An experimental study on durability properties of concrete containing zeolite as a highly reactive natural pozzolan

Meysam Najimi [a,b], Jafar Sobhani [b], Babak Ahmadi [c,d,*], Mohammad Shekarchi [d]

[a] Department of Civil and Environmental Engineering, University of Nevada-Las Vegas, USA
[b] Concrete Technology Department, Building and Housing Research Center, Tehran 13145-1696, Iran
[c] Department of Civil & Environmental Engineering, Amirkabir University of Technology, Tehran 15875-4413, Iran
[d] Construction Materials Institute, Department of Civil Engineering, University of Tehran, Tehran, Iran

HIGHLIGHTS

▶ Zeolite showed more pozzolanic activity than amorphous natural pozzolans.
▶ The use of 15% zeolite improved strength and durability of concrete.
▶ Zeolite improved chloride penetration and corrosion rate of concrete.
▶ The shrinkage of zeolite incorporated samples was lower than the control sample.

ARTICLE INFO

ABSTRACT

The concrete industry is known to be responsible for a great amount of CO_2 emissions generated during the production of Portland cement. In this paper, the application of natural zeolite as a supplementary cementitious material has been investigated. To this aim, some mechanical and durability properties of concrete made with 15% and 30% of natural zeolite are studied in comparison with concrete without natural zeolite replacement. The results revealed considerable effectiveness of natural zeolite application on water penetration, chloride ion penetration, corrosion rate and drying shrinkage of concrete; however, satisfactory performance was not observed in acid environment. Altogether, from the practical point of view, the incorporation of 15% natural zeolite was found as an appropriate option for improving strength and durability properties of concrete.

1. Introduction

Today, concrete is the most widely used man-made construction material in the world due to its low price, appropriate mechanical and durability characteristics as well as ease of being formed into various shapes and sizes. Despite these advantages, environmental problems are arising from the manufacture of Portland cement as a component of concrete. The cement industry alone is estimated to be responsible for about 7% of all CO_2 generated [1,2]. Therefore, reducing the cement consumption is considered a solution towards sustainable development. In addition, prolonging the service life of cement and concrete composites through enhancing the mechanical and durability properties has gained great importance in recent years. The use of natural or artificial pozzolans as partial replacement of Portland cement is well known as a widespread effective way to reach these goals; For instance, the majority of European cement production is allocated to blended cements [3].

Natural zeolite, a hydrated aluminosilicate of alkali and alkaline earth cations with a three dimensional frame structure, has been widely utilized in constructions since ancient times; however, its application as a popular type of natural pozzolans in the manufacture of pozzolanic cements began from the first decades of the 20th century and shows a growing trend in the recent decades [4]. Recently, the most important utilization of natural zeolite in cement and concrete industry has been reported in China [5]. As mentioned by Feng and Peng [5] in 2005, the total quantity of zeolite consumed in this field was as much as 30 million tons per year in China. Zeolitic tuffs have been also used as pozzolanic materials in some cement plants of Russia, Germany, Slovenia, Cuba, Serbia and Spain [4]. It is reported that a volcanic material containing 45% zeolite

* Corresponding author. Address: No. 8, Behnam Alley, Vessal St., Enghelab Ave., Tehran, Iran. Tel.: +98 912 1640793; fax: +98 218 8959740.
 E-mail address: bahmadi@aut.ac.ir (B. Ahmadi).

deposited in Black Forest of Germany is utilized in concrete industry of Germany, Switzerland and France [6]. This material has been applied in the production of paving stones, concrete slabs, ready mixed concrete, and high-strength concrete pipes [6]. In addition, the use of natural zeolite as a pozzolanic material is gaining an increasing trend in Iran recently. However, due to the limited resources and/or other profitable usages, its application in cement and concrete industry is restricted to some regions of the world.

Simultaneously with the growing trend of applying natural zeolite in the cement and concrete industry, several research studies have been conducted to study its effect on concrete properties and compare this natural pozzolan with other pozzolanic materials. In most cases, natural zeolites possess proper pozzolanic activity and their use as partial replacement of Portland cement lead to durability enhancement of cement and concrete composites. However, due to the various types, structures and purities of natural zeolites [7], the obtained results are not expected to be similar in all experimental studies and even in some cases were in contradiction.

The performance of natural zeolite in cement and concrete composites has been also compared with that of other pozzolanic materials [8,9]. Poon et al. [8] found that the pozzolanic activity of natural zeolite is higher than fly ash and lower than silica fume. Chan and Ji [9] also compared the effectiveness of zeolite in enhancing the performance of concrete in comparison with silica fume and pulverized fuel ash (PFA). They concluded that zeolite is more effective than PFA in improving the compressive strength and decreasing the initial surface absorption and chloride diffusion but it is less beneficial than silica fume.

A summary of the related research studies on the application of natural zeolite in cement and concrete composites is presented in Table 1 [8–54]. As it is shown in this table, in spite of various valuable research studies conducted to investigate the strength properties, alkali silica reaction and transport properties of concretes and mortars containing natural zeolite, the other durability aspects; in particular carbonation, freeze and thaw, and, above all, sulfate and acid attack, chloride-induced corrosion of reinforced concrete and shrinkage are rarely found in the literature. Accordingly, this paper aims to study the effects of using natural zeolite as a supplementary cementitious material (SCM) on the mechanical and durability properties of concrete, with a special consideration on transport properties, chloride-induced corrosion of reinforcement, drying shrinkage, and acid deterioration.

2. Materials and mixture proportions

A clinoptilolite type of natural zeolite coming from Semnan province, center of Iran was utilized in this study. The chemical composition and mineralogical compounds of the natural zeolite used in this study are presented in Table 2. In addition, its chemical and physical properties are compared with the requirements of ASTM C618 and reported in Table 3. As it can be seen, the summation of silica, alumina and iron oxide, which are considered to be responsible for pozzolanic activity, is 82.9% for this natural zeolite, exceeding the 70% minimum level for class N raw and calcined natural pozzolans specified in ASTM C618. The results of strength activity index presented in Table 3 reveal that the strength activity index of natural zeolite is not only higher than the natural pozzolan and fly ash requirements of 75% according to ASTM C618, but also more than 100%. This result means that the compressive strength of the mortar containing 20% natural zeolite reached higher values than the control mortar.

It should be mentioned that the strength activity index may not be considered an effective criterion for determining the pozzolanic activity of a material as discussed in previous studies [55–58].

Therefore, a thermo-gravimetric analysis, a more accurate analysis, was also performed on the natural zeolite to investigate its pozzolanic activity. This method is based on the thermal decomposition of crystalline calcium hydroxide to calcium oxide and water in a temperature range of 400–500 °C. The pozzolanic activity was measured by combining 50% natural zeolite and 50% calcium hydroxide powder in presence of enough water for pozzolanic reaction and workability. The results of this test, which are presented in Table 4 in comparison with some other popular Iranian natural pozzolans, verify the good pozzolanic activity of the studied natural zeolite. As can be seen, natural zeolite gained the highest pozzolanic activity. Similarly, other authors [52–54] found that the rate of the pozzolan–lime reaction of natural zeolites, which are crystalline, is generally superior to the reactivity of traditionally used amorphous natural pozzolans. This behavior can be justified by the mineralogical compounds presented in Table 2. The main components of the natural zeolite are identified as clinoptilolite and opal CT, accompanied by other components consisted of Smectite/illite, Plagioclase, Quartz and K-feldspar. The high amounts of active phases, i.e. clinoptilolite and opal CT, confirm the high pozzolanic activity of this natural zeolite. The high internal surface area of natural zeolites due to their porous microstructure can be considered another reason for its high activity. The porous and platy microstructure of the studied zeolite can be observed in the scanning electron microscopy (SEM) images (Fig. 1). This porous and rough structure can also suggest the reason of its high water requirement (see Table 3).

The particle size distribution of natural zeolite is presented in Fig. 2. According to this figure, the studied natural zeolite has particles in the range of 1–200 μm. The majority of these particles are in the range of 1–45 μm and about 28% of particles are larger than 45 μm.

