



Use of natural zeolite as a supplementary cementitious material

Babak Ahmadi *, Mohammad Shekarchi

Construction Materials Institute, Department of Civil Engineering, College of Engineering, University of Tehran, Tehran, Iran

ARTICLE INFO

Article history:

Received 27 August 2008

Received in revised form 19 October 2009

Accepted 20 October 2009

Available online 27 October 2009

Keywords:

Zeolite

Clinoptilolite

Pozzolanic reaction

Durability

ABSTRACT

Natural zeolite, a type of frame-structured hydrated aluminosilicate mineral, is used abundantly as a type of natural pozzolanic material in some regions of the world. In this work, the effectiveness of a locally quarried zeolite in enhancing mechanical and durability properties of concrete is evaluated and is also compared with other pozzolanic admixtures. The experimental tests included three parts: In the first part, the pozzolanic reactivity of natural zeolite and silica fume were examined by a thermogravimetric method. In this case, the results indicated that natural zeolite was not as reactive as silica fume but it showed a good pozzolanic reactivity. In the second part, zeolite and silica fume were substituted for cement in different proportions in concrete mixtures, and several physical and durability tests of concrete were performed. These experimental tests included slump, compressive strength, water absorption, oxygen permeability, chloride diffusion, and electrical resistivity of concrete. Based on these results, the performance of concretes containing different contents of zeolite improved and even were comparable to or better than that of concretes prepared with silica fume replacements in some cases. Finally, a comparative study on effect of zeolite and fly ash on limiting ASR expansion of mortar was performed according to ASTM C 1260 and ASTM C 1567. Expansion tests on mortar prisms showed that zeolite is as effective as fly ash to prevent deleterious expansion due to ASR.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Zeolite tuff–lime mixtures have been widely used in constructions since ancient times. Today, more than 50 natural and 150 synthetic zeolite minerals are known and are used in various industries. In the cement industry, natural zeolite is a popular natural pozzolan in some regions of the world. In China, it is widely used as a cement blending material. It is reported that the total quantity of zeolite consumed for this purpose is as much as 30 million tons per year in China [1,2].

Natural zeolite as volcanic or volcano-sediment material has a three dimensional frame structure and is classified as a hydrated aluminosilicate of alkali and alkaline earth cations. Crystals are characterized by a honeycomb like structure with extremely small pores and channels, varying in size from 3×10^{-4} – 4×10^{-4} μm . It has an equivalent total specific surface (internal and external) area of 35–45 m^2/g [3]. Therefore, zeolite is well known for its ability to lose and gain water by over 30% of its dry weight; furthermore, constituent cations can be exchanged with no major changes in the structure of crystals [3–5].

Mostly, reactive components of pozzolanic materials such as silica fume, fly ash and natural pozzolans are glassy or amorphous.

Though, natural zeolites, which are crystalline, can act as pozzolanic materials [6].

It has been ascertained that natural zeolite is an excellent supplementary cementitious material. 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 C–S–H gel and aluminates, resulting in the improvement of microstructure of hardened cement [2,7–9]. Like other pozzolanic materials, replacement of cement by natural zeolite can improve the mechanical properties of cement and concrete composites [10–13]. Although the replacement of cement by zeolite reduces slump and increases water demand of fresh concrete, high strength (over 80 MPa) and flowing (slump 180 mm) concrete with 10% substitution level of zeolite was produced by means of sufficient amount of superplasticizer [12]. No segregation or bleeding was observed in the flowing fresh concrete because the viscosity of fresh concrete increases by the added zeolite [12]. The strengthening effect of zeolite on concrete is due to reduction in the total pore content and improvement of transition zone structure between zeolite blended cement paste and aggregates of hardened concrete [13]. In another work, it is shown that high-volume natural zeolite mixture (50% mass replacement) is producible for structural concrete applications [14].

A number of research studies have been confirmed that natural zeolite effectively prevents the deleterious expansion of concrete due to alkali silica reaction [15–18]. The mechanism by which

* Corresponding author. Tel.: +98 21 66400480.
E-mail address: bahmadi@aut.ac.ir (B. Ahmadi).

natural zeolite inhibits alkali silica reaction is by decreasing the alkaline ions (Na^+ , K^+) concentration in the pore solution through ion exchange, adsorption and pozzolanic reaction of natural zeolite [15].

In some experimental studies the effectiveness of zeolite in enhancing the performance of cement is compared with that of other pozzolanic materials. It is observed that the pozzolanic reactivity of natural zeolite is between that of silica fume and fly ash [2]. Other research has shown that, with the replacement level of 10%, zeolite performs better than pulverized fuel ash but is inferior to silica fume in terms of increasing the compressive strength, decreasing the initial surface absorption and the chloride diffusion of concrete [19].

Generally, despite the good performance of zeolite as pozzolanic material, limited researches are performed and published about this subject, especially about the durability aspects of concrete.

Natural zeolite is abundantly deposited in Iran and it can be easily quarried and processed while usual pozzolans such as fly ash, silica fume, high-reactivity metakaolin and slag are rarely available and are relatively expensive. Additionally, with the focus on increasing the durability of concrete structures especially in aggressive environments such as the Persian Gulf region [20–22], finding of an available and economical supplementary cementitious material have gained great importance in Iran. Therefore, the objective of this study was to evaluate the effect of natural zeolite, coming from Semnan in the center of Iran, on properties of concrete using various testing methods.

