

Diffusion of Chloride Ions in Polymer-Mortar Composites

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ABSTRACT: In recent years, the rapid deterioration of various reinforced concrete structures has been a widely recognized problem in the world. Penetration of chloride ions into the concrete structures was found to be the major cause of premature corrosion of reinforcing steel and to promote their deterioration. The present articles deals with the resistance to chloride penetration of polymer-mortar, which are often used as low-cost promising materials for preventing or repairing various reinforced concrete structures. To gain more knowledge on the efficiency of polymer-mortar, four mortar mixtures: one specimen with Portland cement (control sample) and three mixtures with

2.5, 5, and 7.5 wt % of the replacement of cement by polyethylene terephthalate (PET) were tested for chloride ion permeability under immersion in 5% sodium chloride solution. Their chloride ion penetration behavior is discussed by applying Fick's second law. In conclusion, the chloride ion penetration depth and apparent chloride ion diffusion coefficient of the polymer-mortar composites are smaller than those of unmodified mortar. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1600–1605, 2008

Key words: polymer-mortar; composite; sodium chloride solution; polyester; PET; diffusion

INTRODUCTION

The resistance to chloride penetration of mortar and concrete is one of the most important issues concerning the durability of concrete structures. When the chloride concentration of mortar or concrete exceeds a certain threshold value, depassivation of steel occurs and reinforced steel starts to corrode.^{1–4} The cement which is alkaline (pH = 13) oxidizes embedded steel bars, forming a chemically and electrically inactive layer (passive film) of ferric oxide. Consequently the development of protective materials with excellent resistance to chloride penetration is demanded for the concrete structures. Polymer-modified mortars^{5,6} using various polymer dispersions are often used as low-cost promising materials for preventing the chloride-induced corrosion and for repairing the concrete structures damaged by it.^{7–9}

The polyethylene terephthalate (PET) bottles have taken the place of glass bottles as storing vessel of beverage due to its lightweight and ease of handling and storing. As the beverage consumption increases drastically, the production of PET bottles increased exponentially as it was reported that PET bottles were produced about 87,000 ton at the end of 2002 in Korea.¹⁰ If waste PET bottles were reused as light-

weight aggregates for concrete, positive effects are expected on the recycling of waste resources and the protection of environmental containment.^{11,12} The purpose of this study is to evaluate the resistance of the polymer-mortar composites using typical polymer to chloride ion penetration.

Chloride-induced corrosion of steel reinforcement is known to be a major cause of concrete deterioration. It has been established^{13–15} that the water-soluble and free chlorides play a significant role in the corrosion of steel in concrete. A simple method of spraying 0.1 N silver nitrate aqueous solution on a cross section of split concrete to determine a depth of chloride penetration became very attractive because Otsuki et al.¹⁶ and Collepardi¹⁷ published the results of their work.

This practice is often called a colorimetric method because the spraying of 0.1 N AgNO₃ solution on a freshly broken mortar and concrete surface leads to the formation of white and black regions with well-distinguished boundaries. The white region is due to precipitation of AgCl, and hence, represents the area that contains chloride. The black region is assumed to correspond to the “no chloride zone.”¹⁸

The white colorimetric front seems to correspond to free and water-soluble chlorides, and measuring the depth of the white front will give an idea of how far chloride has penetrated into polymer-mortar composites and concrete.

In this article, polymer-mortar composites using PET polymer are prepared with different polymer-cement ratios, and tested for chloride ion penetration

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TABLE I
Chemical and Mineralogical Properties of Cement Used

Constituent	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	CaO free	Loss	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Cement	21.82	6.57	4.01	63.43	0.21	1.86	0.24	2.09	40.20	32.25	10.64	12.19

under immersion in test solution with 5% sodium chloride (NaCl). Their chloride ion diffusion behavior is discussed by applying Fick's second law.

MATERIALS AND METHODS

The mortar and/or mortar-polymer composites mixtures were prepared in collaboration with two laboratories, at the laboratory of the Civil Engineering Department, ENSET Oran (Algeria) and the laboratory of Polymer Chemistry, University of Oran Es-Senia, using the following materials.

