

## THE USE OF FLY ASH TO IMPROVE THE CHLORIDE RESISTANCE OF CEMENT MORTARS

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### ABSTRACT

This paper presents a laboratory study on the strength and chloride penetration resistance of fly ash and ordinary portland cement concretes and mortars. The concrete mixes were 30/20 structural concrete with different workabilities with target slump values of 50, 75 and 125 mm. The mortar specimens were sieved from the site concrete mixes and cured for various ages before exposure to a sodium chloride water solution.

Two laboratory techniques of chloride exposure were used to assess the behaviour of opc and opc/fa mortars. These were the intermittent test and the continuous capillary absorption test. The exposure to chloride salt in the laboratory was an attempt to simulate site exposure conditions, i.e. splash zone in road bridges and direct contact with wet contaminated soil. In each case the chloride concentration profile was obtained at different exposure periods and used for the calculation of chloride diffusion coefficients.

The results of the study confirm the unique advantage of fly ash as a workability enhancer, i.e. reduction of the water content without impairing the concrete workability. The results show that the concrete with and without fly ash achieves approximately the same strength at the age of 28 days. It is found that the coefficient of diffusion is not dependent on the method to salt exposure and most importantly that even at short ages the use of fly ash enhances the chloride penetration resistance of concrete. This technological advantage is enhanced by the environmental impact caused by using fly ash which, on the one hand reduces the energy required to produce concrete, and on the other, avoids the disposal of fly ash as inert waste.

## Introduction

In many civil engineering materials applications the use of industrial waste is not only environmentally desirable, but it is beneficial in technological terms, since wastes used in appropriate circumstances can and do improve the properties of materials for construction.

Durable concrete demands resistance to aggressive environments. Reinforced concrete not designed for the appropriate environmental conditions may sustain chemical or/and physical damage, which in the event leaves the reinforcing steel unprotected and susceptible to corrosion. The resistance to fluid and ion penetration is directly related to the permeability and diffusion properties of concrete. In turn these properties are strongly affected by the pore structure characteristics, the degree of hydration and the nature of the cement hydrates. A durable concrete is defined as that which exhibits adequate and expected performance during its design life. This definition is not related to the environmental conditions and therefore, it is implicit within it that the performance level required increases as the environment becomes more aggressive.

Designing for performance not only requires designing for strength, but also designing for resistance to fluid and ion penetration. The measurable parameters are then intrinsic permeability and diffusion coefficient. Permeability is measured by monitoring the rate of fluid flow which occurs due to a pressure gradient (1). It is calculated by assuming non-turbulent flow and using the Darcy's numerical model (2). Because ions move within concrete in a solvated state, permeability gives a good indication of the resistance of concrete to ion penetration (3).

Diffusion is defined as the process of ion movement through a solid which is caused by a concentration gradient. The rate of ion movement is used to calculate the diffusion coefficient by using the first (steady state) or second (non-steady state) Fick's Law.

In practice the movement of ions occurs through a combination of pressure and concentration gradients and therefore it is important to be clear on what it is that a test indicates with reference to the potential durability of concrete.

Chloride ions in solution penetrating concrete may reach the reinforcing steel and initiates a process of corrosion which eventually leads to the loss of steel section and reduction of serviceability of the reinforced concrete (4, 5).

Exposure to chlorides occurs by:

- a) continuous exposure of the concrete surface to salt laden water,
- b) by intermittent splashing of salt water,
- c) by chlorides carried by wind in a solvated state, particularly close to sea shores.

These different exposure modes may result in different chloride concentrations at the concrete surface and depending on the moisture content of the concrete, might penetrate the concrete by diffusion and/or permeation with the additional complication that if the concrete is dry, capillary water absorption will occur.

To reduce the rate of chloride penetration, concrete should be designed for minimum total porosity particularly by reducing the capillary voids (6, 7) and by providing a “chemical trap” so that chlorides can be immobilised by reacting with the hydrated phases forming the walls of the concrete voids.

It is now accepted that the best method to reduce the rate of ion penetration into concrete is to use water reducing agents and/or pozzolanic or hydraulic additions (8, 9).