The experimental tests included three parts: In the first part, the pozzolanic reactivity of natural zeolite (NZ) and silica fume (SF) were examined by a thermogravimetric method. In the second part, several physical and durability tests of plain concrete and concretes incorporating NZ and SF with water to total cementitious ratio of 0.40 were performed. The performances of mixtures were assessed in terms of slump, compressive strength, water absorption, oxygen permeability, chloride diffusion, and electrical resistivity of concrete. NZ was replaced 5%, 10%, 15% and 20% of cement by weight while replacement levels of SF were 5%, 10%, and 12.5% by weight. Finally, effect of NZ and fly ash (FA) on suppressing ASR expansion of mortar was performed based on ASTM C 1260 and ASTM C 1567. NZ and FA were in turn used to replace 10%, 20%, 30%, and 40% by weight of cement. SF and FA were chosen for comparison because of their effective application and wide usage as pozzolanic admixtures.

2. Materials

The cement used was a commercially available ASTM Type II Portland cement with a specific gravity of 3.14 and a fineness of $290 \text{ m}^2/\text{kg}$. The source of NZ (clinoptilolite type) used in this project was the mines from north of Semnan, Iran. Quantitative X-ray diffraction phase analysis of NZ of the mine had shown 90–95% zeolite in the mineralogy composition [23]. NZ had a specific gravity of 2.20, a fineness of $320 \text{ m}^2/\text{kg}$ and an average particle size of $16.84 \mu\text{m}$. The total content of SiO_2 , Al_2O_3 , and Fe_2O_3 in the zeolite was found to be approximately 83% which is more than the minimum requirement (70%) specified in ASTM C 618 for natural pozzolans. SF was obtained from Azna ferro-silicon alloy manufacture with a specific gravity of 2.20 and a specific surface area of $20,000 \text{ m}^2/\text{kg}$. FA was produced in South Africa, having a specific gravity of 2.22 and a fineness of $410 \text{ m}^2/\text{kg}$. The chemical compositions of these four fine materials are listed in Table 1.

The fine and coarse aggregates used for casting concrete mixtures were from the Karaj River region. The coarse aggregate had a maximum size of 19 mm, a specific gravity of 2.78, and a water absorption of 1.97%. The fine aggregate had a specific gravity of

Table 1
Chemical properties of binders.

	OPC	Natural zeolite	Silica fume	Fly ash
<i>Oxide composition % by mass</i>				
CaO	63.25	1.68	–	1.05
SiO_2	22.42	67.79	93.16	61.30
Al_2O_3	4.68	13.66	1.13	28.80
Fe_2O_3	3.68	1.44	0.72	4.98
MgO	3.63	1.2	1.6	0.63
Na_2O	0.25	2.04	–	0.24
K_2O	0.75	1.42	–	1.40
SO_3	1.74	0.5	0.05	0.13
Loss on ignition	0.45	10.23	1.58	0.70

2.59, an absorption of 2.58%, and a fineness modulus of 3.27. Fine aggregate from the Aras River region was used in mortar bars for performing ASR experiments. This aggregate is to be used in Aras dam construction. According to previous studies, it is of high alkali silica reaction potential [24]. Petrography of this aggregate according to ASTM C 295 indicated that the rock is igneous with reactive minerals of dolomite and quartz.

Naphthalene based superplasticizer (40% solid) was used for the concrete mixtures in order to improve the workability of fresh concrete.

3. Specimen preparation and testing methods

3.1. Assessment of pozzolanic reactivity

Thermogravimetric method (TG) [25,26] was used to evaluate the pozzolanic activity of pozzolans. For this purpose, two pastes were prepared by mixing NZ and SF with hydrated lime. These pozzolanic materials and hydrated lime were mixed in the ratio of 1:1 by weight. The water to solid material ratio was kept at 0.50. The pastes were placed in containers made of glass and stored in a water bath kept at 60°C . Prior to testing, samples were taken from container and the hydration was stopped with subjecting the samples to acetone. The percentage of $\text{Ca}(\text{OH})_2$ fixed through pozzolanic reaction was calculated (Eq. (1)) at time of 1, 3, 7, 14, and 28 days of curing for each sample using thermogravimetric analysis with a constant heating rate of $30^\circ\text{C}/\text{min}$ from 60 to 1000°C in a static air atmosphere.

$$\text{Fixed Ca}(\text{OH})_2 (\%) = \frac{(\text{CH})_i - (\text{CH})_p}{(\text{CH})_i} \quad (1)$$

where $(\text{CH})_i$ is the initial mass of $\text{Ca}(\text{OH})_2$ in the paste (g) and $(\text{CH})_p$ the mass of fixed $\text{Ca}(\text{OH})_2$ in the paste at a given age (g).

3.2. Strength and transport property measurements

Several experiments were performed on concrete mixtures incorporating different replacement levels of NZ or SF at a water to total cementitious materials ratio (w/cm) of 0.40. The cementitious materials content was kept at $400 \text{ kg}/\text{m}^3$. For all of the mixtures, the ratio of fine aggregate to coarse aggregate was maintained at 1:1 and the aggregate content was $1850 \text{ kg}/\text{m}^3$. Superplasticizer was added in order to attain a slump of about 70 mm. The mixture proportions and fresh concrete properties are shown in Table 2. The dry materials were mixed first followed by the addition of water into the mixer. Finally, the superplasticizer was added to the mixture. Immediately after mixing the concrete mixtures were 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 demoulded and moist cured at $23 \pm 1^\circ\text{C}$ until the age of tests. The concretes were tested for compressive

Table 2
Binder content and properties of fresh concrete.

