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Time-Dependency of Chloride Diffusion in Concrete: A Brief Review and Preliminary Results

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Abstract

Chloride ingress into concrete has long been known to decrease the service life of built infrastructure. Inadequate knowledge of the physical reasons associated with chloride diffusion into concrete could generate chloride penetration profiles that become meaningless for prediction of service life. In this study, the effects of pore closure (physical effect) and changes in chloride binding (chemical effect) on chloride diffusion through Australian General Purpose (GP) cement pastes were investigated. Through-diffusion tests and “in-and-out” diffusion tests were conducted to monitor the time-dependent chloride diffusion through cement pastes cured from 1 to 28 days. The through-diffusion test quantified the overall chloride diffusion behaviour at different stages of cement hydration, which was a combined result of physical and chemical processes controlling diffusion. The “in-and-out” test differentiated the contributions of the physical and chemical processes on the chloride diffusion at different stages of cement hydration. As expected, the reduction of chloride diffusivity was significant during the first two weeks of curing, most likely attributed to the significant reduction of porosity as well as establishment of capillary discontinuities within the pore structure. It was also observed that the amount of bound chloride was not constant but increased significantly from 1 to 28 days of curing age.

Keywords: Chloride diffusion, Time dependency, Chloride binding, Curing age.

INTRODUCTION

Rehabilitation and replacement of reinforced concrete structures exposed to the corrosive marine environment incurs considerable disruption and costs, mostly associated with chloride (Cl-') ingress through the concrete, which initiates corrosion of reinforcement. The passage of chloride into concrete can be modelled using semi-empirical estimations of Cl- diffusivity, D. However, this diffusivity must be considered as an approximation only since it has been commonly found that D is not a constant but follows the power law \( D = D_0 (t/t_0)^m \), where \( t \) is the time of diffusion, \( t_0 \) is the reference time when \( D = D_0 \) and \( m \) is a fitting parameter [1-6]. It was pointed out by others [7] that the parameters, specially the age factor, used to explain the time dependency of chloride diffusion have little physical meaning and these are purely empirical parameters determined by regression analysis. Incomplete knowledge of the physical reasons associated with the fitting parameter (m) could generate penetration profiles that become meaningless for the prediction of service life.

We assume here that the diffusion of Cl- through cement paste is primarily controlled by two mechanisms: the advective permeability of the cement paste and the relative strengths of Cl- binding mechanisms. It is known that permeability plays an important role in ion ingress as it controls the rate of advective flow of solutes [8]. It then follows that porosity and pore structure of the cement paste predominantly control the permeability of the cement paste.

Following the interpretation of Yong and Hansen [9] on the Powers-Brownyard [10] theory, the pores in cement paste can be classified as either capillary pores or gel pores based solely on pore diameter. Pores >10 nm effective diameter (\( d_{eff} \)) are defined to be capillary pores and gel pores have \( d_{eff} < 10 \) nm. In cement pastes and concretes, the capillary pores are the remnants of water-filled space that existed between solid phases; the gel pores are regarded as an intrinsic part of cement hydration products [8]. The amount of capillary pores would be higher at very low degree of hydration, however, the total volume as well as the \( d_{eff} \) of capillary pores continue to decrease with increasing hydration.

In an important review, Garboczi [11] concluded that other than the decreasing porosity of cement paste with hydration, pore size and their...
connectivity predominantly control the solute transport properties of cement pastes. At early stages of cement hydration, capillaries have an interconnected network of large diameter channels, and the movement of the water is dominated by advective flux. During hydration, the effective capillary pore diameter as well as the overall capillary porosity decrease due to the production of hydration products that occupy the capillary pore space. Thus the capillary pore diameter decreases thereby reducing the permeability of the cement paste. In addition, with blocking of capillary pores by cement hydration gel during hydration, isolated and discontinuous capillary cavities are formed, which may be connected through the gel pores only. This reduces the fraction of the pores that form a connected pathway for transport and increases the tortuosity of the flow path. As this process continues, the capillary pore space can lose all long range-connectivity, so that advective transport of water or ions through the relatively large capillary pore system becomes negligible and diffusive transport, which is regulated by the tortuous network of smaller gel pores, dominates. Therefore the importance of the pure capillary pore (advective) transport decreases with time due both to decreasing capillary pore size as well as to decreasing their connectivity (increasing the tortuosity of the flow paths), and at a critical degree of hydration, the fraction of connected capillary pores (defined by the volume fraction of capillary pores that make up a connected path through the sample divided by the total volume of capillary porosity) would become zero.