Cement

The cement used was a blended Portland cement type CPJ-CEM II/A (pouzzolanic cement) obtained from Zahana factory located in the western Algeria, having a 28-day compressive strength of 32.5 MPa and an absolute density of 3.09 g/cm³. Initial and final setting times of the cement were 2 h and 3 h 20 min, respectively. Its Blaine specific area was 2987 cm²/g. Its chemical and mineralogical properties are given in Table I.

Polymer

The polymer used was PET (polyester); it has an approximate melting point of 248°C. The PET powder is obtained by finely crushing the drink bottles (plastic); its particle size distribution is shown in Figure 1. After preliminary tests, we decided to use in

this study the polymer particles of size lower than 1 mm.

Sand

Crushed sand obtained from career of Kristel was used (Oran, Algerian West). The principal characteristics are given in Table II, and particle size distribution is shown in Figure 1.

Preparation and casting of test specimens

Four mixtures were made to compare the effect of adding PET as a cement replacement material. First was control sample (without PET).

The other three polymer-mortar composite mixtures were made by replacing cement with 2.5, 5, and 7.5% of PET by mass. The specimens will be graded PET and the numbers 0, 2.5, 5, and 7.5 represent the percentage of the replacement of Portland cement by PET at 0, 2.5, 5, and 7.5% by weight of cementitious material, respectively.

The mortar mixes had proportions of 1 binder: 3 Sand (by weight). The binder consisted of cement and PET. The water to binder ratio was kept constant at 0.5. The physical properties of the pastes of mortars were determined in accordance with EN 196-3.¹⁹ The detailed mix proportions of the mortars are shown in Table III. The mortar was placed in prismatic steel molds having dimensions of 10 cm × 10 cm × 10 cm. After casting, specimens were left covered with a plastic sheet. After removal from the molds at 24 h of age, all specimens were cured in a condition of 20°C ± 3°C and immersed in water saturated with lime for a period of 28 days.

Before the test, the finished and bottom surfaces and two sides of cube mortar specimens were coated with an epoxy resin paint (Fig. 2).

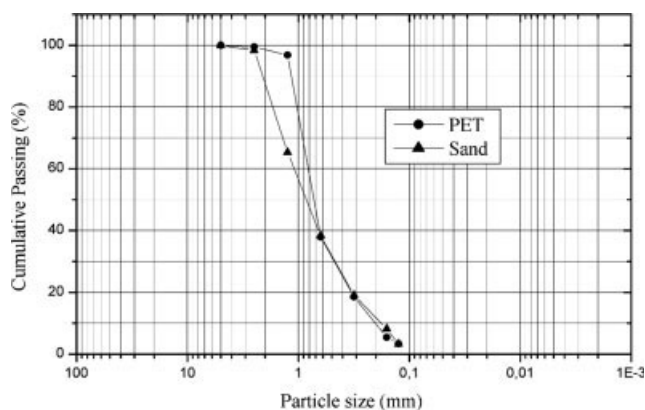


Figure 1 Particle size distributions of polyethylene terephthalate (PET) and Sand.

TABLE II
Physical Properties of Sand Used

Absolute density (g/cm ³)	2.53
Equivalent of sand (%)	84
Fineness modulus	2.55
Nature	Limestone
Absorption coefficient (%)	0.5

TABLE III
Mix Proportions of Polymer-Mortar Composites

Mix design	Cement:sand (by weight)	Polymer-cement ratios (%)	Water-cement ratios (%)
PET 0	1 : 3	0	50
PET 2.5	1 : 3	2.5	50
PET 5.0	1 : 3	5.0	50
PET 7.5	1 : 3	7.5	50

Chloride ion penetration test

The resistance to chloride penetration was determined in accordance with UNI 7928²⁰ and JIS A 1171.²¹ The cured cube mortar specimens were immersed in test solutions at 20°C for 7, 28, and 91 days for chloride ion penetration. The test solution used was 5% of NaCl. The test solution was changed every 7 days up to an immersion period of 28 days, and then every 28 days.

