Properties of Cement-based Composite Materials under Different Storing Environment Temperature

T L Weng¹, S H Weng², S W Cho²

¹Physics Division, Tatung University, Taipei City 104, Taiwan.
²Department of Architecture, China University of Science and Technology, Taipei City 115, Taiwan

E-mail:¹wengabc@ttu.edu.tw, ²s.h.weng0816@gmail.com, ³swcho@ms19.hinet.net

Abstract. This study reports on the properties of cement-based composite materials (mortars) under different storing environment temperature, as determined using the accelerated chloride migration test (ACMT). Mortars with a water/cement ratio of 0.45 and five fine aggregate volume fractions (0%, 15%, 30%, 50% and 60%) under various environment temperatures (25, 40, 60 and 80°C) were evaluated according to the passage of chloride ions through the specimens using ACMT. Calculate chloride migration coefficients on the steady-state. Cement-based composite materials with 60% fine aggregate presented a migration coefficient higher than that of other specimens, whereas mortar with 30% fine aggregate was lower, due to the effects of dilution and tortuosity.

1. Introduction

Interfacial Transition Zone (ITZ) has a higher concentration of calcium hydroxide crystals and porosity far exceeding that of the matrix paste [1,2,3], Reduces resistance to the diffusion of chloride ions.

Temperature is one of the fundamental factors affecting the pore structure of cement-based composite materials (mortars), which makes it an important factor in ion transport. The size of pores and extent of micro-cracking has been shown to increase in specimens stored at temperatures of 40°C, 60°C, or 80°C over a period of 56 days, even after undergoing curing in water for 28 days. These effects have been shown to increase the ion transport properties of mortar, due to the effects of dilution, tortuosity, and percolation between the ITZ and the surrounding paste [4].

The Steady-state chloride migration coefficient, rate (K) was calculated using linear regression based on experiment data, in order to determine the extent of chloride ion penetration, as follows:

\[ C = K t + c \], for steady state

The Nernst–Planck equation was used to calculate the steady-state migration coefficient \( M_s \), as follows [5]:

\[ M_s = \frac{RT}{[\bar{z}][C_0 FE]} \frac{VK}{A} \]  (2)

where V is the volume of the solution in the anodic cell (m³), and A is the surface of the specimen exposed to chloride ions (m²). The chloride migration rate (K).
This study used the ACMT to investigate the ion transport properties of cement-based composite materials (mortars) stored at 40 °C, 60 °C, and 80 °C for 56 days [2-4]. Our aim was to determine the steady-state migration coefficients in unheated (air, 25 °C) and heated mortar specimens.

2. Experiments

2.1. Composite materials (Mortars) and specimen preparation

In this study, mortar specimens with a water/cement ratio of 0.45, were a cement-based composite materials comprising fine aggregate embedded within a matrix of cementitious paste [6]. In characterizing the influence of aggregate on the chloride migration coefficient of mortar, the volume fraction of fine aggregate in the mix proportions (\(V_f\), the volume of aggregate/mortar) was varied between 0 % and 60 %, as shown in Table 1.

| Mix | Water | Cement | SP* | Sand | Fine Aggregate |
|-----|-------|--------|-----|------|----------------|
| M0  | 574.6 | 1276.9 | 0   | 0    | 0              |
| M15 | 486.6 | 1081.3 | 0   | 390.3| 0.15           |
| M30 | 398.8 | 886.2  | 0   | 779.6| 0.3            |
| M50 | 278.2 | 618.2  | 6.18| 1299.8| 0.5            |
| M60 | 217.7 | 483.8  | 9.68| 1559.8| 0.6            |

* The dosage of superplasticizer (SP) was adjusted to obtain a slump closed to 150 mm.

Cast cylindrical mortar specimens (ø100 × 200 mm) were cured in water (23 ± 2 degree) for 28 days and then stored at 40 °C, 60 °C, or 80 °C for 56 days in an oven. Samples were cut from the middle section of the cylindrical specimens and the thickness of the specimen was 30 mm due to reduction the Joule effect [2,3,6], whereupon the lateral surface was coated with epoxy before being placed in vacuum desiccators at a pressure of less than 1 mm Hg (133 MPa) for 3 h. The specimens were then immersed in water 18 h prior to ACMT, in accordance with ASTM C1202 specifications.

2.2. Experimental procedure

The ACMT was used to measure the cumulative concentration of chloride ions that passed through the specimens, as shown in Figure 1. We employed a modified version of the RCPT method in accordance with ASTM C1202 [7,8].

