the compressive strengths were determined by taking the average of six test results.

The evaluation of the water absorption, porosity and unit weight was performed on prism specimens with size of 40 × 40 × 160 mm after 28 days of curing in conformity with TS 3624 [18]. The values were expressed by taking the average of three test results.

In the carbonation tests, the prism specimens cured in the humidity chamber (21 ± 1 °C, 50% RH) were used and the tests were conducted at 2, 7, 28, 56 and 90 days of age. The values were expressed by taking the average of three prismatic specimens. A phenolphthalein method was used to monitor the pH of mortar specimens in carbonation experiments. In this method, phenolphthalein is used as an indicator of the pH change in the mortar pore solution. The usual method of studying carbonation is to measure the depth of neutralisation as indicated by a phenolphthalein solution, which has been sprayed onto the fractured concrete surface. This indicator shows a magenta coloured region on the concrete where the pH value exceeds about 9 and a colourless region at the originally exposed surface where carbonation has reduced the pH to below 9. At the time of measurement, a 1% phenolphthalein solution in alcohol was sprayed on a surface of the mortar prism cut perpendicularly to the longitudinal axis of symmetry.

For the determination of freeze and thaw resistance, series of three prismatic mortar specimens of 40 × 40 × 160 mm were prepared with each mortar. Tests were carried out after 28 days. At this time, mortars were submitted to 50 freezing/thawing cycles. Each day, two cycles were carried out: 3 h at −20 °C, 0.5 h immersed in water, 3 h at −20 °C, and again another 0.5 h immersed in water, and for the rest of the time (17 h), the specimens were kept immersed in water. Also three specimens from each mixture were kept in water at 20 °C during the freeze–thaw test of the other specimens. After 50 cycles, all specimens were tested at the same age and their flexural and compressive strengths were determined.

The fire resistance tests of the mortar mixtures were performed on prism specimens with size of 40 × 40 × 160 mm. The specimens were demoulded after 24 h and stored in water at 21 ± 1 °C for 27 days. Later, the specimens were removed from water and kept in laboratory conditions for 24 h. Flexural and compressive strengths of control group specimens were determined. From each mixture six samples were exposed to 250, 500, 750 and 1000 °C temperatures for 1 h in furnace. The heating rate was set at 10 °C/min. It should be accentuated that this heating rate is very high for large specimens because of thermal stress formations. For example, a rapid fire exposure of 10 or 20 °C/min in an oven will bring about a considerable temperature difference of approximately 400 °C between surface and core giving rise to thermal stresses, which will damage the specimen before it is tested [19]. Afterwards, the hot mortar specimens were cooled in two regimes. One group of specimens were left in laboratory conditions for air cooling while second group of specimens were shock cooled in water at 21 ± 1 °C. After the cooling period to room temperature, the prismatic specimens were subjected to flexural and compressive strength test according to TS EN 1015-11 [17] and three specimens were tested at each stage and average values were reported. The test results were compared with those of unheated control mortar.

3. Results and discussion

3.1. Physical properties

The physical properties of the cement paste containing different replacement levels of clinoptilolite are given in Table 3.

The effect of replacement of 5–30% of cement with clinoptilolite is an increase in the water demand necessary for maintaining consistency. This might be due to the relatively high fineness and porous structure of clinoptilolite. The increase in clinoptilolite content increases the initial and final setting times. The amount of gypsum and C_3A content both decrease as the blend amount increases in the mixtures. When dissolution of C_3A component slows down, diffusion of water and the transition of Ca^{2+} ion into soluble state in water slow down [20,21]. Hence, this situation leads to increasing

Fig. 1. Particle size distributions of cement and clinoptilolite.

Table 3
Physical properties of the cement pastes.

	Clinoptilolite (%)					
	0	5	10	15	20	30
Water demand (%)	32.1	34.8	37.5	40.3	43.0	47.5
Initial setting time (min)	177	171	190	212	229	253
Final setting times (min)	220	254	273	283	290	337
Soundness (mm)	1	1	2	2	3	4

of setting times. The soundness of the samples shows a gradual increase with the increase in the replacement level, but volume expansions of clinoptilolite-substituted cement mixtures are below the limits given by TS EN 197-1 [22].

3.2. Compressive strength

The compressive strength of the mortars was determined at 2, 7, 28, 56 and 90 days, and the test results are presented in Fig. 2.