After 7-, 28-, and 91-day immersions, the composite specimens were split, and the split cross-sections were sprayed with 0.1 N silver nitrate (AgNO₃) indicator¹⁶ as prescribed in UNI 7928 (concrete-determination of the ion chloride penetration). The depth of the rim of each crosssection changed to white color was measured with slide calipers as a chloride ion penetration depth as shown in Figures 3 and 4.

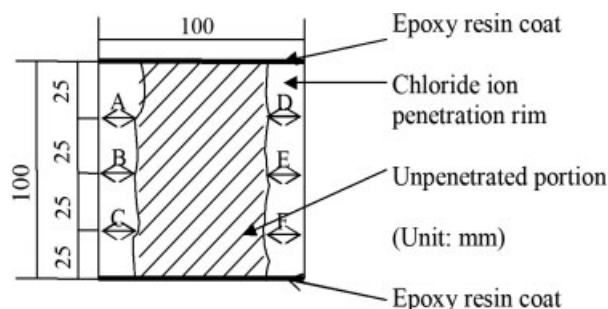
RESULTS AND DISCUSSION

Chloride penetration immersion test

Figure 5 illustrates the chloride ion penetration depth (Cl⁻ penetration depth) of unmodified mortar



Figure 2 The cube mortar specimens with an epoxy resin paint. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



A, B, C, D, E, and F: Measured for chloride ion penetration depth and averaged.

Figure 3 Crosssection of specimen after chloride ion penetration test.

and polymer-mortar composites immersed in 5% NaCl solution for 7, 28, and 91 days.

Generally the Cl⁻ penetration depth of unmodified mortar PET0 and different composites PET2.5, PET5, and PET7.5 increases with additional immersion period. Regardless of the types of polymer-cement ratios, the Cl⁻ penetration depth of polymer-mortar composites is markedly smaller than that of unmodified mortar and reduced with an increase in polymer-cement ratio. These results are in agreement with those reported by Ohama et al.²²

In ordinary cement concrete, it is generally considered that the Cl⁻ permeates easily through pores with radii under 20 Å because the pore surfaces are electrically positive due to the adsorption of calcium ion (Ca²⁺).²³ By contrast, the Cl⁻ penetration into the polymer-mortar composites seems to be inhibited by the incorporation of PET polymer. It (PET polymer) makes the cementing matrix denser and reduces the porosity of the hardened paste.^{24,25}

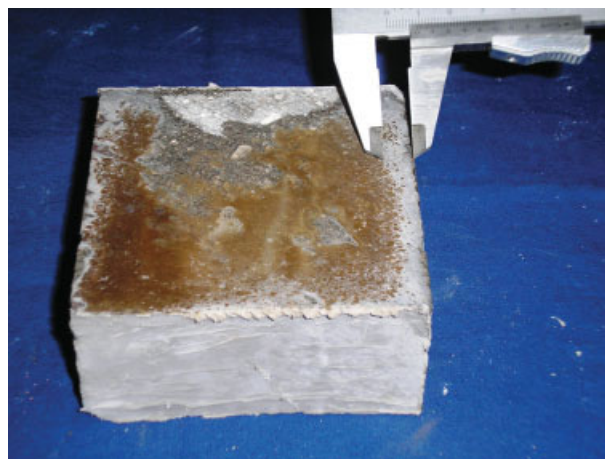


Figure 4 Crosssection of specimen after using 0.1 N of silver nitrate indicator test. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

