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LOW POROSITY AND EARLY DURABILITY OF CONCRETE

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Abstract
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 the low capillary porosity such a concrete is able to resist sulfate attack, chloride penetration and freezing-thawing cycles even after a curing time of 3 days only.

Key words: Durability, Sulfate Attack, Chloride Penetration, Freezing-Thawing, Porosity, Permeability, Superplasticizer, Air-Entraining Agent.

1. Introduction

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

If air bubbles, caused by the addition of air-entraining agent, are excluded, there are two types of porosity: macroporosity, due to a defective compaction of of fresh concrete, and capillary porosity, mainly due to the presence of free water. Equation (1), based on the Powers theory (T.C. Powers and T.L. Brownyard, 1945-1947), indicates the percentages of capillary pores by volume of cement paste (V_p) as a function of the water/cement (w/c) ratio and the degree of cement hydration (α):

$$V_p = \frac{w/c\ 100 - \alpha\ 36\ 15}{w + 100/g}\ 100 \qquad (1)$$

where g (in g/cm^3) is the cement specific gravity.

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, provided that very low water/cement ratios compensate the lower degree of hydration caused by the shorter curing.

Superplasticizers allow macroporosity to be reduced, as they make concrete more flowable and compaction easier, even with moderate vibration or, in some cases, without vibration at all. Moreover, they reduce capillarity porosity considerably by reducing the water/cement ratio.

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 heaviliy 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, even using ordinary Portland cements (ACI Committee 201, 1983).

However, in some exceptional cases, such as concrete to repair bridge decks exposed to the severe action of deicing salts based on chlorides, particularly durable concrete, with much lower water/cement ratio (0.32) is recommended (ACI Committee 201, 1983).

Moreover, even with "normal" aggression (where 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 extendeed curing of concrete is not practicable. That is the case, for instance, in sea underwater pours, where chloride and sulfate penetration could be soon prevented only by concrete watertightness achieved in a few days because of a very low water/cement ratio. Moreover, in case of aggregates containing sporadic amounts of gypsum or anhydrite, sulfate attack can start immediately in wet concrete, and ettringite or thaumasite production does not stop until concrete is watertight. Again, a very low w/c ratio such as 0.32, should allow concrete to become watertight in a few days so that sulfate attack should be immediately blocked.

The purpose of the present work was to verify if the use of superplasticizers at high dosage could allow the manufacture of flowing concretes which are able to resist immediately chemical and physical attacks even after a short curing time such as 3 days.

2. Experimental

Plain and superplasticized concretes, both at slump of about 220 mm, were produced with a water/cement ratio of about 0.55 and 0.32 respectively (Table 1). A relatively high dosage of superplasticizing admixture (based on a 40% aqueous solution of sulfonated naphtalene 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. An air entraining agent (0.04%) was also used only to manufacture concrete specimens for frost resistance test.

After a curing time of 3 or 28 days concrete specimens were tested to evaluate sulfate resistance, chloride penetration and frost resistance. Moreover, capillary porosity, permeability and compressive strength have been carried out.

Table 1. Composition, and characteristics of concrete mixes.

Concrete Type	Plain	Superplasticicized	Air-Entrained	Air-Entrained & Superplasticized
Cement content (Kg/m^3)	398	403	401	402
Water (kg/m^3)	220	129	212	125
Slump (mm)	220	220	215	225
Air Volume (%)	1.2	2.1	5.4	5.9
Air-Entraining Admixture (%)	--	--	0.04	0.04
Superplasticizer (%)	--	2.5	--	2.5
Durability Tests	SO$_4^{=}$ resistance Cl$^-$ penetration	SO$_4^{=}$ resistance Cl$^-$ penetration	Freezing-Thawing Resistance	Freezing-Thawing Resistance

3. Discussion of results

Figure 1 shows the compressive strength as a function of curing time for the a) plain mix, b) superplasticized concrete, c) air-entrained concrete and d) air-entrained and superplasticized mix. Due to the reduction in mixing water, superplasticizer addition causes a remarkable increase in strength for both plain and air-entrained concrete.

