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MEASUREMENT OF CHLORIDE PENETRATION INTO SILICA FUME CONCRETE

by

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ABSTRACT

Chloride induced corrosion is a major factor affecting the service life of concrete structures. The likely effect of using silica fume to reduce chloride penetration has been measured using a ponding type experiment and an electrical method. It is concluded that due to the special properties of the silica fume mixes the electrical test is not a reliable way of measuring the effect but they are less permeable than the OPC mixes.

INTRODUCTION

Chloride induced corrosion of the reinforcement is a major cause of deterioration of concrete structures. Increasing use of salt is especially damaging to road bridges. Silica Fume (sf) addition to ordinary portland cement (opc) concrete has been proposed as a solution. Tests based on electrical resistivity (1, 2, 3) indicate that sf concrete performs many times better than opc concrete. In this paper results from electrical measurements are compared with those from a simple ponding test. The effect of different curing conditions on chloride penetration resistance is also evaluated.

MIX DESIGN

Two sf mixes were tested with water/cementitious ratios of 0.3 and 0.46. These mixes had 20% of the cement replaced by sf supplied by Elkem Chemicals from Norway. Two control mixes with the same water/cementitious ratios but made only with opc were also tested. Details of the mixes are given in Table 1.

Mix	A	B	C	D
Cement (Kg/m^3)	344	430	252	315
Silica fume (Kg/m^3)	86	0	63	0
Water/(sf + opc)	.3	.3	.46	.46
Superplasticisers (% of sf + opc)	1.4	1.4	1.9	1.9
5-20 mm. aggregate/(sf + opc)	3	3	4	4
Fine aggregate/sf + opc	1.5	1.5	2.3	2.3
28 day strength (MPa)	113	80	88	55

Table 1 Composition of Mixes

A napthalene formaldehyde condensate superplasticiser was used to make the mixes workable and thus suitable for site use. The workability of all four mixes was 100 ± 15 mm.

Mortar was made with the same proportions without the coarse aggregate.

CURING CONDITIONS

Three different curing conditions were used.

1. Curing in fog room (20°C and 100% R.H.) until test age (CC1).

2. Treated with a curing membrane and stored at 20 degrees at 70 % R.H. for 7 days and then in water at 6 degrees (CC2).

3. Curing in water at 6 degrees (CC3).

The lowest temperature recommended by the suppliers for the placement and curing of Silica Fume concrete as a bridge deck overlay is 4.5°C (40°F) (1).

GRAVITY ASSISTED CHLORIDE DIFFUSION

Experimental Method

Concrete beams were cast in moulds 500 mm long by 100 mm square. A rebate 20 mm deep by 40 mm wide and 300 mm long was formed in the top of each beam. After curing, four 32 mm diameter holes were drilled in each beam in the bottom of the rebate just deep enough to form the shape of the tip of the drill (approximately 10 mm deep at the centre). A heavy rotary hammer drill was used. The rebate was then filled with saturated sodium chloride solution and the beam was kept at approximately 20 degrees centrigrade. After 28 days samples were drilled from the bottom of the holes and tested

for acid soluble chloride content by the titration method described in BS 1881, 1971 (4). The depth of drilling for samples was controlled by the drilling time because it was not possible to provide accurate direct control. The exact procedure for sampling was as follows:

1 Remove salt solution and wash off remaining salt with cold water.

2 Wait for concrete to surface dry at room temperature.

3 Drill for 10 seconds and discard dust.

4 Drill for 5 seconds and retain dust as sample 1 (approx 5 mm depth).

5 Drill for 5 seconds and discard dust.

6 Drill for 5 seconds and retain dust as sample 2. (approx. 10 mm depth).

This method produced samples of about 2-4 grammes. Material from the 4 holes in the same beam was mixed to provide sufficient for testing.

Calculation of results

The depth was calculated by weighing the total amount of material collected. (This method was checked by measuring with a vernier caliper for one third of the samples).

The penetration of chloride into the samples was caused by diffusion and gravity driven flow. If the permeability of the samples is assumed to be low the diffusion process will dominate. The solution to the equations for diffusion from a flat surface is a complimentary error function (5) and a good approximation to this can be obtained with an exponential which has the advantage that it can be integrated. The results were therefore calculated by fitting an exponential decay function to the two readings.