As expected, the compressive strength increased with age. The rate of increase depended upon the level of clinoptilolite replacement and age. As seen in Fig. 2, it is observed that the control mortar achieved a compressive strength of 21.85 MPa at the age of 2 days, 32.37 MPa at the age of 7 days, 43.90 MPa at the age of 28 days, 50.00 MPa at the age of 56 days and 51.20 MPa at the age of 90 days. The compressive strength of the mortars containing clinoptilolite ranged from 14.23 MPa to 22.87 MPa at the age of 2 days, 30.69 MPa to 38.31 MPa at the age of 7 days, 47.84 MPa to 52.52 MPa at the age of 28 days, 51.01 MPa to 56.88 MPa at the age of 56 days, and 52.41 MPa to 59.44 MPa at the age of 90 days. It appears that clinoptilolite used in this study has a suitable strengthening effect because of its high pozzolanic activity. When these values compare with the control mortar, it can be seen

that the mortars containing clinoptilolite have higher compressive strength than that of the control mortar. At the age of 2 days, the compressive strengths of the mortars with 5% and 10% clinoptilolite content were higher than that of the control mortar due to probably its high fineness value. After that, the compressive strengths of the mortars decreased with an increase in clinoptilolite content. This reason is owing to lack of sufficient $Ca(OH)_2$ in the medium despite an increase in reactive clinoptilolite phases [20]. At the age of 7 days, there was a continuing improvement in the performance of the mixtures. When curing times were extended to 28, 56 and 90 days, an increase in the performance of the mixtures was noticed. This is likely due to the large pozzolanic contribution of clinoptilolite. Zeolite has a high pozzolanic activity. Hence, during the hydration of cement, it easily reacts with $Ca(OH)_2$ and converts into the compounds that possess cementitious properties. As a result, the strength of hardened concrete is improved [23].

3.3. Flexural strength

The flexural strength of the mortars was determined at 2, 7, 28, 56 and 90 days, and the test results are presented in Fig. 3.

As seen in Fig. 3, the flexural strength test results are similar to the compressive strength test results. Most of the flexural strength values of all the mortars containing clinoptilolite are better than that obtained from the reference mixture. The control mortar achieved a flexural strength of 4.01 MPa at the age of 2 days, 5.98 MPa at the age of 7 days, 7.15 MPa at the age of 28 days, 7.31 MPa at the age of 56 days, and 8.91 MPa at the age of 90 days. The flexural strength of mortars containing clinoptilolite varied between 2.88 MPa and 4.55 MPa at the age of 2 days, 5.16 MPa and 6.56 MPa at the age of 7 days, 7.21 MPa and 8.20 MPa at the age of 28 days, 7.24 MPa and 8.57 MPa at the age of 56 days, and 8.91 MPa and 10.02 MPa at the age of 90 days. This phenomenon
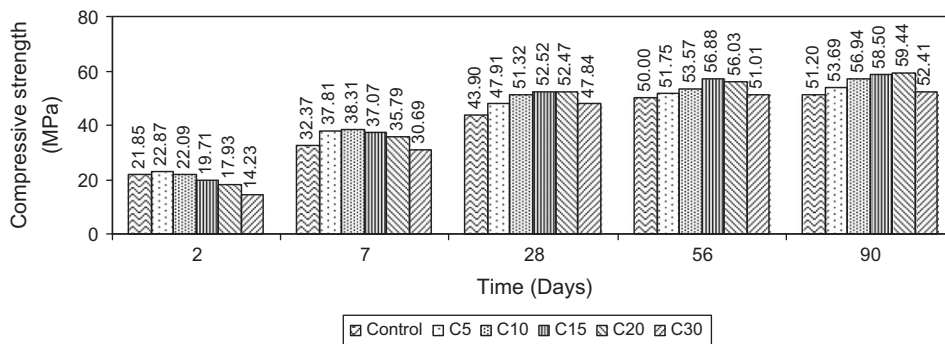