This paper evaluates the effect of fly ash on the chloride resistance of concrete exposed to salt water and presents diffusion measurement data under two simulated exposure conditions:

- a) intermittent splashing,
- b) capillary-osmosis absorption

The paper explores the effect of fly ash replacement on the water demand of concrete designed to different workability levels. Finally, it discusses the environmental and durability consequences of using fly ash to produce concrete.

### **Materials and Sample Preparation**

Specimens for the study were prepared from in-situ structural concrete mixes used in the construction of Drax power station in the North of England (10). The mixes contained 33% (by weight) fly ash as cement replacement. Three specific workabilities of 50, 75 and 125 mm, as measured by the slump test, were used in this study. For control purposes, opc concrete mixes of similar workabilities were also made and tested. Details of the different mix constituents are given in Table 1.

The effect of fly ash inclusion on reducing the water demand without impairing the workability of concrete has been acknowledged for a long time. In fact the mix design concept proposed by Cabrera in 1985 (11) and used by Hassan et al (12) in a recent design procedure is based on the effectiveness of fly ash to reduce water demand without impairing workability. Hassan et al showed that a 10% replacement of opc by fly ash will reduce the water demand by 3-4%.

The mixes designed for this study show that the reduction of water to maintain constant workability (see Table 1) increases when the target workability increases. i.e. for the mix with 50 mm slump 10% opc substitution gave a 4% water reduction, while for the mix with 125 mm slump, the water reduction per each 10% substitution was 6.4%.

Mortars were sieved from the different concrete mixes and cast into 100 mm cubes. The mortar cubes were cured for a period of either 3 or 28 days according to BS 1881 (13). The cubes were then stored in an environmental chamber maintained at 20°C and 65% relative humidity until the age of 77 days prior to chloride exposure.

## **PROGRAMME OF TESTING**

### **Compressive Strength**

Mortar and concrete cubes (100 mm side) were used to measure compressive strength for the different mixes studied in this programme. The test was carried out in accordance with BS 1881: Part 116 (14).

### **Intermittent Splashing**

An apparatus was designed to discharge by fine overhead spray a small amount of 3.2% sodium chloride and water solution, this is shown in Figure 1. The mortar cubes were placed on an open grid set in a shallow bath. Mounted overhead were 12 No. spray heads connected to a header tank and compressed air supply. A bulk storage tank with internal agitator contained a 3.2% sodium chloride solution which continuously filled the smaller header tank. An electrically time control system caused the overhead spray to operate at 15 minute intervals, dousing the cubes arranged below. The solution then ran to waste.

The splashing test was completed in a stable 20°C environment. Each series of tests, which ran through 84 days, contained an equal number of fly ash and ordinary Portland cement cubes. The chloride concentration profiles were measured at exposure ages of 14, 28, 56, 70 and 84 days.

### **Capillary Osmosis Absorption Test**

For the continuous exposure condition a simple metal bath was prepared and fitted with an internal plastic support. The mortar cubes were placed upon the support and all adjacent faces of all cubes and the cube tank sides were sealed with a polymer sealing compound to exclude air. A clear plastic tube was fitted to the bath to allow filling to the underside of all cubes with a 3.2% solution of sodium chloride. This arrangement is shown in Figure 2. At intervals of 14, 28, 56, 70 and 84 days the cubes were tested for chloride content at different depths so that a concentration profile could be obtained.

### **Chloride Concentration Profile**

After the desired exposure period, the cubes were removed from the chloride environment and carefully wiped dry with clean tissue, before sample drilling. Powder samples were collected from the surface down to depths of 0-10 mm, 10-20 mm and 20-30 mm using a Hillti hammer with 12 mm diameter drill. The procedure was repeated for cubes prepared with 50, 75 and 125 mm slumps. The powder samples obtained from each experimental set up were mixed with boiling water and tested for chloride content using the Quantab titration methods (15).

The Quantab titration method used in this work was checked against X-ray spectrometry on samples taken from the mortar cubes. Figure 3 plots results of the two methods giving a correlation of 0.714. When major outliers were excluded a correlation of 0.894 was obtained. This confirmed that the Quantab Titration method is an acceptable method for determining chloride concentration in this experimental series.