Code	Cement replacement material and level (%)	Content of cement replacement material (kg/m ³)	Cement (kg/m ³)	Superplasticizer (L/m ³)	Slump (mm)	Air content (%)
Control		–	400	2.7	65	2.4
NZ5	Zeolite, 5	20	380	3.2	75	3.4
NZ10	Zeolite, 10	40	360	4.3	60	3.3
NZ15	Zeolite, 15	60	340	6.3	65	3.8
NZ20	Zeolite, 20	80	320	7.0	75	3.6
SF5	Silica fume, 5	20	380	3.2	45	3.2
SF10	Silica fume, 10	40	360	3.7	80	2.8
SF12.5	Silica fume, 12.5	50	350	4.0	70	3.6

strength, oxygen permeability, water absorption, chloride diffusion, and electrical resistivity.

- (1) *Compressive strength*: At 3, 7, 28, and 90 days of age, three 150-mm cube specimens of each concrete mixture were tested for compressive strength with a 2000 kN hydraulic press and a loading rate of 0.5 N/mm²/s.
- (2) *Water absorption*: Three concrete cores, 75 mm in diameter and 130 mm in height, were obtained from three 200 mm cubes for each concrete mixture after the concretes were cured for 28 days. Water absorption tests were performed after the cores were oven-dried for 72 h. The absorption of each specimen was measured by calculating the increase in mass resulting from immersion in water for 30 min as a percentage of the mass of the dry specimen.
- (3) *Oxygen permeability*: Oxygen permeability tests were carried out on cylindrical specimens, 150 mm in diameter and 50 mm in height, according to the Cembureau method [27]. Following curing for 28 days, specimens were oven-dried at 105 ± 1 °C for a period of 7 days. Based on this method, oxygen under pressure was applied on one end of the specimens while providing a tightly fitting seal to the curved surface. The rate of gas flow from the other flat side was then measured using a soap bubble flow meter, once the flow rate stabilized. The relationship proposed by Hagen–Poiseuille (Eq. (2)) was used to determine specific permeability coefficient. The flow is assumed to be laminar and unidirectional.

$$K_0 = \frac{2 \cdot Q \cdot p_a \cdot L \cdot \eta}{A(p_2 - p_a^2)} \quad (2)$$

where K_0 is the specific permeability coefficient (m²), Q the volume flow rate of the fluid (m³ s⁻¹), A the cross-sectional area of specimen (m²), L the thickness of the specimen in the direction of flow (m), η the viscosity of gas (2.02 × 10⁻⁵ N s m⁻² for oxygen at 22 °C), p the inlet pressure (N m⁻²), p_a the outlet pressure (N m⁻²). In this study, a single test result corresponds to the average of the specific permeability coefficient measured at five absolute inlet pressure levels of 1, 1.2, 1.4, 1.6, and 1.8 N m⁻² relative to outlet pressure.

- (4) *Chloride diffusion*: Bulk chloride diffusion samples were prepared according to ASTM C 1556. Cylindrical specimens (150 mm diameter × 300 mm thick) were cast, followed by 45 days curing, for each concrete mixture. Afterwards, the cylinders were sawn to provide a 100 mm thick slice from the top of the specimen. The slices were sealed with epoxy polyurethane coating on all sides except the sawn surface to simulate one-dimensional diffusion. These specimens

were immersed in a sodium chloride solution with a concentration of 165 g/l and a temperature of 23 °C. After an exposure period of 90 days, the specimens were removed from the salt solution. A hole with a diameter of 45 mm was drilled to produce pulverized material samples at incremental depths from the uncoated face. The resulting powder samples from each layer were collected separately to analyze acid-soluble chloride content according to ASTM C 1152 and ASTM C 114. The resulting output of the test is a plot of acid-soluble chloride concentration versus depth from the exposed surface. The apparent diffusion coefficient, D_a and surface concentration, C_s were calculated from the established chloride concentration profile based on Fick's Second Law of Diffusion and Crank's solution (Eqs. (3) and (4)).

$$\frac{\partial C}{\partial T} = D_a \frac{\partial^2 C}{\partial x^2} \quad (3)$$

$$C(x, t) = C_s \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_a \cdot t}} \right) \right] \quad (4)$$

where x is the depth from the surface (m), t the exposure duration (s), $C(x, t)$ the chloride concentration at depth x and time t , C_s the chloride concentration at the surface, and D_a the apparent diffusion coefficient (m²/s).

- (5) *Electrical resistivity*: Electrical resistivity testing was conducted on three 100 mm cubes prepared for every concrete mixture during a period of 90 days after the casting of concretes. The specimens were submerged in water until the testing age. The electrical resistivity of the cubes was measured based on AC Impedance Spectrometry (ACIS) method using a concrete resistance meter [28,29]. The resistivity then was calculated by:

$$\rho = \frac{A \cdot R}{L} \quad (5)$$

where ρ is the resistivity (kΩ cm), A the area (cm²), R the resistance (kΩ), L the length of specimen (cm).

