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EFFECT OF WATER/CEMENT RATIO, POZZOLANIC ADDITION AND CURING TIME ON CHLORIDE PENETRATION INTO CONCRETE

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Abstract

Concrete specimens with different water/cement ratios with and without fly ash or silica fume, and different curing times have been manufactured and then immersed in a 10% $CaCl_2$ aqueous solution. Chloride penetration has been tested in concrete specimens.

The results of the present work indicate that:

a) since the intrinsic properties of concrete such as porosity and permeability are changing during the immersion in the chloride solution, the experimental values of chloride penetration deviate from the theoretical curve of Fick's law, particularly when young concretes are tested;

b) the lower the water/cement ratio, the lower the chloride diffusion coefficient;

c) the longer the curing time, the lower the chloride diffusion coefficient;

d) even with early curing time such as 3 days, chloride penetration is dramatically reduced provided that a very low water/cement ratio, such as 0.32, is adopted;

e) the combined addition of superplasticizer and silica fume or fly ash furtherly reduces chloride penetration.

1. Introduction

It is well known that chloride can attack both concrete (1-3) and steel (4,5) in reinforced concrete structures. This occurs, for instance, in concrete marine structures or highway concrete structures exposed to de-icing salts based on sodium or calcium chloride.

Chloride can penetrate concrete by diffusing through the continuous pore system of the cement paste enveloping the aggregates (6-8).

There are two types of porosity wihich can affect chloride diffusion into a concrete: macroporosity, due to a defective compaction of fresh concretes, and capillary porosity, mainly due to the presence of free water. There are chemical admixtures (superplasticizers) which reduce macroporosity since they make concrete more workable and compaction easier, even with moderate vibration or, in some cases, with no vibration at all. Moreover they can reduce capillary porosity considerably by decreasing the water cement ratio. Equation [1] based on the Powers theory (9), indicates the percentage of capillary pores (V_p) by volume of cement paste as function of the water/cement (w/c) ratio and the degree of cement hydration (a):

$$V_p = \frac{w/c\ 100 - a\ 36.15}{w + 100/g}\ 100 \qquad [1]$$

where g (in g/cm^3) is the cement specific gravity and w is the amount of mixing water (kg) per 100 kg of cement.

Capillary porosity can be reduced by decreasing the w/c ratio and/or by increasing the curing time which in turn increases the degree of hydration. This means that low capillary porosity can be obtained even in concretes at earlier curing times, provided that very low water/cement ratios compensate the lower degree of hydration caused by the shorter curing.

Reduction in porosity causes reduction in concrete permeability and therefore increases durability, since aggressive agents penetration is remarkably decreased.

Highly workable concrete, therefore easily compactable even in heavily reinforced structures and under poor vibration, manufactured with low water/cement ratio and extensively cured, produces a durable structure. Several standards, or recommendations of technical committees, state the adequate water/cement ratio according to the degree of attack of aggressive agents. As a general rule, if concrete is fully compacted and sufficiently cured, a water/cement ratio in the range of 0.40 to 0.50 provides durable structures (10).

However, in some exceptional cases, such as concrete for bridge decks exposed to the severe action of deicing salts, a particularly durable concrete, with very low water/cement ratio, such as 0.32, is recommended by the ACI Committee 201 (10).

Moreover, even with "normal" aggression (were a water/cement ratio in the range of 0.40 to 0.50 is generally sufficient to guarantee durability provided that a long curing has been carried out) a very low water/cement ratio, such as 0.32, may be needed to obtain an "early" durability, if an extended curing time such as 28 days is not practicable. That is the case, for instance, in sea underwater pours, where chloride penetration could be soon prevented only by concrete watertightness achieved in a few days because of a very low water/cement ratio. Moreover, also in "normal" works the curing time is hardly ever prolonged over 7 days so that even a w/c ratio in the range of 0.40 to 0.50 may not be sufficient to guarantee durability because of the relatively low degree of cement hydration at the time of concrete exposure to aggressive agents.

The purpose of the present work was to verify if the use of superplasticizers could allow the manufacture of flowing concretes which are able to resist chloride penetration even after a short curing time such as 3 days. Moreover the effect of artificial pozzolans such as fly ash and silica fume, on chloride penetration has been examined since these materials should be able to furtherly reduce capillary porosity due to the combination with calcium hydroxide - produced by cement hydration - by transforming it into calcium silicate hydrate.