The effect of natural zeolite on setting time which was measured according to ASTM C191 is shown in Table 5. By increasing the amount of natural zeolite up to 40% in cement paste, the setting time decreased. This phenomenon can be attributed to the high surface area of natural zeolite and absorbing some parts of paste water by natural zeolite. Similar results were also obtained by Canpolat et al. [20] and Uzal et al. [34]. Although the setting time of cement paste do not correlate with that of concrete [59], it can be expected that the use of natural zeolite in concrete result in setting time reduction. Jana [28] found that using natural zeolite up to 30% lead to a lower concrete setting time, so that about 25% reduction in setting time was reported for the concrete mixture containing 30% zeolite. However at 40% level, the setting time of concrete showed a significant increase from that of control mixture.

In addition to natural zeolite, a commercially available ASTM type II Portland cement and fine (0–4.75 mm) and coarse (4.75–19 mm) aggregates meeting the requirements of ASTM C33 were used in this investigation. The chemical composition and physical properties of the cement are presented in Tables 2 and 6, respectively. Also, the physical and mechanical properties of aggregates are reported in Table 7.

Table 8 summarizes the concrete mixture proportions. In addition to the control concrete without natural zeolite (NZ0), two mixtures were made by replacing 15% and 30% of cement mass with natural zeolite; hereafter named as NZ15 and NZ30, respectively. The use of natural zeolite decreased the workability of concrete which was compensated by using a commercially available melamine-based superplasticizer. In this regard, by addition of superplasticizer, the slump of the mixtures was maintained in the range of 70–90 mm. As shown in Table 8, by increasing the replacement level from 15% to 30%, the superplasticizer consumption was not increased linearly. Replacing 30% natural zeolite demanded three times more superplasticizer than 15% level of replacement. From this aspect, although natural zeolite is cheaper than Portland ce-

Table 1
Previous research studies of using natural zeolite in cement and concrete composites [8–54].

Test	Natural Zeolite replacement (%)				
	0–10	11–20	21–30	31–40	41–50
Strength properties	Chan and Ji [9], Ahmadi and Shekarchi [10], Ahmadi [11], Shekarchi et al. [12], Najimi [13], Pargar et al. [14], Feng et al. [15–17], Fragoulis et al. [18], Perraki et al. [18], Canpolat et al. [20], Kasai et al. [21], Ikotun and Ekolu [22], Ikotun [23], Ikotun et al. [24], Yilmaz et al. [25], Bilim [26], Karakurt and Topcu [27]	Poon et al. [8], Chan and Ji [9], Ahmadi and Shekarchi [10], Ahmadi [11], Shekarchi et al. [12], Najimi [13], Pargar et al. [14], Feng et al. [19], [16,17] Fragoulis et al. [18], Perraki et al. [19], Canpolat et al. [20], Kasai et al. [21], Yilmaz et al. [25], Bilim [26], Karakurt and Topcu [27], Jana [28], Tokushige et al. [29], Ding et al. [30], Fu et al. [31]	Poon et al. [8], Chan and Ji [9], Pargar et al. [14], Canpolat et al. [20], Kasai et al. [21], Bilim [26], Karakurt and Topcu [27], Yilmaz et al. [25], Jana [28], Tokushige et al. [29], Fu et al. [31], Janotka and Števula [32]	Canpolat et al. [20], Yilmaz et al. [25], Karakurt and Topcu [27], Jana [28], Cioffi et al. [33]	Karakurt and Topcu [27], Uzal et al. [34]
Alkali–silica reaction	Ahmadi and Shekarchi [10], Ahmadi [11], Shekarchi et al. [12], Ikotun [23], Karakurt and Topcu [27], Jana [28], Sersale and Prigione [35], Feng et al. [36], Feng and Hao [37]	Ahmadi and Shekarchi [10], Ahmadi [11], Shekarchi et al. [12], Karakurt and Topcu [27], Sersale and Prigione [35], Feng et al. [36], Feng and Hao [37], Pei-wei et al. [38]	Ahmadi and Shekarchi [10], Ahmadi [11], Shekarchi et al. [12], Karakurt and Topcu [27], Jana [28], Feng et al. [36], Feng and Hao [37], Feng et al. [39]	Ahmadi and Shekarchi [10], Ahmadi [11], Shekarchi et al. [12], Karakurt and Topcu [27], Sersale and Prigione [35], Feng et al. [36], Feng and Hao [37], Pei-wei et al. [38]	–
Transport properties	Chan and Ji [9], Ahmadi and Shekarchi [10], Ahmadi [11], Shekarchi et al. [12], Najimi [13], Pargar et al. [14], Feng et al. [15,16], Ikotun and Ekolu [22], Ikotun [23], Ikotun et al. [24], Bilim [26], Jana [28], Feng et al. [40]	Poon et al. [8], Chan and Ji [9], Ahmadi and Shekarchi [10], Ahmadi [11], Shekarchi et al. [12], Najimi [13], Pargar et al. [14], Bilim [26], Jana [28], Feng et al. [40]	Poon et al. [8], Chan and Ji [9], Pargar et al. [14], Bilim [26], Jana [28]	Jana [28]	Uzal et al. [34]
Sulfate and acid resistance	Ikotun [23], Ikotun et al. [24], Karakurt and Topcu [27], Jana [28]	Karakurt and Topcu [27], Janotka et al. [41]	Karakurt and Topcu [27], Jana [28], Janotka and Števula [32] Janotka et al. [41]	Karakurt and Topcu [27] Janotka et al. [41]	Karakurt and Topcu [27], Janotka et al. [41]
Freeze and thaw resistance	Bilim [26]	Bilim [26]	Bilim [26]	–	–
Carbonation	Bilim [26]	Bilim [26]	Bilim [26]	–	–
Corrosion of reinforcement	–	–	–	–	–
Drying shrinkage	Kasai et al. [21], Jana [28]	Kasai et al. [21], Jana [28]	Kasai et al. [21], Jana [28]	–	–
Heat of hydration	Krolo et al. [42,43]				
Pozzolanic activity	Poon et al. [8], Ahmadi and Shekarchi [10], Ahmadi [11], Shekarchi et al. [12], Jana [28], Varela et al. [44], Snellings et al. [45], Mertens et al. [46], Burriesci et al. [47], Perraki et al. [48,49], Caputo et al. [50], Liguori et al. [51], Sersale [52], Malquori et al. [53], Zhang et al. [54]				

Table 2
Chemical composition of utilized cement and natural zeolite.

Compound/property	Cement	Natural zeolite
Chemical analysis (%)		
Calcium oxide (CaO)	61.32	1.68
Silica (SiO$_2$)	21.68	67.79
Alumina (Al$_2$O$_3$)	4.85	13.66
Iron oxide (Fe$_2$O$_3$)	4.40	1.44
Magnesium oxide (MgO)	2.60	1.2
Sodium oxide (Na$_2$O)	0.25	2.04
Potassium oxide (K$_2$O)	0.71	1.42
Sulfur trioxide (SO$_3$)	1.90	0.52
Mineral compounds (%)		
Clinoptilolite	–	70.6
Opal CT	–	18.8
Quartz	–	1.6
Plagioclase	–	2.4
K-feldspar	–	1.5
Smectite/illite (clay minerals)	–	5.2

Table 4
Results of thermo-gravimetric measurements.

Natural pozzolans	Pozzolanic activity (%)	
	8 days	30 days
Trass (Jajrood region)	34	40.5
Pumice-I (khash region)	36	38.5
Pumice-II (Sahand region)	21.5	28.5
Tuff (Abyek region)	22.0	22.5
Zeolite-clinoptilolite (aftar region, Semnan province)	45.8	54.3

Note that, thermo-gravimetric analysis is done by combining 50% natural pozzolan with 50% Ca(OH)$_2$ powder.

ment, the high superplasticizer demand for concretes containing high levels of natural zeolite may result in more production costs. The higher demand of superplasticizer in zeolite incorporated concrete mixtures can be attributed to the porous and platy microstructure of the natural zeolite (see Fig. 1). In most studies, higher superplasticizer demand has been reported for zeolite incorporated mixtures [10–14,26,28,29,34]. Ahmadi and Shekarchi [10] and Tokushige et al. [29] reached the conclusion that the dosage of superplasticizer increased substantially with incorporation of zeolite. However, no significant slump loss of concretes containing natural zeolite was reported by Chan and Ji [9].

