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

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SUMMARY

By using a high dosage of superplasticizer, the mixing water has been reduced by about 40% and a flowing concrete with a water/cement ratio of 0.32 has been manufactured. Because of a low capillari porosity such a concrete is able to resist chloride penetration even after a curing time of 3 days only.

INTRODUCTION

Concrete porosity is a basic property which affects not only mechanical properties, such as strength, but also durability.

Porosity of well compacted concrete mixes can be decreased by reducing the water/cement ratio and/or by increasing the curing time which in turn increases the degree of hydration. This mean that the earlier the curing time, the lower the water/cement ratio required to attain to low porosity and therefore to high durability of concrete. This aspect of the problem becomes very important when the concrete is exposed to the attack of aggressive agents after few days of curing.

The aim of the present work was to examine the effect of water/cement ratio and curing time of concrete on the kinetics of chloride penetration. It is well known that chloride can attack both concrete (1-3) and steel reinforcement (4-6).

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EXPERIMENTAL

Plain and superplasticized concretes, both at slump of about 220 mm, were manufactured with a water/cement ratio of about 0.55 and 0.32 respectively (Table 1). A relatively high dosage of superplasticizing admixtures (based on a 40% aqueous solution of sulfonated naphthalene polymer) was used (2.5% by weight of cement) so that a very high reduction (about 40%) in the mixing water was achieved. Ordinary portland cement (400 kg/m^3) and natural aggregate (maximum size of 20 mm) were used for both plain and superplasticized concretes).

Table 1
Composition and characteristics of concrete mixes

Concrete type	Plain	Superplasticized
Cement Content (kg/m^3)	400	400
Water (kg/m^3)	221	129
Water/cement	0.55	0.32
Slump (mm)	220	230
Superplasticizer (% by weight of cement)	0.0	2.5

After a curing time of 3 or 28 days at 20°C, concrete specimens were immersed in a 10% NaCl aqueous solution to evaluate chloride penetration by a colorimetric test based on the spraying of fluoresceine and $AgNO_3$ aqueous solution on the concrete surface of the splitted specimens. The concrete depth penetrated by chloride becomes pink coloured, whereas the area which is chloride free becomes dark coloured (Fig. 1). Moreover, tests on capillary porosity, permeability and compressive strength have been carried out.

DISCUSSION OF RESULTS

Figure 2 shows the compressive strength as a function of curing time for the plain mix and the superplasticized concrete. Due to the reduction in mixing water, superplasticizer addition causes a remarkable increase in strength in comparison with the plain concrete.

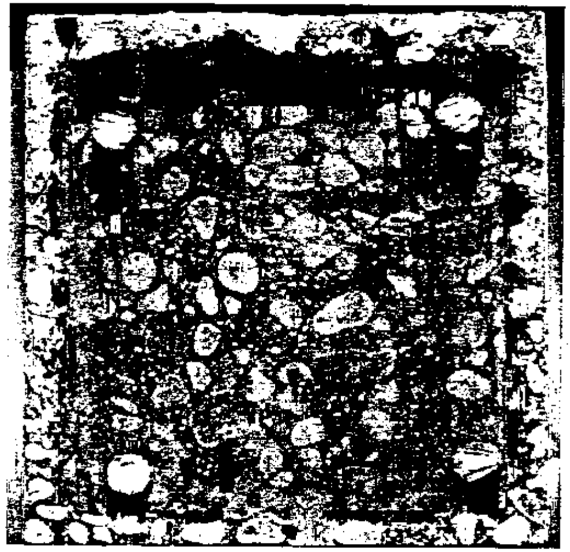

Fig. 1
The light area corresponds to the concrete depth penetrated by chloride.

Moreover, due to the remarkable reduction in the w/c ratio, capillary porosity of superplasticized concretes at early ages (3 days) is much lower than that of plain concrete at longer ages (28 days). Figure 3 shows the cumulative volume of pores as a function of the pore size for cement pastes wet-screened from plain and superplasticized concretes on No. 200 sieve (0.075 mm). Both total volume and size of pores are strongly reduced by the decrease in the w/c ratio (from 0.55 to 0.32) caused by 2.5% superplasticizer addition, so that the 3 days superplasticized cement mix is much less porous than the 28 days plain cement mix.

The porosity reduction results in a dramatic decrease of permeability of the superplasticized concrete with respect to the plain mix. This means that the curing time required to reach a certain permeability value is reduced in the presence of superplasticizer. In the absence of this admixture, concrete must be cured for about one month and a half in order to reach the above mentioned permeability coefficient. This aspect of the problem is quite important from a practical point of view, since in plain concretes watertightness can be really obtained only by prolonging the moist curing or demoulding after a long time.