2. Experimental

Three concrete mixes with the same cement content (400 kg/m^3) and different amounts of mixing water (320-175-129 kg/m^3) have been manufactured. In order to keep the same level of workability (slump of 220 mm), different dosages of a superplasticizer (0-1.1-2.5% by weight of cement) have been used to compensate the reduction in mixing water. Table 1 indicates mix proportions and compressive strength of mixes A, B, and C with w/c of 0.55, 0.44 and 0.32 respectively. As concrete components have been used: Portland cement, sand with a fineness modulus of 2.60, gravel with a maximum size of 20 mm, and a superplasticizer based on a 40% aqueous solution of naphthalene sulfonated polymer.

Table 1
Mix proportions and strength of concrete mixes in the absence of fly ash and silica fume (slump = 220 mm)

MIX	A	B	C
Cement (kg/m^3)	398	400	403
Water (kg/m^3)	220	175	129
Superplasticizer (% by weight of cement)	0.0	1.1	2.5
w/c ratio	0.55	0.44	0.32
Compressive strength (MPa) at:			
1 day	15.1	24.9	40.1
7 days	39.9	55.0	70.4
28 days	45.1	60.1	80.2
90 days	52.3	69.2	88.3

In a second set of concrete mixes fly ash or silica fume have been used. About 60 kg/m^3 of fly ash or silica fume have been used as additional components without any reduction in the cement content. The dosage of the superplasticizer has been adjusted in order to obtain the same w/c ratio (0.44) and the same slump (220 mm) as those of the mix B. Table 2 indicates the mix proportions and the compressive strengths of this second set of concrete mixes (D and E) in comparison with the concrete mix having the same w/c ratio and slump but without fly ash or silica fume (mix B).

At a curing time of 3 or 28 days concrete specimens were put in contact with a 10% $CaCl_2$ aqueous solution. After a certain period of time, the concrete specimens were splitted and the chloride penetration depth was evaluated (6) by spraying fluoresceine and $AgNO_3$ aqueous solution on the fractured surface. Because of this treatment, the concrete area penetrated by chloride ions became pink coloured, whereas the area which is chloride free became dark coloured.

Table 2

Mix proportions and strength of concretes in the presence of fly ash or silica fume (slump = 220 mm)

MIX	B	D	E
Cement (kg/m^3)	400	398	401
Water (kg/m^3)	175	175	175
Fly ash	---	60	---
Silica fume (kg/m^3)	---	---	58
Superplasticizer (% by weight of cement)	1.1	1.5	1.8
w/c ratio	0.44	0.44	0.44
w/b* ratio	0.44	0.38	0.38
Compressive strength (MPa) at:			
1 day	24.9	26.1	26.9
7 days	55.0	60.3	65.3
28 days	60.1	68.3	74.9
90 days	69.2	75.0	86.3

* b = binder = cement + fly ash (or silica fume)

3. Results

The chloride penetration into the concrete follows the Fick's law (6-8)

$$J = -D \frac{dC}{dx} \qquad [2]$$

were **J** is the chloride flow, **C** is the chloride concentration into the concrete, **x** is the concrete depth penetrated by chloride at a given time, and **D** - diffusion coefficient - is an intrinsic property of the concrete. The lower is the **D** value, the more difficult is the chloride penetration into the concrete. When the concentration of the chloride aqueous solution in contact with concrete is kept constant, the diffusion coefficient **D** can be calculated (6,7) through the equation:

$$x = 4 \sqrt{Dt} \qquad [3]$$

where **t** is the time required for chloride to penetrate a certain concrete depth

Figures 1 and 2 show the penetration depth (**x**) as a function of $\sqrt{t}$ for concrete specimens having different w/c ratios after a curing time of 3 and 28 days respectively. The experimental values of penetration depth (**x**) deviate from the theoretical and linear curve x versus $\sqrt{t}$ - equation [3] - particularly when young concretes (3 days of curing, Fig. 1) with high w/c ratio are tested. This is due to the fact that, in such a case, concrete porosity and the **D** diffusion coefficient are not constant but they decrease during the chloride penetration because of the increase in the degree of cement hydration.

Independently of the curing time (3 or 28 days), the lower is the w/c ratio, the slower is the chloride penetration. Because of the reduction in the w/c ratio, capillary porosity is decreased so that superplasticized concretes with a shorter curing time (3 days, Fig. 2) resist chloride penetration much better than the plain concrete cured for a longer age (28 days, Fig. 1). In other words, the reduction in the w/c ratio is able to compensate a lower degree of cement hydration, caused by a shorter curing time, in order to attain to a low concrete porosity and then to a slow chloride diffusion. By taking into account the difficulties in prolonging the curing time on a job site, a reduction in the w/c ratio gives a practical solution in manufacturing durable concrete structures exposed to the chloride attack even at early ages or without adequate curing.