## RESULTS

### Compressive Strength

The compressive strength results, moisture contents and densities of the concretes and mortars are given in Table 2, the compressive strengths are also presented graphically in Figure 4. Typically the lower water/cementitious ratio mix gave higher compressive strength and the opc mixes gave high compressive strength when compared with the pfa mixes at 7 days and comparable strengths at 28 days. It is clear that the difference in strength is narrowed down with time from 7 to 28 days and from other research (11, 17) it is expected that at a later age the pfa mixes will eventually give higher strength than the opc mixes.

### Chloride Penetration

The chloride concentration profiles for the different opc and opc/fa mortars were obtained after 84 days of exposure to chloride environments either by splashing or capillary absorption. Typical examples for the chloride concentration versus depth are shown in Figure 5 and 6. The results show that the chloride concentration decreases across the mortar depth.

The chloride distribution with depth of the specimen is a decay function, which can be statistically represented by the following expression:

$$Cl = ae^{bd} \quad (1)$$

Where:

- Cl = chloride concentration
- d = mortar depth
- a,b = constants
- e = natural logarithm base

The chloride diffusion coefficients are then calculated using the following expression:

$$\frac{C_x}{C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2)$$

Where:

- $C_o$  = the chloride concentration at the surface of the specimen  
 $C_x$  = the chloride concentrations at depth  $x$  of the exposed surface of the specimen  
 $D$  = diffusion coefficient  
 $t$  = time  
 $\text{erf}$  = the error function (16)

The diffusion coefficients of the different opc and opc/fa mortars cured for 3 days or 28 days are listed in Table 3.

## DISCUSSION

### Water Demand and Strength

Replacement of a proportion of cement with fly ash modifies the rheology of plastic concrete allowing a reduction in water demand for the same workability (17). Based on the results given in Table 1, a statistical equation with  $r^2 = 0.99$  was obtained. This equation can be used to determine the approximate water reduction for any target slump when designing trial mixes. The equation is:

$$R_w = 9.7 + 0.08 (S) \quad (3)$$

Where:

- $R_w$  = water reduction (%)  
 $S$  = slump (mm)

This equation is presented graphically in Figure 7.

Since for any concrete the water/cementitious ratio limits the maximum strength achievable (11) it should be expected that in the short term (28 days) the compressive strength of the fly ash mixes should equal the strength of the equivalent opc mixes, since in reality, there is a trade off between reduction of opc and reduction in  $w/c + fa$  ratio, i.e. less opc lower strength. but lower  $w/c+fa$  ratio higher strength.

In the long term (beyond 28 days) the reaction between fly ash and the lime generated by the hydration of cement reduces the porosity of the concrete and most importantly reduces the average pore size, leading to higher strength and improvements in performance related parameters (11, 18). Table 2 shows that the strength of the opc and opc+fa mixes at 28 days is statistically approximately the same. It also shows the effect of increasing the water cementitious ratio. An increase from 50 to 125 mm slump ( $2\frac{1}{2}$  times) reduces the strength by one third on the opc concrete, but only by a quarter in the opc-fa concrete. This is the result of the lower water cementitious ratio of the fly ash concretes and mortars.

## Chloride Diffusion

The chloride concentration on the surface of the specimens tested was found to be different in the two tests carried out. The surface chloride concentration on the specimens subjected to capillary absorption were higher than the chloride concentrations of specimens subjected to the intermittent splash experiment.

However, the most important finding was that the diffusion coefficient calculated from any of the tests carried out was approximately the same and was not affected by the estimated surface concentration. Figure 8 shows that statistically the diffusion coefficients are the same for both modes of exposure. Thus the idea that the exposure mode affects the value of the chloride coefficient of concrete is not supported by the findings of this study.

The results presented in Table 3 show that even at short age, before the beneficial effect of the fly ash lime reaction has taken place, the chloride diffusion coefficient of the opc concrete is reduced by at least 25% for low workability (50 mm slump) to 42% for the high workability (125 mm slump) when fly ash is used. This reduction in terms of enhanced service life is considerable, to say the least.

Apart from this obvious technological advantage, fly ash that is not utilised is disposed of in landfill sites for which there is a cost, this becomes unnecessary if all available fly ash is incorporated into concrete. The energy reduction arising from the reduction of cement content is also considerable as has been shown in reference (19).