It should be added that natural zeolite increased the viscosity of fresh concrete. This is because the cement was partially replaced with natural zeolite by weight and therefore, according to the lower specific gravity of natural zeolite (2.2 g/cm^3) in comparison with that of cement (3.1 g/cm^3), the paste volume of the zeolite incorporated mixtures were higher than that of the control mixture. Another reason for this phenomenon is high surface area of natural zeolite. Chan and Ji [9] and Ahmadi and Shekarchi [10] reported similar observation. Şahmaran et al [60] suggested that natural zeolite can be used as a viscosity-modifying agent in cement-based grouts. Natural zeolite showed an insignificant decreasing effect on concrete density, which can be attributed to its lower specific gravity (2.2 g/cm^3) in comparison with that of cement (3.1 g/cm^3).

3. Specimen preparation

The dry materials were mixed first, followed by the addition of water into the mixer. Then, the superplasticizer (if any) was added to the mixture to achieve a desirable workability. Immediately

after mixing, the concrete mixtures were molded and consolidated by a vibrating table. After casting, all the specimens were left covered in the casting room for 24 h. The test samples were then demolded and moist cured at 23 ± 1 °C until the specified age for each test.

4. Experimental results and discussions

4.1. Mechanical properties

The compressive strength of the mixtures was measured on 150 mm cubic specimens and the results are presented in Table 9. In general, the higher cement replacement by natural zeolite led to lower compressive strength. As it can be seen, the compressive strength of NZ15 and NZ30 were lower than the control concrete at all ages. However, the percentages of strength reduction were generally decreased by increasing the age. This behavior can be related to the pozzolanic activity of natural zeolite.

In term of compressive strength, it seems that natural zeolite performs better in blended cement composites with lower w/cm ratios. Poon et al. [8] used natural zeolite as part of cement and investigated the effect of w/cm ratio on the pastes. It was concluded that zeolite in cement pastes with a lower w/cm ratio contributed more to the strength of the pastes. Also, it was found by Chan and Ji [9] that when w/cm ratio was higher than 0.45, the strength of the concretes incorporating zeolite was lower than that of the control concrete, whereas at w/cm values lower than 0.45, higher compressive strengths were obtained for the concretes containing zeolite compared to the control concrete. Moreover, as presented in the previous paper [10], the concretes containing natural zeolite with w/cm ratio of 0.40 displayed higher compressive strength than the control mixture at the ages of 3, 7, 28 and 90 days, whereas contrary results were obtained for the concretes with w/cm of 0.5 in the present study (see Table 9). The studied natural zeolites are the same in these two studies.
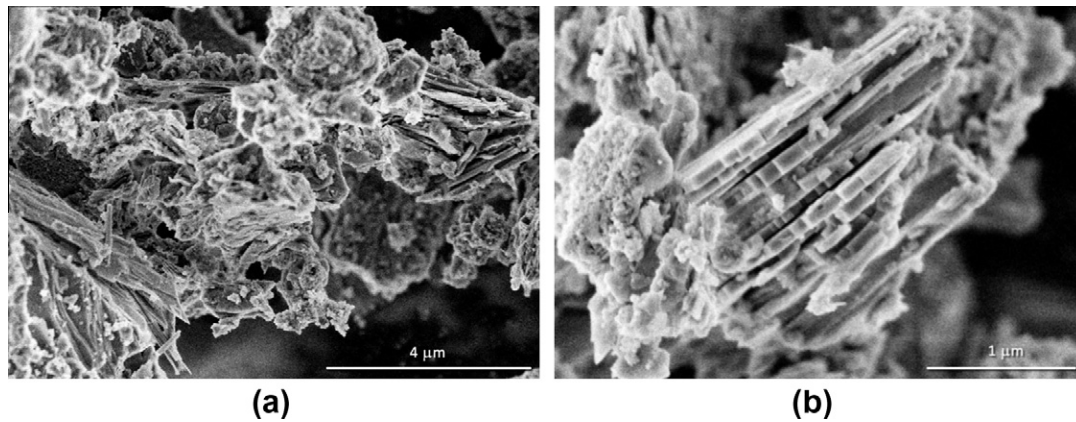
Table 3
Chemical and physical properties of natural zeolite according to ASTM C618.

Requirements			Natural zeolite results (clinoptilolite)
		Class N, ASTM C618	
Chemical requirements	SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ (%)	Min, 70.0	82.89
	Sulfur trioxide (SO$_3$) (%)	Max, 4.0	0.52
	Moisture content (%)	Max, 3.0	2.9
	Loss on ignition (%)	Max, 10.0	9.85
Physical requirements	Amount retained when wet-sieved on 45 μm sieve (%)	Max, 34	28
	Strength activity index, at 7 days, percent of control[a]	Min, 75	120
	Strength activity index, at 28 days, percent of control[a]	Min, 75	127
	Water requirement, percent of control	Max, 115	114
	Autoclave expansion or contraction (%)	Max, 0.8	0.02

[a] Note that, the activity index of natural zeolite is determined based on ASTM C311 by replacing 20% of cement with natural zeolite.
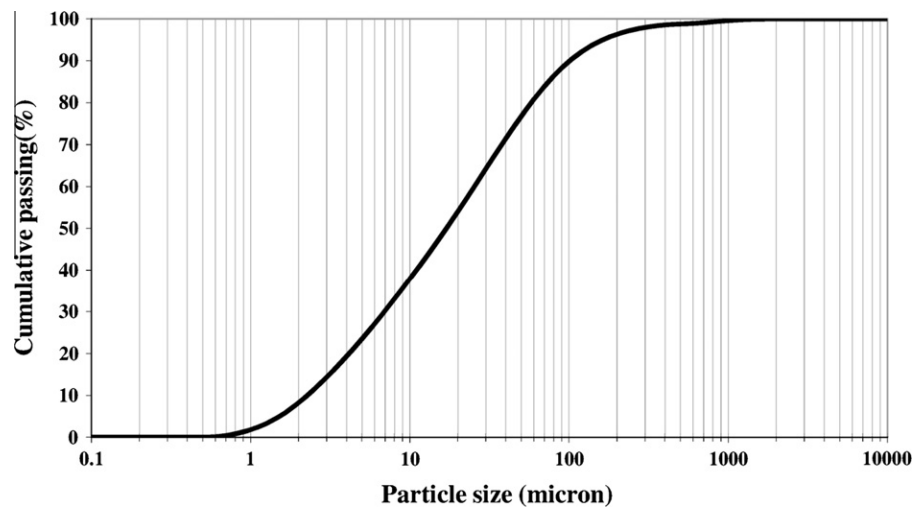
Fig. 1. SEM image of natural zeolite.

Fig. 2. Particle size distribution of natural zeolite.

Table 5
Results of setting time.

Natural zeolite percentage	Initial setting (min)	Final setting (min)
0	168	218
10	121	174
20	110	143
40	49	124

Table 6
Mechanical and physical properties of cement.

Tricalcium silicate (C_3S) (%)	40.57
Dicalcium silicate (C_2S) (%)	31.55
Tricalcium aluminate (C_3A) (%)	5.41
3 day compressive strength (MPa)	14.4
7 day compressive strength (MPa)	21.9
28 day compressive strength (MPa)	32.1
Initial setting time (min)	168
Final setting time (min)	218
Specific surface (m^2/kg)	284
Specific gravity (g/cm^3)	3.10
Loss on ignition (975 °C) (%)	1.74
Insoluble residue (%)	0.72
Autoclave expansion (%)	0.30

Table 7
Aggregate properties.