Figures 3 and 4 indicate the effect of fly ash or silica fume addition on the chloride penetration curve (concrete mixes B, D and E of Table 2). Figure 3 concerns concrete specimens with a 3 day curing time, whereas Fig. 4 indicates the chloride penetration in concrete specimens with a curing time of 28 days before the exposure to $CaCl_2$ aqueous solution. As fly ash and silica fume have been used as additional components (concrete mixes D and E) the w/c ratio is the same as that of the control concrete (mix B in Table 2). The beneficial effect of fly ash and silica fume in reducing concrete chloride penetration appears both at early (Fig 3) and longer ages (Fig. 4) of exposure to $CaCl_2$ aqueous solution.

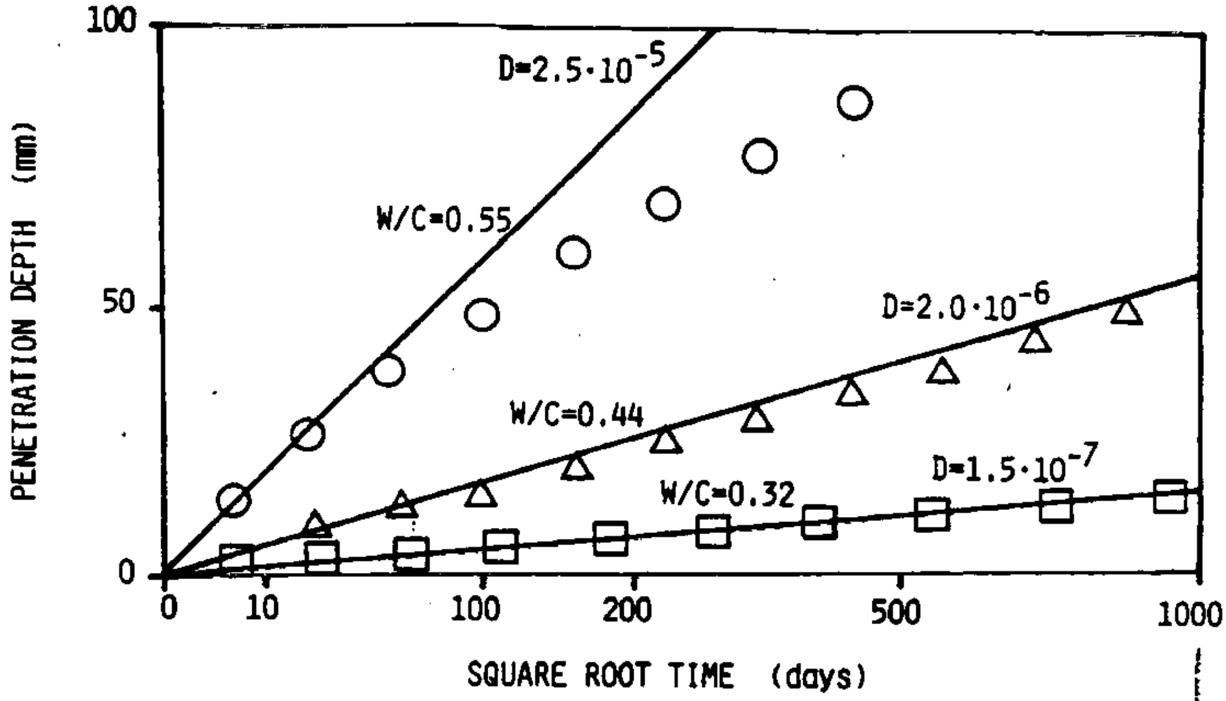

Fig. 1
Chloride penetration depth versus time. Figures on the curves indicate D values (mm^2/s) and w/c ratios. Curing time before exposure to $CaCl_2$ solution: 3 days.

