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Beneficial effect of fly ash on chloride diffusivity of hardened cement paste

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Abstract

The rate at which chloride ions penetrate into concrete determines the time period after which the passivity of reinforcing bars begins to break down for corrosion. It is also related to the quality and thickness of the concrete cover and determines the service life of the structure. This study is aimed at investigating the effect of fly ash on chloride diffusivity of hardened cement pastes using the accelerated chloride ion diffusion test method. The results obtained from this test were used to calculate the diffusion coefficient of chloride ions using the Nernst-Plank equation for steady state condition. The results confirmed that the diffusion coefficient of chloride ions values for cement-fly ash pastes lie within the range of 10^{-7} and 10^{-9} cm^2/s. It was also found that blending cement with fly ash significantly decreases the diffusion coefficient of chloride ions only at the later ages of curing. Furthermore, it was observed that fly ash replacement ratio of 40% gives the best results with respect to chloride diffusivity through cement-fly ash pastes. Water/binder ratio was also found to affect the chloride ion diffusion coefficient through cement-fly ash pastes appreciably at the early ages of curing, but became less important at the later ages of curing.

Keywords: Accelerated chloride ion diffusion test; Pore size distribution; Mercury porosimetry; Microstructure; Fly ash

The diffusion of chloride ions through concrete is a major cause of corrosion of reinforcing bars in off-shore structures as well as highway bridges in cold countries where deicing salts (NaCl and $CaCl_2$) are used during the winter. In countries like Japan, which has long beaches as well as a long winter period, this is a major problem. Theoretically, bars embedded in concrete structures are protected both chemically and physically against environmental corrosion by the concrete cover. The high alkalinity of the pore solution of the concrete cover provides the chemical protection by the formation of a protective oxide film or passive layer on the surface of the bars. The impermeability of the concrete cover is expected to provide a physical protection against the ingress of deleterious materials like chloride ions that are known to cause a breakdown of this passive layer when the $[Cl^-]/[OH^-]$ ratio at the surface of the bars reaches a threshold value of 0.3 [1]. The diffusivity of chloride through concrete therefore depends on the microstructure of the concrete cover. Blending cement with fly ash is known to produce concrete with a dense microstructure [2] and hence an improvement in the physical protection of any embedded bars. In addition to this, if there is the chloride binding by the aluminate phase of the fly ash to form Friedel's salt, then the concentration of the free chloride ions in the pore water of concrete would be expected to decrease. Currently, there is no consensus among the research community on chloride binding in cement-fly ash paste/concrete.

This study aims at determining the beneficial effect when cement is blended with fly ash with respect to the diffusivity of chloride ions through the resulting paste. It is also aimed at investigating the chloride binding ability of fly ash to form Friedel's salt. In this study, since the conventional test method for determining the diffusion coefficient of chloride ion through cement paste/concrete using the diffusion cell is time consuming, the accelerated chloride ion diffusion (ACID) test method [3–5], which is an improvement over the rapid chloride permeability test (AASHTO T277) [6] method that was used.

1. Experimental procedures

1.1. Materials and mix proportions

The following materials were used: ordinary portland cement (OPC) (specific gravity: 3.13, Blaine fineness: 3300 cm^2/g) and fly ash (FA) (specific gravity: 2.28, Blaine fineness: 3960 cm^2/g). Their chemical compositions are presented in Table 1. These materials were used to prepare ce-

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Table 1
Chemical compositions of OPC and fly ash (%)

Type	Ig. loss	Insol	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Total
OPC	1.6	0.3	21.7	5.3	2.9	63.7	1.2	2.1	0.33	0.54	99.67
Fly ash	1.49	63.14	28.75	2.59	1.08	0.63	<0.01	0.55	0.39	1.04	99.66

ment paste (water/binder ratio: 35, 45, 55, and 65%; fly ash replacement ratio: 0, 20, and 40%). Cylindrical specimens, 10 cm diameter and 20 cm high, were made and cured in water at 20°C and tests conducted at 7, 28, and 91 days, and 1 year.

