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EXPERIMENTAL MEASUREMENTS OF CHLORIDE ION DIFFUSION RATES USING A TWO-COMPARTMENT DIFFUSION CELL: EFFECTS OF MATERIAL AND TEST VARIABLES

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ABSTRACT

Chloride ion diffusion rates in cementitious paste have been determined using a modification to the "standard" two-compartment diffusion cell. Ordinary Portland cement samples of varying water/cement ratios were investigated together with similar materials to which varying amounts of pyrolysed scrap automotive polymer (Sheet Moulding Compound - SMC) had been added. The effects of changes in the experimental conditions (sample thickness, chloride ion concentration in first compartment) were also investigated. The chloride ion diffusivity was reduced by either reducing the water/cement ratio or by the incorporation of pyrolysed SMC into the mix. There was a small decrease in effective chloride ion diffusivity with increase in sample thickness. The concentration of chloride ion in Cell 1 had no significant effect on the measured diffusivity. However, by increasing the concentration, the time required to make the diffusivity measurements can be significantly reduced.

Introduction

The interaction between the concrete service environment and the concrete itself can lead to deterioration of reinforced concrete structures, in some cases rendering the structure unsuitable for its design purpose. Often these interactions are with chemical species in the environment (1). One of the more common modes of deterioration associated with reinforced concrete is the chloride ion induced corrosion of the embedded reinforcing steel. The chloride ion changes both the passive condition of the embedded reinforcing steel, and those aspects of the concrete environment which allowed the passive condition of the steel to develop in the first place. The main protection systems for preventing this deterioration focus on preventing chloride ion from reaching the embedded steel (2). Since the chloride ion is required to move from the surface of the concrete to the surface of the steel bar and to accumulate to sufficient quantity before corrosion induced deterioration of the reinforced concrete takes place, it is the rate of this mass transfer which controls the rate of deterioration, at least in the initial stages. The mass transfer of a given material by virtue of a concentration gradient is defined as diffusion. The mass transfer coefficient, in this case known as diffusivity, is defined by Fick's first law as the ratio between the concentration gradient and the change in concentration with time (3).

In the present study, we investigate the usefulness of a simple device for measuring the diffusivity of chloride ion in cementitious materials, and determine the effects of changes in experimental and materials parameters on the measured diffusivity. In particular, investigations were undertaken to determine the effect(s) of (i) changing the mix proportions and hence the pore distribution of the cement under study, and (ii) adding supplementary potentially cementitious materials, on the diffusivity of the chloride ion in cement.

The potentially-cementitious material chosen for study was pyrolysed sheet moulding compound. Sheet moulding compound (SMC) is a mineral and glass fibre reinforced polyester, and is currently used by most of the major international automobile manufacturers (4). One of the major problems which is associated with the use of this material is that due to its thermosetting properties it cannot be readily or effectively recycled. In order to improve the cost effectiveness of this material, a cheap disposal method is required (5). The SMC Automotive Alliance has developed an environmentally sound method of pyrolyzing the polymer, the products of the pyrolysis being energy, an oil product and ash. It has been suggested that the ash be utilized as an additive to concrete to economically dispose of the ash and modify the properties of the concrete itself. A chemical analysis of the ash component of the pyrolysed sheet moulding compound, or PSMC, is found in Table I. The finely divided components of the E-glass should have pozzolanic properties. Addition of PSMC to concretes and mortars has been shown to increase both the compressive strength of these materials and their resistance to alkali-aggregate reactions (5).

TABLE 1 Chemical Composition of PSMC

Component	Component Composition (%)
$CaCo_3$	55
C	12
E-glass	33
Consisting of:	
SiO_2	54
Al_2O_3	14
CaO	20
Boric Acid	8
Oxides of K, Na, Mg, Ti and Fe	Trace

Experimental Details

Description of Diffusion Cell

The effective diffusivity of chloride ion in cement paste was determined using a modified version of the two compartment diffusion cell first utilized in 1981 by Page et al at the University of Aston (6). One of the main modifications to the present experimental set-up compared to what has been used previously (6-8) is the incorporation of stirrers in both cells. This should help prevent chloride ion gradients building up at the cement paste disc-solution interfaces.