It was observed that the predicted concentration was near zero by 20 mm depth. The integral was therefore calculated over the range 0-20 mm and from it the average concentration in that area was obtained.

HIGH VOLTAGE CHLORIDE MIGRATION

Experimental method.

Mortar samples were tested for chloride transmission with a voltage of 40 volts applied across them. The penetration rate was recorded by measuring the current passing. This method is very similar to the FHWA test developed by Whiting (6). The apparatus used and test procedure has been fully reported by Cabrera and Lynsdale (7). A schematic diagram of the cell is shown in Figure 1. At the test age the samples were placed in the test cells with NaCl (30g/l) on the negative side and NaOH (12g/l) on the positive side. Before testing the 3 day (CC2) samples were saturated in water under an applied vacuum for 2 hours because they were dry. All other samples were wet from curing.

The current was recorded by measuring the voltages across 0.1 Ohm shunts in the circuit as shown in Figure 1. The temperature was also recorded with a thermocouple in the sodium chloride.

Calculation of results

A typical output of the raw data is shown in Figure 2. Correction for the effect of temperature on the resistivity has not been applied. If temperature correction was applied it would increase the spread of the readings because the samples with lower resistances generally reached higher temperatures.

The initial current, final current and total charge passing during the 6 hours of measurement were calculated. The lengths of the samples were measured and a small correction factor was applied to normalise the results to exactly 55 mm length, (i.e. if the length of the sample was 56 mm the

readings were multiplied by 56/55).

RESULTS AND DISCUSSION

Results

The chloride concentration value and the total charge passing with age at the time of testing are shown in Figure 3 and Figure 4. The relationship between the two is shown in Figure 5. Although the relationship between them which was observed by Whiting (6) is confirmed inspection of the data reveals that the major dependence of charge passing on the age and curing condition of the sf mixes is not reflected in the chloride sampling results. Figure 6 shows the relationship between initial and final current and it may be seen that this is different for the sf mixes when compared with the opc mixes.

The simplest way of comparing the results for the charge passing is in terms of the ratio between the charge passing through the control mix and that for the silica fume mix. The ratios for the high and low strength mixes at 28 days (cured at $20^{\circ}C$) are 26 and 7.5. These values are in line with those obtained by other workers. Table 2 shows the ratios reported for a concrete mix and for a cement paste, both cured at a temperature of at least $20^{\circ}C$.

Type of mix	% sf replaced	W/(sf + opc)	age days	Ratio	Reference
concrete	13	.33	28	14	Christensen et.al. (1984)
paste	10	.5	28	2.6	Li et.al. (1986)

Table 2. Examples of ratios (opc/sf) of charge passed..

Reports of chloride penetration carried out by ponding (gravity assisted) are not consistent. Wolsiefer (8) for example carried out tests using the FHWA ponding test and reported that chloride penetration in a sf mix similar to mix A (see Table 1), was 9 times less than the chloride penetration of a control opc mix but other data reported by Marusin (9) indicated that reductions were less than 50%. In the experiments reported in this paper the ratios of sf mixes over the opc mixes varied with the age of testing, curing condition and the type of mix. In general the ratio increased with age and decreased with temperature of curing. The ratios were higher for the low strength mixes. Values varied from 1.2 to 1.67 for mix B/mix A and from 1.22 to 2.65 for mix D/mix C.

While there is clearly a considerable variation between the types of samples used the data generally indicates that the results obtained from the electrical method give higher ratios than those from the gravity methods. For some types of macro-corrosion cell the electrical resistivity of the concrete will have a major direct effect on the corrosion rate independent of its influence on the chloride concentration. Thus the electrical cell gives only an indication of actual corrosion rates while the gravity systems give the true measure of the chloride penetration. It is of interest to consider the mechanism of the electrical experiment to see why it gives a low reading for permeability.