The specimens were placed between two acrylic cells with #20 brass mesh screen electrodes (10 cm diameter) placed against the sides of the specimens. In ACMT, electrical fields are manipulated to pass through specimens. In this case, one cell was filled with 4500 ml of 0.30N NaOH solution and the other cell was filled with 4500 ml of 3.0 % NaCl solution. As shown in Figure 1, the two cells were connected to a 24-V DC power source with the NaOH electrode acting as the anode and the NaCl electrode acting as the cathode [7,8]. The chloride concentration in the anode cell was measured periodically using an ion chromatograph.
3. Results and Discussion
ACMT provides a method by which to characterize the permeability of materials. The chloride concentration was determined by sampling the solution in the anodic cell of ACMT. As shown in Figure 2, this process includes three stages: non-steady-state, transition period, and steady-state [2,6].

3.1. Chloride migration coefficient
The steady-state migration coefficients (Ms) for all specimens can be calculated using Eq. (2), as shown in Table 2. Cement-based Composites (Mortars) with 60 % fine aggregate presented a migration coefficient higher than that of other specimens, due to the formation of connections between ITZs, whereas mortar with 30 % fine aggregate was lower, due to the effects of dilution and tortuosity. The chloride ion transport behavior of cement-based composite materials (mortar) is affected by the temperature at which it is stored. Table 2 shows that the steady-state migration coefficient of mortar increases with temperature due to the effects of micro-cracking caused by an increase in temperature associated with percolation the formation of ITZs [9]. In cement-based composite materials (mortar) with a fine aggregate volume fraction of 0.3, the steady-state migration coefficient in Ms45_40 was 1.86 × that of Ms45_25. The steady-state migration coefficient of Ms45_60 was 4.11 × that of Ms45_25 and the steady-state migration coefficient of Ms45_80 was 4.37 × that of Ms45_25. In mortar with a fine aggregate volume fraction of 0.6, the steady-state migration coefficient of Ms45_40 was 1.57 × that of Ms45_25, the steady-state migration coefficient of Ms45_60 was 2.75 × that of Ms45_25, and the steady-state migration coefficient of Ms45_80 was 2.79 × that of Ms45_25.

Table 2. Steady-state migration coefficient (M_s×10^{12} m^2/sec) under 25°C, 40°C 60°C and 80°C

| Migration coefficient of Chloride Migration in steady-state, M_s(×10^{-12} m^2/sec) | Rs |
|-----------------|-----|
| M45             |     |
| Vf=0%           |     |
| 25°C (a)        | 11.6| 16.8| 38 | 48 | 1.45| 3.28| 4.14|
| 40°C (b)        | 11.2| 15.6| 33.3| 39.7| 1.39| 2.97| 3.54|
| 60°C (c)        | Vf=30%| 7.3| 13.6| 30 | 31.9| 1.86| 4.11| 4.37|
| 80°C (d)        | Vf=50%| 10.3| 27 | 40 | 45 | 2.62| 3.88| 4.36|
| Vf=60%          | 20.4| 32 | 56 | 57 | 1.57| 2.75| 2.79|

3.2. Influence of aggregate volume fraction on chloride migration coefficient
3.2.1 Dilution and tortuosity. Even if the bond between the aggregate and cement paste were perfect,
the migration coefficient of fine aggregate would be far below that of cement paste, due to the effects of dilution. The blockage of flow paths by aggregate reduces the area of the mortar that provides permeability (as measured in cross-section) [10]. The dilution effect depends on the volume fraction of aggregate, wherein the relative impermeability of the aggregate results in a linear parallel chloride ion flow [2].

Taking into account the effects of dilution, the chloride migration coefficient of mortar $M_s$ can be expressed as follows [10]:

$$M_s = M_0 (1 - V_f)$$  \hspace{1cm} (3)

where $M_0$ is the migration coefficient of cement paste, and $V_f$ is the volume fraction of fine aggregate.

