Hydraulic cement pastes: their structure and properties

Proceedings of a Conference held at University of Sheffield
8-9 April 1976

Cement and Concrete Association

THE INFLUENCE OF WATER-REDUCING ADMIXTURES ON THE CEMENT PASTE AND CONCRETE PROPERTIES.

M. Collepardi - Department of Materials, Science, Engineering Faculty,
University of Ancona, Via della Montagnola, Ancona, Italy.
L. Massidda, Institute of Applied Chemistry and Metallurgy, Engineering
Faculty, University of Cagliari, Piazza d'Armi, Cagliari, Italy.

Summary

The effect of two very common water reducing admixtures were studied. The first one it's a traditional type admixture, the second one it's a synthetic polymer type. Samples of Portland cement paste and concrete with and without admixture has been prepared at room temperature.

The effect of admixtures on the hydration degree, the capillary porosity, the morphological structure and the strength of cement paste were examined. A decrease of capillary porosity and increase of strength is obtained by using admixtures. The effect is higher for the synthetic polymer admixture. Moreover the hydration of tricalcium silicate is accelerated by the presence of admixtures, probably by an increased dispersion of solid particles. The composition and morphology of hydrated cement are not modified by the addition of admixtures. The effect on strength and paste porosity is mostly caused by reduction of water-cement ratio and in a smaller degree by a greater hydration degree.

The effect of admixtures on compressive strength, shrinkage, permeability, and sulphate resistence of concrete were also studied. In particular, synthetic polymer admixture causes a higher compressive strength increase also in a very flowable concrete. That may be because besides to cut down mixing water, this admixture reduces bleeding also in very fluid concrete, so assuring a better adhesion between aggregates and cement paste. Using admixtures a reduction of shrinkage and permeability, and higher durability were obtained. Obviously the higher effect is produced when using synthetic polymer admixture.

Introduction

It is well-known that a reduction in the water/cement ratio (w/c) gives rise to an improvement in each and all the characteristics of the hardened concrete. Nevertheless, for a given system of compaction, when the quantity of mixing water is reduced below a certain value, the flowability of the fresh concrete is so reduced that complete compaction is not possible, and the mechanical properties of the concrete diminish as the w/c ratio is reduced.

This is schematically illustrated in Fig. 1 where curve C represents completely compacted concretes and curves A and B represent the behaviour in practice of concretes which are compactable to a different extent. The behaviour represented by curve A can be altered to that illustrated by curve B, by improving vibration efficiency and/or by realizing a more flowable concrete making use of additives. In other words, the addition of water-reducing additive can result in a double improvement in the concrete: the first is due to a reduction in the mixing water; the second to the increased flowability and therefore to easier placeability.

This article deals with the influence of two water-reducing or fluidifying additives on the properties of Portland cement paste and concrete: the first additive is of the traditional type, while the second is a new product recently introduced on to the market, having a fluidifying power considerably greater than the first. Using the latter product it is possible to prepare the so-called "rheoplastic" concretes (1,2), that is, concretes which are extremely flowable (slump $\geq$ 20 cm) but which at the same time, are plastic, very cohesive, and hardly segregable (bleeding capacity $\leq 2.x10^{-3}$).

Experimental procedure

Various concrete mixes were prepared all using high-strength Portland cement (conforming to the Italian Standards)and containing 300 Kg of cement and 1936 Kg of dry aggregate per cubic metre of concrete. The percentages of fine aggregate (0-5 mm) medium aggregate (5-15 mm) and large aggregate (15-25 mm) were 32%, 38% and 30% respectively.

A concrete mix was prepared having a w/c ratio of 0,57 and a slump of 10 cm measured by Abrams cone. Other concrete mixes were also prepared having the same slump but having w/c ratios reduced due to the presence of the additives.

The first additive, A, was of the traditional type containing an hydroxylated product (type A and class 5, according to the ASTM classification C494); the second, B, was a product containing a hydrocarbon syntethic polymer with sulphonic, aminic, carboxylic and hydroxylic groups (Rheomac). Lastly, using this latter product, a fourth concrete mix was prepared having a very high flowability (slump = 20 cm) but at the same time being very cohesive (bleeding capacity = 1.6×10^{-3}). Table I shows the properties of the four types of concrete mix and the real w/c ratios of their corresponding cement pastes, calculated by taking into account also the water absorbed by the aggregates (0.02%). At the same time, four pastes of cement and of tricalcium silicate were prepared, with and without additives, and with the w/c ratios as indicated in the last column of Table I.