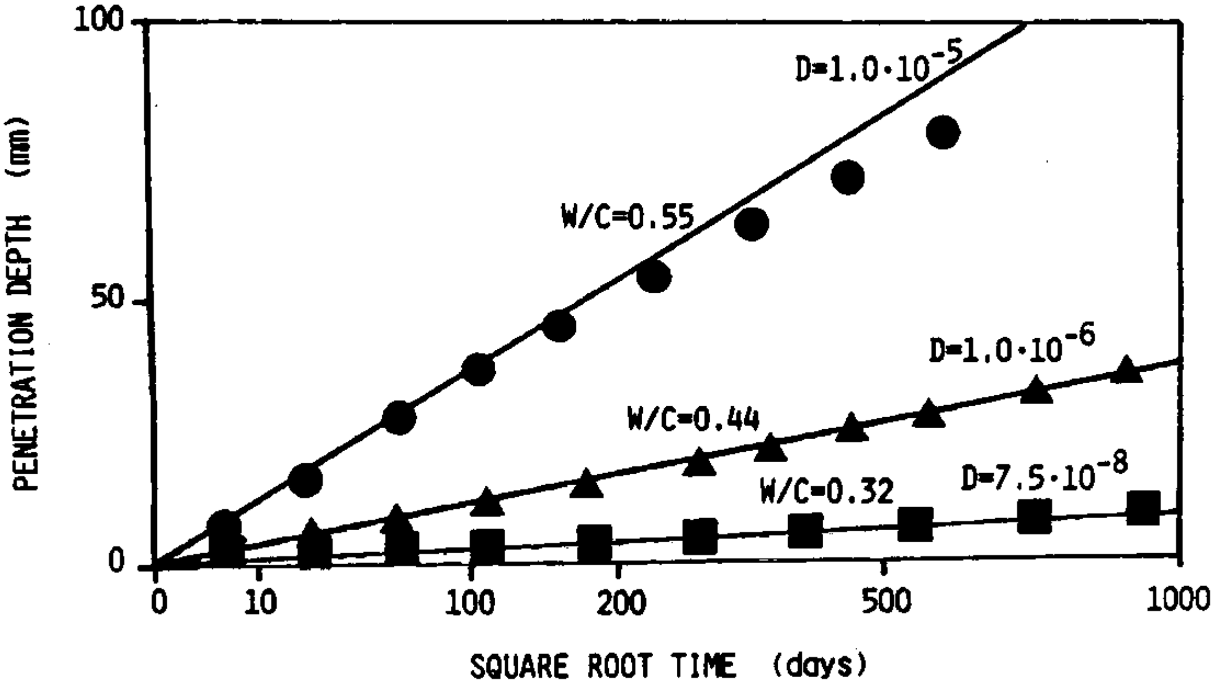

Fig. 2
Chloride penetration depth versus time. Figures on the curves indicate D values (mm^2/s) and w/c ratios. Curing time before exposure to $CaCl_2$ solution: 28 days.

