Effect of Superplasticizer Type on the Performance of High-Volume Fly Ash Concrete

By A. Borsoi, S. Collepardi, L. Coppola, R. Troli and M. Collepardi

Superplasticized high-volume fly ash concretes with 50% of portland cement replacement were manufactured by using two different chemical admixtures based on sulfonated naphthalene (*SN*) or acrylic polymer (*AP*).

Portland cement with a Blaine fineness of about 400 or 500 m^2/Kg was replaced by 50% of ground or un-ground fly ash. The content of the cementitious material (portland cement + fly ash) was about 470 kg/m^3. The concretes with *SN* were manufactured with a slump in the range of 190-200 mm, whereas the slump of the concretes with *AP* was in the range of 220-230 mm. Due to the different effect of the superplasticizers, the water-cementitious material ratio (*w/cm*) was 0.32 or 0.29 for the *SN* or *AP* admixture respectively, although the dosage was slightly lower for the latter.

Cube specimens were cured at 5°C or 20°C and compressive strength was measured at 1 to 90 days. Due to the lower *w/cm*, the strength of the concretes with the acrylic polymer was significantly higher with respect to those with *SN*.

The better performance of the *AP* superplasticizer, in terms of compressive strength, was obtained at early and later ages independently of the curing temperature (5 and 20°C) and the fineness of the portland cement and fly ash.

Due to the lower *w/cm* in concrete with the *AP* admixture with respect to those with the *SN* superplasticizer, the durability behavior of high-volume fly ash concrete can be furtherly improved in terms of lower penetration rate of CO_2 or chloride ions.

Antonio Borsoi is a laboratory technician of Enco. He is active in the area of concrete mixture design. He is author of several papers in the field of superplasticized concrete mixtures.

Silvia Collepardi is a research civil engineer of Enco, Spresiano, Italy. She is working in the field of concrete durability and superplasticized concrete mixtures and has published several papers in this area.

Luigi Coppola is a research civil engineer and technical director of Enco, Spresiano, Italy. He has authored numerous papers on various aspects of concrete technology, durability and mix-design. He was acknowledged by a CANMET-ACI award for his contribution to the fundamental knowledge of concrete durability.

Roberto Troli is a research civil engineer and director of the Enco laboratory. He is author of several papers in the field of concrete technology, particularly in the area of chemical and mineral admixtures as well as in the durability of concrete.

Mario Collepardi is Professor of Materials Science and Technology at the Ancona University, Italy. He is author or co-author of numerous papers on concrete technology and cement chemistry. He is also the recipient of several awards for his contributions to the fundamental knowledge of superplasticizers and their use in concrete.

INTRODUCTION

Previous works on high volume fly ash (*HVFA*) concrete characterized by high portland cement replacement (50-65% by mass), low water-cementitious material ratio (*w/cm),* and use of naphthalene-based superplasticizer were carried out by Malhotra and coworkers (1-4).

The main purpose of the present work was to study the influence of the superplasticizer type in terms of different chemical composition on the performance of *HVFA* concrete. Superplasticizers based on sulfonated naphthalene (*SN*) or acrylic polymer (*AP*) were studied.

Another purpose of this work was to study the influence of the specific surface area of the blended cements on the performance of *HVFA* concrete.

MATERIALS

Cementitious materials: The chemical analysis of the two ingredients (portland cement and fly ash) used to manufacture blended cements are shown in Table 1.

Portland cement was available at the Blaine fineness of 395 and 504 m^2/Kg. Each portland cement was blended with fly ash which was available at three different Blaine fineness levels: 351 m^2/kg (unground fly ash), 395 and 482 m^2/kg (both ground). Four blended cements (*A*,*B*,*C*, and *D)* were manufactured (Table 2), all with 50% by mass of portland cement replaced by fly ash, and characterized by different Blaine fineness (from 368 m/Kg for cement *A* to 487 m^2/Kg for cement *D*). Other properties of these cements, such as setting time, compressive strength, and classification according to the European Norm were published in a previous paper (5).

Aggregates: Natural sand (fineness modulus of 3.09) and two coarse aggregates were used. For all concrete mixtures a combined aggregate was used with 25% of sand, 40% of gravel (4-16 mm) and 35% of coarse aggregate (10-25 mm).