Aggregate type	Specific gravity	Water absorption (%)	Fineness modulus	%<75 μm
Fine (0–4.75 mm)	2.53	2.60	3.1	1.1
Coarse (4.75–19 mm)	2.56	1.46	–	0.2

Table 8
Mixture proportions.

Mixture identification	Natural zeolite percentage	Cement (kg/m^3)	Natural zeolite (kg/m^3)	Superplasticizer (% of cement)	Fresh density (kg/m^3)
NZ0 (control)	–	350	0	0	2318
NZ15	15	297.5	52.5	0.4	2310
NZ30	30	245	105	1.2	2291

Note: the followings are valid for all mixtures: w/cm = 0.5, water = 175 kg/m^3, fine aggregate = 870 kg/m^3 and coarse aggregate = 870 kg/m^3.

Considering the results of concrete compressive strength test (see Table 9) and strength activity index test on mortar specimens (see Table 3), no relationship can be concluded between them. The compressive strength of mortars containing natural zeolite is con-

Table 9
Compressive strength results.

Mixture identification	Compressive strength (MPa)				
	7 days	14 days	28 days	90 days	356 days
NZ0 (control)	16.1	34.1	38.0	40.8	49.0
NZ15	14.5	29.2	36.6	39.7	45.6
NZ30	10.0	23.8	28.7	38.0	42.4
	Compressive strength reduction compared to the control concrete (%)				
NZ15	−9.9	−14.4	−3.7	−2.7	−6.9
NZ30	−37.9	−30.2	−24.5	−6.9	−13.5

Table 10
Transport properties.

Mixture identification	Water penetration depth (mm)		24 h-Water absorption (%)		Chloride ion penetration (C)	
	28 days	90 days	28 days	90 days	28 days	90 days
NZ0 (control)	15	15	6.88	6.50	6970	6340
NZ15	13	11	7.97	7.95	1914	958
NZ30	9	10	7.75	7.60	572	408
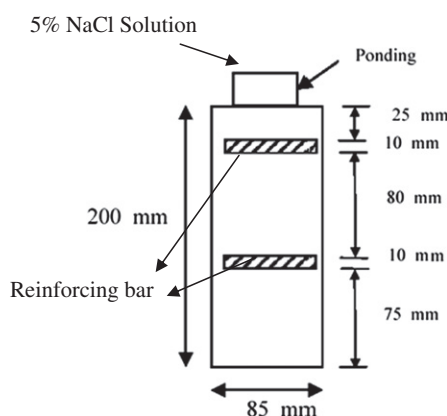
Fig. 3. Schematic configuration of ponding setup for reinforced sample.

siderably higher than that of mortar without natural zeolite, whereas concretes containing natural zeolite had lower compressive strength comparing to the control concrete. Therefore, the strength activity index cannot be considered an effective tool for determining behavior of a pozzolan in concrete. This phenomenon was similarly observed in other research studies [55–58].

4.2. Transport properties

The results of water penetration depth of the concrete mixtures, evaluated via EN 12390-8 at 28 days, are given in Table 10. Generally, by application of the natural zeolite, the water penetration depth decreased. The more natural zeolite replaced, the more water penetration decreased. After 28 days of curing, the water penetration depth of NZ15 and NZ30 were respectively reduced about 13% and 40% in comparison with the control specimens (NZ0). At the age of 90 days, the performances of NZ15 and NZ30 were almost similar and about 33% better than NZ0.

In contrast with the results of water penetration test, the water absorption of the concrete mixtures containing natural zeolite was higher than that of the control concrete. This phenomenon can be related to the different origin and the measurement process of these two tests. The water penetration is related to the microstructure, so the concrete mixtures containing natural zeolite have less pores due to the pozzolanic activity and consumption of $Ca(OH)_2$.

On the other hand, it seems that water absorption is influenced by the water absorption of utilized materials, specially by the paste at concrete surface. Therefore, since the water absorption of natural zeolite is significantly higher than that of cement, the more water absorption is inevitable.

Similar to the results of water penetration test, using natural zeolite decreased the chloride ion permeability. Table 10 also represents the rapid chloride penetration (RCPT) results of the specimens, measured according to ASTM C1202 at 28 and 90 days. The RCPT values of NZ15 and NZ30 were about 27.5% and 8.2% of those of the control mixture after 28 days of curing and were about 15.1% and 6.4% of those of the control mixture after 90 days of curing, respectively. Based on the these results, the effectiveness of using natural zeolite on decreasing chloride ion permeability is more considerable at later ages which can be attributed to the pozzolanic reaction of natural zeolite. It should be noted that Jana [28], Uzal et al. [34] and Feng et al. [40] similarly observed reductions in chloride ion penetration values; however, the amount of reduction for the utilized natural zeolite is considerably higher than those obtained in previous studies. This can be attributed to the high pozzolanic activity of the studied natural zeolite due to its high amounts of active phases, i.e. clinoptilolite and opal CT. Rapid chloride penetration test is dependent on the pore solution of concrete structure in addition to the pore structure. Some authors [61,62] declared that the current flow (in coulomb) is significantly dependent on the amount of OH^- in pore solution. Pozzolans with higher activity consume more $Ca(OH)_2$ and so reduce the amount of OH^- in the pore solution. In fact, the higher the pozzolanic activity, the higher the decrease in OH^- and the lower the rapid chloride penetration value. Therefore, the applied natural zeolite which has a high pozzolanic activity showed a greater reducing effect on the rapid chloride penetration results.

4.3. Electrochemical corrosion measurements

4.3.1. Experimental setup

Cylindrical specimens of size 85×200 mm, reinforced by two deformed 10 mm steel bars which were horizontally located at distances of 80 mm were designed for the electrochemical measurements. A schematic configuration of such specimens is depicted in Fig. 3.

In this test, three parameters including open circuit potential, corrosion rate and polarization resistivity were evaluated through Potentiodynamic and open circuit potential measurements.

For each measurement, two reinforced samples were made and wet cured for 28 days. Afterward, samples were subjected to cyclic ponding including 2 weeks of 5% NaCl solution exposure followed by 2 weeks left in dry condition. A Solartron 1287 electrochemical interface controlled by a personal computer (PC) was used. A Hg/Hg$_2$SO$_4$ in saturated K$_2$SO$_4$ (0.64 V/NHE) reference electrode and a platinum counter electrode were used for the electrochemical measurements. CorrWare software was applied to perform the measurements and CorrView software was utilized for data acquisition and fittings purposes.

4.3.2. Open circuit potential

The open circuit test setup was used to monitor the open circuit potential (OCP) (or free corrosion potential) as a function of time. The experiments were performed for a fixed time of 100 s. During this time period, the OCP values were obtained on the fix rate of five points per second. The results of the open circuit potential test are presented in Fig. 4. According to ASTM C876, the half cell potential between −200 and 0 for CuSO$_4$ electrode (equivalent to −540 to −340 for the electrode utilized in this study, i.e. Hg/Hg$_2$SO$_4$ in saturated K$_2$SO$_4$) represents too low possibility of corrosion, so the specimens probably have not experienced corrosion during the test period. Moreover, the use of natural zeolite as partial replacement of cement led to the improvement of concrete quality, especially for NZ30 which significantly improved the OCP.

4.3.3. Potentiodynamic measurements

A potentiodynamic polarization (PDP) test over a potential range of about OCP value ±200 mV was performed to obtain the polarization curve. This curve was then analyzed to calculate corrosion rate and polarization resistance. Again, CorWare and CorView softwares were utilized to perform the electrochemical tests and analyze the gained data, respectively.