The concretes and pastes were cured at 20°C and at a saturated vapour conditions. The results registered were: (a) the strengths at 1,7 and 28 days; (b) the degree of hydration and the hydrolysis calcium hydroxide (3) only in the tricalcium silicate pastes; (c) the capillary porosity by mercury intrusion (4) in the cement pastes; (d) the permeability of the concrete mixes; (e) the espansion of concretes in a solution containing 20 g/l of sodium sulphate ; (f) the shrinkage of the concretes; (g) the morphology of the hydrated products (5) using the Scanning Electron Microscope (SEM).

Discussion

Table II illustrates the results of the compressive strengths of the cement pastes. It can be seen that the use of additives caused an increase in strengths especially in mix No. 3 containing the synthetic polymer and having the same consistency as mix No. 1 without additives. It should be noted, however, that the increase in strength is not only due to the reduction in the w/c ratio; a comparison between mixes No. 2,3 and 4, and mixes No. 5,6 and 7, respectively, demonstrates that even at equal w/c ratios, with the presence of additives, slightly higher strenghts are obtained.

Table III illustrates the hydrolysis calcium hydroxide and the hydrated C_3S* ;

* Cement Chemistry Notation is used: C = CaO; S = SiO_2; H = H_2O

both referred to 1 g of initial anydrous C_3S. From these values, the C/S molar ratio of calcium silicate hydrate (C-S-H), was calculated. It can be seen that the degree of hydration is actually of the order of 5-10% higher in the samples containing the additives. This explains why even at equal w/c ratios, the strength is slightly higher in the mixes containing additives (Table II). It is probable that the increase in the degree of hydration can be ascribed to the major dispersion of the cement particles.

The composition of C-S-H observed in the presence of additives, and evaluated by means of the molar ratio C/S (Table III), is substantially equal to that obtained in the absence of additives provided that the comparison is made between samples having the same w/c ratio. On reducing the w/c ratio, it is seen that the C/S molar ratio increases, thus conferming the results obtained by Brunauer et al (6). As well as their composition, also the morphology of the hydrated products is independent of the presence of additives. The SEM micrographs in Fig. 2 show the morphological structure of C_3S and cement paste with and without the synthetic polymer additive.

Fig. 3 shows the polymer additive influence on the cumulative pore size distribution, in the 1-0,01 μm range, in the cement pastes after 3 days curing. Similar effects were obtained for the other curing periods . The range examined is that which contains the capillary pores, and is very important because these determine the permeability, and the durability, of the concrete (7). If a comparison is made between pastes of the same consistency (w/c = 0,44 without additive and w/c = 0,30 with additive), a large reduction both in the total porosity and in the pore diameter can be observed, as is illustrated by the inflection of the curve at much smaller diameter values for those samples containing the additive. Again, at equal w/c ratios, the presence of additive diminishes the total porosity, and the pore diameter: which is, at least, partly attributable to the higher degree of cement hydration (Table III). Analogous effects, though to a less marked degree, are observed when the "traditional" additive is present.

Fig. 4 shows the permeability of concrete in function of the time. It can be observed that when additives are present, the permeability is greatly reduced. The effect is particularly noticeable in the concrete mix containing the polymer based additive. This must be ascribed to the reduction both of total porosity and of the pore diameter.

It should be taken into account, however, that all the concrete mixes regardless of their workability were vibrated to the point of complete compaction (entrapped air less than 1%). Therefore, the differences in permeability must be ascribed only to the differences in w/c ratio and, to a less degree, to the percentage of hydrated cement. In site practice, however, the permeability of the concrete can be higher than that determined under laboratory conditions due to the difficulty of placing, and of control of the amount of vibration. From this point of view, the "rheoplastic" concrete examined in this work (slump = 20 cm; bleeding capacity = $1,6 \cdot 10^{-3}$) behaves in a decidedly better manner than others since, due to its easier placing properties and the scarce segregation, the concrete structure depends much less on the care taken over proper compaction, thus becoming more homogeneous and resembling more the laboratory-produced mix.

The reduction of permeability leads to an increase in the durability of the concrete, as is shown by the curves in Fig. 5, which illustrates the volume increase due to sulphate attach in function of the time. The concretes were cured 7 days and then immersed in the sulphate solution. The lower the w/c ratio, the less permeable is the concrete to aggressive solutions, and therefore the less is the sulphate attach which the concrete undergoes.