One cell, referred to as Cell 1, is filled with a sodium chloride solution of known concentration. The other cell, referred to as Cell 2, is filled with distilled water. The concentration of the solution in Cell 2 was monitored with respect to time using a chloride ion selective electrode (9). Based on these measurements, the effective diffusivity of chloride ion in the cement paste can be calculated using the equation (6):

$$C_2 = \frac{D_{Cl_{eff}} \cdot A \cdot C_1}{V \ell} \cdot t$$

where, C_1, C_2 is the concentration of chloride ion in cells 1 and 2, respectively; $D_{Cl_{eff}}$ is the effective diffusivity of chloride ion in hardened cement paste; A is the cross-sectional area of cement paste disk available for diffusion; V is the volume of Cell 2 of the diffusion cell; ℓ is the thickness of the cement paste disk; and t is time.

Experimental Investigations

The experiments performed were designed with two purposes. The first was to measure the effect of changes in the physical and chemical structure of the cementitious material on the diffusivity of chloride ion. To this end, two experiments were carried out, namely: a) to investigate the effect of the water:cement ratio on the effective diffusivity of the chloride ion in hardened cement paste. Cement disks were prepared with water:cement ratios of 0.4, 0.5, 0.6 and 0.7; b) to investigate the effect of replacing a portion of the type 10 portland cement with pulverized PSMC on the effective diffusivity of chloride ions in hardened cement paste. Cement disks were prepared with 5, 10, 20 and 30 percent of the portland cement replaced by PSMC. All samples were prepared with a water:binder ratio of 0.5, where binder refers to the total of the portland cement and the pozzolanic components of the PSMC.

The second set of experiments were designed to determine the effect of changes in the experimental conditions normally utilized (3 mm sample thickness, C_1 = 1M) on the measured chloride diffusivity, as well as to investigate the dependence of the effective chloride ion diffusivity on the magnitude of the concentration gradient. The cement disks used in these experiments had a water cement ratio of 0.45 and consisted only of ordinary portland cement. As noted, this was a two-part study in order to c) investigate the effect of different chloride ion concentrations in Cell 1 on the time required to measure the effective chloride ion diffusivity. In addition, this experiment investigated the dependence of the effective diffusivity of chloride ion on the magnitude of the concentration gradient; d) investigate the effect of the sample thickness on the measured effective chloride ion diffusivity in cement paste. Twelve disks of varying thickness were studied.

The cement paste disks used in all these experiments were cast in 50 mm diameter cylindrical moulds approximately 300 mm in length. The samples were filled in thirds and each layer was rodded a total of 25 times. The second and third layers were rodded with care to ensure that the rod did not penetrate into the underlying layers. After allowing 24 hours for the cylinder to set, the specimens were demoulded and placed in an automatically controlled curing room at 23 ± 2°C and 100 percent relative humidity. The samples were allowed to cure under these conditions for 8 weeks. The samples were then cut to the desired thickness using a rock saw with a diamond blade. The edges were turned to ensure a good fit into the diffusion cells. Each side of the disk was then abraded using 60 grit silicon carbide abrasive powder. The specimens were then bolted into the diffusion cells, the seal checked and the respective compartments were filled with solution. The charged cell was then placed into the holder, the stirring apparatus was put into place and the experiment was allowed to proceed. The chloride ion concentration in Cell 2 was then measured at different times using a chloride ion selective electrode and the slope of the concentration versus time plot was used to compute the effective chloride ion diffusivity.

Results

The results from these tests will be summarized by looking at the basic trends noted in the variation of effective chloride in diffusivity, $D_{Cl_{eff}}$, with changes in material or experimental parameters.