3.3. Assessment of ASR potential

The efficacy of natural NZ in controlling ASR expansion of mortar bar was compared with that of FA using the accelerated test method of ASTM C 1260 and ASTM C 1567. Nine different mortar mixtures containing 0, 10%, 20%, 30%, and 40% by mass replacement of cement with NZ or FA were prepared. Based on the test method, mortar bars were produced by using 1 part of cement to 2.25 parts of sand. Additionally, the water to total cementitious materials (w/cm) was kept at 0.47. Binder content of mortar bars are shown in Table 3. Three mortar bars (25 × 25 × 225 mm) were cast for each mortar mixture. After 24 h in their molds, the bars

Table 3
Binder content of mortar bars.

Code	Cement replacement material and level (%)	Content of cement replacement material (g)	Cement (g)
C	–	–	440
Z10	Zeolite, 10	44	396
Z20	Zeolite, 20	88	352
Z30	Zeolite, 30	132	308
Z40	Zeolite, 40	176	264
FA10	Fly ash, 10	44	396
FA20	Fly ash, 20	88	352
FA30	Fly ash, 30	132	308
FA40	Fly ash, 40	176	264

were removed from the molds and stored in a water bath filled with tap water at 80 °C for a period of 24 h. After this precondition-

ing, the length of mortar bars was measured (initial reading). Then placed into storage containers filled with a 1 N NaOH solution at 80 °C for the duration of the test. Subsequent length readings were made for 35 days after initial reading.

4. Results and discussion

4.1. Pozzolanic reactivity

Fig. 1 presents the percentage of reacted Ca(OH)₂ versus time for the NZ and SF pastes. It can be noticed that the reactivity of NZ was lower than that of SF. At the age of 14 days, approximately the total amount of Ca(OH)₂ was reacted in SF paste, whereas 94% of the initial quantity of Ca(OH)₂ was fixed by NZ. Nevertheless, NZ exhibited high rate of consumption of lime. For this pozzolanic material about 100% of the initial amount of Ca(OH)₂ was fixed at the time of 28 days.

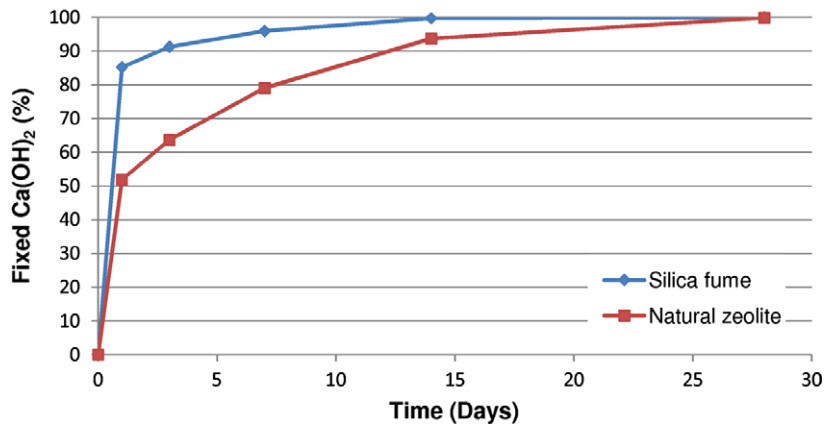


Fig. 1. Percentage of fixed Ca(OH)₂ versus time in natural zeolite and silica fume pastes (NZ or SF, Ca(OH)₂, water: 1, 1, 1).

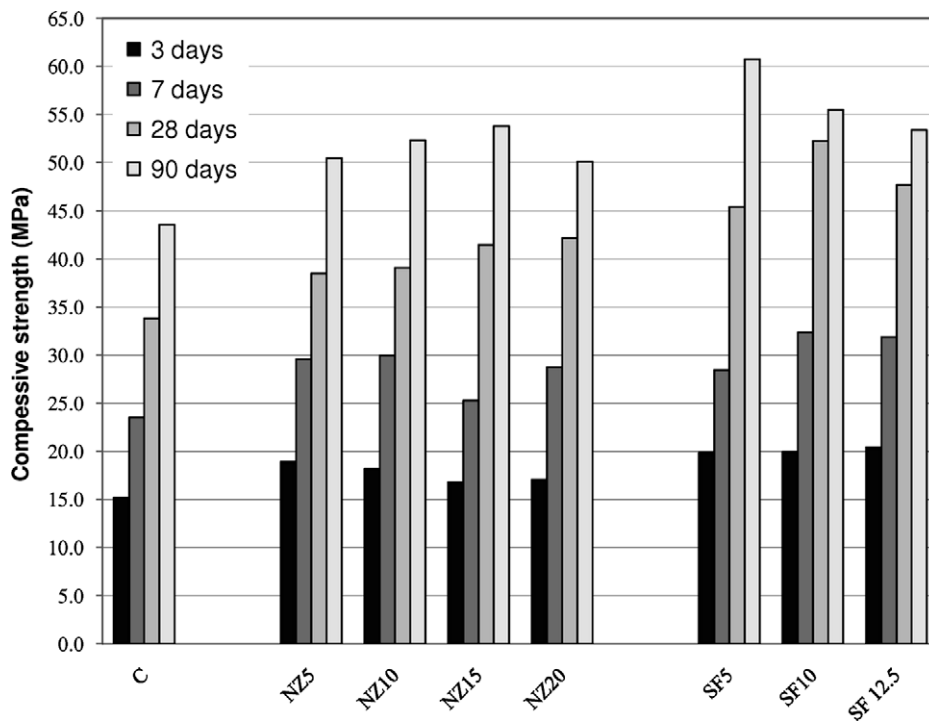


Fig. 2. Compressive strength of control and natural zeolite and silica fume concrete.