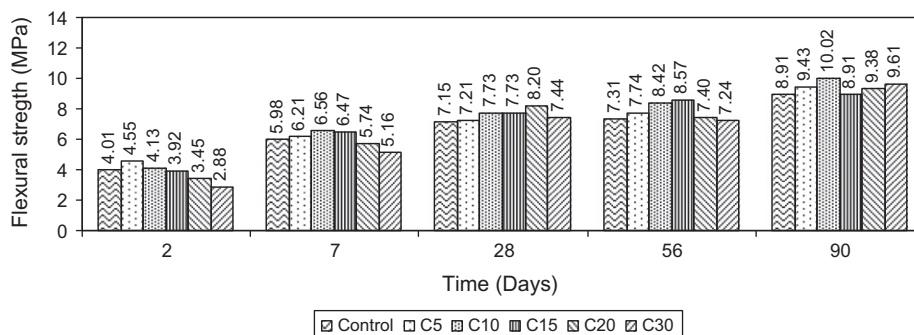**Fig. 2.** Compressive strength of the cement mortars.

Fig. 3. Flexural strength of the cement mortars.

Table 4
Water absorption, porosity and dry unit weight of the cement mortars.

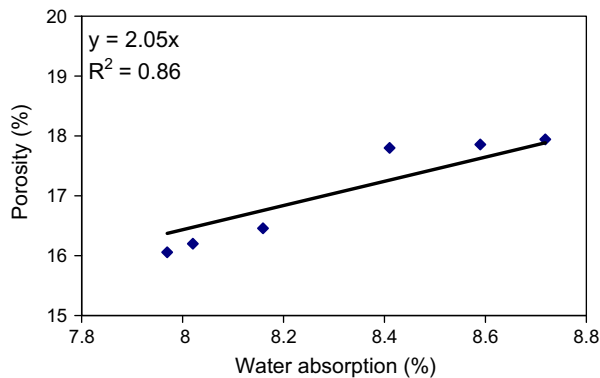| Mixture	Water absorption (%)	Porosity (%)	Dry unit weight (kg/m^3)
Control	8.72	17.93	2078
C5	8.59	17.85	2020
C10	8.41	17.79	2016
C15	8.02	16.21	2004
C20	7.97	16.06	1997
C30	8.16	16.47	1913

Fig. 4. The relation between porosity and water absorption values.

could be attributed to the pozzolanic effect of the zeolite as discussed above.

3.4. Water absorption, porosity and dry unit weight

Water absorption, porosity and dry unit weight of the mortar mixtures containing clinoptilolite are given in Table 4.

The results indicate that dry unit weight decreases with an increase in clinoptilolite content. Dry unit weight changed between 1913 kg/m^3 and 2078 kg/m^3 for mortar specimens aged 28 days. The dry unit weight of the mortars containing clinoptilolite was lower than the control mortar because of high porosity and the low specific gravity of clinoptilolite compared to the cement. Water absorption values changed between 7.97% and 8.72% while porosity values ranged from 16.06% to 17.93% for the mortars containing clinoptilolite aged 28 days. Water absorption and porosity values of the mortars decreased with the increase of clinoptilolite content up to 20% replacement ratio and all the mortars including clinoptilolite exhibited lower water absorption and porosity values than the control mortar. This situation may be explained in this way: The large quantity of reactive SiO_2 and Al_2O_3 in zeolite chemically combines with the calcium hydroxide produced by the hydration of cement to form additional CSH gel and aluminates, resulting in the improvement of microstructure of hardened cement [5,24–26].

In this study, a linear regression analysis was carried out between porosity and water absorption to evaluate if a relationship existed. Result of regression analysis is presented in Fig. 4. As seen in Fig. 4, good relationship existed between porosity and water absorption with 0.86 correlation coefficient of R^2.

3.5. Carbonation

The evolution of the depth of the carbonated layer in time for the mortars is given in Fig. 5.

Concrete has naturally high pH due to $Ca(OH)_2$ formed when Portland cement reacts with water. The pH of the ionic water solu-
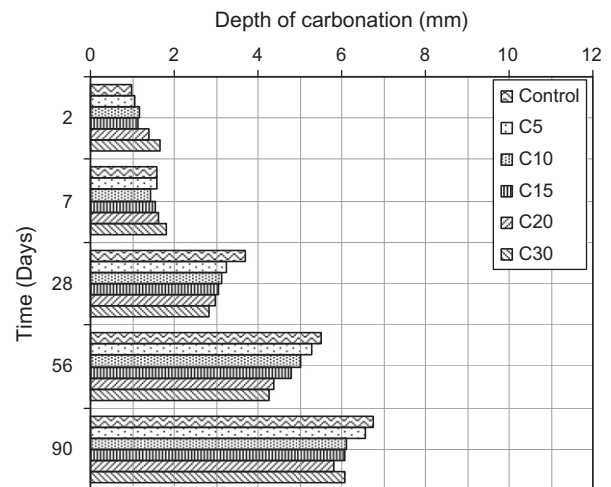