Using computer simulation, Bentz and Garboczi [12] showed that the fraction of capillary pores of C3S pastes with w/c ratios of 0.35, 0.45 and 0.5 reached zero when the degrees of hydration were about 55, 75 and 85%, respectively; cement pastes with w/c ratios of 0.6 or above always had a continuous and connected capillary pore system independent of the degree of hydration. Capillary pores become disconnected when the capillary porosity of the C3S pastes reached to 18 ± 5% [12]. Referring to Powers et al [13], Young [14] also pointed out that the time at which the capillary pores become completely discontinuous strongly dependent on the w/c ratio of the paste, and cement pastes with w/c ratio of 0.4 can achieve a discontinuous capillary pore network within as early as 3 days of hydration. It is expected that the development of such a discontinuous pore network will limit Cl⁻ transport to diffusion processes only.

It is generally agreed that Cl⁻ that has penetrated concrete is present in two forms: free Cl⁻ and bound Cl⁻ [15-17]. In addition to porosity and pore structure described above, it is known that Cl⁻ binding plays an important role in the Cl⁻ diffusion into concrete [18]. Binding of chloride refers to the adsorption of free Cl⁻ ions by cement gel and/or their chemical reactions with hydrated cement. When free Cl⁻ from the environment penetrate the pore network of concrete, some Cl⁻ may be captured by the hydrated products through chemical binding or physical binding. Chemical binding refers to binding of Cl⁻ as a result of chemical reactions between the Cl⁻ and cement paste. Unlike chemical binding, physical binding is believed to be due to the absorption of the Cl⁻ on the surface of cement paste. The physical binding is due to the weak Van der Waals or electrostatic force between the Cl⁻ and cement paste surface [19].

It is generally accepted that the C₃A phase of Ordinary Portland Cement (OPC) plays an important role in Cl⁻ binding by chemically reacting with the Cl⁻ during hydration to form calcium chloroaluminate hydrate (C₃A.CaCl₂.10H₂O) generally known as Friedel’s salt [20-25]. Recent studies also pointed that Friedel’s salt can also from due to the replacement of OH⁻ ions of the hydroxyl AFm [Ca₂Al(OH)₆.2H₂O] structure, by Cl⁻ present in the pore solution [25]. It is also alleged that the C₃AF phase also reacts with Cl⁻ and forms a similar product known as calcium chloroferrite (C₃F.CaCl₂.10H₂O) [20, 23-25]. Unlike chemical binding, it is believed that hydrated C-S-H also binds chloride by physical absorption on its surface [19]. Since binding processes remove Cl⁻ from the pore solution of the cement paste, the net changes could alter the movement of Cl⁻ into cement paste.

Due to the complexity of the Cl⁻ binding mechanisms in cements and concretes, researchers have used Cl⁻ adsorption isotherms to describe the bound Cl⁻ as a function of the free Cl⁻ of cement-based materials [19, 26-32] and they have applied a modified version of Fick’s second law to consider Cl⁻ binding in cement based materials [33]. Although a considerable amount of literature has been published on Cl⁻ the chloride binding in cement paste, however, there is a lack of knowledge on the effect of curing age of the cement paste on the chloride binding.

This paper presents preliminary results of studies on the effect of pore closure on time dependent Cl⁻ diffusion, and the change in Cl⁻ binding with curing age of cement pastes. We assume that when concrete is exposed to Cl⁻, diffusion of chloride is governed by Fick’s laws. It is likely that at early ages the power laws should produce the greatest predicted changes to the diffusion. We hope to confirm that capillary transport diminishes within two weeks of hydration, and subsequently, Cl⁻ diffusion follows a power law. It is also expected that the amount of bound Cl⁻ might not be constant, but instead expect that it changes with curing age.
In this study, a 1-day cured cement paste (6mm thick x 10mm dia) with water-to-cement ratio (w/c) of 0.42 was used to investigate time-dependent diffusion behavior of chloride into cement paste. In addition to this, specimens (20mm thick x 100mm dia) with same w/c were also prepared to determine the effect of curing age from 1 to 28 days on the chloride binding of cement pastes. Australian General Purpose (GP) cement and deionized water was used for pastes. The diffusion of chloride can be determined using either the through diffusion method or the penetration profile method. As it was impractical to use the penetration profile testing at early ages, the through diffusion testing after one day of cement hydration was used to observe if the expected power law behavior was followed. While the through-diffusion test probes the overall diffusion behavior, a test named “In and Out diffusion” enables separation between binding and pore closure as binding is different between In diffusion and Out diffusion, while diffusion is given by the slope of the out diffusion Vs. square root of time graph (discussed in a later section).