4.2. Fresh concrete properties

The higher the replacement of cement by NZ, the more the superplasticizer was required to maintain the slump of concrete, which can be attributed to the large amount of pores in its frame structure and high surface area. In addition, using more NZ led to increase of viscosity of fresh concrete, which can be suitable for producing of pumping concrete. Similar results were obtained about the properties of fresh concretes incorporating natural zeolite by other authors [12,13]. However, it is reported that workability of fresh concrete was not affected by natural zeolite noticeably [19].

4.3. Compressive strength

Fig. 2 shows the effect of NZ or SF on the compressive strength of concrete. It is clear that regardless of replacement level, NZ and SF increased concrete strength at all ages. In terms of 90-day compressive strength, it is apparent that the optimum replacement level for NZ was at 15%. At this age the strength results of NZ concretes were comparable to those of SF10 and SF12.5. Based on the results, higher 28-day compressive strengths were achieved when NZ was further used. The compressive strength of concrete mixtures NZ5, NZ10, NZ 15, and NZ 20 were 14%, 16%, 23%, 25%

Table 4
Results from chloride diffusion tests (90-day exposure).

Concrete code	$D_r (\times 10^{-12} \text{ m}^2/\text{s})$	C_s (percent concrete)	Coefficient of regression
Control	12.5	0.82	0.992
NZ5	12.2	0.74	1.000
NZ10	5.5	0.92	0.995
NZ15	5.1	0.96	0.999
NZ20	4.4	1.04	0.997
SF5	5.2	0.73	0.993
SF10	3.1	0.65	0.990
SF12.5	1.4	0.69	0.995

higher than that of the control mixture. It appears that the zeolite used in this study has a suitable strengthening effect because of high purity (90–95%). Feng et al. [12,13] studied on compressive strength of concretes containing a natural zeolite with a purity level of about 60%. They reported that replacement of cement by zeolite at different levels increased the 28-day compressive strength of concrete about 10–15%. Also, according to the results reported by Chan and Ji [19], the 28-day strength of zeolite concrete with a replacement level at 15% (as an optimum replacement level) was 14% higher than that of control concrete.

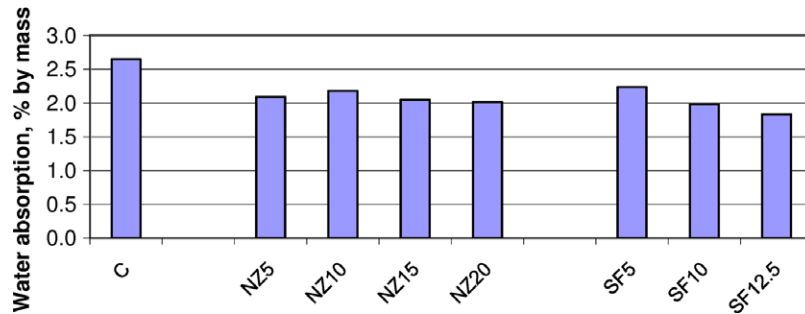


Fig. 3. Water absorption of control and natural zeolite and silica fume concrete (28-day curing).

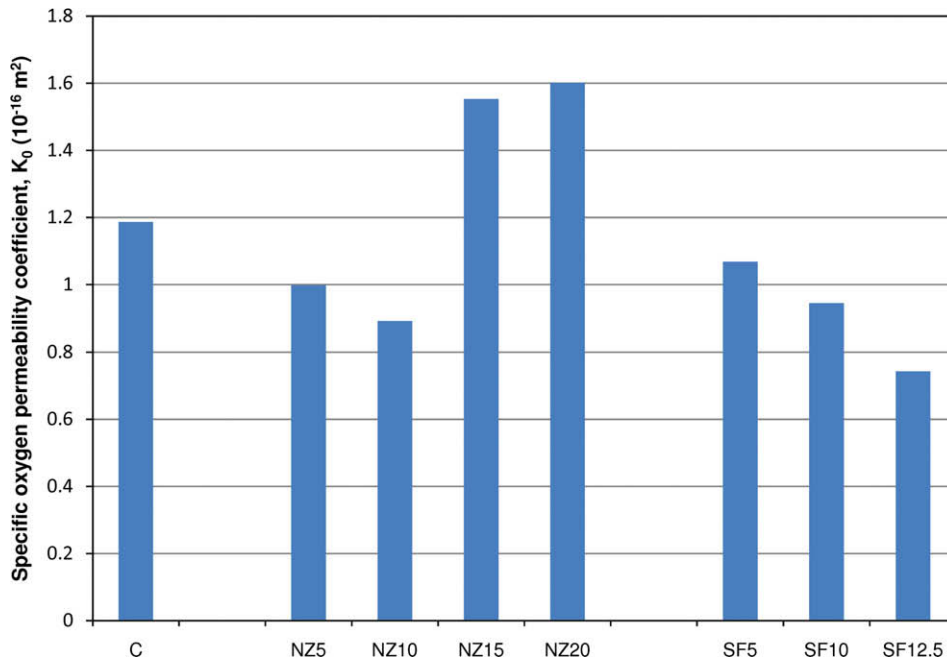


Fig. 4. Oxygen permeability of control and natural zeolite and silica fume concrete (28-day curing).