The mechanism of conduction of d.c.
It has been established (10) that the conduction is almost all through the pore water, conduction through the cement matrix and aggregate is negligible. (It has been observed by Hansson (11) that a closed pore structure would allow almost no current). Thus the current at the cathode may be assumed to be largely composed of chloride ions migrating towards the

sample. Assuming normal isotope concentrations the ions will have an average mass of 35.5 atomic units i.e. 5.94 E-26 Kg and one electronic charge i.e. 1.6 E-19 coulomb. Thus for each Coulomb of charge recorded 0.37 mg of chloride ions will enter the sample.

When the ions have entered the sample the situation becomes more complicated. Each ion will penetrate a given distance and then stop. Whiting (6) measured the concentrations of chloride in samples after the diffusion test and found that they decay to zero within the thickness of the sample and do not extend to the opposite face. From the point where the chloride ion stops another ion such as an hydroxyl ion must start in order to conduct the electron to the anode.

The precise point at which the ion stops will be dependent on the existing concentration and other factors such as the ability of the matrix to bind the ion. If the only factor is the initial concentration the current may be expected to increase linearly with time. (The resistance must be lower in the areas with chloride in them or the ions would go straight through). Whatever the final distribution is, it follows that the first ions to enter the sample will initially stop at the surface. Thus the initial current will be dependent on the mobility of the ions already in the sample (primarily hydroxide ions) and not the chloride ions.

It may be seen from Figure 6 that the current flow in the opc samples increases during the test indicating that the main controlling factor is the extent of the existing penetration into the sample. For the sf samples, however, it decreases, especially for the samples with high current flow, indicating a different mechanism. It is proposed that this mechanism is the depletion of hydroxide ions. This would explain the strong dependence on

age and curing condition because the supply of these ions will be reduced with the progress of the pozzolanic reaction. This depletion is purely a property of the electrical test and has no direct connection with the chloride permeability under normal circumstances.

EFFECT OF CURING CONDITIONS

Figures 3 and 4 show the chloride concentration and the total charge passed for the three test ages. It can be seen that the resistance to chloride permeability increased with age and decreased with increases in w/opc+sf ratio for any of the curing conditions.

It is also evident that curing at 20°C and 100% R.H. provides the best environment for resistance to chloride ingress.

The results at 90 days of age show that the worst condition for chloride ingress as measured by the electrical method is curing condition CC3. When the resistance is measured by the ponding test, condition CC2 and CC3 gave the worst results. It is interesting to note that even at the worst curing condition (CC3) sf addition provides a mix with higher resistance to chloride penetration than a mix with higher cement content and lower w/c ratio, i.e., mix C compared with mix B.

CONCLUSIONS

1 A simple measure of chloride penetration into concrete has been obtained by filling drilled holes with chloride solution and sampling by continuing drilling with the same bit.

2   The results from comparing the gravity assisted chloride penetration test with the electrical test show that the relationship between charge passing in the rapid chloride permeability test and chloride penetration into opc samples does not hold for silica fume samples. The reason for this difference is that the current is controlled by the hydroxide ions in the silica fume samples and by the chloride ions in the opc samples.

3   Both tests however, indicate that the silica fume replacement reduces the chloride permeability of the concrete mixes.

4   Low temperature water curing or curing membrane protection at 70% R.H. increase chloride ingress at all testing ages.