In this measurement, the polarization resistance (R_p) was calculated as the inverse of the slope of the current versus potential graph. For this calculation, the part of curve located near OCP value was applied. The density of corrosion current (i_{corr}) was then calculated from the Stern–Geary equation [63]:

$$i_{corr} = B/R_p \tag{1}$$

where B is the so-called "Stern–Geary constant" and its value was taken as 26 mV [64–66]. The gained current is a measure of the corrosion rate. The corrosion rate was calculated as follows:

$$CR = K\frac{i_{corr}}{\rho}EW \tag{2}$$

where CR is the corrosion rate (mm/year), K is a constant for converting units, i_{corr} is the corrosion current (amp/cm^2), ρ is the iron density (gram/cm^3) and EW is the iron equivalent weight (gram/equivalent).
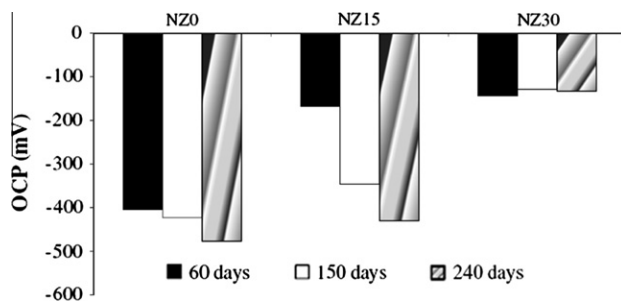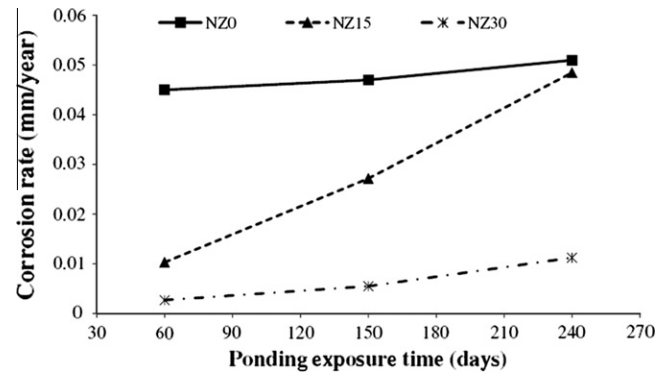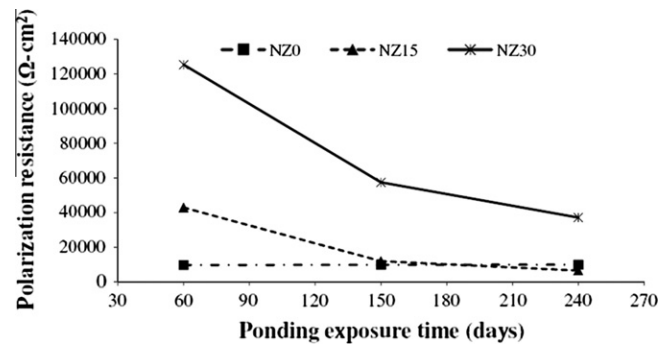
Fig. 5. Corrosion rate.

Fig. 6. Polarization resistance.

The corrosion rate and polarization resistance results of the mixtures are presented in Figs. 5 and 6, respectively. Generally, the corrosion rate of the mixtures containing natural zeolite was lower than that of the control concrete and their polarization resistance was found to be higher than that of the control concrete. Accordingly, the more natural zeolite replaced, the better performance was observed. Although the corrosion rate of NZ15 reached the control concrete after 240 days of ponding exposure, NZ30 showed a significantly lower corrosion rate even at this age.

4.4. Drying shrinkage

The effect of utilizing natural zeolite as a supplementary cementitious material on drying shrinkage of concrete has been rarely investigated. In this study, the drying shrinkage measurements were performed on 75 × 75 × 285 mm concrete prisms after 28 days of curing in water. It should be noted that during the
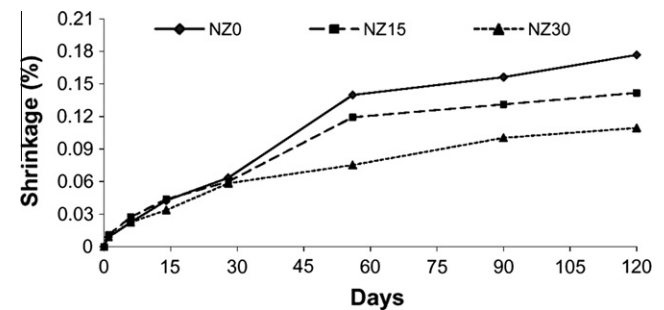
Fig. 4. Open circuit potential.
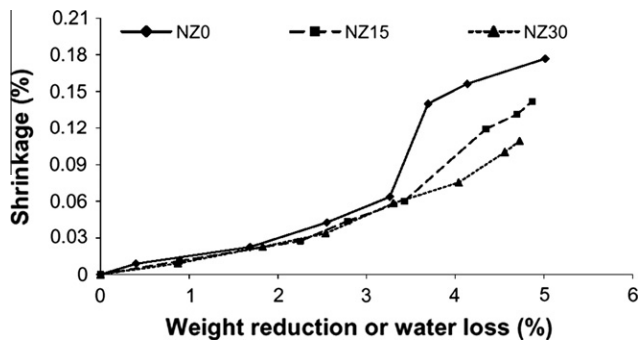
Fig. 7. Drying shrinkage versus age.

Fig. 8. Drying shrinkage versus moisture loss.

measurements, the concrete prisms were stored in a room with a temperature of 23 °C and a relative humidity of 50%.

Fig. 7 presents the drying shrinkage of mixtures, which are plotted versus age. According to this figure, the application of natural zeolite led to a considerable decrease in drying shrinkage. The drying shrinkage of NZ15 and NZ30 were about 84% and 64% of the control concrete after 90 days, respectively. These results are in contrast with the results of Jana's research [28]. Jana observed that the drying shrinkage of natural zeolite mixtures at 10% and 20% Portland cement replacement levels were similar or slightly higher than that of the control mixture, whereas by replacing 30% of cement with zeolite, the drying shrinkage was about 20% more than the control mixture [28]. However, it should be noted that Jana [28] carried out the shrinkage tests on mortar bars and just after

7 days of moist-curing. In addition, Kasai et al. [21] examined drying shrinkage for the mortars blended with clinoptilolite or mordenite type zeolite. Both clinoptilolite and mordenite blended mortars experienced higher shrinkage than the control mortar and the mordenite blended mortar showed slightly greater shrinkage than clinoptilolite blended mortar.

From another point of view, the drying shrinkage is plotted versus the moisture loss of the samples in Fig. 8. As it can be seen, up to 3.3% moisture loss, the drying shrinkage was similar and in the low range for all the mixtures, whereas thereafter the shrinkage of NZ15 and NZ30 were significantly lower than that of the control concrete. For instance, at 4% moisture loss, the drying shrinkage of NZ15 and NZ30 were about 67% and 50% of control concrete, respectively. These results can be attributed to the internal curing ability of natural zeolite. It means that natural zeolite as a porous material absorbs a part of water in fresh state of concrete and this water gradually migrates out of natural zeolite during drying of hardened concrete. This phenomenon is well-documented for concrete mixtures incorporating lightweight aggregates [67–70].

4.6. Sulfuric acid deterioration

An special chamber was designed to simulate the sulfuric acid attack on the concrete specimens, as shown in Fig. 9. Acid attack is more corrosive in lower pH, so the setup of the chamber was regulated in a manner that the pH of the solution always remains at 2.

Cube specimens of 100 mm size were made and cured in a standard moist condition for 28 days. Subsequently, these specimens were left for 28 days in the laboratory condition to ensure the

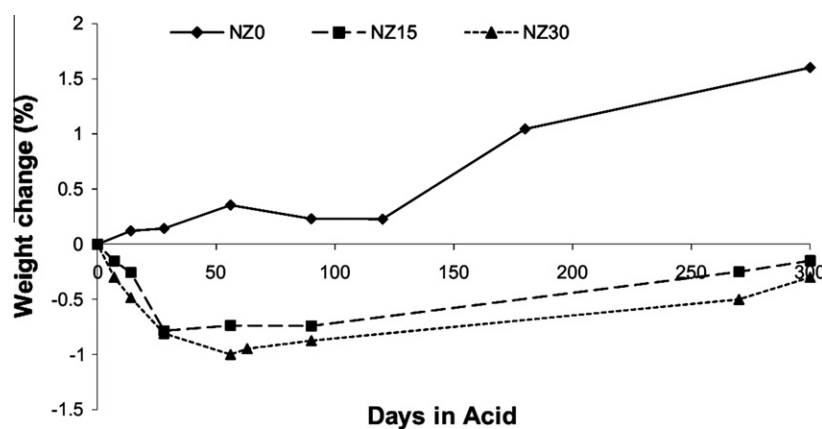

Fig. 9. Simulated chamber for sulfuric acid attack.