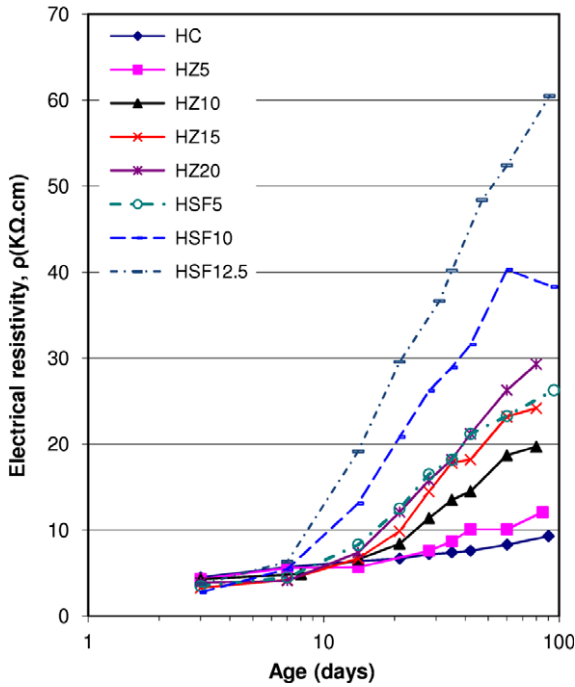


Fig. 5. The development of electrical resistivity of control and natural zeolite and silica fume concrete with age.

4.4. Water absorption

The water absorption results of concrete specimens are presented in Fig. 3. It can be seen that both the NZ and SF concrete mixtures displayed lower water absorption than the control mixture. All the mixtures incorporating NZ did not show considerable difference in percentage of water absorption. It can be found NZ was more effective than SF in reducing the water absorption at the level of 5%. For SF concrete, the higher the replacement level, the more the reducing effect in water absorption.

4.5. Oxygen permeability

Fig. 4 demonstrates the effect of level of SF or NZ replacement on the specific oxygen permeability coefficient K_o (see Eq. (2)) of concrete mixtures. It can be found that the concrete mixtures with

5% and 10% replacement levels of NZ had a lower permeability compared with that of the control and SF concretes with equal replacement levels.

At 15% and 20% replacement levels, there was an increase in specific permeability coefficient of NZ concrete and these values were also higher than that of control concrete mixture. A potential reason for increase in oxygen permeability with the higher NZ replacement is that a partial amount of NZ is still unreacted in hardened concrete paste. Passing of oxygen through porous structure of unreacted NZ particles may be an additional justification of higher oxygen permeability of concrete.

SF12.5 was the most impermeable specimen.

4.6. Chloride diffusion

The values of apparent diffusion coefficient (D_a) and surface chloride concentration (C_s) determined for various concrete mixtures from Eq. (4) are given in Table 4. Furthermore, the coefficients of regression R^2 calculated for the curve of Crank's solution fitted to the plot of chloride content versus depth are presented in the same table. The results show that at 10–20% NZ, there was a marked decrease in diffusion coefficient compared to control concrete. However, SF concretes had a better effect on improving diffusion characteristics of concrete than NZ concretes at the same level of replacement. It was shown that the natural zeolite was more effective than pulverized fuel ash in term of chloride diffusion of concrete but it was less effective than silica fume [19].

Because the test conducted in this study was based on measuring the acid-soluble chloride content, the chloride binding effect of natural zeolite was not studied. This subject and the corrosion behavior of concrete containing NZ in Persian Gulf are under investigation by the authors.

4.7. Electrical resistivity

The electrical resistivity, ρ developments versus time (up to 90 days) of specimens are presented in Fig. 5. As shown in this figure, NZ and SF increased resistivity of concrete. Increase in resistivity was occurred with using more NZ or SF content, and with increasing age. At all ages, the resistivities of the concrete mixtures with natural zeolite were lower than those recorded for silica fume concretes with the same replacement level. It seems that NZ increased resistivity of concrete by creating a finer pore size distribution [12] and decreasing ionic concentration [15].

The resistivity of the concrete has an important influence on the rate of corrosion of embedded reinforcing steel after the break-

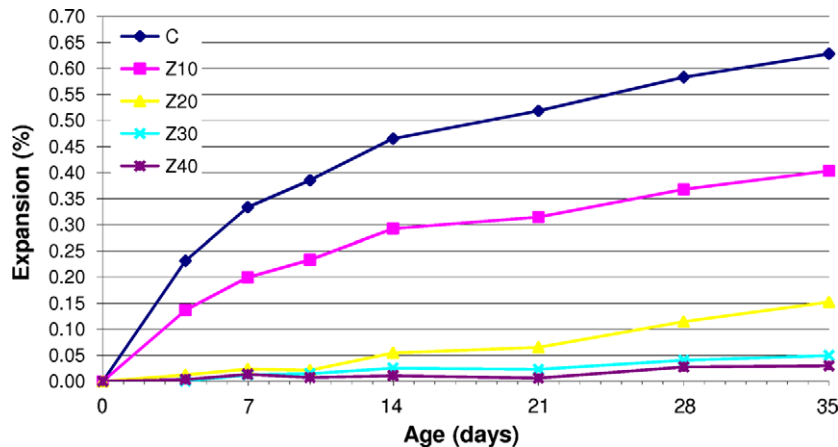


Fig. 6. Expansion of mortar bars made with zeolite versus time.