## CONCLUSIONS

From the results of the short term laboratory experiments the following conclusions are offered:

1. Fly ash replacing part of the ordinary portland cement in concrete reduces the amount of water required to maintain a target workability value. This reduction increases as the workability increases.
2. Concrete mixes designed to a target workability show that at 28 days of age, 33% replacement of opc by fly ash gives approximately the same compressive strength as opc mixes.
3. The chloride diffusion coefficient of opc concrete is reduced from between 25% to 42% by the substitution of opc by fly ash. The beneficial effect of fly ash is enhanced for mixes with high water-cementitious ratio.
4. The incorporation of fly ash in concrete results not only in a better durable material but reduces the energy required to produce concrete, thereby reducing pollution levels arising from the high temperatures required to produce clinker. Furthermore, the problems associated with the disposal of fly ash in landfill sites are potentially eliminated.

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Table 1. Mix constituents of opc and opc/fa concrete.

Slump (mm)	OPC Concrete				OPC/FA concrete					reduction in water content (%)
	w/c ratio	opc	sand	gravel	w/c ratio	opc	fa	sand	gravel	
50	0.52	300	700	1220	0.45	200	100	700	1220	13.5
75	0.56	300	700	1220	0.47	200	100	700	1220	16.1
125	0.62	300	700	1220	0.49	200	100	700	1220	21.0

Table 2. Compressive strength of opc and opc/fa mortars and concretes.

50 mm slump	At 7 days of age			At 28 days of age		
	Compressive strength (MPa)	Moisture Content (%)	Wet Density (kg/m <sup>3</sup> )	Compressive strength (MPa)	Moisture Content (%)	Wet Density (kg/m <sup>3</sup> )
opc mortar	49.1	6.35	2260	60.8	5.85	2250
opc/fa mortar	37.7	6.70	2249	55.0	6.20	2249
opc concrete	47.5	5.00	2440	57.6	5.00	2443
opc/fa concrete	40.3	4.50	2434	49.6	4.50	2420
75 mm slump						
opc mortar	43.8	7.10	2219	50.9	6.70	2235
opc/fa mortar	36.7	7.40	2230	48.2	7.15	2217
opc concrete	39.6	4.60	2432	52.3	4.00	2448
opc/fa concrete	34.2	4.80	2422	48.1	4.50	2417
125 mm slump						
opc mortar	33.0	7.40	2203	47.8	6.90	2213
opc/fa mortar	23.8	7.45	2228	43.6	6.65	2208
opc concrete	32.0	-	2468	42.6	4.50	2415
opc/fa concrete	25.6	-	2423	37.5	5.5	2400

Table 3. Non-steady state chloride diffusion coefficients.

	Slump (mm)	OPC mortar $\times 10^{-11}(\text{m}^2/\text{sec})$		OPC/FA mortar $\times 10^{-11}(\text{m}^2/\text{sec})$	
		3 days curing	28 days curing	3 days curing	28 days curing
SPLASH TEST	50	2.31	2.59	2.29	1.82
	75	1.79	1.57	1.40	1.66
	125	4.05	3.50	2.77	1.81
CAPILLARY ABSORPTION TEST	50	2.00	2.38	2.34	1.80
	75	1.47	2.07	1.28	1.52
	125	5.01	3.42	2.85	2.11