Effects of Varying the Water:Cement Ratio

Cement paste disks were made up with water:cement ratios of 0.4, 0.5, 0.6 and 0.7 and the

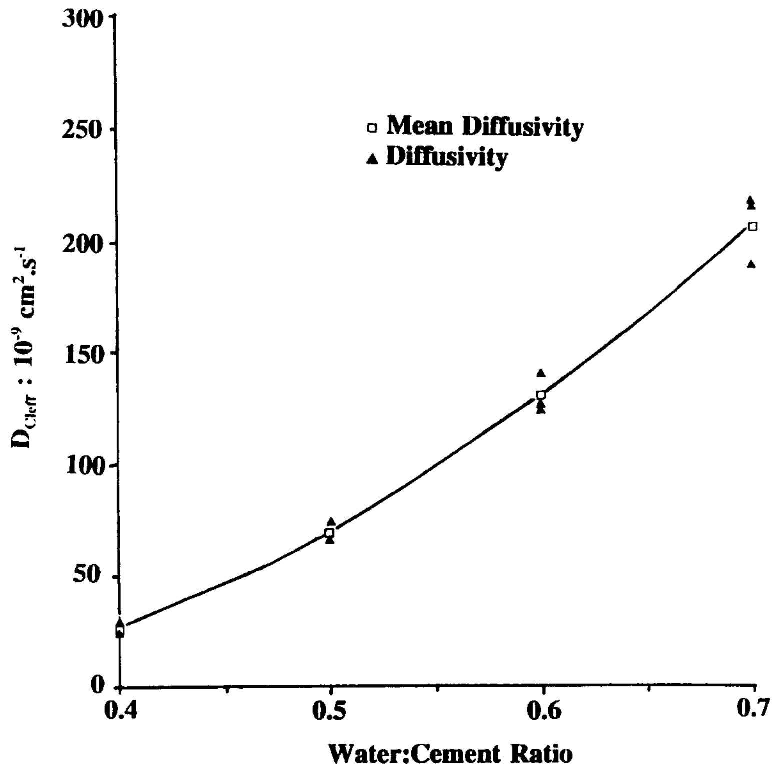

FIG. 1
Plot of effective chloride ion diffusivity versus water:cement ratio.

effective diffusivity was measured in triplicate for each set of samples. The results are presented in Figure 1 as a plot of $D_{Cl_{eff}}$ vs. water:cement ratio. There is a very clear trend of increasing $D_{Cl_{eff}}$ with increasing water:cement ratio.

Variation of PSMC Content

Cement paste discs of water:cement ratio 0.5 were made up with PSMC contents of 5, 10, 20 and 30% and the effective diffusivity was measured in triplicate for each set of samples. A plot of measured $D_{Cl_{eff}}$ vs. PSMC content is given in Figure 2. An increase in PSMC content of the cement paste gives rise to a decrease in $D_{Cl_{eff}}$.

Variation of Chloride Ion Concentration in Cell 1

The chloride ion concentration in Cell 1 of the diffusion cell was varied from the normally used value of 1 molar. Using cement paste disks of water:cement ratio of 0.45, the concentration in Cell 1 was varied from 0.5 to 2.0 to 3.0 to 4.0 molar. From Figure 3, which is a plot of $D_{Cl_{eff}}$ vs. chloride ion concentration in Cell 1 it is apparent that $D_{Cl_{eff}}$ is virtually independent of the chloride ion concentration in Cell 1.