Also, the resistence to freezing and thawing cycles increases when the additives examined in this work are present. The effect is much more notable in the case of the polymer-based additive, especially if it is used in conjunction with an air-entraining additive.

Table IV illustrates the shrinkage of the concrete mixes, cured for 7 days and then exposed for 3 and 6 months at a relative humidity of 65%. The results obtained demonstrate that the use of additives leads to a reduction in shrinkage. The greater the reduction in the w/c ratio the greater is the reduction in shrinkage, this being of the same order as that which appears in the literature dealing with analogous concrete mixes without additives, but with different w/c ratios (7).

Fig. 6 shows the compressive strength of the concrete mixes in function of the time. The increase is particularly apparent in those concrete mixes containing the synthetic polymer-based additive, arriving at values of 100% for concretes of equal w/c ratio, and of 50% for those with different slumps. Also in this case, as has been seen in the case of permeability, it should be noted that the strength increases of "rheoplastic" concrete prepared on the job site are higher than those obtained when this same concrete is prepared in the laboratory. This depends on the fact that if, in practice, one passes from a more efficient vibration system (curve B in Fig. 1) to a less efficient one (curve A in Fig. 1), the resulting effect is negligible in the case of a "rheoplastic" concrete, while it is much more marked in a "normal" concrete. Furthermore, the low segregation exhibited by "rheoplastic" concrete, assures a greater "homogeneity" of the concrete properties throughout the structure, which is of importance to the project engineer particularly when dealing with high-rise structures.

Conclusions

The reduction of the w/c ratio by the use of fluidifying additives gives rise to an improvement of all the properties of the cement paste and, therefore, of the hardened concrete; strengths increase, capillary porosity, pore diameter, permeability and shrinkage all decrease, and durability increases. The effect is particularly noted when using the high-power fluidifying additive recently introduced onto the market. In this case, however, it is preferable to use the characteristics of this additive partly for reducing the w/c ratio, and partly for increasing the flowability of the fresh concrete. This makes it possible to obtain on the job site an excellent concrete of constant quality. In practice, the improvements in the concrete properties obtainable in the laboratory

cannot always be systematically translated into job practice because of the difficulties of placing and compaction control.

When a very flowable concrete (slump ≈ 20 cm) is used, it is necessary, even at a low w/c ratio, to keep the bleeding and the segregation of the aggregates within relatively low limits, as is the case with the so-called "rheoplastic" concrete. This is extremely important in garanteeing the "homogeneity" of the structure, the adhesion between aggregate particles and cement paste and, finally, the protection of the reinforcing steel (8).

References

1. Collepardi M. Behaviour of "Rheoplastic" Concrete, 78th Annual Meeting of the American Ceramic Society, Cincinnati, May, 1976.

2. Collepardi M. Assessment of the "Rheoplasticity of Concretes, publication pending on Cement and Concrete Research.

3. Collepardi M. and Massidda L. Hydration of Tricalcium Silicate, Journal American Ceramic Society, vol. 54, No. 9 September 1971, pp. 419-422.

4. Collepardi M., Rossi G. and Spiga M.C. Influence of calcium chloride on the paste hydration of tricalcium silicate, (in Italian) Accademia Nazionale dei XL, serie IV, vol. XVIII, 1968, pp. 3-12.

5. Collepardi M. A discussion of the paper "Studies on the Hydration of Tricalcium Silicate Pastes. I Scanning Electron Microscope Examination of Microstructural Features" by F.V. Lawrence and J.F. Young, Cement and Concrete Research, Vol. 3, No. 5 September 1973, pp. 645-647.

6. Kantro D.L., Weise C.H. and Brunauer S. Paste Hydration of Beta-Dicalcium Silicate, Tricalcium Silicate and Alite, Symposium on Structure of Portland Cement Paste and Concrete, Special Report 90, Highway Research Board, Washington, DC, 1966, pp. 309-27.

7. Neville A.M. Properties of Concrete, Ed. Pitman Paperback, London,(1975); pag. 325.

8. Powers T.C. The Properties of Fresh Concrete, John Wiley and Sons, Inc. New York (1968), pp. 533-603.

Table I – Composition and properties of the mixes containing 300 Kg of Portland cement and 1936 Kg of aggregate per m^3 of concrete.