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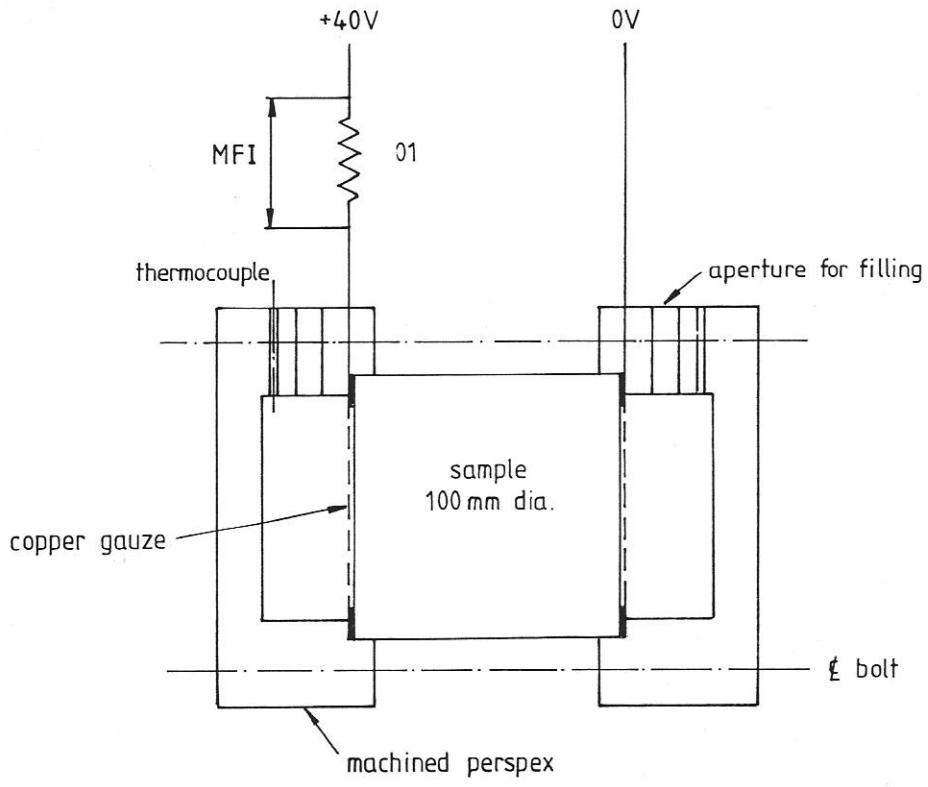