1.2. Test methods

The ACID test was used to measure the chloride ion diffusion coefficient (D_{cl}) through cement and cement-fly ash pastes. In addition, the following tests were also conducted: electrical resistivity test, scanning electron microscopy (SEM), fluorescence microscopy, mercury intrusion porosimetry, and differential scanning calorimetry (DSC).

1.2.1. The ACID test

In this test, a diffusion cell (volume: 785 mL, cathode: 3% NaCl solution, anode: 0.3N NaOH solution) cement paste specimen (ϕ 10 cm $\times$ 2 cm) was used. The cement paste specimen was placed between the electrodes and an electric field of 3 V/cm applied to the electrodes, as shown in Fig. 1. The amount of chloride ions that migrate from the cathode through the cement paste specimen to the anode of the cell was determined by measuring the concentration of the chloride ions in the anode solution periodically. A graph of the amount of chloride ions that pass through the specimen and arrive at the anode, which is indicated by the concentration of the Cl^- ions, vs. the number of days gives a straight line as shown in Fig. 2. The slope of this straight line, which is termed the chloride ion flux (J_{cl}), is used in the Nernst-Plank's equation to calculate the D_{cl} as shown in Eq. (1), below [3,4]:

$$\mathrm{Dcl} = \frac{R \cdot T}{Z_c \cdot F \cdot C_{cl} \cdot \Delta V} \cdot \mathrm{J_{cl}} \tag{1}$$

Where: D_{cl} = chloride ion diffusion coefficient in cm^2/s, R = universal gas constant = 8.31 J/K · mol, T = temperature in kelvin, Z_c = ionic charge of chloride ion, F = Faraday constant = 9.65×10^4 C/mol, C_{cl} = chloride ion concentration in the anode chamber of the diffusion cell, ΔV = electric field in volts/cm.

1.2.2. Electrical resistivity measurements

The electrical resistivity was measured with an automatic LCR meter by applying a 10-mV AC at 1 kHz across saturated specimens (ϕ5 cm $\times$ 5 cm) using copper plate electrodes. The instrument gives a digital display of the value of the electrical resistance. The value of the resistance measured is then used to calculate the electrical resistivity of the specimens.

1.2.3. DSC

The DSC test was performed to determine the quantity of Friedel's salt formed (if any) due to chloride binding and also the quantity of $Ca(OH)_2$ formed in the cement and cement-fly ash pastes.

1.2.4. Mercury intrusion porosimetry

The above test was used to measure the total pore volume of the cement and cement-fly pastes.

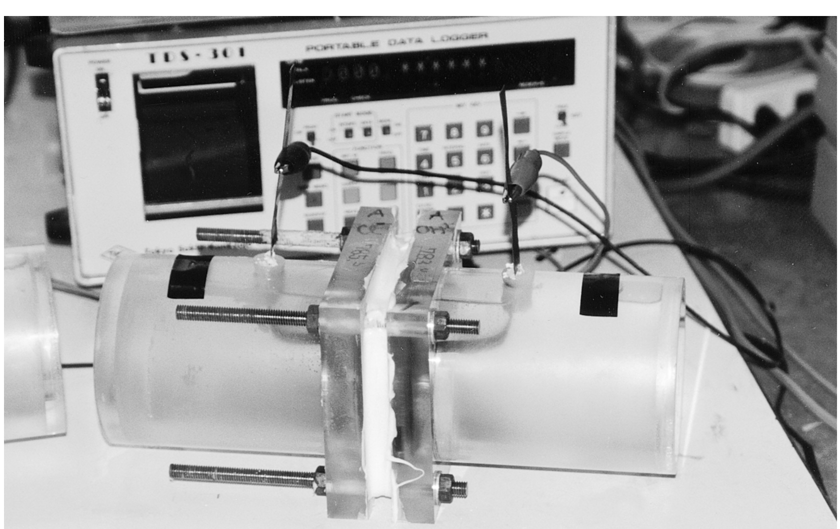

Fig. 1. Setup of the ACID test.

