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Influence of exposure temperature on chloride diffusion in concretes incorporating silica fume or natural zeolite

Ali Dousti [a], Reza Rashetnia [a], Babak Ahmadi [a,b,*], Mohammad Shekarchi [a]

[a] *School of Civil Engineering, College of Engineering, University of Tehran, Tehran, Iran*
[b] *Department of Civil & Environmental Engineering, Amirkabir University of Technology, Tehran 15875-4413, Iran*

HIGHLIGHTS

- The effect of exposure temperature on chloride diffusion into concrete was studied.
- In the mixtures, cement was partially replaced by natural zeolite and silica fume.
- Use of natural zeolite and silica fume enhances chloride resistance of concrete.
- Activation energy was obtained for zeolite, silica fume and control concretes.
- Temperature rise leads to lower chloride resistance of concrete.

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ABSTRACT

This paper examines the effect of exposure temperature ranging from 22 °C to 50 °C on chloride diffusion in concretes containing different percentages of silica fume or natural zeolite. The results indicate that concrete diffusivity and chloride penetration depth increase with exposure temperature, which is in agreement with the Arrhenius theory. Resistance of concrete mixtures against chloride diffusion was improved with the use of silica fume and zeolite. Irrespective of exposure temperature, chloride resistance of concrete enhanced with increasing silica fume and zeolite replacement level. Additionally, silica fume was more effective than zeolite in improving chloride resistance at the same replacement level. The activation energy values of zeolite and silica fume incorporated concretes were 20–29 kJ/mol and 26–31 kJ/mol, respectively and were lower than that of control concrete (32 kJ/mol). However, no certain trend was found for the effect of replacement level of silica fume and zeolite on activation energy value of concrete. Furthermore, at the same replacement level of 10%, the activation energy value of the concrete containing zeolite was higher than that of the concrete containing silica fume.

1. Introduction

Chloride-induced corrosion is one of the main causes of deterioration of reinforced concrete structures in aggressive environments such as marine environments. Normally, the alkalinity of concrete around a steel bar provides a passive environment. The passive state can be broken down by presence of sufficient chloride ions in concrete at the surface of steel bar leading to corrosion initiation. Corrosion propagates with presence of sufficient O_2 and H_2O. Corrosion damage in concrete structures is often observed by rust-staining of the surface, cracking and spalling of the concrete cover due to formation of expansive corrosion products. Corrosion can also lead to structural distress due to loss of reinforcing steel cross sectional area as well as loss of bond between steel reinforcement and concrete [1–3]. Hence, service life of reinforced concrete structures exposed to chloride ions is closely related to the rate of chloride ion diffusion through the concrete.

Research studies about kinetics of chloride ingress have shown that diffusion of chloride ions is greatly influenced by a range of parameters but mainly water/binder ratio, environmental conditions (such as temperature variations), type of cementitious materials and concrete microstructure [4]. Generally, the rate of material diffusion and the chemical reactions rise with increase in temperature. The effect of temperature on chloride ion diffusion has been investigated in some research studies [4–12]. Exposure temperature affects the transport of chloride ions in concrete in two ways. For one thing, the movement of chloride ions can be accelerated by increasing the temperature because molecular speed increases with higher temperature; for another, amount of bound chloride by hydrated cement products can be influenced by temperature. Elevated temperature can decrease physical binding of chloride because of higher thermal vibration of chloride ions.

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[*] Corresponding author. Address: No. 8, Behnam Alley, Vessal St., Enghelab Ave., Tehran, Iran. Tel.: +98 9121640793; fax: +98 218 8959740.
E-mail address: bahmadi@aut.ac.ir (B. Ahmadi).

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Conversely, elevated temperature can increase the content of chemically bound chloride due to increase of reaction rate [1,5,6].

Actually, most of research studies have been dealt with investigated chloride diffusion of conventional concrete with overlooking the effect of temperature as a dominant parameter. Usually, most of the studies are performed at lab temperature. However, in reality, concrete structures can be subjected to various exposure temperatures. Consequently, changes in exposure temperature have serious impact on chloride diffusion into concrete structures. Therefore, it would be of great practical interest and importance to consider such a temperature effect on the chloride diffusion process in concrete.

Some theories have been presented to describe the effect of exposure temperature on chloride diffusion in concrete, but there is a shortage of actual laboratory experiments to satisfactorily verify these theories. Specially, there are not enough appropriate performed experiments which able to explain the diffusion of chloride ions in concrete based on the Arrhenius theory [7]. In general, the influence of temperature on diffusion is theoretically propounded by Arrhenius as shown in the following equation.

$$D(T) = D_0 \exp\left(\frac{E_a}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \tag{1}$$

where D_0 (m^2/s) and $D(T)$ (m^2/s) are the diffusion coefficients at T_0 (K) and T (K), respectively, E_a is the activation energy of diffusing substance (in this case chloride) transport in concrete (kJ/mol) and R is the ideal gas constant (8.31×10^{-3} kJ/°K/mol).