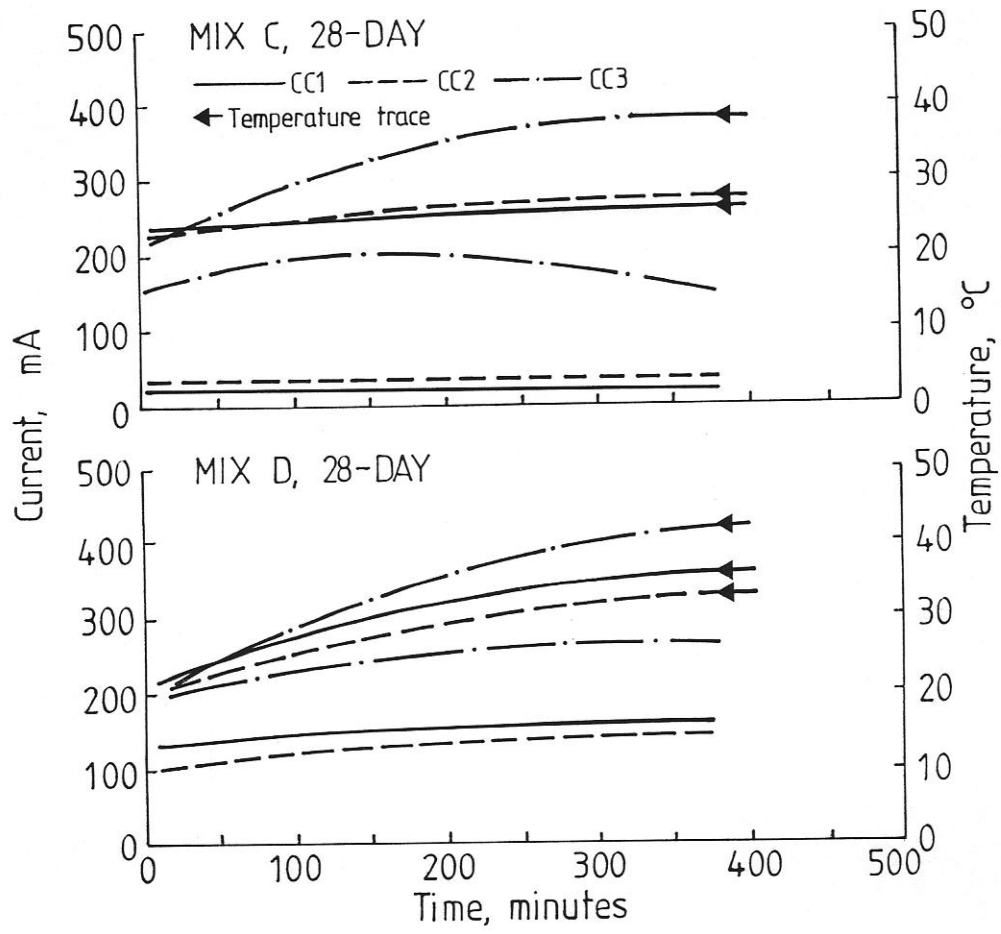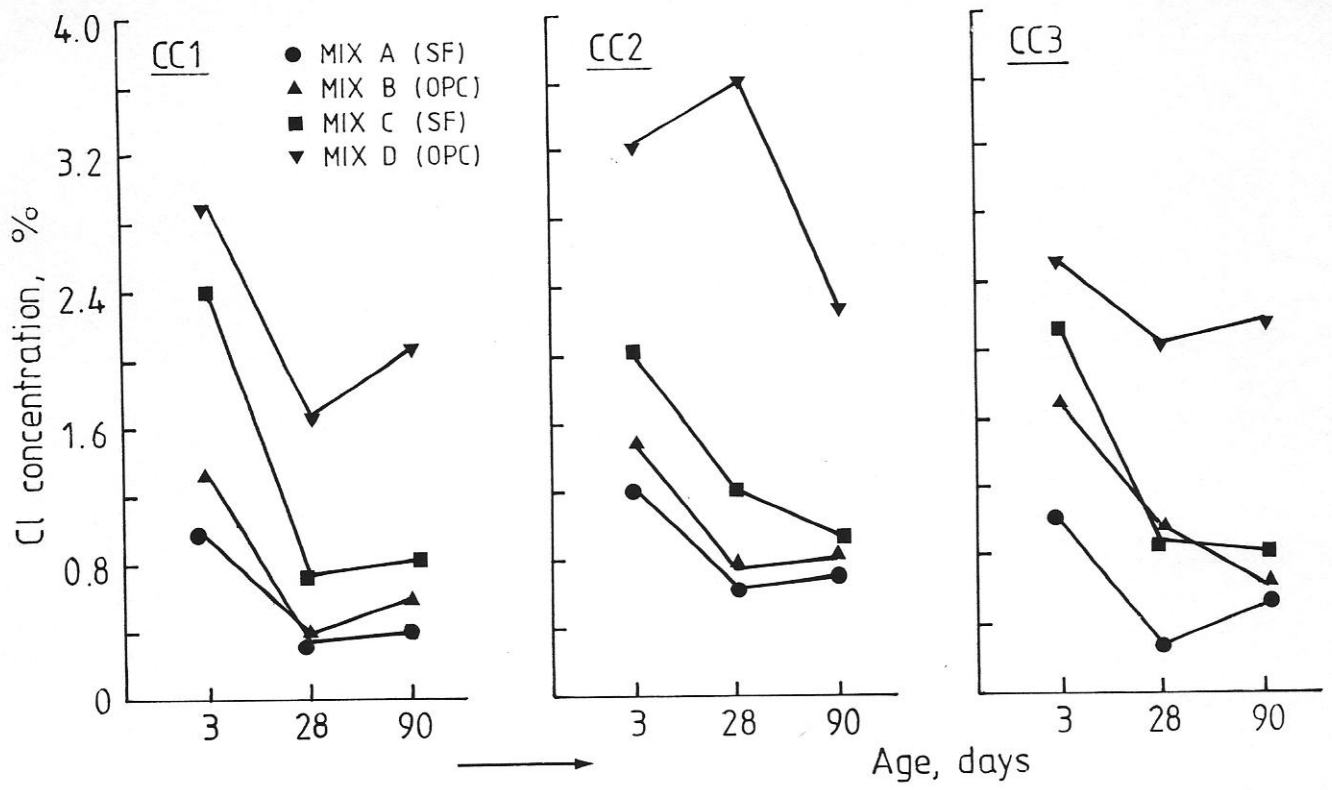
Fig 1