Fig. 5. The evolution of the depth of the carbonated layer in time for the mortars.

tion present in the pores of fresh concrete may be over 14. When concrete is exposed to the atmosphere or when ground waters that contain some CO_2 seep into concrete, a reaction takes place between CO_2 and $Ca(OH)_2$ of the hydrated cement paste leading to the formation of $CaCO_3$. This situation can reduce the pH to 9, although that reaction usually is restricted to a thin layer at the surface and causes a decrease in the alkalinity of the concrete, which makes the steel reinforcement more vulnerable to corrosion. As seen in Fig. 5, carbonation depth of the mortars increased with age since CO_2 penetrates from the surface to the interior of mortar in time. The experimental results showed that the carbonation depth of mortars containing clinoptilolite was higher than that of the control mortar at early ages. However, this negative effect disappeared at longer term ages depending on the pozzolanic reactions. After 90 days of exposure to carbonation, the depth of the layer having pH below 9 was 6.75 mm in control mortar, whereas the carbonation depth changed between 5.82 and 6.58 mm in clinoptilolite incorporated mortars. Additionally, the resistance of the mortar made with clinoptilolite to carbonation increased with increasing the clinoptilolite replacement level and minimum depth of carbonation was obtained from the mortars containing 30% clinoptilolite at the end of carbonation experiments. This phenomenon may be attributed to the lower $Ca(OH)_2$ content in the hardened cement paste at a given age due to less $Ca(OH)_2$ produced and the higher amount of $Ca(OH)_2$ consumed by the pozzolanic reaction.

3.6. Freeze–thaw resistance

The mechanical behavior of mortars after 50 freezing/thawing cycles is shown in Table 5.

When concrete is in a saturated or nearly saturated condition, it is subjected to great internal stresses that take place upon freezing

Table 5
The flexural and compressive strength of the cement mortar after freeze–thaw test.

Mortars	Without cycles		50 cycles	
	Flexural (MPa)	Compressive (MPa)	Flexural (MPa)	Compressive (MPa)
Control	7.50	52.63	7.43	45.97
C5	8.79	54.28	8.15	51.12
C10	8.67	56.39	3.75	42.94
C15	9.02	59.87	2.93	42.59
C20	7.79	58.56	3.63	42.84
C30	7.62	53.69	3.40	43.00

Table 6
Compressive strength of all mixtures after exposure to high temperatures.

Mixture	Compressive strength (MPa)								
	20 °C	250 °C		500 °C		750 °C		1000 °C	
		SC	FC	SC	FC	SC	FC	SC	FC
Control	42.50	37.67	32.13	33.19	23.22	18.45	8.19	2.48	–
C5	45.34	41.36	34.95	43.79	23.38	15.77	7.41	2.73	–
C10	50.41	42.78	38.67	44.84	29.20	19.78	11.98	3.01	2.06
C15	51.28	43.19	41.90	49.35	33.49	20.05	15.63	3.77	2.25
C20	51.44	47.86	42.91	50.84	35.04	25.23	13.14	3.95	2.72
C30	46.50	49.59	43.05	52.08	37.27	23.13	17.22	5.42	3.16