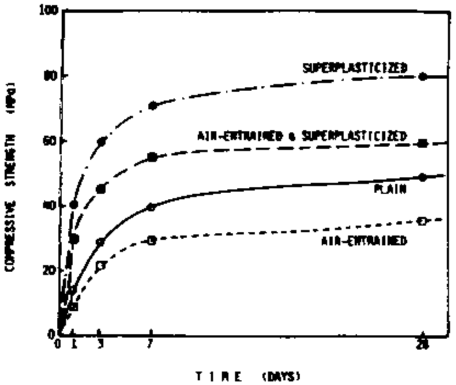

Fig. 1 Compressive strength of concrete mixes.

Moreover, due to the remarkable reduction in the w/c ratio, capillary porosity of superplasticized concretes at early ages are much lower than that of plain concrete at longer ages. Figure 2 shows the cumulative volume of pores as a function of the pore size for cement pastes wet-screened from plain and superplasticized concretes. Both total volume and size of pores are strongly reduced by the 2.5% superplasticizer addition, so that the 3 day superplasticized cement mix is much less porous than the 28 day 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. Table 2 shows that, as a result of the remarkable reduction in the w/c ratio, the permeability coefficient value of $5\cdot10^{-12}$ m/s - corresponding practically to a "watertight" concrete structure - is attained in only 2 days in the presence of 2.5% sulfonated naphtalene superplasticizer. In the absence of this admixture, concrete must be cured for about one mounth 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.

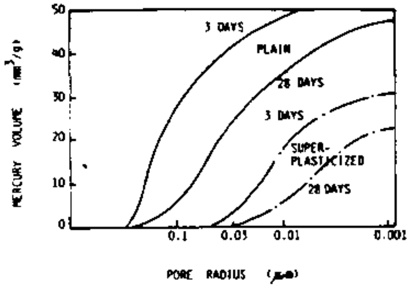

Fig. 2 Cumulative volume of mercury penetrating cement pastes wet- screened from plain and superplasticized concretes on No. 200 sieve (0.075 mm). Figures on curves indicate the curing time in days.

Table 2. Curing time required to attain a permeability coefficient of $5\cdot10^{-12}$ m/s.

Concrete type	Plain	Superplasticized	Air-Entrained	Air-Entrained & Superplasticized
w/c	0.55	0.32	0.53	0.31
Curing time (days)	48	2	44	2

Figure 3 shows the change in length of plain or superplasticized concrete specimens immersed at 20°C in a 10% $MgSO_4$ aqueous solution after a curing time of 3 or 28 days. In consequence of the very low permeability, the behaviour of superplasticized concrete in this very aggressive environment is quite good even after a curing time of only 3 days. On the other hand, the resistance of plain concrete to the sulfate attack is very poor in the specimens cured for the shorter curing time (3 days). Incidentally some specimens immersed in the sulfate solution at 3°C were completely destroyed in less than 6 months as a result of ettringite and thaumasite formation revealed by X-ray diffraction analysis. Even with a longer curing time (28 days), the durability of the plain mix appears to be much lower than that of the superplasticized concrete cured for only 3 days.

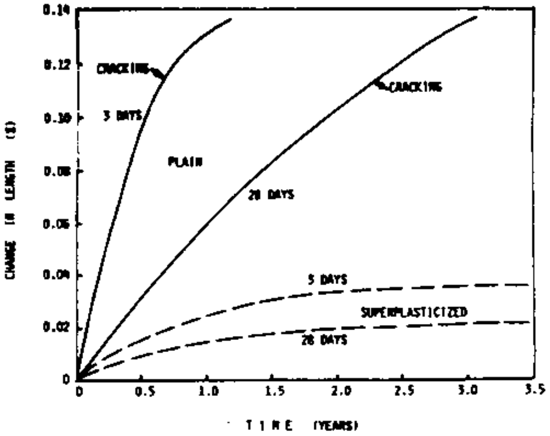

Fig. 3 Change in lenght of concrete specimens cured for 3 or 28 days before immersion in a 10% $MgSO_4$ aqueous solution.

Penetration of chloride into reinforced and prestressed or post-tensioned concretes can cause reinforcement corrosion. Choride penetration into concrete follows the Fick's low (M. Collepardi, A. Marcialis and R. Turriziani, 1970, 1972 a, 1972 b):

$$J = -D \frac{dC}{dx} \qquad (2)$$

where J is the chloride flow, C is the chloride concentration into the concrete and x is the concrete lenght penetrated by chloride at a given time. 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 (M. Collepardi, A. Marcialis and R. Turriziani, 1970, 1972 a) through the empiric equation (3).

$$x = 4\sqrt{Dt} \qquad (3)$$

by measuring the chloride penetration lenght - for instance, through a chromatic indicator such as floresceine and silver nitrate (M. Collepardi, A. Marcialis and R. Turriziani, 1970) - after a given period of time (t).