The tortuosity effect can be attributed to the impermeability of fine aggregates, which forces migrating chloride ions to navigate around aggregate particles, thereby increasing the length of the flow paths and reducing the flow rate. The effects of tortuosity and dilution can be combined to express the chloride migration coefficient of mortar using the Bruggeman equation, as follows [10]:

$$M_s = M_0 (1 - V_f)^{3/2}$$  \hspace{1cm} (4)

Figure 3 present specimens at $25^\circ$C, $40^\circ$C, $60^\circ$C, and $80^\circ$C, showing that when the volume fraction of the fine aggregate is below 0%, 15%, 30%, 50%, and 60% any increase in the volume fraction of the aggregate reduces the migration coefficient (Steady-state) of the mortar. Figure 4 present a comparison of the theoretical chloride migration coefficient of specimen with a w/c ratio of 0.45 and $M_s$ values calculated using Eq.(3) and (4). The theoretical chloride migration coefficient $M_s/M_0$ is defined as the ratio of the chloride migration coefficients of mortar and cement paste.

A comparison of experiment data with chloride migration coefficient for various volume fraction of fine aggregate in Figure 4 illustrates how the chloride migration coefficient at $25^\circ$C is influenced by dilution and tortuosity when the volume fraction of the fine aggregate is below 0.3. At $V_f=0.3$, taking into account only the effects of dilution reduces the theoretical chloride migration coefficient from 1.0 to 0.7, whereas taking into account the effects of tortuosity reduces the theoretical chloride migration coefficient from 1.0 to 0.65. Increasing the volume fraction of fine aggregate to beyond 0.3 led to an increase in the length of the flow paths. As indicated by the experiment data in Figure 4, the chloride migration coefficient is influenced by the effects of dilution as well as tortuosity.

As shown in Figure 4, at temperatures of $40^\circ$C, $60^\circ$C, and $80^\circ$C, increasing the volume fraction of aggregate leads to a decrease in the migration coefficient of mortar, in cases where the volume fraction of the aggregate is below 30%.

3.2.2 ITZ and percolation effects. In this study, mortar is regarded as a three-phase composite materials
(cement paste, fine aggregate, and ITZ). The ingress of chloride ions leads to the formation of an ITZ between the fine aggregate and the matrix, thereby increasing the chloride migration coefficient of the mortar. The connected-pore paths between ITZs would allow harmful ions such as chlorine ion to penetrate the concrete quickly [9].

As shown in Figure 4, mortar with a volume fraction of the fine aggregate exceeding 0.4–0.5 can is susceptible to percolation of ITZs at 25°C. The apparent width of the ITZs in which the higher porosity is interconnected as observed by the previous study [11]. As shown in Figure 4, samples with a volume fraction of 0.3–0.4 at 25°C presented a chloride migration coefficient of 0.5–0.7. This means that the ITZ did not exert a significant influence, due to the fact that percolation does not occur at such low volume fractions of fine aggregate. As shown in Figure 4, increasing the volume fraction of fine aggregate to beyond 0.3 led to a sharp increase in the chloride migration coefficient, particularly at 0.6. In samples with a fine aggregate volume fraction of 0.3 stored at temperatures exceeding 40°C, the appearance of micro-cracking is an indication of percolation resulting from the overlap of porous regions and increased tortuosity in ITZs [12]. This is consistent with previous findings based on prediction models [13,14]. In addition, a higher storage temperature also increased the amount of shrinkage and subsequent microcracking. It also indicated that the aggregate size and volume fraction on shrinkage induced micro-cracking as well as consequently greatly increased tortuosity and permeability in ITZ regions correspond with the results of previous findings [15]. Generally, constituent phases and their geometric arrangement are the primary factors determining ion migration in concrete. Dilution and tortuosity tend to decrease the permeability of mortar, whereas the formation of connections between ITZs tend to increase permeability.

4. Conclusions

This study demonstrated how the transport properties of composite materials (mortar) are influenced by temperature (25, 40, 60 and 80°C). Based on the results obtained in these experiments, the following conclusions can be drawn:

1. Specimens with a 30% volume fraction of fine aggregate presented the lowest steady-state migration coefficient among the mixes in this study, whereas mortar with 30% fine aggregate was lower, due to the effects of dilution and tortuosity.
2. Cement-based composite materials (Mortars) with 60% fine aggregate presented a migration coefficient higher than that of other specimens, due to the formation of connections between ITZs.
3. at temperatures of 40°C, 60°C, and 80°C, increasing the volume fraction of aggregate leads to a decrease in the migration coefficient of mortar, in cases where the volume fraction of the aggregate is below 30%.
4. constituent phases and their geometric arrangement are the primary factors determining ion migration in concrete. Dilution and tortuosity tend to decrease the permeability of mortar, whereas the formation of connections between ITZs tend to increase permeability.

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