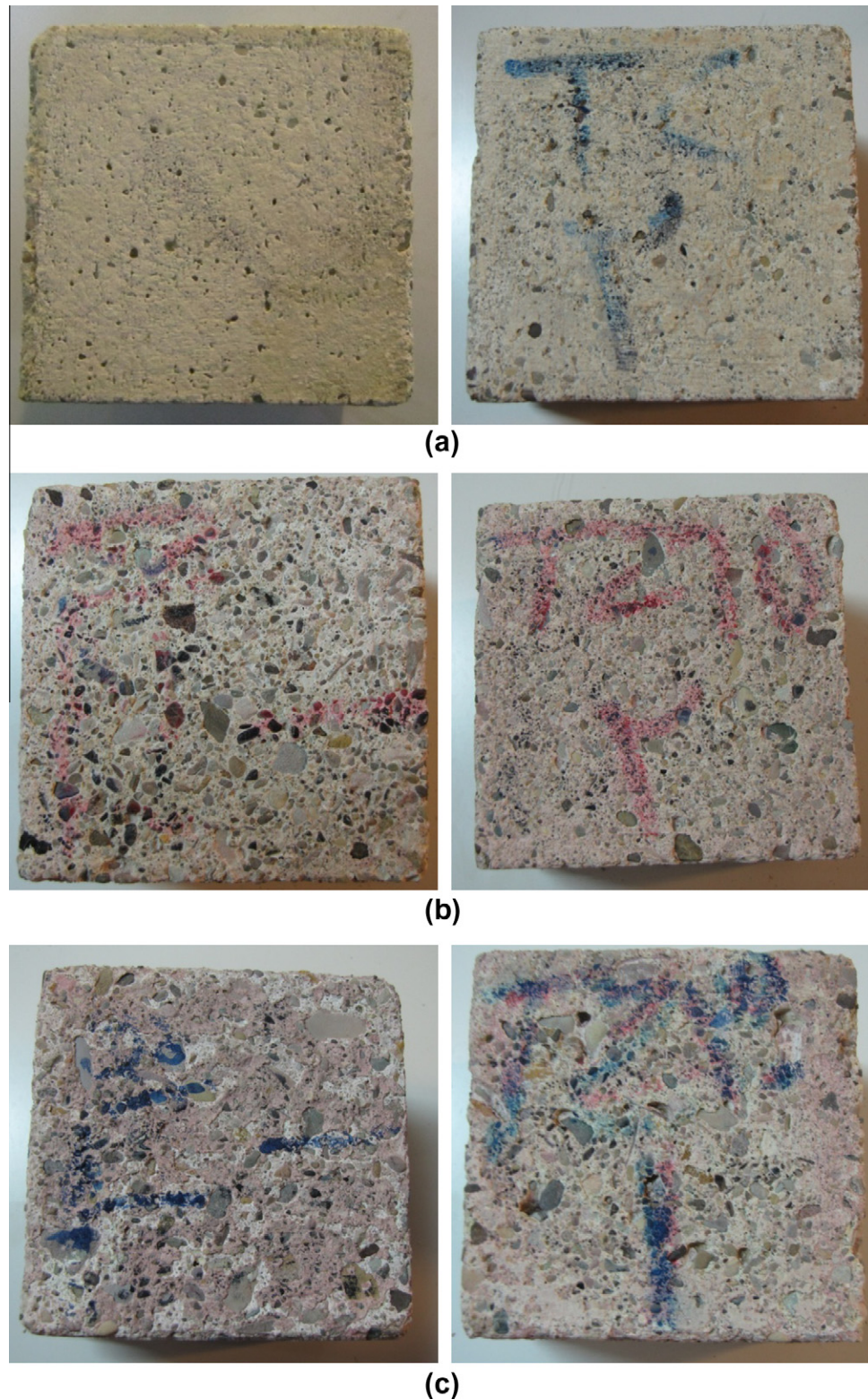
Fig. 10. Weight change in sulfuric acid.

Fig. 11. The surface appearance of specimens after 300 days of exposure in sulfuric acid: (a) NZ0 (control), (b) NZ15 and (c) NZ30.

stable state. At this age, the weight was measured and then the specimens were transferred to the simulating chamber. At different ages, the specimens were removed, brushed, weighted and re-stored in the simulating chamber. The results of weight measurements are presented in Fig. 10. As can be observed, the weight of NZ0 increased during the immersion in acid, while weight of NZ15 and NZ30 firstly decreased and then increased. According to the results of weight measurements presented in Fig. 10, it seems that the H_2SO_4 penetration was the cause of weight increase. For concrete mixtures containing natural zeolite, the deteriorated paste on the surface was brushed and so these samples lost their weight. After deteriorating the surface layer of

Table 11
Compressive strength after 300 days immersion in acid.

| Mixture identification	Compressive strength (MPa)		Strength reduction in acid (%)
	28 days in water + 28 days in lab condition + 300 days in acid exposure	356 days in water	
NZ0 (control)	46.3	49.0	5.5
NZ15	36.1	45.6	20.8
NZ30	32.5	42.4	23.3
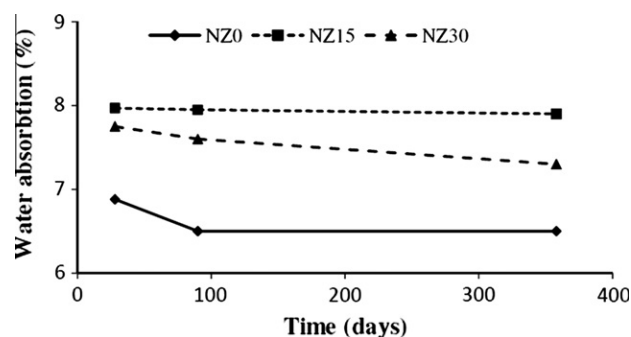
Fig. 12. Water absorption.

paste and reaching the aggregates, the weight of NZ15 and NZ30 started to increase due to the penetration of acid solution. As shown in Fig 11, an evident decomposition can be observed on the surface of NZ15 and NZ30 after 300 days of exposure in sulfuric acid, so that the aggregates became visible. This kind of deterioration was not found for NZ0.

In addition, after 300 days of immersion in acid, the compressive strength of the specimens was measured to find the effect of acid attack on strength properties. The compressive strength results of samples cured in water until 356 days and the specimens immersed in acid for 300 days (age of 356 days; i.e. 28 days in water + 28 days in lab condition + 300 days in acid exposure) are presented in Table 11. The compressive strength of NZ0 in acid were only 5.5% lower than that of the specimen cured in water, while the strength of NZ15 and NZ30 in acid decreased about 20.8% and 23.3%, respectively.

The inappropriate performance and lower compressive strength of natural zeolite concrete can be related to the reaction of acid sulfuric with $Ca(OH)_2$, which may have inhibited natural zeolite pozzolanic reaction, and higher absorption of NZ15 and NZ30.

Since the specimens were transferred to the simulating chamber at the age of 56 days, pozzolanic reaction was incomplete at this age. On the other hand, sulfuric acid could react with $Ca(OH)_2$ which is necessary for pozzolanic reaction. This reaction is as follow:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O \qquad (3)$$
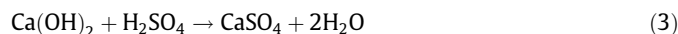
Based on this reaction, probably there have not been sufficient $Ca(OH)_2$ for pozzolanic reaction, so the concrete mixtures containing natural zeolite have lost some parts of C–S–H gel which is responsible for compressive strength of concrete.