FIG1

Fig 2

FIG2

Fig 3   FIG3
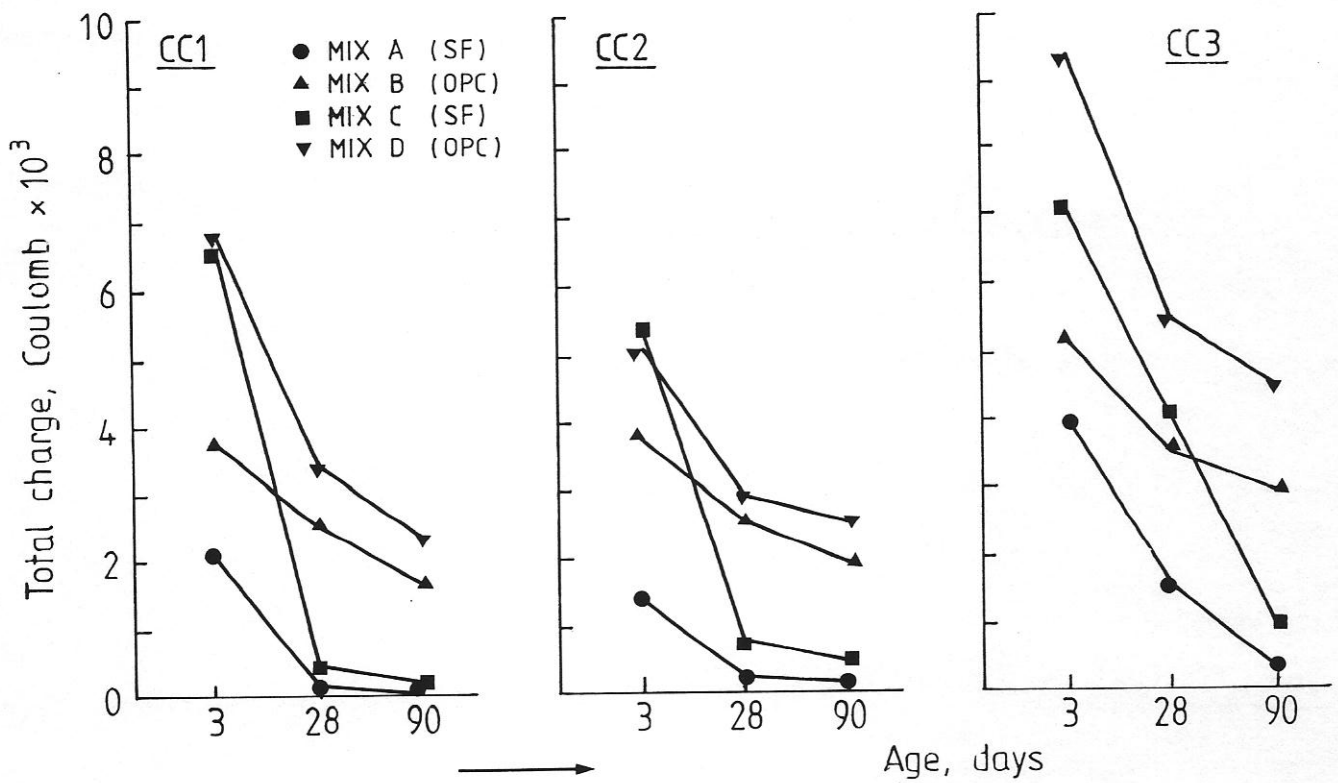

Fig 4   FIG4

MIX A (SF)
MIX B (OPC)
MIX C (SF)
MIX D (OPC)

Equation for line:
$Y = 386.15 + X = 1858.3$
$R^2 = 0.478$

Fig 5 FIG5

MIX A (SF)
MIX B (OPC)
MIX C (SF)
MIX D (OPC)