Concrete No.	Additive %	Slump (cm)	Bleeding capacity	w/c Concrete	w/c * Paste
1	-	10	$4.0\cdot10^{-3}$	0.57	0.44
2	A (0,2%)	10	$2.1\cdot10^{-3}$	0.55	0.42
3	B (3%)	10	$1.1\cdot10^{-3}$	0.43	0.30
4	B (3%)	20	$1.6\cdot10^{-3}$	0.48	0.35

*These figures are calculated from the absorbed water of the aggregates (0.02%)

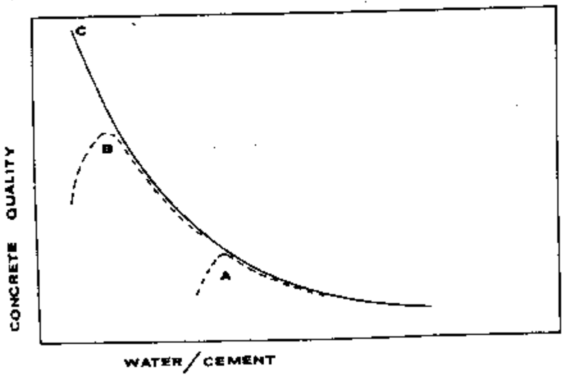

Fig. 1 Effect of water/cement ratio on the concrete quality

Table II. Composition and strength of cement pastes.

PASTE N°	ADDITIVE	w/c	COMPRESSIVE STRENGTH (KG/CM^2)		
			1 DAY	7 DAYS	28 DAYS
1	-	0.44	85	381	548
2	-	0.42	91	402	590
3	-	0.35	106	588	790
4	-	0.30	120	615	820
5	A	0.42	93	417	596
6	B	0.30	124	660	898
7	B	0.35	112	612	815

Table III. Degree of hydration and C/S molar ratio of tricalcium silicate paste with and without additives.

AGE	ADDITIVE	w/c	DEGREE OF HYDRATION (g/g)	FREE $Ca(OH)_2$ (g/g)	C/S $\frac{MOLE}{MOLE}$
3	-	0.44	0.49	0.22	1.72
7	-	0.42	0.61	0.27	1.68
7	-	0.30	0.58	0.25	1.73
3	A	0.42	0.50	0.21	1.70
7	A	0.42	0.63	0.27	1.70
3	B	0.30	0.53	0.23	1.74
7	B	0.30	0.65	0.27	1.72

Table IV. Shrinkage (R.H.=65%) of concretes cured for 7 days.

CONCRETE N°.	SHRINKAGE ($X10^6$)	
	90 DAYS	180 DAYS
1	310	450
2	270	420
3	170	250
4	190	280

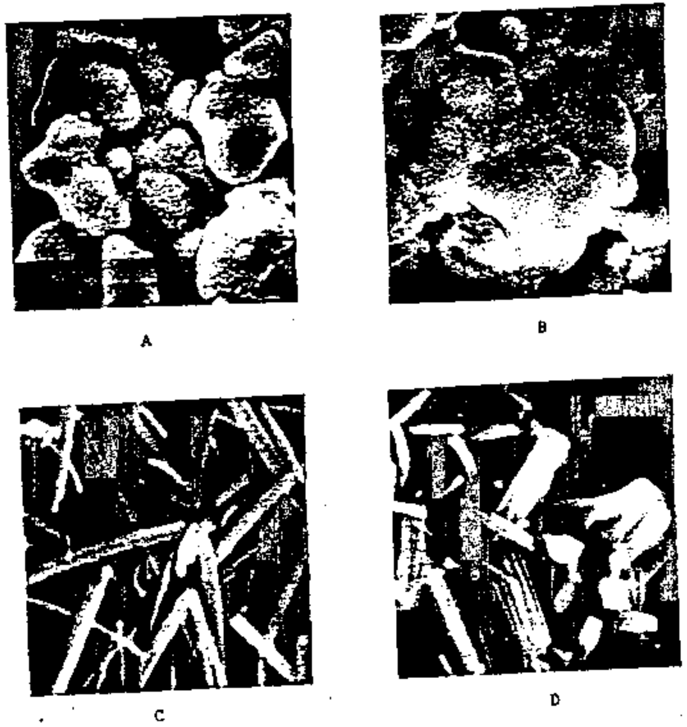

Fig.2. Scanning electron micrographs of C_3S and cement paste (w/c = 0.42)

A(x 3,000) : C_3S cured 1 day without additive

B(x 3,000) : C_3S cured 1 day with Rheomac

C(x 15,000) : cement paste cured 7 days without additive

D(x 15,000) : cement paste cured 7 days with Rheomac.