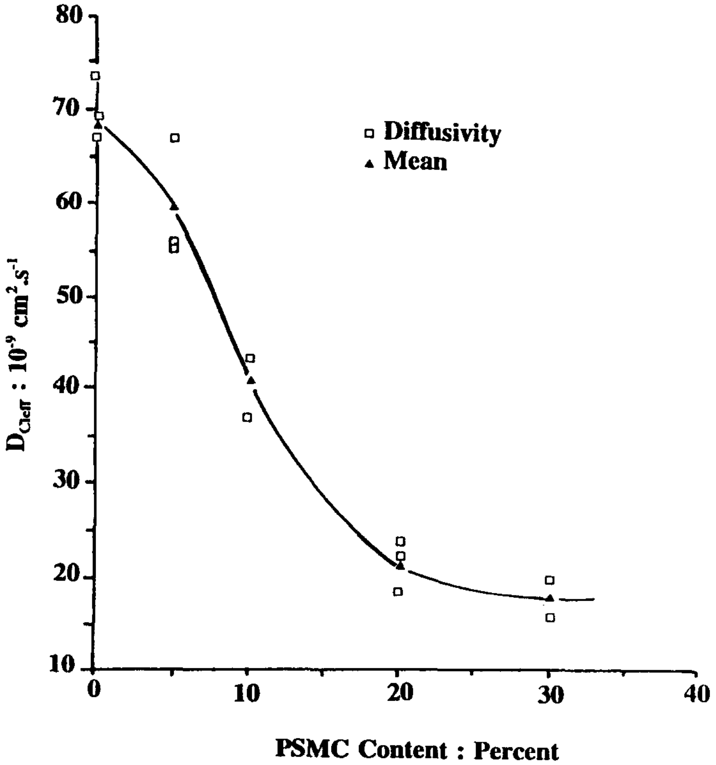

FIG. 2
Plot of effective chloride ion diffusivity versus PSMC content for cement pastes of water:binder ratio 0.5.

Variation of Sample Thickness

Cement paste disks of thicknesses ranging from 1.78 mm to 5.22 mm were prepared (the 'standard' thickness is 3 mm). These disks were prepared using a water:cement ratio of 0.45. From Figure 4, which is a plot of $D_{Cl_{eff}}$ vs. sample thickness, there would appear to be a slight dependence of $D_{Cl_{eff}}$ on sample thickness. An increase in sample thickness gives rise to a decrease in the measured effective chloride ion diffusivity.

Discussion

Looking first at the effects of experimental parameters on the measured effective chloride ion diffusivity, $D_{Cl_{eff}}$, we recall that as the sample thickness is increased there is a slight decrease in $D_{Cl_{eff}}$, but as the chloride ion concentration in Cell 1 is increased from 0.5M to 4.0M there is no significant change in $D_{Cl_{eff}}$. If, however, we look at the general reproducibility of the $D_{Cl_{eff}}$ measurements, we find that the sample to sample variation is of the same order of magnitude as the decrease due to increasing sample thickness. Thus the results would suggest that effective chloride ion diffusivities of different cement pastes can be compared even if the measurements were made using samples of different thicknesses, provided sample thickness are in the range of thicknesses surveyed in the present tests, i.e., approximately from 2 to 5 mm.

Although the magnitude of the chloride ion concentration in Cell 1 did not affect the value of $D_{Cl_{eff}}$, the time required to reach a specific chloride ion concentration in Cell 2 decreased significantly with increasing chloride concentration in Cell 1. For instance, the time required to reach a chloride concentration of 100 m Moles/litre in Cell 2 decreased from approximately 3000 hours for a Cell 1 concentration of 0.5 molar to approximately 400 hours for a Cell 1

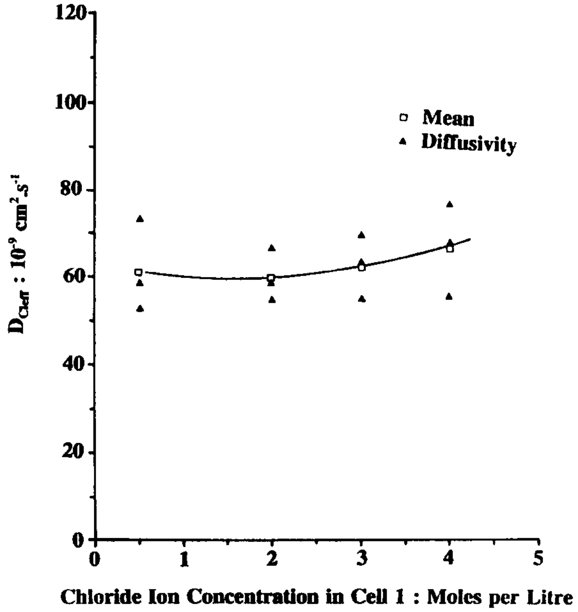

FIG. 3

Plot of effective chloride ion diffusivity versus chloride ion concentration in Cell 1.

concentration of 4.0 molar. Thus the time required to carry out the $D_{Cl_{eff}}$ determinations can be much reduced by increasing the concentration in Cell 1 from the 'normal' value of 1.0 molar. This reduction in time, makes the test more 'useful' as a sorting test to investigate the effects of variations in materials parameters on $D_{Cl_{eff}}$.