and thus expanding of the water in its capillaries. These internal stresses lead to cracking and surface deterioration of the concrete [27]. As seen in Table 5, the flexural and compressive strength of the mortars decreased after 50 freezing/thawing cycles due to the formation of cracks caused by great internal stresses occurred as a result of volume expansion. The mortar containing 5% clinoptilolite exhibited higher durability resistance to freezing and thawing damage compared to the control mortar. However, as from this replacement level, clinoptilolite incorporation resulted in decrease of both compressive and especially, flexural strength of mortar specimens after freezing/thawing cycles. The decrease is dramatic above 10% clinoptilolite replacement. At 15% clinoptilolite replacement, compressive and flexural strength reduction was about 7% and 60%, respectively. Compared to the mortars without cycles, the strength decrease, which was observed with the increase of clinoptilolite content in the mortars subjected to 50 freezing/thawing cycles, can be explained as in the following. It is known that the pozzolanic reaction is responsible for refining the pore structure of blended cement. The formation of secondary CSH gel by means of the pozzolanic reaction improves the pore structure and decrease the capillary porosity of the mortar [2]. Since, the capillary pores which are connected with each other reduces, there is no enough free space to accommodate the volume increase due to ice formation in mortar. Since freezing of water results in a volume increase of about 9%, the part that has already frozen and expanded exerts a force on the unfrozen water in the pore, and drives the unfrozen water out of the pore. Consequently, the surrounding material is subjected to stress, and this situation causes the rupture of the material [27]. In the mortars containing clinoptilolite, the utilization of air-entraining agents might be beneficial to improve the durability against freezing and thawing cycles.

3.7. Fire resistance

3.7.1. Residual compressive strength

The residual compressive strengths of slow cooled (SC) and fast cooled (FC) mortar specimens are presented in Table 6.

As seen in Table 6, clinoptilolite replacement resulted in an increase in compressive strength of mortar specimens at room temperature. At 20% clinoptilolite replacement, the increment was reached 21% compared to control mixture. At 250 °C, the compressive strength of SC mortars was lower than the mortar specimens at room temperature of about 20 °C. It could be due to thermal stress formations resulting from the temperature differences between surface and core depending on the high heating rate of 10 °C/min. Nevertheless, when the temperature was elevated to 500 °C, an increase in the compressive strength of SC mortars containing clinoptilolite was observed compared to the specimens at 250 °C. The strength gain occurring at this temperature may be elucidated partially due to the closer configuration of hydrated cement paste after the evaporation of free water, which leads to greater van der Waal's forces as a result of the cement gel layers moving closer to each other [28–30]. Since transportation of mois-

Table 7
Flexural strength of all mixtures after exposure to high temperatures.

Mixture	Flexural strength (MPa)								
	20 °C	250 °C		500 °C		750 °C		1000 °C	
		SC	FC	SC	FC	SC	FC	SC	FC
Control	7.27	5.04	4.57	4.63	2.34	1.60	1.17	0.94	–
C5	7.50	6.33	5.39	6.21	3.01	1.65	1.50	1.41	–
C10	8.32	6.68	5.07	6.33	3.75	1.79	1.64	1.37	0.90
C15	7.62	6.56	5.04	5.86	3.50	1.88	1.64	1.17	0.47
C20	8.32	6.31	4.88	6.00	3.61	2.11	1.88	0.95	0.35
C30	7.97	5.98	5.37	5.60	3.52	1.76	1.18	0.35	0.82

ture in mortar is rather gradual, residual moisture in mortar allowed accelerated hydration at the early stage of heating mortars to high temperatures. Further hydration of cementitious materials is another important cause of the hardening of hydrated cement paste. The temperature increase leads to additional hydration products from the unhydrated cement grains. For clinoptilolite incorporated mortars, besides unhydrated cement, unhydrated clinoptilolite particles can react with $Ca(OH)_2$ and produce CSH like gels [28,30,31]. The strength losses occurring in mortar mixtures at 750 °C increased significantly when the temperature was elevated to 1000 °C. The severe strength loss of mortar specimens between 750 and 1000 °C is due to the decomposition of CSH gel [32,33].

Rapid cooling in water caused additional compressive strength losses compared with slow cooling in air at all test temperatures and the mortars containing 0% (control) and 5% clinoptilolite content completely disintegrated at 1000 °C. This result is attributed to conversion of free calcium hydroxide to CaO (quick lime) by losing water above 400–500 °C. When CaO gets in contact with water, it rehydrates to form $Ca(OH)_2$ accompanied by an expansion in volume [34]. Additionally, sudden differences at temperatures can lead to cracks which cause the strength losses. However, strength differences between SC and FC were diminished with the increase of temperature up to 1000 °C. This might be due to the beneficial effect of $Ca(OH)_2$ formation which leads to an increase in residual strength by filling cracks and voids in case of water cooling [19].

3.7.2. Residual flexural strength

The effects of temperatures over the range of 20 °C–1000 °C on flexural strength of slow cooled (SC) and fast cooled (FC) mortar specimens are given in Table 7.