Table 3 indicates that the chloride diffusion coefficient in a concrete at a given curing time can be reduced by about 100 times by reducing the w/c ratio by 40% through the addition of 2.5% sulfonated naphtalene superplasticizer. Again, 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. 2), and consequently in permeability, improves the concrete resistance to the potential chloride attack on the iron reinforcement.

Table 3. Coefficient of chloride penetration in concrete specimens cured 3 or 28 days before the immersion in 10% $CaCl_2$ aqueous solution.

Concrete Type	Plain		Superplasticized	
Curing time (days)	3	28	3	28
Coefficient of chloride diffusion (mm^2/s) at:				
10 days	$3\ 10^{-5}$	$11\ 10^{-6}$	*	*
100 days	$2\ 10^{-5}$	$9\ 10^{-6}$	$2\ 10^{-7}$	$8\ 10^{-8}$
1000 days	$2\ 10^{-5}$	$8\ 10^{-6}$	$1\ 10^{-7}$	$7\ 10^{-8}$

* undeterminable

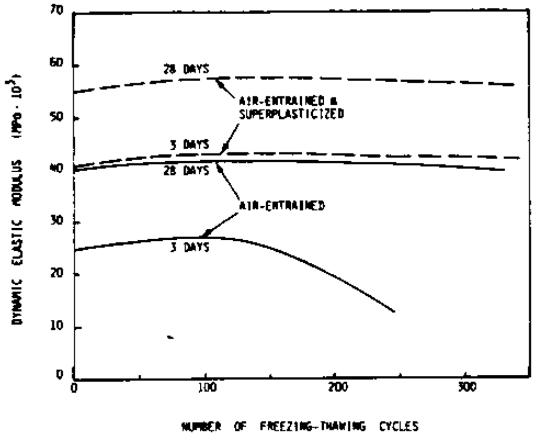

Fig. 4 Dynamic elastic modulus versus freezing-thawing cycles for concrete cured 3 or 28 days.

As a last example of early durability of superplasticized concrete with a very low w/c ratio, Fig. 4 shows the dynamic elastic modulus versus the number of freezing-thawing cycles (ASTM C-666, procedure A). The combined addition of air-entraining agent and superplasticizer allows flowing concrete to be manufactured with a 0.32 w/c ratio. As a result of the low w/c ratio, high strength (Fig. 1) and low permeability (Table 2) are attained at very early ages. Consequently a frost resistant concrete can be produced even after a curing time of only 3 days. On the other hand, the control mix containing only the air entraining agent appears to be frost resistant only in the case of an adequate curing time (28 days).

5. Conclusions

A relatively high dosage (2.5%) of superplasticizer, based on sulfonated naphtalene polymer, allows flowing concrete to be manufactured with low porosity and "early" durability. With a w/c ratio of 0.32 flowing superplasticized concrete is able to resist even at early ages, the sulfate attack and the chloride penetration. Moreover, the combined addition of air-entraining agent and superplasticizer allows flowing concrete to be frost resistant even after a relatively short curing time.

References

T.C. Powers and T.L. Brownyard (1945-1947), "Studies of the physical properties of hardened Portland cement paste" (Nine parts), J. Amer. Concr. Inst. 43 (Oct 1945 to April 1947).

ACI Committee 201 (1983), "Guide to Durable Concrete", ACI Manual of Concrete Practice 1983, Part 1, 101.2R- 1/201.2R-37, ACI Publication, Detroit.

M. Collepardi, A. Marcialis and R. Turriziani (1970), "Kinetics of Penetration of Chloride Ions in Concrete", Ind. Ital. Cem. 4, 157-164.

M. Collepardi, A. Marcialis and R. Turriziani (1972, a) "Penetration of Chloride Ions into Cement Pastes and Concretes", J. Amer.Cer. Soc. 55, 534-535.

M. Collepardi, A. Marcialis and R. Turriziani (1972, b)"The Penetration of de-icing Agents in Cement Pastes", Ind.Ital.Cem.69, 143-150.