The results showing an increase in $D_{Cl_{eff}}$ with increasing water:cement ratio, Figure 1, are in general agreement with previously reported results (6, 10-15). This increase in effective diffusivity has been attributed to an increase in total porosity of the paste, since an increase in water:cement ratio leads to an increase in theoretical porosity at 100% hydration (16). It is interesting to note that the magnitude of the scatter in the diffusivities measured in this study and by others, is often up to 25% of the mean value at any given water:cement ratio. This may indicate that there are variations in the pore structures of the samples used in the various studies. These variations may be due to the different maturities or different curing regimes of the samples. It is also to be noted that the specimen-to-specimen variation for a given w/c ratio increases with increasing w/c ratio. This is probably indicative of more segregation in the higher w/c ratio pastes. It may however, be indicative of the effect of using relatively thin cement paste disk samples. Sample of thickness less than 10 mm may be affected by the presence of small entrapped air voids, and as has been noted previously (7,8), the diffusing cell technique is normally limited in usefulness to samples less than 10 mm thick. Characterizing the cement in terms of the lithologic factor (17,18) or some other parameter which accounts for

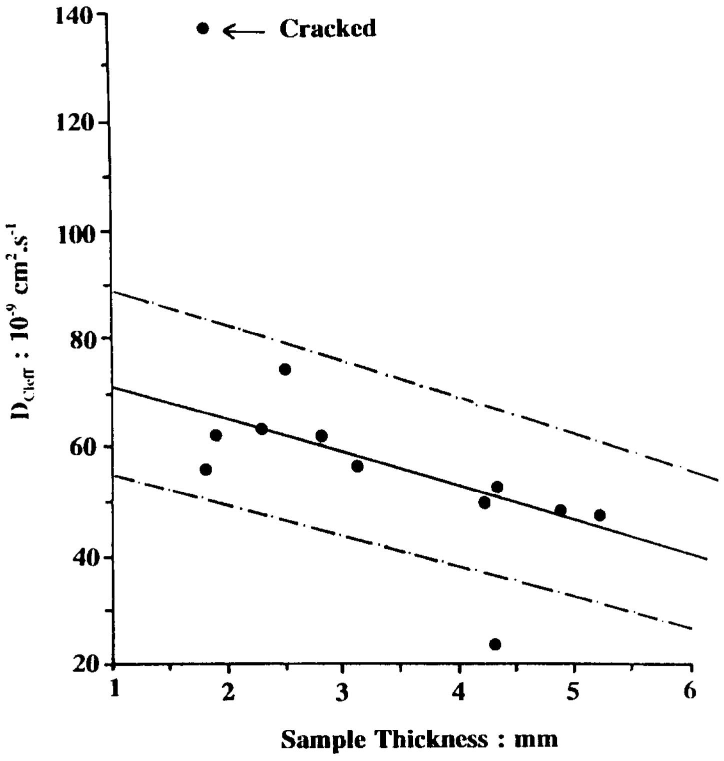

FIG. 4

Plot of effective chloride ion diffusivity versus sample thickness.

both the total porosity, i.e., void volume, and other aspects of the pore distribution of the cement, could reduce the effect of these local variations.

The results for the effects of PSMC additions on the effective chloride ion diffusivity in cement paste, Figure 2, show that PSMC reduces the diffusivity. The porosity of these cement pastes containing PSMC was measured (19) and the effective chloride ion diffusivity was found to be directly proportional to the porosity, Figure 5. Based upon the chemical composition of the 'E' glass, some pozzolanic activity of the PSMC is expected. Results for other pozzolans, e.g., ground granulated blast furnace slag and pulverized fly ash (20), show that when incorporated into OPC they give a less porous and/or finer pore size microstructure with significantly diminished diffusion rates of chloride ions. Resistivity measurements on pastes at early ages indicates similar behaviour between PSMC, Silica Fume and Flyash. The effects of decreasing water:cement ratio and increasing PSMC content are thought to be similar in that they both produce a decrease in both the number of pores above a threshold diameter and the number of pores which are connected and unblocked.