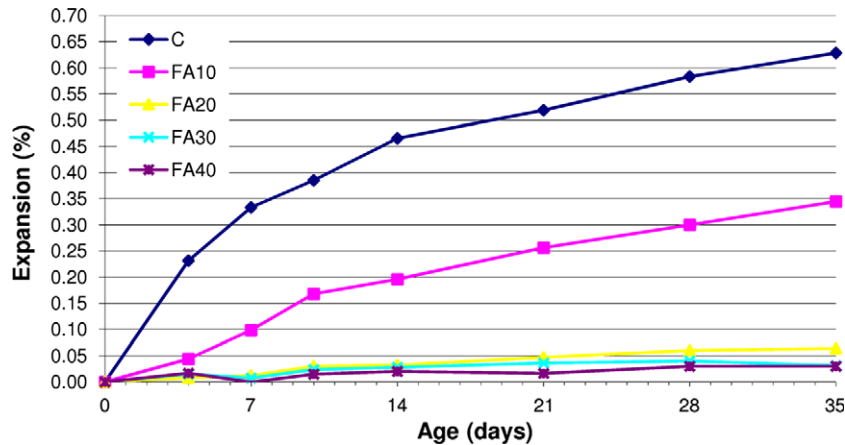


Fig. 7. Expansion of mortar bars made with fly ash versus time.

down of passivity. Generally, the larger the resistivity of the electrolyte (in this case concrete), the smaller the corrosion rate of the reinforcement will be [30,31]. It is reported that the corrosion rate of reinforcing steel is low when the resistivity of concrete exceeds 20 k Ω cm [32].

4.8. ASR expansion

Results of the expansion of the NZ and FA mortar bars compared to control mortar bar are shown in Figs. 6 and 7 respectively. According to the expansion limits mentioned in ASTM C1260, after 14 days of exposure to 1-N NaOH solution, if the average of the expansion of mortar bar (without pozzolanic materials) exceeds 0.20%, the aggregate is considered deleteriously reactive. As seen in Figs. 6 or 7, the 14-day expansion of control mortar bar is 0.47%. Therefore, the sand used in this portion of study is highly reactive. Additionally, the results showed that when an increasing amount of cement was replaced by NZ or FA, expansion of mortar bars due to ASR decreased significantly. A comparison of Figs. 6 and 7 shows that the behavior of NZ was almost identical to that of FA in controlling expansion due to ASR.

Based on ASTM C 1567, after 14 days of exposure to 1-N NaOH solution, combinations of cement, pozzolanic material and aggregate that expand less than 0.1% are likely to have a low risk of deleterious expansion when used in concrete under field conditions. Fig. 8 reveals the effect of different levels of cement replacement by NZ or FA at the age of 14 days. It can be seen that replacing more

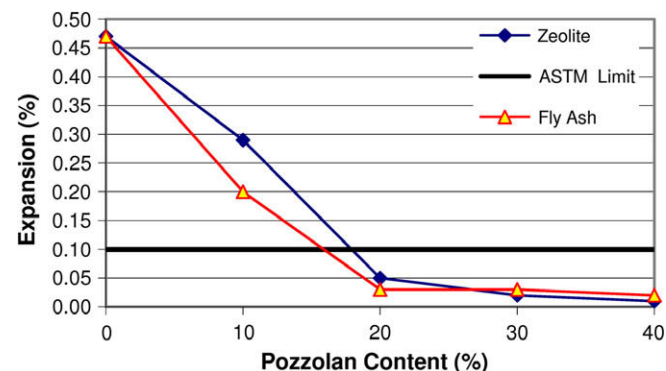


Fig. 8. Comparing the expansion of mortar bars made with zeolite and fly ash at the age of 14 days.

than 20% of cement by zeolite or fly ash fulfilled the ASTM C 1567 limit.

It is reported that the mechanism by which natural zeolites inhibits alkali silica reaction is by decreasing the alkaline ion concentration in the pore solution through ion exchange, adsorption and pozzolanic reaction of natural zeolite [15].

5. Conclusions

The main conclusions of this study on a locally quarried and produced natural zeolite from Iran can be summarized as follows:

1. Based on thermogravimetric analysis, although natural zeolite showed lower pozzolanic reactivity than silica fume, this pozzolan revealed high rate of consumption of lime and fixed almost total amount of Ca(OH)₂ after 28 days of curing.
2. The higher the replacement of cement by natural zeolite led to much superplasticizer demand in order to maintain the slump of fresh concrete, though the viscosity of concrete increased.
3. Both the natural zeolite and silica fume concrete mixtures displayed higher strengths than the control mixture at 3, 7, 28, and 90 days. Natural zeolite was not as effective as silica fume in increasing the compressive strength. Nevertheless, at 90 days, the results of natural zeolite concretes were comparable to those of concretes incorporating 10% and 12.5% silica fume. Comparing to the results obtained in other researches, it seems that natural zeolite used in the present study is more effective in term of enhancing compressive strength of concrete because of high purity.
4. The substitution of cement with up to 20% natural zeolite reduced water absorption and chloride diffusion coefficient of concrete. Also, the oxygen permeability of concrete was reduced by replacement of cement with up to 10% natural zeolite.
5. The use of 5% and 10% zeolite lowered the oxygen permeability of concrete even more effectively than the use of the same levels of silica fume. The water absorption of concrete containing 5% zeolite was also lower than that of concrete containing 5% silica fume.
6. According to the decrease in chloride diffusion coefficient and the increase in electrical resistance, it can be expected that reinforced concretes with natural zeolite added have capacity for corrosion resistance.
7. The use of 20–40% zeolite or fly ash was similarly efficient in controlling deleterious expansion of mortar containing highly reactive aggregate.