2.1 Specimen preparation and curing
Pastes were mixed in a high-shear mixer according to ASTM C1738–14 [34]. A 6mm thick X 10mm dia cylindrical sample was cast for through-diffusion testing. Two 20mm thick and 100mm dia samples were cast for chloride binding testing. After casting, the molded specimens were cured in a sealed condition for the first 24 hours to prevent moisture loss. After demolding the specimens, they were cured at 20 °C in an air-tight box (with wet towel inside of the box to supply adequate moisture during curing) until tested. The through-diffusion test was conducted on a 1-day cured paste sample. The Cl⁻ binding by paste samples was determined at 1, 7, and 28 days.

2.2 Through-diffusion test
Time dependent diffusion behaviour of chloride through cement pastes was evaluated using a two-cell diffusion test setup. This through-diffusion experiment monitored the chloride ion transmission from 1L of a 0.6M NaCl solution (solute cell) separated by the 6mm thick paste barrier from 1L of a 0.6M KOH solution (buffer cell). The test was conducted at a constant temperature of 20 °C. An ion selective electrode (ISE) was used for continuous measurement of the Cl⁻ concentration in the buffer cell. Liquid samples were also collected at different times during the test, and were analyzed by Inductively Coupled Plasma (ICP) method.

2.3 In and out diffusion test
During the -In diffusion test, cylindrical slab of cement paste was exposed to 0.5L of 0.6 M NaCl solution for 7 days after a specific curing age and concentrations of Cl⁻ ion in the test solution were measured using ICP. During the -out diffusion test, the solution was changed to distilled water and Cl⁻ concentration leached from the specimens into the water was measured over 7 days using the ISE. Liquid samples were also collected at different time intervals and analysed by ICP.

RESULTS AND DISCUSSION
3.1 Through-diffusion
Figure 1 shows the concentration of Cl⁻ with time in the buffer cell for 11 weeks. The ICP test results of selected samples are also plotted which are in reasonable agreement with the ISE data. It was observed that the diffused chloride reached the buffer cell after about 2 days (Point A). This initial breakthrough was followed by a rapid increase of the chloride concentration with time for another 2 days (Stage B). Between 4 and 15 days, the Cl⁻ concentration did not change significantly (Stage C). This was followed by a significant increase of Cl⁻ concentration (Stage D), however, the rate of increase of the chloride concentration decreased significantly at about 17 days (Point E). Subsequently the Cl⁻ concentration increased at a steady rate.

![Fig. 1: Diffusion of chloride ion into the buffer cell during through-diffusion test.](image-url)

It can be assumed that prior to the initial breakthrough of Cl⁻ (point A) into the buffer cell, the ingress of Cl⁻ may be primarily related to the binding of Cl⁻ by cement paste as well as filling of pore spaces of the cement paste as pointed out by Atkinson and Nickerson [35, 36]. The rapid increase of Cl⁻ concentration after point A might be predominantly due to the fast diffusion of Cl⁻ attributed to the continuous capillary pores existed in the cement paste. During stage C, the insignificant increase of chloride concentration may be attributed to two possible reasons. Firstly, establishment of a discontinuous capillary pore at the end of stage B, which significantly reduced the ease of Cl⁻ movement through cement paste. Thus Cl⁻ movement may be primarily controlled by the gel pores formed. Secondly, Cl⁻ binding might have also resulted in a lower Cl⁻ diffusion through the paste.
The increasing trend of the chloride concentration during stage D might be attributed to the leaching of Ca(OH)$_2$. Diamond et al. [37] concluded that pore space of the C-S-H gel is filled by Ca(OH)$_2$ and leaching of Ca(OH)$_2$ is expected to significantly increase the volume of large gel pores. Moreover, it is also known that leaching of Ca(OH)$_2$ also increases the porosity of capillary pores. Thus, it can be hypothesized that these phenomena opened some of the blocked capillary pores which increased Cl$^-$ penetration in the short term. However, continuous cement hydration may have resulted a discontinuous capillary pore network within 2 days which subsequently reduced Cl$^-$ penetration at Point E. It might be assumed that at the end of stage D, essentially a linear concentration gradient across the paste sample was established and a steady state diffusion condition (refers to a linear increase of chloride concentration with time) was attained. It should be noted that simple time dependent diffusion does not explain the graph in Fig. 1. 