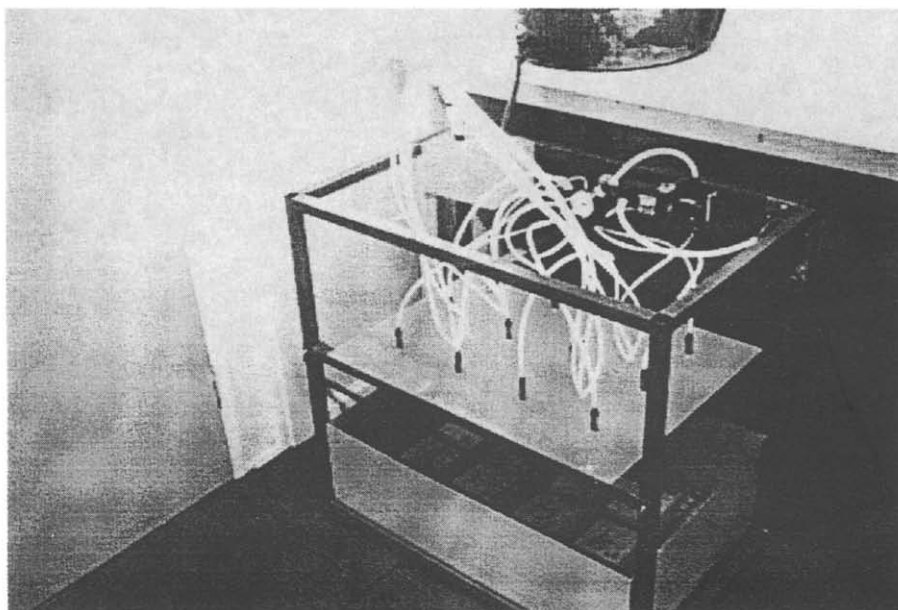


Figure 1. Intermittent splashing apparatus.

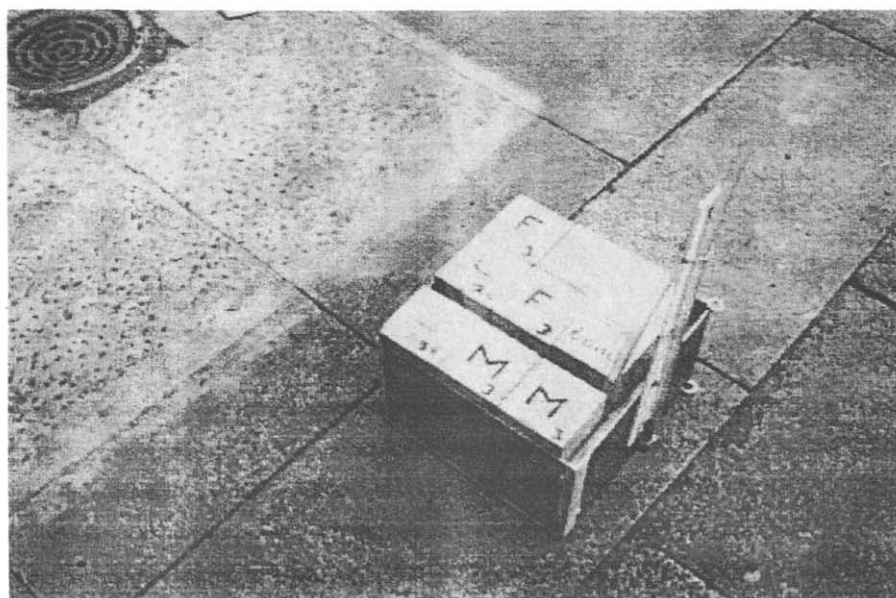


Figure 2. Capillary-osmosis absorption set-up.

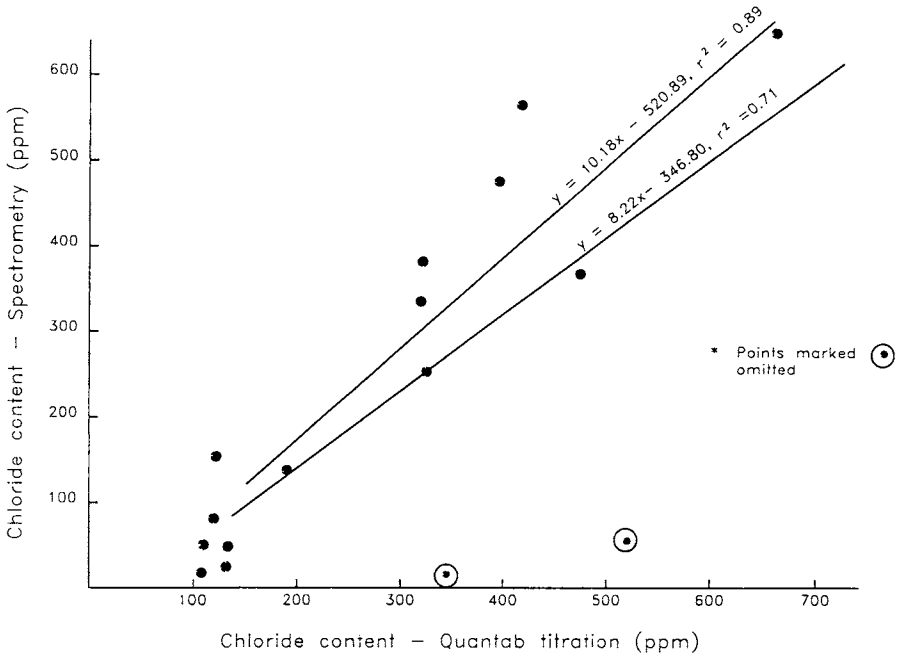


Figure 3. Relation between chloride results from spectrometry and quantab titration.