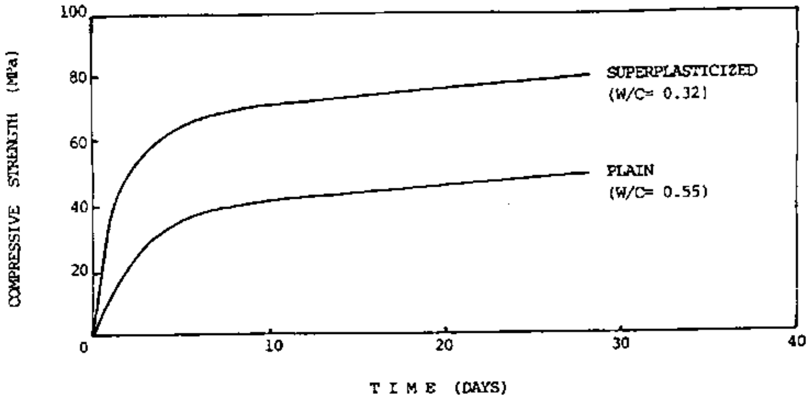

Fig. 2
Compressive strength of concrete mixes

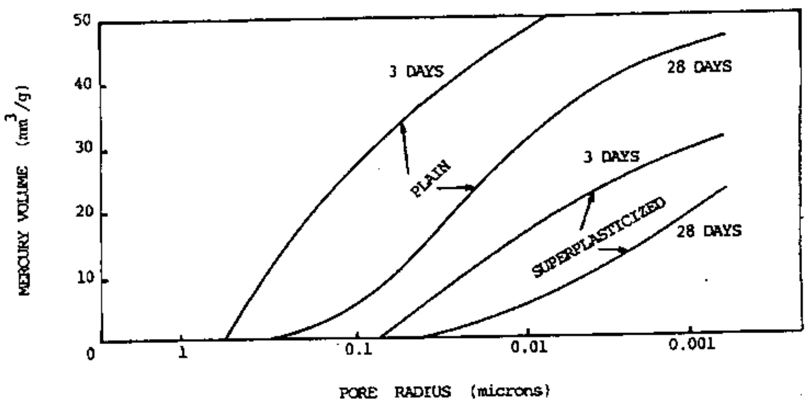

Fig. 3
Cumulative volume of mercury penetrating cement pastes wet-screened from concrete mixes on No. 200 sieve (0.075 mm).

Chloride penetration into concrete follows the Fick's low:

$$J = -D \; dC/dx$$

where J is the chloride flow, C is the chloride concentration into the concrete and x is the concrete length penetrated by chloride at a given time (7-9). The diffusion coefficient D is an intrinsic property of the concrete and it is related to the concrete resistance to chloride penetration. The lower is the D value, the more difficult is chloride penetration into a concrete. The diffusion coefficient can be calculated (7,8) through the empiric equation:

$$x = 4 \sqrt{Dt}$$

by measuring the chloride penetration depth (x) after a given period of time (t).

Figure 4 shows the penetration depth (x) as a function of $\sqrt{t}$. The experimental values of penetration depth deviate from the theoretical curve x versus $\sqrt{t}$ of Fick's law particularly when young concretes (3 days) with high w/c ratio are tested. This is due the fact that, in such a case, concrete porosity and thereby the D diffusion coefficient are not constant but they change during the immersion in the chloride solution. This change is greater for young concretes (3 days) than for the older ones (28 days). From the linear part of the x versus $\sqrt{t}$ curves the D values have been calculated and reported in Table 2.

Table 2 indicates that the chloride diffusion coefficient in a concrete at a given curing time can be significantly reduced by reducing the w/c ratio. The superplasticized concrete with a 0.32 w/c ratio, even with a short curing time (3 days), appears to be much more resistant to chloride penetration than a long cured (28 days) plain mix with a w/c ratio of 0.55. Also in this case, the decrease in capillary porosity (Fig. 3), and consequently in permeability, improves the concrete resistance to the potential chloride attack on the iron reinforcement.

CONCLUSIONS

The results of the present work demonstrate that:

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

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

c) 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;

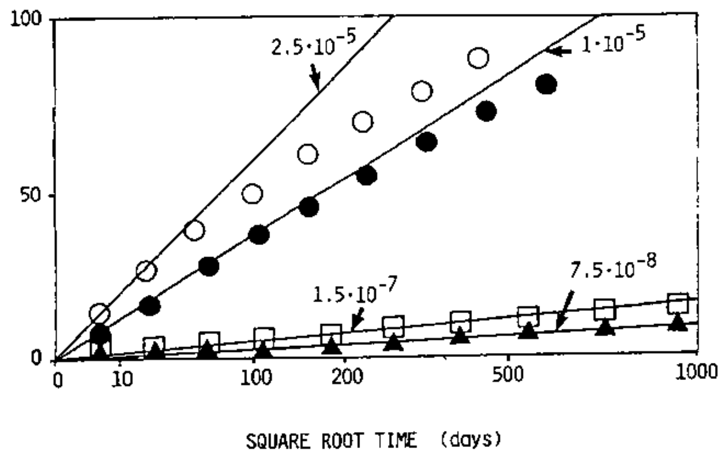

Fig. 4
Chloride penetration depth versus time: curves follow the Fick's law with D coefficient values on the curves

Tab. 2
Diffusion coefficient of chloride penetration in concrete specimens cured 3 or 28 days before the immersion in 10% NaCl aqueous solution.

Concrete type	Plain		Superplasticized	
w/c ratio	0.55	0.55	0.32	0.32
Curing time (days)	3	28	3	28
Coefficient of chloride diffusion (mm^2/s)	$2.5 \cdot 10^{-5}$	$1.0 \cdot 10^{-5}$	$1.5 \cdot 10^{-7}$	$7.5 \cdot 10^{-8}$

d) 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 concretes with early curing time and high w/c ratio are tested.

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