In addition, according to Fig. 12, the higher absorption of NZ15 and NZ30 comparing to that of NZ0 can be considered a reason for absorbing more acid. Therefore, surface deterioration and weight loss leading to strength reduction could occur more in the concretes incorporating natural zeolite.

It should be mentioned that Janotka et al. [41] found that the acid (HCl and H_2SO_4) resistance of the zeolite blended mortar was greater than that of the control mortar. They attributed this

improvement to less permeable structure of zeolite blended mortar than the control mortar. It seems that more comprehensive studies are required in this field.

5. Conclusion

This paper addressed the application of natural zeolite as a supplementary cementitious material. In this study, different properties of concrete made with 15% and 30% of natural zeolite were investigated in comparison with concrete without natural zeolite replacement.

The following conclusions can be drawn from this investigation:

1. The clinoptilolite type of natural zeolite utilized in this study showed more pozzolanic activity than other Iranian natural pozzolans. It also met the ASTM C618 specifications for a type N pozzolan.
2. The rough and porous structure of utilized natural zeolite as well as its high surface area resulted in a significant decrease in concrete workability and paste setting time. Accordingly, mid-range and preferably high-range water reducing admixtures are necessary for maintaining the desirable workability.
3. The compressive strength of concretes containing natural zeolite were lower than that of control concrete at all ages. However, the percentages of reduction were lower at later ages, which can be attributed to the pozzolanic activity.
4. Generally, the durability properties of concrete were improved by partial replacement of cement with natural zeolite. The most effectiveness of natural zeolite application was observed in the chloride ion penetration, corrosion rate, drying shrinkage and water penetration; however, satisfactory performance was not observed in acid environment.
5. Although the more replacement level led to the better durability performance, from the practical point of view, the incorporation of 15% natural zeolite is promising. The concrete contained 15% natural zeolite reached a suitable compressive strength, water penetration, chloride ion penetration, corrosion rate, drying shrinkage and it also did not demand too much superplasticizer.

References

[1] Mehta PK. Concrete technology for sustainable development. Concr Int 1999;21(11):47–52.
[2] Damtoft JS, Lukasik J, Herfort D, Sorrentino D, Gartner EM. Sustainable development and climate change initiatives. Cem Concr Res 2008;38(2):115–27.
[3] The European Cement Association. CEMBUREAU annual report 2001. Brussels: CEMBUREAU; 2001.
[4] Colella C. In: Čejka J, van Bekkum H, Corma A, Schueth F, editors. Introduction to zeolite science and practice. Amsterdam: Elsevier; 2007. p. 999–1035.
[5] Feng N, Peng G. Applications of natural zeolite to construction and building materials in China. Constr Build Mater 2005;19(8):579–84.
[6] Hauri F. Natural zeolite from southern Germany: applications in concrete. In: Bowman RS, Delap SE, editors. Proceedings of 7th international conference on the occurrence, properties, and utilization of natural zeolites. Socorro; 2006. p. 130–1.
[7] Misaelides P. Natural zeolites: still a subject of innovative research? In: Petrov O, Tzvetanova Y, editors. Proceedings of 8th international conference on the occurrence, properties, and utilization of natural zeolites. Sofia; 2010. p. 27–8.
[8] 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(8):427–32.

[9] Chan SYN, Ji X. Comparative study of the initial surface absorption and chloride diffusion of high performance zeolite, silica fume and PFA concretes. Cem Concr Compos 1999;21(4):293–300.

[10] Ahmadi B, Shekarchi M. Use of natural zeolite as a supplementary cementitious material. Cem Concr Compos 2010;32(2):134–41.

[11] Ahmadi B. Feasibility study of using natural zeolite as pozzolanic material in concrete. MSc thesis. Tehran: University of Tehran; 2007.

[12] Shekarchi M, Nejad JE, Ahmadi B, Rahimi M. Improving concrete properties by using natural zeolite, Part I – Mechanical and durability properties. Iran Concr J 2008;30:34–42.

[13] Najimi M. Investigating the properties of concrete containing natural zeolite as supplementary cementitious materials. Report No.: AF.TO-PO.N89/1. Tehran: Building and Housing Research Center; 2010.

[14] Pargar F, Valipour M, Shekarchi M, Tahmasbi F. Study on the effect of exposure conditions on the chloride diffusion of concretes incorporating silica fume, metakaolin and zeolite located in Qeshm Island. Iran Concr J 2010;35.

[15] Feng N, Yang H, Zu L. The strength effect of mineral admixture on cement concrete. Cem Concr Res 1988;18(3):464–72.

[16] Feng N, Li GZ, Zang XW. High-strength and flowing concrete with a zeolitic mineral admixture. ASTM Cem Concr Aggr 1990;12(2):61–9.

[17] Feng N, Mukai T, Ehara K. A study on the effect of zeolite when used as a strength increasing admixture of concrete. J Struct Constr Eng 1988;388:9–17.

[18] Fragoulis D, Chaniotakis E, Stamakis G. Zeolitic tuffs of Kimolos Island, Aegean sea, Greece and their industrial potential. Cem Concr Res 1997;27(6):889–905.

[19] Perraki T, Kakali G, Kontoleon F. The effect of natural zeolites on the early hydration of Portland cement. Microporous Mesoporous Mater 2003;61(1–3):205–12.

[20] Canpolat F, Yilmaz K, Kose MM, Sumer M, Yurdusev MA. Use of zeolite, coal bottom ash and fly ash as replacement materials in cement production. Cem Concr Res 2004;34(5):731–5.

[21] Kasai Y, Tobinai K, Asakura E, Feng N. Comparative study of natural zeolites and other inorganic admixtures in terms of characterization and properties of mortars. In: Malhotra VD, editor. Proceedings of the 9th Canmet/ACI international conference on fly ash, silica fume, slag, and natural pozzolans in concrete. Istanbul: Farmington Hills; 1992. p. 615–34.

[22] Ikotun BD, Ekolu S. Strength and durability effect of modified zeolite additive on concrete properties. Constr Build Mater 2010;24(5):749–57.

[23] Ikotun BD. The effect of modified zeolite additive as a cement and concrete improver. MSc thesis. Johannesburg: University of the Witwatersrand; 2009.

[24] Ikotun BD, Ekolu S, De Freitas VG. Effect of modified zeolite additive on properties of cement mortars. In: Oyawa WO, Kimura M, editors. Proceedings of the 2nd international civil engineering conference on civil engineering and sustainable development. Mombasa; 2008. p. 187–96.

[25] Yilmaz B, Ucar A, Oteyaka B, Uz V. Properties of zeolitic tuff (clinoptilolite) blended portlad cement. Build Environ 2007;42(11):3808–15.

[26] Bilim C. Properties of cement mortars containing clinoptilolite as a supplementary cementitious material. Constr Build Mater 2011;25(8):3175–80.

[27] Karakurt C, Topcu IB. Effect of blended cements produced with natural zeolite and industrial by-products on alkali-silica reaction and sulfate resistance of concrete. Constr Build Mater 2011;25(4):1789–95.

[28] Jana D. A new look to an old pozzolan, clinoptilolite – a promising pozzolan in concrete. In: Proceedings of the 29th ICMA conference on cement microscopy. Quebec City: Curran Associates Inc.; 2007. p. 168–206.

[29] Tokushige H, Kamehima H, Kawakami M, BIER TA. Effect of use of natural zeolite as a mineraladmixture and an aggregate on physical properties of cement mortar and porous concrete. In: Proceedings of the 4th international conference on construction materials: performance, innovations and structural implications. Nagoya; 2009. p. 1231–6.

[30] Ding J, Fu Y, Beaudoin JJ. Stratlingite formation in high alumina cement-silica fume systems: significance of sodium ions. Cem Concr Res 1995;25(6):1311–9.