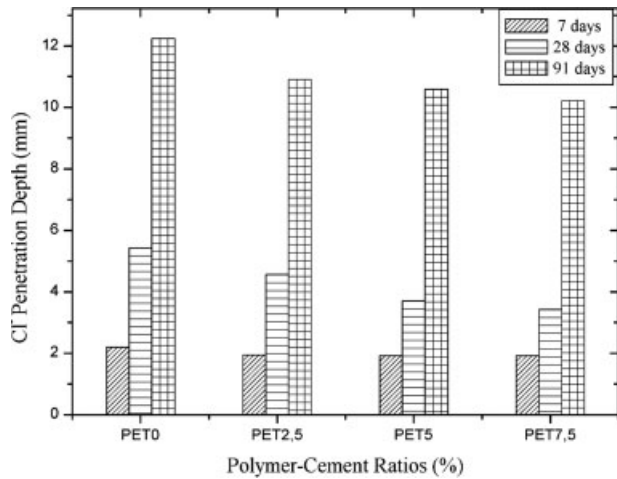


Figure 5 Polymer-cement ratios versus Cl⁻ penetration depth of polymer-mortar after 5% NaCl solution immersion.

Application of Fick’s second law of diffusion

As chloride ion penetration through polymer-mortar composites in test solution with 5% NaCl concentration follows Fick’s second law²⁶ under nonsteady state conditions for diffusion, the solution to the law is given by the following equation:

$$\frac{C}{C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{1}$$

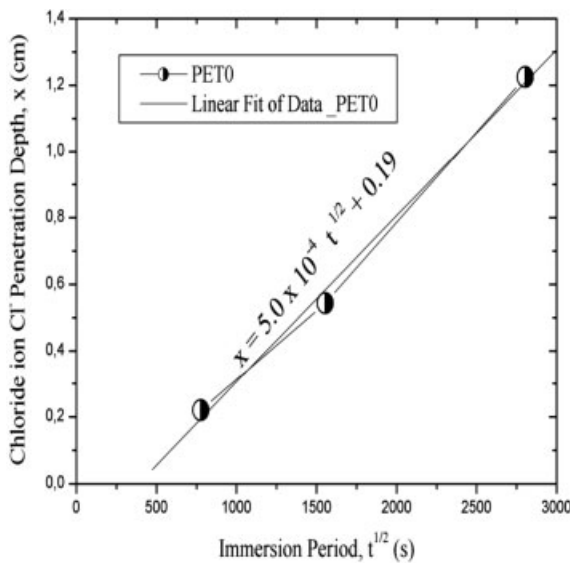
where *C* is the concentration of chloride ions at a chloride ion penetration depth, *x* is distance from the polymer-mortar composites surface (the penetra-

tion depth), *C*₀ is the concentration of chloride ions at the exposed surfaces of the polymer-mortar composites, *t* is the immersion period in the NaCl test solutions, *D* is chloride ion diffusion coefficient, and erf is error function available in standard mathematical tables. An approximation to eq. (1) is expressed as follows²⁷:

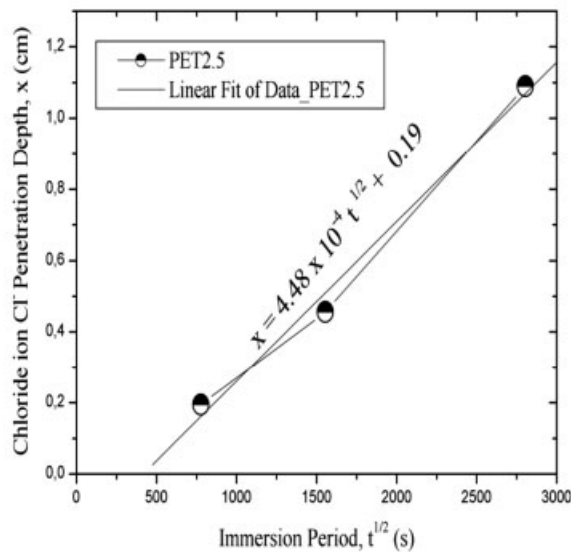
$$x = 4\sqrt{Dt} \tag{2}$$

The typical examples of the relationships between the immersion period and chloride ion penetration depth of polymer-mortar composites are illustrated in Figures 6 and 7.