Equation for line: $Y = X$
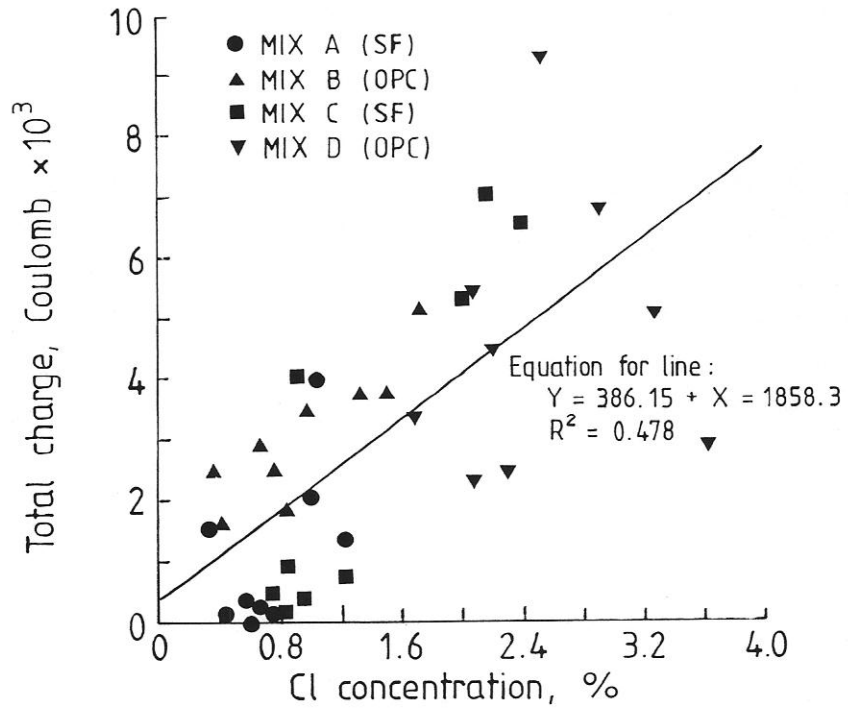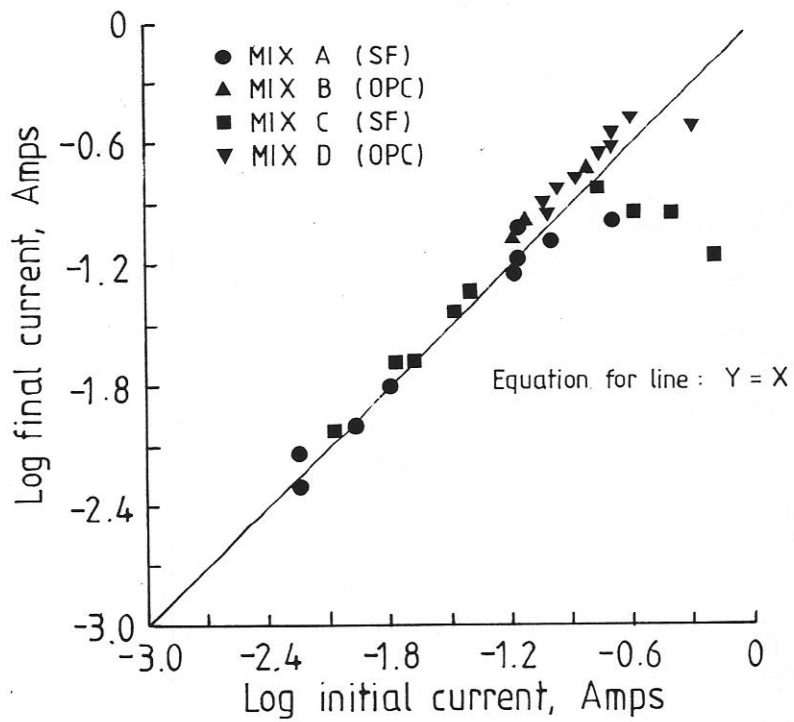
Fig 6 FIG6

FIGURE TITLES

Figure 1.   Sample holder for high voltage chloride permeability test

Figure 2.   Typical outputs from the high voltage chloride test apparatus

Figure 3.   Average chloride concentration in the depth range 0-20 mm
             expressed as a percentage of the weight of opc+sf

Figure 4.   Total charge passing during the six hours of testing with an
             applied voltage of 40 Volts

Figure 5.   Relationship between the two measurements of chloride
             penetration. The graph shows total charge passing vs. average
             chloride content within 20 mm thickness expressed as a
             percentage of total cementitious content.

Figure 6.   Relationship between initial and final current for the high
             voltage experiment.