The negative effect of elevated temperatures on flexural strength was more severe than compressive strength case. Although, all tested SC mortars did not exhibit severe loss in compressive strength up to 500 °C, most of them have lost some flexural strength as from 250 °C. The existence of cracks reduces a valid area of cross-sections and the existence of tensile stress causes expansion of cracks [35,36]. The residual flexural strength of SC mortars made with clinoptilolite after the high temperatures was higher than that of the control mortar. At the end of the tests,

the maximum residual flexural strength for SC mortars was obtained from the mortars containing 5% clinoptilolite.

Due to the formation of crack occurring as a result of instantaneous temperature changes which the shock cooling method generated, residual flexural strength of FC mortar specimens was lower than SC, similar to compressive strength results. The mortars containing 0% (control) and 5% clinoptilolite content completely disintegrated at 1000 °C.

4. Conclusions

The following conclusions can be drawn from this study:

(1) Water demand of cement paste containing clinoptilolite increased with clinoptilolite substitution ratio due to microspores inherently found in their structures. Depending on clinoptilolite blend ratios, plasticity time of cement pastes increased. Although soundness of cement pastes increased with an increase in clinoptilolite content, these expansions were lower than the minimum values given in standards.

(2) The demand for chemical admixture for the mortars containing clinoptilolite increased with rising replacement ratio due to its high porosity and specific surface.

(3) The replacement of clinoptilolite with cement affected the early strengths positively due to its high fineness value. The later strengths improved depending on the amount of $Ca(OH)_2$ in the binder paste. The strength of the mortars containing clinoptilolite was higher than control mortar. It was seen that the mortars containing up to 30% clinoptilolite exhibited comparable or higher strength results compared to control mixture at all curing time.

(4) The dry unit weight of the mortars containing clinoptilolite was found to be lower than the control mortar due to low specific gravity of clinoptilolite compared to the cement. Water absorption and porosity of the mortars decreased with the increase of clinoptilolite content.

(5) The control mortar showed less durability to carbonation compared to the mortars made with clinoptilolite after 90 days of exposure to carbonation.

(6) The mortar containing 5% clinoptilolite exhibited higher durability resistance to freezing and thawing damage compared to the control mortar.

(7) After exposure to high temperatures, the residual compressive and flexural strength of mortars containing clinoptilolite were higher than those of control mortar. Fast cooling resulted in severe strength loss when compared to slow cooling.