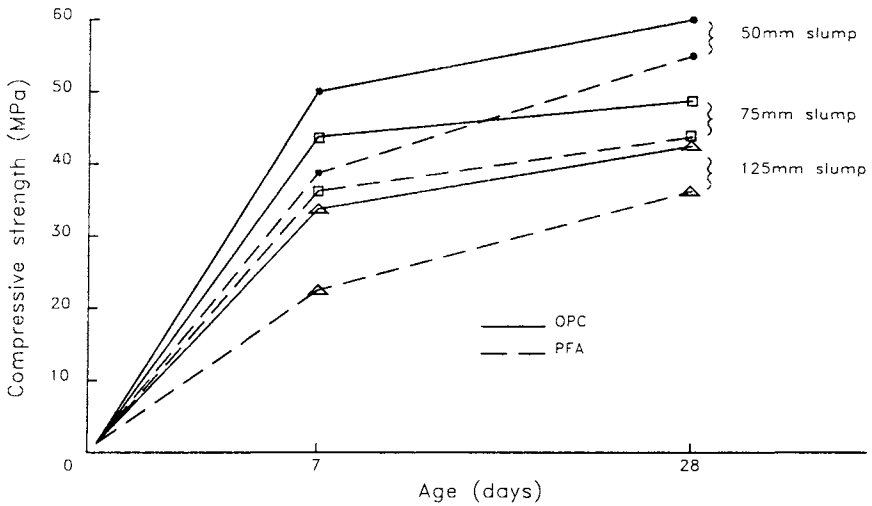


Figure 4. Compressive strength of opc and opc-pfa concrete mixes.

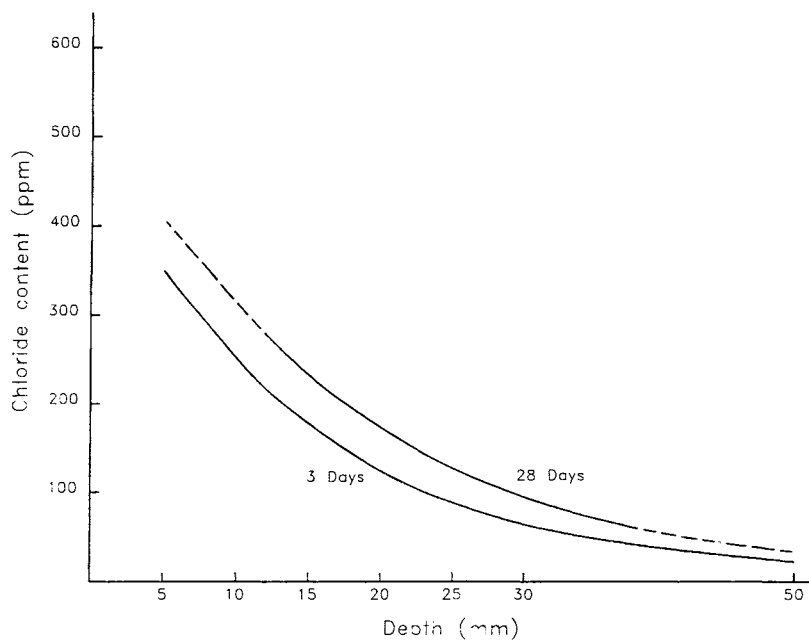


Figure 5. Typical chloride profile of specimens exposed to the splashing environment.