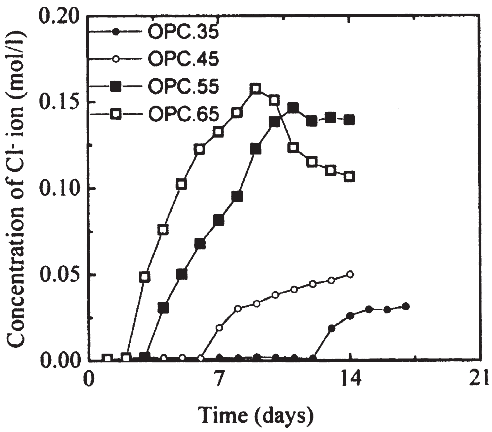

Fig. 2. Variations of Cl^- concentration in cell (OPC pastes, 7 days curing).

2. Results and discussion

2.1. Chloride ion diffusion coefficients

Table 2 shows the values of D_{cl} through the cement and cement-fly ash pastes at curing ages of 7, 28, 91, and 365 days. It could be observed that the D_{cl} values lie between 10^{-9} cm^2/s and 10^{-7} cm^2/s. A closer look at the D_{cl} values depicts that fly ash has beneficial effect on chloride diffusivity only at the later days of hydration. For a given fly ash replacement ratio, an increase in the water/binder ratio causes an appreciable increase in the D_{cl} value; however, as the curing age increases this change becomes less significant. It is important to note that for the specimens with water/binder ratio of 0.35, the time duration for the Cl^- ions to migrate from the cathode chamber through the cement and cement-fly ash paste to the anode chamber was more than the time prescribed for the test. It could therefore be inferred that at such low water/binder ratio fly ash replacement may not cause any significant change in the diffusivity of the resulting paste.

2.2. Electrical resistivity

Fig. 3 shows a graph of electrical resistivity vs. curing time. It is seen that the electrical resistivity of the cement-fly ash pastes increases rapidly with curing time, whereas that of the OPC increases at a slower rate. Since the flow of electrical current through hydrating cement paste is electrolytic, that is, mainly due to the flow of ions through the pore spaces, its resistivity is an indirect measurement of porosity and hence diffusivity [7]. In reinforced concrete structures at the onset of corrosion of the bars, the corrosion current and hence the rate of corrosion is influenced by the electrical resistivity of the concrete. The high electrical resistivity of cement-fly ash pastes would cause the overall resistivity of cement-fly ash concrete to increase and hence a lower rate of bar corrosion after the breakdown of passivity.

2.3. Relation between electrical resistivity and total pore volume

Fig. 4 shows a scatter diagram between the logarithm of electrical resistivity and total pore volume (TPV) of the cement and cement-fly ash pastes. It is seen that there is a correlation between electrical resistivity and total pore volume of the pastes. However, the correlation coefficient decreases with an increasing fly ash content. It shows that the logarithm of the electrical resistivity is inversely proportional to the total pore volume.

2.4. DSC

Fig. 5 shows the results of DSC for the cement and cement-fly ash pastes at a curing age of 1 year. The graph shows that the quantity of $Ca(OH)_2$ formed in the hydration of the pastes decreases with the addition of fly ash. This implies that the pH of the pore solution of the pastes also decreases with the addition of fly ash and hence if bars are embedded, their passivation period based on $[Cl^-]/[OH^-]$ ratio would be expected to decrease. However, the ratio of $[Cl^-]/[OH^-]$ is unreliable when applied to blended cement pastes [8,9]. Thus, even though $[Cl^-]/[OH^-]$ ratio of blended cements are lower compared to OPC pastes, the chloride threshold concentration for the breakdown of passivity is similar to or slightly higher than that of OPC pastes [10]. Therefore, notwithstanding the decrease in the OH ion concentration or pH of the pore solution in the cement-fly ash pastes/concretes, if bars are embedded their passivity period