References

[1] Worrell E, Martin N, Price L. Potentials for energy efficiency improvement in the US cement industry. Energy 2000;25:1189–214.
[2] Ghrici M, Kenai S, Meziane E. Mechanical and durability properties of cement mortar with Algerian natural pozzolana. J Mater Sci 2006;41:6965–72.
[3] Mehta PK. Greening of the concrete industry for sustainable development. Concr Int 2002;24:23–8.
[4] Lea FM. The Chemistry of cement and concrete. 3rd ed. London: Edward Arnold Ltd.; 1970. ISBN: 0 7131 22773.
[5] Poon CS, Lam L, Kou SC, Lin ZS. A study on the hydration rate of natural zeolite blended cement pastes. Constr Build Mater 1999;13:427–32.
[6] Colella C, Gennaro M, Aiello R. Use of zeolitic tuffs in the building industry. Rev Mineral Geochem 2001;45:551–87.
[7] Ikotun BD, Ekolu S. Strength and durability effect of modified zeolite additive on concrete properties. Constr Build Mater 2010;24:749–57.
[8] Kurudirek M, Özdemir Y, Türkmen İ, Levet A. A study of chemical composition and radiation attenuation properties in clinoptilolite-rich natural zeolite from Turkey. Radiat Phys Chem 2010;7 9:1120–6.
[9] Canpolat F, Yılmaz K, Köse MM, Sümer M, Yurdusev MA. Use of zeolite, coal bottom ash and fly ash as replacement materials in cement production. Cement Concrete Res 2004;34:731–5.
[10] Janotka I, Števula L. Effect of bentonite and zeolite on durability of cement suspension under sulfate attack. ACI Mater J 1998;96:710–5.
[11] Fragoulis D, Chaniotakis E, Stamatakis MG. Zeolitic tuffs of Kimolos Island, Aegean Sea, Greece and their industrial potential. Cement Concrete Res 1997;27:889–905.
[12] Quanlin N, Naiqian F. Effect of modified zeolite on the expansion of alkaline silica reaction. Cement Concrete Res 2005;35:1784–8.
[13] Feng N, Li G, Zang X. High-strength and flowing concrete with a zeolitic mineral admixture. ASTM Cement Concrete Aggr 1990;12:61–9.
[14] TSI, TS EN 196-1. Methods of testing cement-Part 1: Determination of strength. Ankara, Turkey: Turkish Standard Institute; 2009 [in Turkish].
[15] TSI, TS EN 196-3. Methods of testing cement-Part 3: Determination of setting time and soundness. Ankara, Turkey: Turkish Standard Institute; 2002 [in Turkish].
[16] TSI, TS EN 1015-3. Methods of test for mortar for masonry-Part 3: Determination of consistence of fresh mortar (by flow table). Ankara, Turkey: Turkish Standard Institute; 2000 [in Turkish].
[17] TSI, TS EN 1015-11. Methods of test for mortar for masonry-Part 11: Determination of flexural and compressive strength of hardened mortar. Ankara, Turkey: Turkish Standard Institute; 2000 [in Turkish].
[18] TSI, TS 3624. Test method for determination the specific gravity the absorption water and the void ratio in hardened concrete. Ankara, Turkey: Turkish Standard Institute; 1981 [in Turkish].
[19] Hertz KD. Concrete strength for fire safety design. Mag Concrete Res 2005;57:445–53.
[20] Yılmaz B, Uçar A, Öteyaka B, Uz V. Properties of zeolitic tuff (clinoptilolite) blended Portland cement. Build Environ 2007;42:3808–15.
[21] Sidheswaran P, Bhat AN. Impact of zeolitic water content on exchange of calcium ions. Thermochim Acta 1997;298:55–8.
[22] TSI, TS EN 197-1. Cement-Part 1: Compositions and conformity criteria for common cements. Ankara, Turkey: Turkish Standard Institute; 2002 [in Turkish].
[23] Chan CF, Mitsuda T. Formation of 11 A tobermorite from mixture of lime and colloidal silica with quartz. Cement Concrete Res 1978;8:135–8.
[24] Ortega EA, Cheeseman C, Knight J, Loizidou M. Properties of alkali-activated clinoptilolite. Cement Concrete Res 2000;30:1641–6.
[25] Perraki T, Kakali G, Kontoleon F. The effect of natural zeolites on the early hydration of Portland cement. Micropor Mesopor Mater 2003;61:205–12.
[26] Caputo D, Liguori B, Colella C. Some advances in understanding the pozzolanic activity of zeolites: the effect of zeolite structure. Cement Concrete Compos 2008;30:455–62.
[27] Erdoğan TY. Admixtures for concrete. Ankara: The Middle East Technical University Press; 1997. ISBN: 975-429-131-6.
[28] Khoury GA. Compressive strength of concrete at high temperatures: A reassessment. Mag Concrete Res 1992;44:291–309.
[29] Dias WPS, Khoury GA, Sullivan PJE. Mechanical properties of hardened cement paste exposed to temperatures up to 700 °C. ACI Mater J 1990;87:160–6.
[30] Hossain KMA. High strength blended cement concrete incorporating volcanic ash: performance at high temperatures. Cement Concrete Compos 2006;28:535–45.
[31] Heikal M. Effect of temperature on the physico-mechanical and mineralogical properties of Homra pozzolanic cement pastes. Cement Concrete Res 2000;30:1835–9.
[32] Xu Y, Wong YL, Poon CS, Anson M. Impact of high temperature on PFA concrete. Cement Concrete Res 2001;31:1065–73.
[33] Poon CS, Azhar S, Anson M, Wong YL. Comparison of the strength and durability performance of normal- and high-strength pozzolanic concretes at elevated temperatures. Cement Concrete Res 2001;31:1291–300.
[34] Aydın S. Development of a high-temperature-resistant mortar by using slag and pumice. Fire Safety J 2008;43:610–7.
[35] Özturan T, Cülfik MS. Effect of elevated temperatures on the residual mechanical properties of high-performance mortar. Cement Concrete Res 2002;32:809–16.
[36] Xu Y, Wong YL, Poon CS, Anson M. Influence of PFA on cracking of concrete and cement paste after exposure to high temperatures. Cement Concrete Res 2003;33:2009–16.