Generally the chloride ion penetration depth of the polymer-mortar composites increases with additional immersion period and is reduced with an increase in polymer-cement ratio at the respective immersion period. As seen in Figures 6(a,b) and 7(a,b), *x* – √*t* plots are linear with negative intercepts on the √*t* - axis regardless of the types of polymer-mortar composites and the polymer-cement ratio. This means that the *x* – √*t* plots do not follow Fick’s second law because of the reaction of the chloride ions with some cement hydrates. The chlorides may be found by reaction in different states: bound chloride, chemically combined with C-A-H in form, for instance, of C₃A.CaCl₂.10 H₂O; bound chloride, adsorbed on C-S-H or free chloride ions within the pore aqueous solution.¹⁷ Goto et al.²⁸ reported that the diffusion of chloride ion through the hardened cement was also accompanied by a chemical reaction. In addition, our results are in agreement with



(a)



(b)

Figure 6 (a,b) Immersion period versus chloride ion penetration depth of polymer-mortar composites during 5% NaCl immersion.

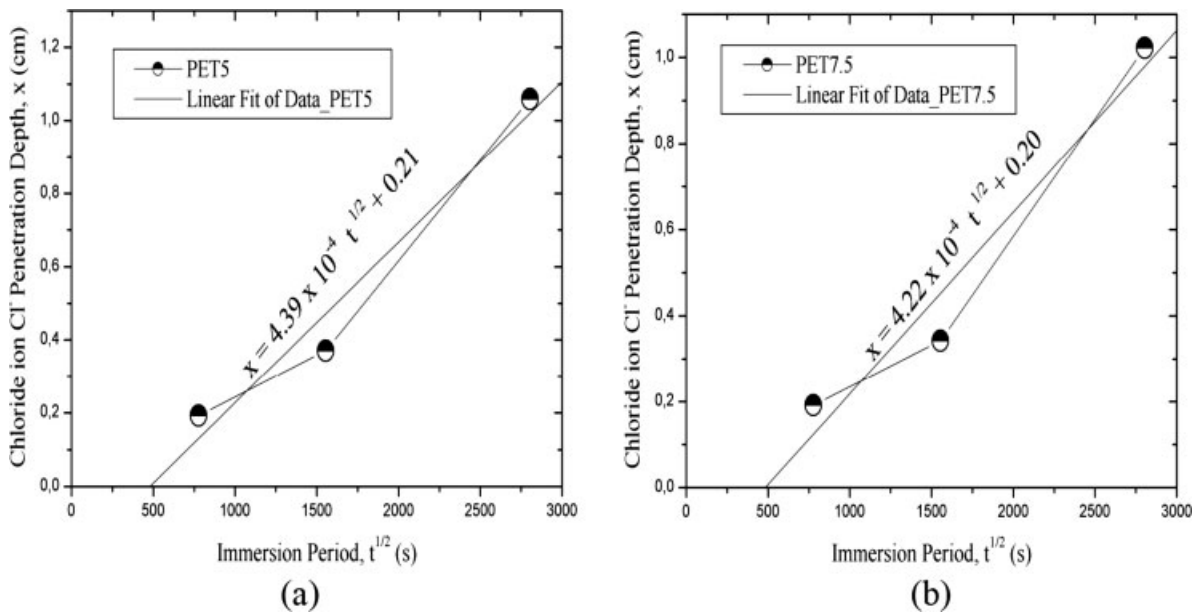


Figure 7 (a,b) Immersion period versus chloride ion penetration depth of polymer-mortar composites during 5% NaCl immersion.

those reported by Ohama et al.²² Accordingly the estimation of the apparent chloride ion diffusion coefficient by the following equation can be recommended²⁹:

$$x = 4\sqrt{D_a t} + k \quad (3)$$

where D_a is the apparent chloride ion diffusion coefficient calculated from the slopes of the $x - \sqrt{t}$ lines, and k is empirical constant. The typical empirical equations based on eq. (3) are shown in Figures 6(a,b) and 7(a,b).