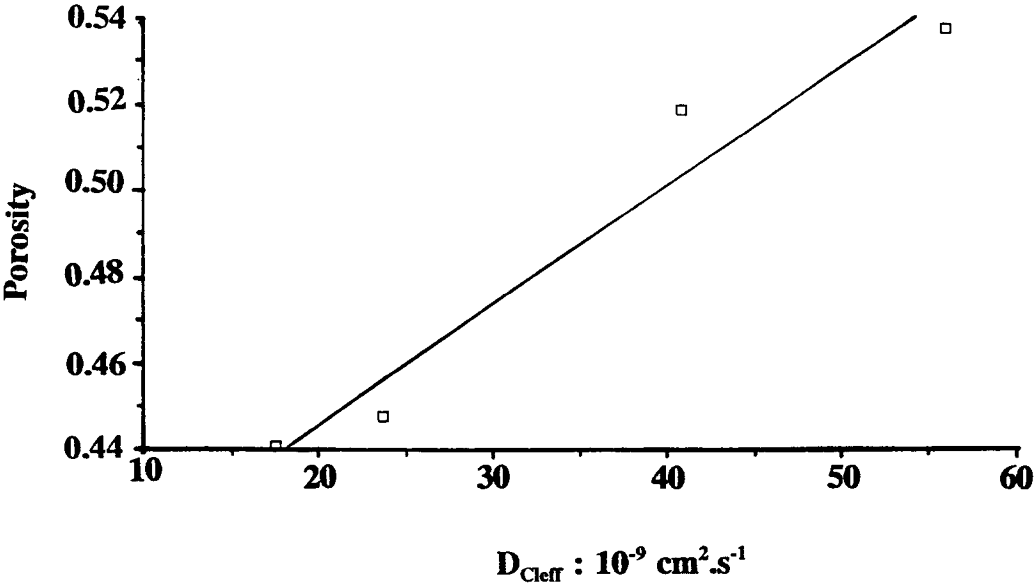

FIG. 5
Plot of porosity versus effective chloride ion diffusivity for PSMC modified cement pastes.

The significance of the present results with respect to the chloride-induced corrosion of steel reinforced structures arises from two aspects, namely: (i) the effective chloride ion diffusivity is one of the main factors controlling the time required for a sufficient chloride ion concentration to build up at the steel rebar to bring about depassivation. Any factor producing a reduction in chloride ion diffusivity would prolong the life of the structure by increasing the time for initiation of corrosion of the rebar. This reduction in effective chloride ion diffusivity can be accomplished either by reducing the water:cement ratio or by adding PSMC. (ii) our work on changing the test parameters for the diffusion cell technique, has shown that the time required to determine the effective chloride ion diffusivity can be reduced by almost an order of magnitude by increasing the chloride ion concentration in Cell 1 from 0.5M to 4.0M. It is thus recommended that when using this type of test to determine the effective chloride ion diffusivity, and hence to obtain a measure of the 'resistance' of a material to chloride ion intrusion, the chloride ion concentration in Cell 1 be maintained at 4.0M.

Conclusions

The main conclusions of the present study are as follows:

(1) The concentration of chloride ion in Cell 1 of the diffusion cell, within the limits examined in this study, has no significant effect on the measured diffusivity of the chloride ion. However, an increase in the chloride concentration in Cell 1 can be used to reduce the time required to make chloride ion diffusivity measurements.

(2) There is a small decrease in measured effective chloride ion diffusivity in hardened cement paste with an increase in the sample thickness.

(3) As has been well documented by other researchers, it was found that the diffusivity of chloride ion in cement paste is a function of the water:cement ratio of the cement mix with an increase in the water:cement ratio causing an increase in the effective chloride ion diffusivity.

(4) Pyrolysed sheet moulding compound (PSMC) utilized as an additive to cement in ordinary cement pastes acts like other pozzolans and is effective in reducing the effective diffusivity of chloride ions.

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