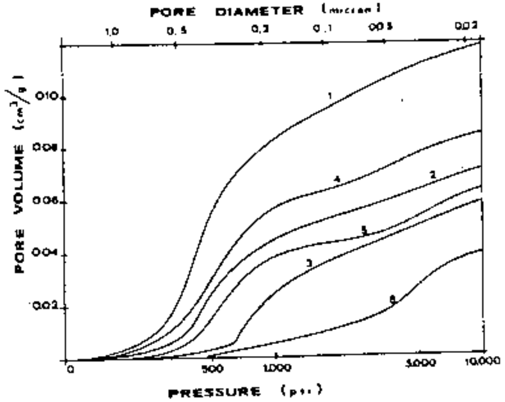

Fig. 3. Cumulative pore volume in function of pore diameter or pressure of intruded mercury. The cement pastes were hydrated for 3 days with the following w/c ratios

1 - w/c = 0.44
2 - w/c = 0.35
3 - w/c = 0.30
4 - w/c = 0.44
5 - w/c = 0.35
6 - w/c = 0.30

1-2-3 without Rheomac
4-5-6 with Rheomac

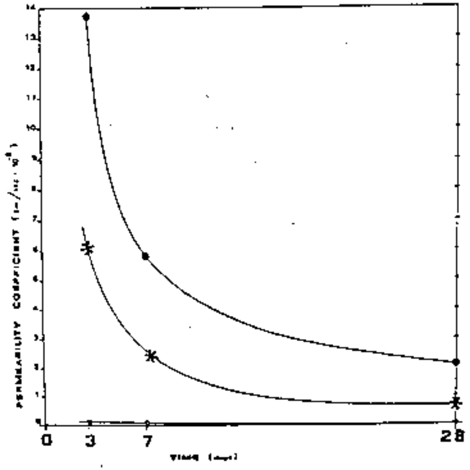

Fig. 4. Permeability of concretes versus curing.

● Concrete N. 1

✱ Concrete N. 2

○ Concretes N. 3 and N. 4

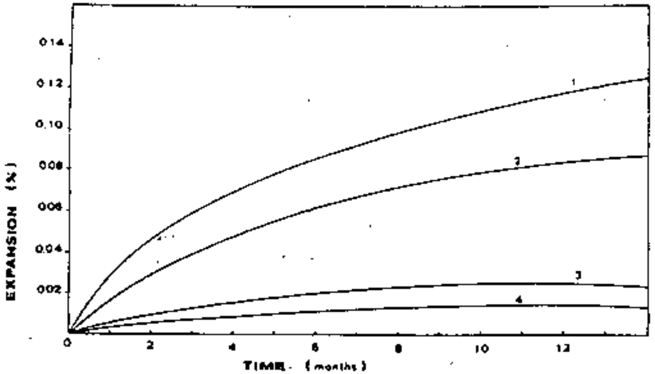

Fig. 5. Expansion due to the sulphate attack in function of time. The figure on the curves shows the concrete numbers indicated in Table I.

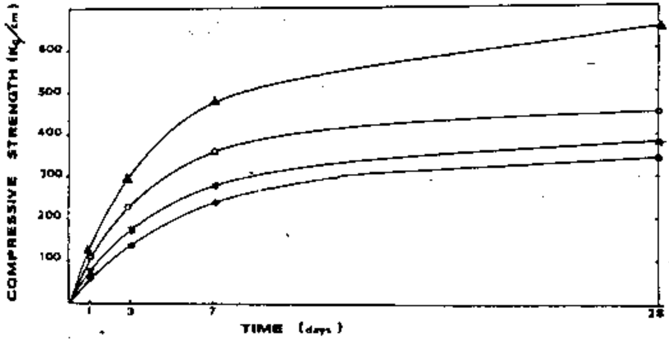

Fig. 6. Compressive strength of concretes in function of curing. ● Concrete No. 1; ✱ Concrete No. 2; ▲ Concrete No. 3; ○ Concrete N. 4.