[31] Fu Y, Ding J, Beaudoin JJ. Zeolite-based additives for high alumina cement products. Adv Cem Based Mater 1996;3(1):37–42.

[32] Janotka I, Števula L. Effect of bentonite and zeolite on durability of cement suspension under sulfate attack. ACI Mater J 1998;95(6):710–5.

[33] Cioffi R, Colangelo F, Caputo D, Ligiori. Influence of high volumes of ultra-fine additions on self-compacting concrete. In: Malhotra VM, editor. Proceedings of the 8th Canmet/ACI international conference on fly ash, silica fume, slag, and natural pozzolans in concrete. Sorrento: Farmington Hills; 2006. p. 118–35.

[34] Uzal B, Turanli L, Mehta PK. High-volume natural pozzolan concrete for structural applications. ACI Mater J 2007;104(5):535–8.

[35] Sersale R, Prigione G. Portland-zeolite-cement for minimizing alkali-aggregate expansion. Cem Concr Res 1987;17(3):404–10.

[36] Feng N, Hongwei J, Enyi C. Study on the suppression effect of natural zeolite on expansion of concrete due to alkali-aggregate reaction. Mag Concr Res 1998;50(1):17–24.

[37] Feng N, Hao T. Mechanism of natural zeolite powder in preventing alkali-silica reaction in concrete. Adv Cem Res 1998;10(3):101–8.

[38] Pei-wei G, Sheng-xing W, Ping-hua L, Zhong-ru W. Influence of composite mineral admixtures on expansion and crack do to AAR. In: Proceedings of the 12th international on alkali-aggregate reaction in concrete. Beijing; 2004. p. 716–20.

[39] Feng N, Changchen M, Xihuang J. Natural zeolite for preventing expansion due to alkali-aggregate reaction. ASTM Cem Concr Aggr 1992;14(2):93–9.

[40] Feng N, Feng X, Hao T, Xing F. Effect of ultrafine mineral powder on the charge passed of the concrete. Cem Concr Res 2002;32(4):623–7.

[41] Janotka I, Krajci L, Dzivak M. Properties and utilization of zeolite-blended portland cements. Clays Clay Miner 2003;51(6):616–24.

[42] Krolo P, Krstulovic R, Dabic P, Bubic A. Hydration and leaching of cement-zeolite composite. Ceram-Silikaty 2005;49(3):213–9.

[43] Krolo P, Krstulovic R, Dabic P, Zmicic A, Bubic A. The stabilization of hazardous zeolite waste in cement composites and its effect on hydration processes. Mater Technol 2003;37(6):327–32.

[44] Varela MTB, Ramirez SM, Erena I, Gener M, Carmona P. Characterization and pozzolanicity of zeolitic rocks from two Cuban deposits. Appl Clay Sci 2006;33(2):149–59.

[45] Snellings R, Mertens G, Hertsens S, Elsen J. The zeolite-lime pozzolanic reaction: reaction kinetics and products by in situ synchrotron X-ray powder diffraction. Microporous Mesoporous Mater 2009;126(1–2):40–9.

[46] Mertens G, Snellings R, Van Balen K, Bicer-Simsir B, Verlooy P, Elsen J. Pozzolanic reactions of common natural zeolites with lime and parameter affecting their reactivity. Cem Concr Res 2009;39(3):233–40.

[47] Burriesci N, Arcoraci C, Giordano N, Antonucci PL. Zeolites from pumice and tuff as evaluation of pozzolanic cement constituents. Zeolites 1985;5:96–100.

[48] Perraki T, Kontori E, Tsivilis S, Kakali G. The effect of zeolite on the properties and hydration of blended cements. Cem Concr Compos 2010;32(2):128–33.

[49] Perraki T, Kakali G, Kontori E. Characterization and pozzolanic activity of thermally treated zeolite. J Therm Anal Calorim 2005;82(1):109–13.

[50] Caputo D, Liguori B, Colella C. Some advances in understanding the pozzolanic activity of zeolites: the effect of zeolite structure. Cem Concr Compos 2008;30(5):455–62.

[51] Liguori B, Caputo D, Marroccoli M, Collela C. Evaluarion of zeolitic-bearing tuffs as pozzolanic addition for blended cements. In: Malhotra VM, editor. Proceedings of the 8th CANMET/ACI international conference on fly ash, silica fume, slag, and natural pozzolans in concrete. Las Vegas: Farmington Hills; 2004. p. 319–33.

[52] Sersale R. Structure and characterization of pozzolans and fly ashes. In: Proceedings of the 7th symposium on the chemistry of cement, vol. 1. Paris; 1980.

[53] Malquori G. Portland-pozzolana cement. In: Proceedings of the 4th international symposium on chemistry of cement. Washington: US Department of Commerce; 1962. p. 983–1006.

[54] Zhang Z, Guo J, Liang C. Contribution of zeolite to the hydration of cement. In: Mumpton FA, editor. Proceedings of the 4th international conference on occurrence, properties, utilization of natural zeolites. New York; 1995. p. 221–3.

[55] Gava GP, Prudencio Jr LR. Pozzolanic activity tests as a measure of pozzolans performance. Part 1. Mag Concr Res 2007;59(10):729–34.

[56] Gava GP, Prudencio Jr LR. Pozzolanic activity tests as a measure of pozzolans performance. Part 2. Mag Concr Res 2007;59(10):735–41.

[57] Pourkhorshidi AR, Najimi M, Parhizkar T, Hillemeier B, Herr R. A comparative study of the evaluation methods for pozzolans. Adv Cem Res 2010;22(3):157–64.

[58] Pourkhorshidi AR, Najimi M, Parhizkar T, Jafarpour F, Hillemeier B. Applicability of the standard specifications of ASTM C618 for evaluation of natural pozzolans. Cem Concr Compos 2010;32(10):794–800.

[59] Mindess S, Young JF, Darwin D. Concrete. Prentice Hall: United State of America; 2002.

[60] Şahmaran M, Özkan N, Keskin SB, Uzal B, Yaman İÖ, Erdem TK. Evaluation of natural zeolite as a viscosity-modifying agent for cement-based grouts. Cem Concr Res 2008;38(7):930–7.

[61] Andrade C. Calculation of chloride diffusion coefficients in concrete from ionic migration measurements. Cem Concr Res 1993;23(3):724–42.

[62] Walsh J, Sock M, Lima J, et al. Quantitative studies of chloride permeability of concrete. Rhode Island Dept. of Transportation, Research Report FHWA-RI-RTD-98-1, December; 1998.

[63] Frankel GS. Electrochemical techniques in corrosion: status, limitations, and needs. J ASTM Int 2008;5(2):1–27.

[64] Ismail M, Ohtsu M. Corrosion rate of ordinary and high-performance concrete subjected to chloride attack by AC impedance spectroscopy. Constr Build Mater 2006;20(7):458–69.

[65] Morris W, Vico A, Vazquez M, De Sanchez SR. Corrosion of reinforcing steel evaluated by means of concrete resistivity measurements. Corros Sci 2002;44(1):81–99.

[66] Pech-Canul MA, Castro P. Corrosion measurements of steel reinforcement in concrete exposed to a tropical marine atmosphere. Cem Concr Res 2002;32(3):491–8.

[67] Kovler K, Jensen OM, editors. Internal curing of concrete, state-of-the-art report of RILEM Technical committee 196-ICC. Report No: RILEM TC-196. RILEM Publications S.A.R.L. Bagneux: RILEM; 2007.

[68] Weber S, Reinhardt HW. A new generation of high performance concrete: concrete with autogenous curing. Adv Cem Based Mater 1997;6(2):59–68.

[69] Holm TA, Bremner TW. State-of-the-art-report on high-strength, high-durability structural low density concrete for application in sever marine environments. Report No: ERDC/SL TR-OO-3. U.S. Army corps of Engineers; 2000.

[70] Villarreal V, Crocker D. Better pavements through internal hydration. Concr Int 2007;29(2):32–6.