Figure 8 illustrates the polymer-cement ratios versus apparent chloride ion diffusion coefficient of polymer-mortar composites. The apparent chloride ion diffusion coefficient was obtained from the slopes of $x - \sqrt{t}$ lines after the fitting of experimental data of the profiles type to eq. (3), as demonstrated in Figures 6(a,b) and 7(a,b). The apparent chloride ion diffusion coefficient of the polymer-mortar composites PET2.5, PET5, and PET7.5 is much smaller than that of unmodified mortar PET0 regardless of the NaCl concentration.

The order of magnitude of chloride penetration in the portland cement and polymer-cement (composites) pastes is 10^{-8} cm²/s at 25°C, and this value is about thousand times smaller than of the same ion in water³⁰ (2.03×10^{-5} cm²/s). The interaction between the pore surfaces of the hydrated cement and chloride ions can be responsible for the decrease in the diffusion rate. These results confirm the order of magnitude of the diffusion coefficients for Cl⁻ ion in the cement pastes is 10^{-8} cm²/s, a value smaller

than D for Cl⁻ ion diffusion in water by a factor of 10^3 obtained by Collepardi et al.^{27,31}

The hydration of cement led to the formation of new hydrates (C-S-H gel...) in time. Its makes the cementing matrix denser and reduces the porosity of the hardened paste, which reduces the penetration of chlorides ions. So, if the period of immersion increases one has a reduction in D and D_a .

Nevertheless, there is the possibility that the difference in the diffusion coefficients might be due to a different mobility of the water molecules inside the pores. Finally, it cannot be excluded that the

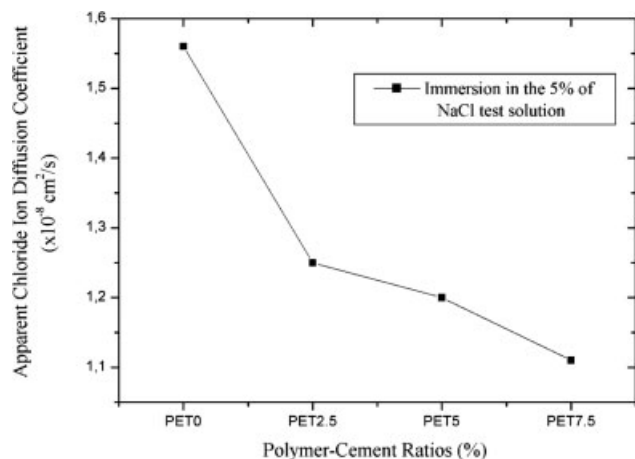


Figure 8 Polymer-cement ratios versus apparent chloride ion diffusion coefficient of polymer-mortar composites.

diffusion coefficient of chloride ion depends also on the type of cation (K^+ or Ca^{2+}) of the salt.

In general, the apparent chloride ion diffusion coefficient tends to decrease with increasing polymer–cement ratio. It is also obvious from the above data that the polymer-mortar composites are generally superior to the unmodified mortar in the resistance to chloride ion penetration.

CONCLUSIONS

The Fick's second law of diffusion was fitted to data from experiment to determine the diffusion coefficient. The conclusions derived from the experimental investigation and analyses are presented below:

The order of magnitude of chloride penetration in the Portland cement and polymer–cement (composites) pastes is 10^{-8} cm^2/s at $25^\circ C$, and this value is about thousand times smaller than of the same ion in water. The interaction between the pore surfaces and the diffusing ions could be responsible for lowering the diffusion coefficient of the Cl^- ion in the hydrated cement.

Regardless of the type of PET polymer, chloride ion penetration depth and apparent chloride ion diffusion coefficient of polymer-mortar composites are remarkably smaller than those of unmodified mortar, and generally tend to decrease with an increase in polymer–cement ratio. This may be explained due to the reduced volume of large-sized pores, and the improved resistance to the absorption of the test solutions with an increase in polymer–cement ratio. Such mortars can be recommended as effective materials for preventing the chloride-induced corrosion of reinforcing steel in various concrete structures.

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