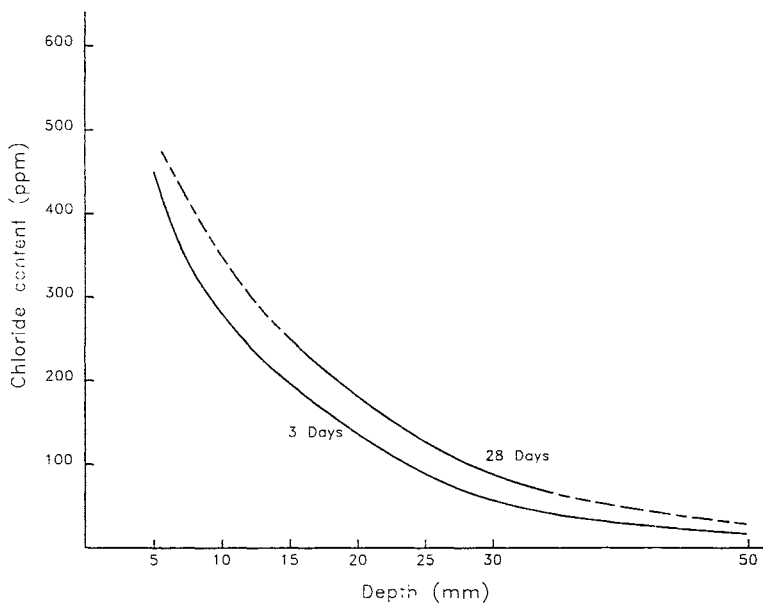


Figure 6 Typical chloride profile from specimens exposed to the capillary osmosis environment.

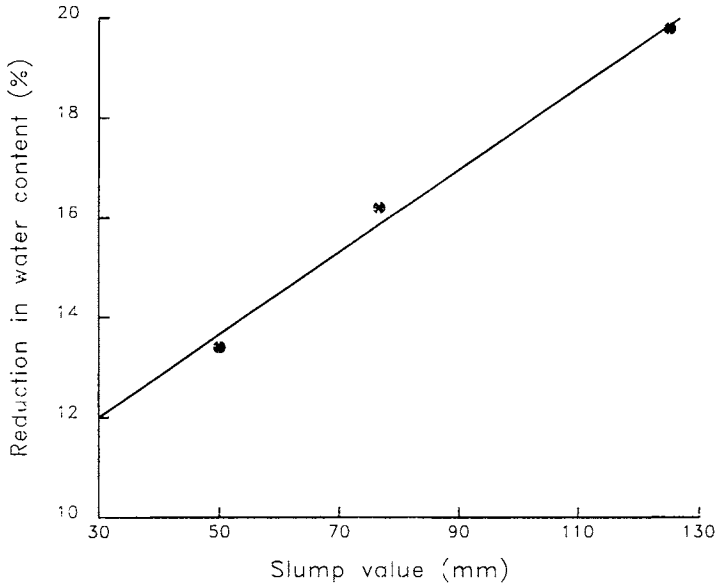


Figure 7. Relation between reduction in water content (arising from substitution of opc by fa) and slump value of concrete.

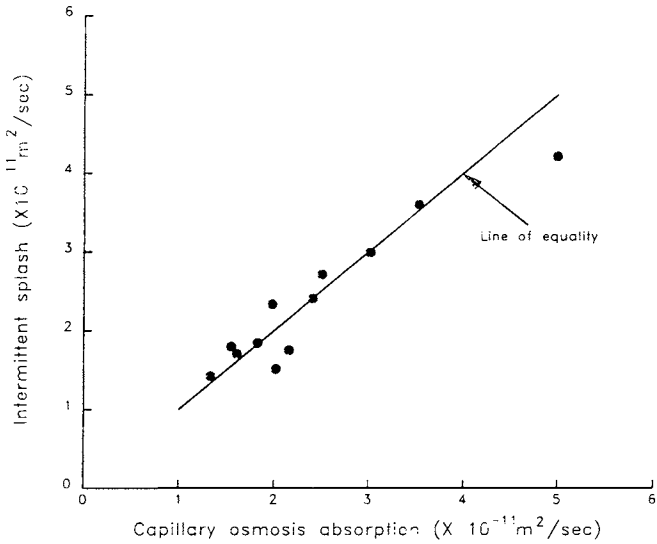


Figure 8. Relationship between chloride diffusion coefficients obtained from splash and capillary absorption tests