3.2 In and out Diffusion

3.2.1 Effect of cement paste curing age on chloride diffusivity

Following the classical diffusion theory and material balanced equation, the mathematical diffusion model of a leaching test proposed in ANS 16.1 standard method [38] is commonly applied [39]. Assuming that the diffusivity is related to the fraction of the ion leached during the -out test, known times of leaching, as well as known area and volume of the cement paste, the following mathematical formula can be deduced [38].

$$\Sigma A_t = (--)$$  \hspace{1cm} (1)

Where $A_0$ is the initial amount of free Cl$^-$ present in the sample (mg)

$\Sigma A_t$ is the cumulative loss of chloride at time t during leaching (mg)

$S$ is the surface area of the sample (cm$^2$)

$V$ is the volume of the sample (cm$^3$)

$D_e$ is the effective diffusivity (cm$^2$/day)

$T$ is the leaching time (day)

The left part of Eqn 1 can be expressed as the cumulative fraction of Cl$^-$ leached (f) at time t. Thus the effective diffusivity can be calculated by taking the slope fitted from a plot of f against the square root of time for a given sample having known $S$ and $V$ by the following relation.

$$\Sigma A_t = D_e \cdot \sqrt{T}$$ \hspace{1cm} (2)

For identical samples, $D_e$ values are proportional to the square of the slope of the corresponding f Vs. $\sqrt{T}$ graph.

Figure 2 shows the fraction of the chloride ion leached with time during the -out diffusion test for pastes cured for different ages. The effective diffusivity of cement pastes at different ages can be calculated using the slope (m) of the initial straight portion of the curves in Fig. 2 using Eqn 2. It is clear from Fig. 2 that the diffusivity of the cement pastes decreased significantly with increasing curing time from 1 to 7 days. The reduced diffusivity was probably due to the reduction of the capillary porosity and pore size attributed to increased cement hydration. However, the reduction in the diffusivity was not significant between the pastes cured for 7 and 28 days. This might be because during early stages of curing, the transport of chloride was dominated by connected capillary pores. The capillary pores might become disconnected within first two weeks of hydration and subsequently, the chloride transport was probably primary controlled by the gel pore. Further curing of the cement pastes might not have reduced the diffusivity significantly. Further investigation is undergoing on samples cured for 56 and 90 days.

3.2.2 Effect of curing age of OPC paste on the leaching rate of chloride

Effect of curing age on Cl$^-$ binding of OPC paste is shown in Fig. 3 and the corresponding free and total Cl$^-$ are shown for discussion. Results show that the amounts of free Cl$^-$ of the OPC pastes were decreased with the increase of curing age from 1 to 28 days, whereas the amounts of the bound Cl$^-$ generally increased with increasing curing. For example, the bound Cl$^-$ of OPC pastes cured for 7-day and 28-day were 29 and 68% higher than that of 1-day, respectively. The increased amount of the bound Cl$^-$ with curing age may be attributed to the higher amount of cement gel. At longer curing, greater amounts of AFm and C-S-H are produced due to increased cement hydration which may bind higher amounts of the Cl$^-$. However, at this point it is difficult to relate the relative contributions of AFm and C-S-H in binding the chloride at different curing age. It was also observed that with increased curing to 28 days (Fig. 3), the amount of total Cl$^-$ also increased. It was expected that at higher curing
age, the porosity of the OPC cement pastes would have reduced, which should have also reduced the total amount of Cl⁻ intruded.

![Graph showing effect of curing age of OPC paste on free, bound and total chloride](image)

**Fig. 3:** Effect of curing age of OPC paste on free, bound and total chloride

However, the increased amount of bound Cl⁻ for longer curing age might reduce the amount of free Cl⁻ in the pore solution of the cement paste, which subsequently increased the Cl⁻ concentration gradient between the pore solution and the outer solution. This increased concentration gradient increased the flux of Cl⁻ to pore solution which increased the total Cl⁻.

**CONCLUSIONS**

Based on initial experimental results to investigate time dependent diffusion behavior of chloride into OPC paste from 1 to 28 days of curing with w/c of 0.42, and using NaCl as a free Cl⁻ source, the following conclusions can be drawn:

1. There was a significant decrease in Cl⁻ diffusivity through cement paste during the first two weeks of hydration.
2. The amount of bound Cl⁻ may be dependent on the curing age of cement paste. With increasing curing age from 1 to 28 days, bound Cl⁻ generally increased.
3. By using both through diffusion and -in and-out diffusion, it was possible to separate differences between binding and pore closure during the first 28 days of curing.

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