Acknowledgment

The authors wish to express their appreciation to the Afrand Tooska Co. for providing facilities needed to carry out the experiments.

References

- [1] Feng N, Peng G. Applications of natural zeolite to construction and building materials in China. *Constr Build Mater* 2005;19(8):579–84.
- [2] 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.
- [3] Mumpton FA, editor. *Mineralogy and geology of natural zeolites*. New York: Reprint of Mineralogical Society of America's Reviews in Mineralogy; 1993.
- [4] Dyer A. Ion-exchange properties of zeolites. *Stud Surf Sci Catal* 2005;157:141–204.
- [5] Colella C. Natural zeolites. *Stud Surf Sci Catal* 2005;157:13–40.
- [6] Mindess S, Young JF, Darwin D. *Concrete*. United State of America: Prentice Hall; 2002.
- [7] Ortega EA, Cheeseman C, Knight J, Loizidou M. Properties of alkali-activated Clinoptilolite. *Cem Concr Res* 2000;30(10):1641–6.
- [8] Perraki Th, Kakali G, Kontoleon F. The effect of natural zeolites on the early hydration of Portland cement. *Micropor Mesopor Mater* 2003;19(1–3):205–12.
- [9] 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.
- [10] Yilmaz B, Uçar A, Öteyaka B, Uz V. Properties of zeolitic tuff (clinoptilolite) blended Portland cement. *Build Environ* 2007;42(11):3808–15.
- [11] Canpolat F, Yilmaz K, Köse MM, Sümer 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.
- [12] Feng N, Li G, Zang X. High-strength and flowing concrete with a zeolitic mineral admixture. *ASTM Cem Concr Aggr* 1990;12(2):61–9.
- [13] Feng N, Yang H, Zu L. The strength effect of mineral admixture on cement concrete. *Cem Concr Res* 1988;18(3):464–72.
- [14] Uzal B, Turanlı L, Mehta PK. High-volume natural pozzolan concrete for structural applications. *ACI Mater J* 2007;104(5):535–8.
- [15] Feng N, Hao T. Mechanism of natural zeolite powder in preventing alkali-silica reaction in concrete. *Adv Cem Res* 1998;10(3):101–8.
- [16] Feng N, Ma C, Ji X. Natural zeolite for preventing expansion due to alkali-aggregate reaction. *ASTM Cem Concr Aggr* 1992;14(2):93–6.
- [17] Feng N, Niu Q. Effect of modified zeolite on the expansion of alkaline silica reaction. *Cem Concr Res* 2005;35(9):1784–8.
- [18] Feng N, Jia H, Chen E. 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.
- [19] Chan SYN, Ji X. Comparative study of initial surface absorption and chloride diffusion of high performance zeolite, silica fume and PFA concretes. *Cem Concr Compos* 1999;21(4):293–300.
- [20] Alizadeh R, Ghods P, Chini M, Hoseini M, Ghalibafian M, Shekarchi M. Effect of curing conditions on the service life design of RC structures in the Persian Gulf region. *J Mater Civil Eng* 2008;20(1):2–8.
- [21] Ghods P, Alizadeh R, Chini M, Hoseini M, Ghalibafian M, Shekarchi M. Service life design of reinforced concrete structures in Persian Gulf region using DuraPGulf model. *Concr Int* 2007;29(12):50–5.
- [22] Shekarchi M, Ghods P, Alizadeh R, Chini M, Hoseini M. DuraPGulf, a local service life model for the durability of concrete structures in Persian Gulf. *Arab J Sci Eng* 2008;33(1B):77–88.
- [23] Eftekharejad J. Evaluation of zeolite occurrence in Aftar mine. Tehran: Special Publications of Ministry of Industries and Mines of Iran; 1996.
- [24] Layssi H, Shekarchi M, Abbasi M, Eftekhar MH. Evaluation of the alkali-silica reactivity of rocks from Iran, ARAS region, In: 13th international conference on alkali aggregate reactions, Trondheim, Norway; 2008.
- [25] Moropoulou A, Bakolas A, Aggelakopoulou E. Evaluation of pozzolanic activity of natural and artificial pozzolans by thermal analysis. *Thermochim Acta* 2004;420(1–2):135–40.
- [26] Panea I, Hansen W. Investigation of blended cement hydration by isothermal calorimetry and thermal analysis. *Cem Concr Res* 2005;35(6):1155–64.
- [27] Kollek JJ. The determination of the permeability of concrete to oxygen by the Cembureau method – a recommendation. *Mater Struct* 1989;22(129):225–30.
- [28] Shekarchi M, Tahersima M, Hajibabae, Laysi H. Concrete mix proportions with ultra-high electrical resistivity, In: 11th international conference on durability of building materials and components, Istanbul, Turkey; 2008.
- [29] Ping Gu, Ping Xie, Beaudoin JJ, Brousseau R. AC impedance spectroscopy (II): microstructural characterization of hydrating cement-silica fume systems. *Cem Concr Res* 1992;23(1):157–68.
- [30] Cusson D, Qian S, Hoogveen T. Field performance of concrete repair systems on highway bridge. *ACI Mater J* 2006;103(5):366–73.
- [31] Protection of metals in concrete against corrosion, ACI 222R-01. American Concrete Institute, Committee 222; 2001.
- [32] Broomfield JP. *Corrosion of steel in concrete*. New York: E&FN Spon; 1997.