Table 2
Chloride ion diffusion coefficients of hardened cement and cement-fly ash pastes

Specimen	7 days cured	28 days cured	91 days cured	365 days cured
OPC 35	3.040×10^{-9} [13]*	**	**	**
OPC 45	7.470×10^{-9} [7]	1.040×10^{-8} [11]	8.610×10^{-9} [11]	2.586×10^{-8} [6]
OPC 55	3.198×10^{-8} [4]	2.737×10^{-8} [6]	8.989×10^{-9} [5]	3.703×10^{-8} [3]
OPC 65	4.663×10^{-8} [3]	3.166×10^{-8} [5]	2.662×10^{-8} [5]	6.336×10^{-8} [3]
FA20%35	1.546×10^{-8} [7]	**	**	**
FA20%45	4.080×10^{-8} [4]	2.445×10^{-8} [6]	1.395×10^{-8} [12]	5.073×10^{-9} [27]
FA20%55	5.170×10^{-8} [2]	3.731×10^{-8} [5]	1.801×10^{-8} [9]	6.462×10^{-9} [18]
FA20%65	5.486×10^{-8} [2]	4.812×10^{-8} [5]	2.114×10^{-8} [4]	1.732×10^{-8} [9]
FA40%35	3.101×10^{-8} [4]	**	**	**
FA40%45	6.278×10^{-8} [2]	2.977×10^{-8} [5]	1.350×10^{-8} [11]	4.069×10^{-9} [16]
FA40%55	1.119×10^{-7} [1]	4.861×10^{-8} [3]	1.652×10^{-8} [8]	3.695×10^{-9} [22]
FA40%65	1.713×10^{-7} [1]	5.848×10^{-8} [3]	1.727×10^{-8} [9]	5.085×10^{-9} [28]

* Number of days for chloride ion to migrate from cathode to anode chamber, ** not migrated within prescribed time.

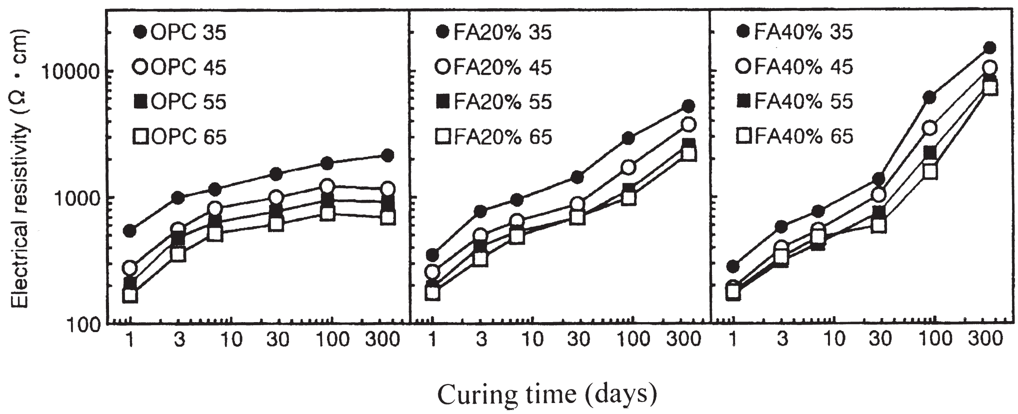

Fig. 3. Variations in electrical resistivity of cement and cement-fly ash paste with curing time.

would be longer in comparison to that of OPC paste. Fig. 5 also shows that the quantity of Friedel's salt increases with the addition of fly ash. This means that blending cement with fly ash would decrease the diffusivity of chloride through the resulting paste, thereby increasing the passivation period of embedded bars. The overall effect of blending fly ash to OPC is therefore to prolong the passivation period of embedded bars in comparison to OPC.