Most of the published search studies on the effect of temperature on chloride diffusion have been performed on cement paste. The reported activation energy values of paste ranges from 32 to 50 kJ/mol [8–10]. Page et al. [8] found that the activation energy of cement paste is dependent on water to cement ratio. Nguyen et al. [11] studied the effect of temperature on chloride diffusion of mortars containing cement type I and type V using an accelerated test method with applying an electrical field. They reached the conclusion that chloride diffusion coefficient and penetration depth increases with temperature level. They found the activation energy values of 35.7 kJ/mol and 32.3 kJ/mol for the mortars incorporating cement type I and type V, respectively. Samsom and Marchand [12] proposed a function, obtained empirically, to estimate variations in diffusion coefficient of concrete when the temperature of the material fluctuates. Yuan et al. [7] reported that activation energy of concrete measured from non-steady-state diffusion tests ranges from 17.9 to 39.9 kJ/mol, while the activation energy obtained from non-steady-state migration coefficient is around 20 kJ/mol and independent of water to cement ratio. Two well-known service life prediction models including FIB model code [13] and Life-365 model [14] assume that the effect of temperature on chloride diffusion coefficient is according to the Arrhenius formula (Eq. (1)). In addition, FIB model code and Life-365 model propose the activation energy value of 40 kJ/mol and 35 kJ/mol, respectively regardless of concrete mixture type. In both of the models, the reference temperature, D_0 is 20 °C (293 K).

This paper examines the effect of temperature ranging from 22 °C to 50 °C on chloride diffusion of concrete mixtures containing various percentages of silica fume (SF) or natural zeolite (NZ) as cement replacement materials. The chosen range of environmental temperatures represents the usual range of temperature for marine environment in south of Iran [2,3]. It should be added that the two studied SCMs are widely available in Iran [15]. The impact of the temperature level of exposure on chloride concentration profile, chloride diffusion coefficient, and activation energy of concrete is determined and discussed. The previous published data about activation energy were mostly studied for cement paste without using SCM [7].

It is worth to mention that this study is complementary for a previous work by the authors which has been presented in another paper [16]. The previous study indicated great performance of this NZ, especially in the case of durability properties including potential of alkali-silica reaction, oxygen permeability, water absorption, electrical resistivity, and chloride diffusion resistance. Ahmadi and Shekarchi [16] showed that performance of concretes containing diverse contents of zeolite is generally improved and the positive results of NZ are comparable to that of SF in some cases. This can be attributed to suitable pozzolanic activity of natural zeolite [16–18].

2. Experimental program

2.1. Materials

The cementitious materials used in this study were portland cement equivalent to ASTM Type II, silica fume (SF) obtained from Azna ferro-silicon alloy manufacture and natural zeolite (NZ). The source of NZ (clinoptilolite type) used in this study was the quarries in the north of Semnan, central regional of Iran. The summation of SiO_2, Al_2O_3 and Fe_2O_3, which are considered to be effective for pozzolanic activity, is 83% for this natural zeolite, exceeding the 70% minimum level for class N raw and calcined natural pozzolans specified in ASTM C618. The chemical composition, density and specific surface area of the cementitious materials as well as mineral compounds of NZ and their contents are listed in Table 1. In addition, the particle size distribution of NZ and SF are illustrated in Fig. 1. The fine aggregate has a specific gravity of 2.59, absorption of 2.58%, and a fineness modulus of 3.27. The maximum size, specific gravity and water absorption of the coarse aggregate are 19 mm, 2.78 and 1.97%, respectively. A naphthalene based high-range water reducer admixture with a solid content of 40% was used in the concrete mixtures in order to increase the consistency of the fresh mixtures.

2.2. Mixture proportions

The experiments were performed on seven concrete mixtures containing different replacement levels of NZ or SF. Natural zeolite was replaced 10%, 15% and 20% of cement by weight while replacement levels of SF were 5%, 10%, and 12.5% by weight. In addition, a control mixture containing no pozzolanic material was also made. All these mixtures were proportioned to have the same cementitious materials content and water to cementitious materials ratio (w/cm) of 400 kg/m^3 and 0.4, respectively, which are typical of those used in the marine concrete structures in Iran. The total aggregate content was 1850 kg/m^3 and the ratio of fine aggregate to coarse aggregate was kept constant at 1:1. High-range water reducer admixture was used in the concrete mixtures to achieve a target slump of about 70 mm. The details of mixture proportions of concrete and the slump values are presented in Table 2.

Table 1
Characteristics of portland cement, silica fume and natural zeolite.

	OPC	Natural zeolite	Silica fume
Oxide composition % by mass			
CaO	63.25	1.68	–
SiO_2	22.42	67.79	93.16
Al_2O_3	4.68	13.66	1.13
Fe_2O_3	3.68	1.44	0.72
MgO	3.63	1.2	1.6
Na_2O	0.25	2.04	–
K_2O	0.75	1.42	–
SO_3	1.74	0.5	0.05
Loss on ignition	0.45	10.23	1.58
Mineral compounds	–	70.6	
Clinoptilolite	–	70.6	–
Opal CT	–	18.8	–
Quarts	–	1.6	–
Plagioclase	–	2.4	–
K-feldspar	–	1.5	–
Smectite/illite (clay minerals)	–	5.2	–
Physical properties	–		
Density (g/cm^3)	3.14	2.2	2.2
Specific surface (m^2/kg)	290[a]	320[a]	20,000[b]

[a] Measured by Blaine method.
[b] Measured by nitrogen-adsorption method.