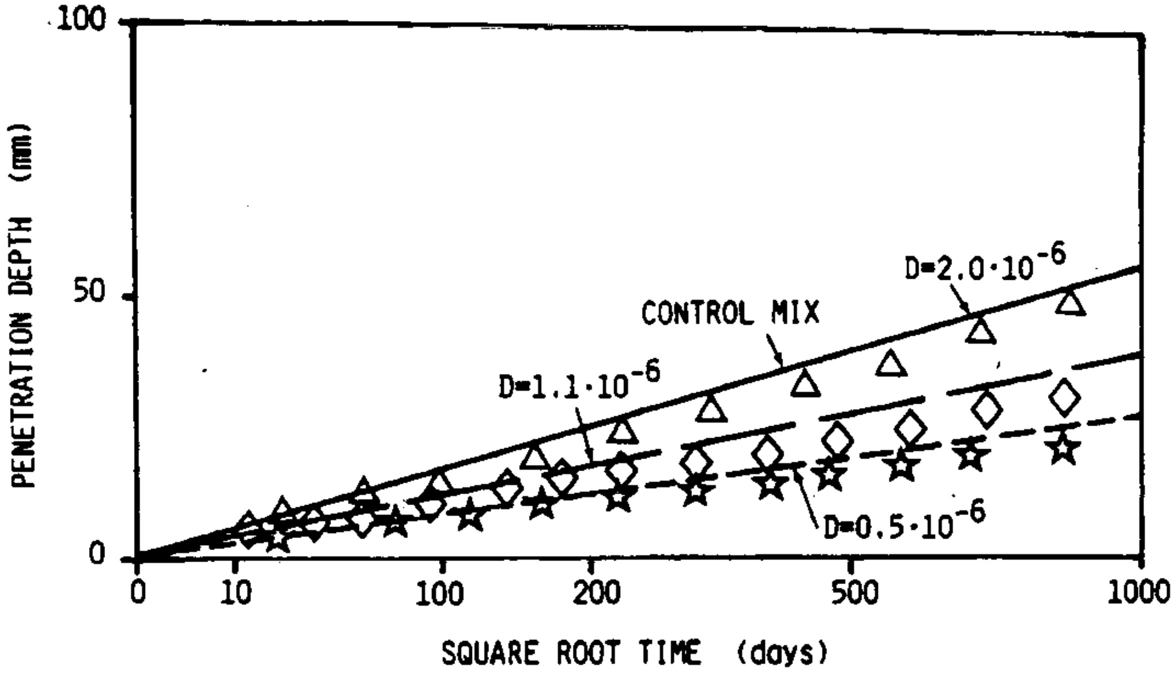

Fig. 3
Effect of fly ash (◇) or silica fume (☆) addition on chloride penetration. Figures on the curves indicate D values (mm^2/s). Curing time before exposure to $CaCl_2$ solution: 3 days.

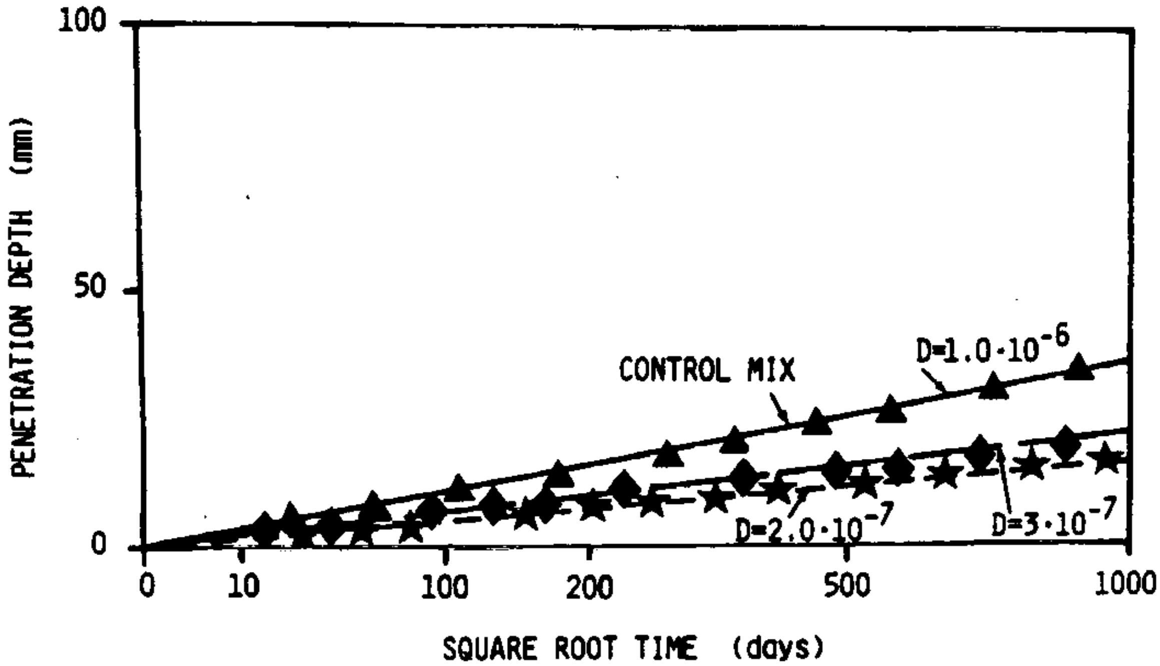

Fig. 4
Effect of fly ash (◆) or silica fume (★) addition on chloride penetration. Figures on the curves indicate D values (mm^2/s) and w/c ratios. Curing time before exposure to $CaCl_2$ solution: 28 days.

Conclusions

a) since the intrinsic properties of concrete, such as porosity and permeability, are changing during the concact with the chloride solution, the experimental values of chloride penetration deviate from the theoretical curve of Fick's law, particularly when young concretes are tested;

b) the lower the water/cement ratio, the lower the chloride diffusion coefficient;

c) the longer the curing time, the lower the chloride diffusion coefficient;

d) even with early curing time such as 3 days, chloride penetration is dramatically reduced provided that a very low water/cement ratio, such as 0.32, is adopted;

e) the combined addition of superplasticizer and silica fume or fly ash furtherly reduces chloride penetration.

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