2.5. Relation between D_{cl} and TPV

Fig. 6 shows a scatter diagram of D_{cl} plotted on a log scale vs. TPV plotted on a normal scale. It is observed that there is a correlation between D_{cl} and TPV. However, the correlation is better in the cement-fly ash pastes than in the OPC pastes.

2.6. Relation between D_{cl} and electrical resistivity

Fig. 7 shows a scatter diagram of D_{cl} and electrical resistivity of the cement and cement-fly ash pastes. It shows a good correlation between D_{cl} and electrical resistivity with D_{cl} being inversely proportional to electrical resistivity. This means that diffusion coefficient of chloride ion through cement pastes could be derived from the value of its electrical resistivity [11]. Since electrical resistivity measurement is simple and nondestructive, such a relation would be very useful for researchers in this field. Further work is therefore required to obtain enough data in order to establish a mathematical or empirical relation between D_{cl} and electrical resistivity.

3. Conclusions

The ACID test method gives quite a reasonable value for the D_{cl} through cement paste/concrete. From the results, it was observed that blending cement with fly ash causes a significant reduction of D_{cl} through the resulting paste only at the later ages of curing. Fly ash replacement of 40% was found to produce the best results. The D_{cl} was also found to decrease as the curing age increases and also as the water/binder ratio decreases. However, at the later ages of curing the effect of water/binder ratio on D_{cl} becomes less significant. At low water/binder ratio of around 0.35 the porosity of OPC paste is low enough with respect to chloride diffusivity, and as such the addition of fly ash may not provide any significant effect.

A correlation was found between (1) D_{cl} and electrical resistivity and (2) the logarithm of electrical resistivity and

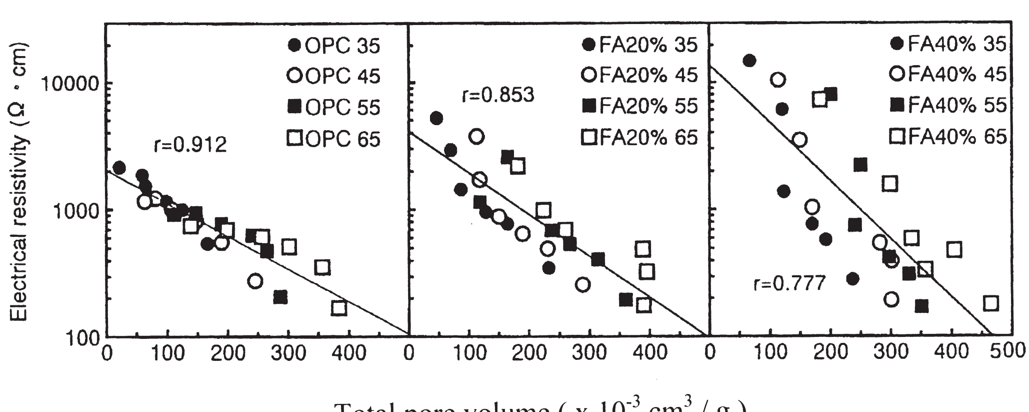

Fig. 4. Relation between electrical resistivity and total pore volume in cement-fly ash pastes.

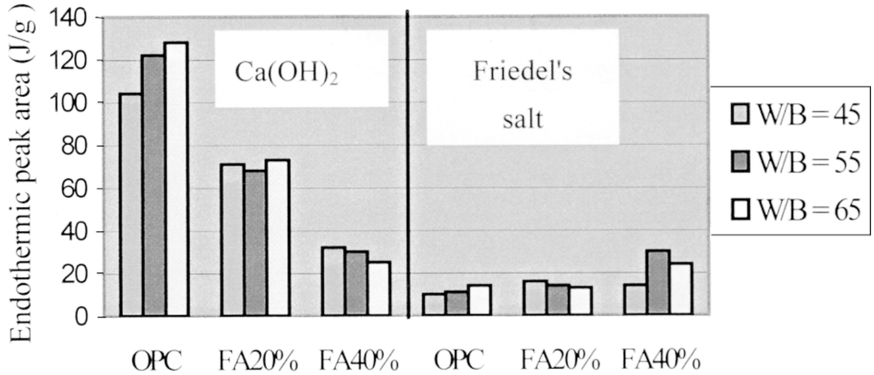

Fig. 5. DSC analysis for cement and cement-fly ash pastes (curing age: 1 year).

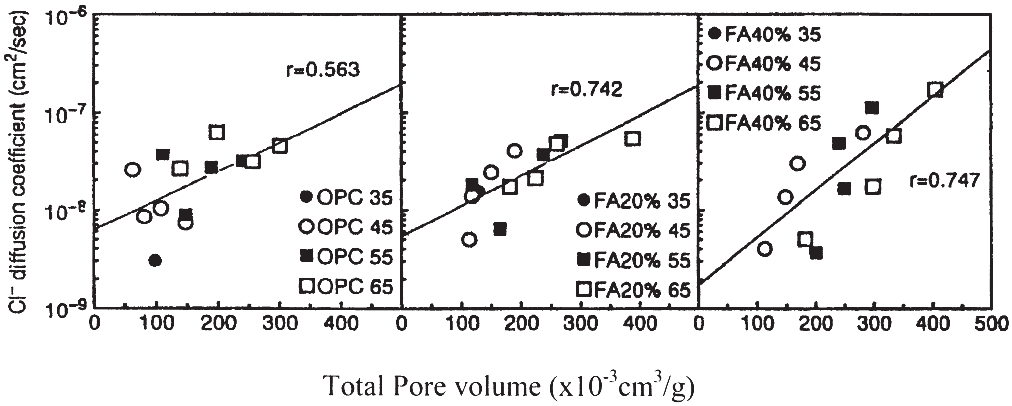

Fig. 6. Relations between Cl^- diffusion coefficient and total pore volume in cement and cement-fly ash pastes.

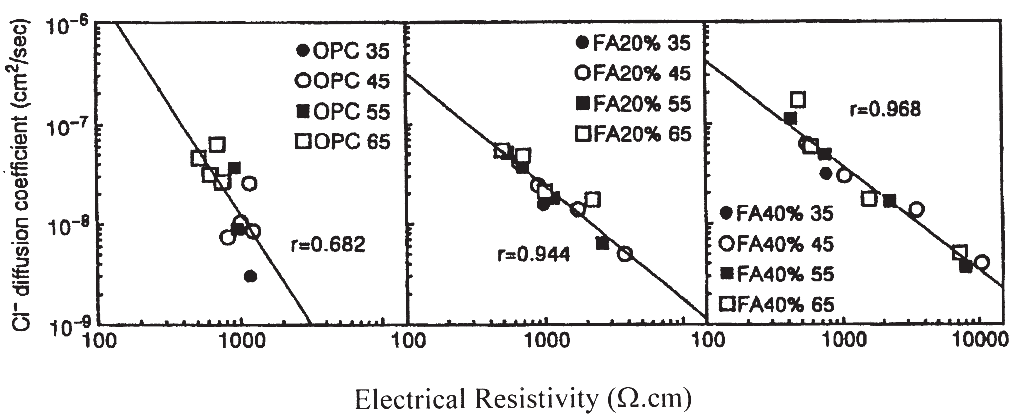

Fig. 7. Relations between Cl^- diffusion coefficient and electrical resistivity.

total pore volume. Thus the electrical resistivity of cement pastes could be used to predict D_{cl} in order to make the latter's measurement very simple due to the ease and nondestructive nature of the former's measurement.

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