Superplasticizers: Two commercial superplasticizers, both from Mapei (Milan, Italy), were used. One admixture was a 40% aqueous solution of sulfonated naphthalene-based polymer (*SN*). The other superplasticizer was a 30% aqueous solution of acrylic polymer (*AP*). More details on the chemical structure and performance of these two superplasticizers can be found in a previous paper (6).

Concrete mixtures: Table 3 shows the composition of the eight *HVFA* mixtures, all manufactured with about 470 Kg/m^3 of cementitious material which corresponds to a content of portland cement of about 235 Kg/m^3. In four mixtures (No. 1-4) the superplasticizer *SN* was used, whereas the other four concretes (No. 5-8) were treated with the superplasticizer *AP*.

METHODS

After measuring specific gravity and slump, fresh concrete was compacted and cured at 5°C or 20°C. Then, the following properties were determined on cube (150 mm) concrete specimens:

- compressive strength up to 90 days at 5°C or 20°C;
- depth of carbonation measured by phenolphthalein test (RILEM CPC-18) of concrete specimens exposed to air at room temperature after demolding at 1 day;
- chloride penetration at 20°C through the $AgNO_3$ and fluorescein test (7) of concrete specimens exposed to a 10% NaCl aqueous solution after a wet curing of 1 week and an air curing at room temperature of 3 weeks.

RESULTS

Workability: Concrete mixture (Table 3) with the *AP*-based admixture performed better, with respect to those with the *SN*-based superplasticizer, in terms of:

- higher slump level (220-230 mm vs. 190-200 mm);
- lower slump loss
- lower *w/cm* (0.29 vs. 0.32).

So, these data confirm the superior performance of the *AP*-based superplasticizer (6,8) even for manufacturing *HVFA* concretes independently of the fineness of the cementitious materials. In particular, more flowable mixtures were obtained, with lower *w/cm*, not only at the end of the mixing time (Table 3) but even, and more importantly, at a given time, up to 60 min, after mixing (Fig. 1).

Moreover, the data shown in Table 3 indicate that when the fineness of both portland cement and fly ash is increased up to about 500 m^2/Kg (cement *D*) a higher amount of superplasticizer (about 20% more) is needed for the *HVFA* concrete to attain the same slump level, at a given *w/cm*, with respect to the corresponding concretes with blended cements *A*, *B*, and *C* at lower fineness (368-415 m^2/Kg).

Compressive Strength: Figures 2,3,4 and 5 show the compressive strength development at 5°C and 20°C up to 90 days for concrete mixtures with cement *A*, *B*, *C* and *D* respectively. In each Figure strength values of *HVFA* concretes with the same cement and different superplasticizer type (*SN* vs. *AP*) are shown.

Independently of the cement type and curing temperature, the compressive strength of *HVFA* concretes with the *AP*-based superplasticizer is significantly higher than that of the corresponding *HVFA* mixtures with the *SN*-based superplasticizer . This behavior is related to the more effective action of the *AP*-based superplasticizer in reducing the *w/cm* (10% less) with respect to the *HVFA* mixture with the *SN*-based admixture. On the other hand, the early retarding action of the *AP* admixture on the portland cement hydration — which is responsible for the negligible slump loss of the fresh *HVFA* concrete within 60 min (Fig. 1) — does not interfere with the early strength development. Therefore, due to these combined actions of the *AP*-based superplasticizer, *HVFA* concretes with 1-day strength of more than 30 MPa and 90-day strength of more than 80 MPa can be manufactured by using only 235 Kg/m^3 of portland cement.

The best combination of cement, fly ash and superplasticizer seems to be:

- very reactive portland cement (Blaine fineness:504 m^2/Kg)
- unground fly ash (Blaine fineness: 351 m^2/Kg)
- *AP*-based superplasticizer (1%).

This combination corresponds to the mixture No. 7 with cement *C* and 1% of *AP*-based superplasticizer (Table 3). This concrete performs very well in terms of low slump loss (Fig. 1) and high compressive strength (Fig. 4). The compressive strength of the concrete No. 8 with cement *D* (Fig. 5) is a little higher than that of the concrete No. 7 with cement C (Fig. 4) due to the higher fineness of the ground fly ash (Blaine: 482 vs. 351 m^2/Kg). However, just because of this fineness increase the amount of the *AP*-based superplasticizer must be increased by 20% to keep the same workability level and *w/cm* (Table 3)

Carbonation: Due to the relatively small amount of portland cement in *HVFA* concrete and the pozzolanic reaction of fly ash, the amount of $Ca(OH)_2$ in *HVFA* concrete is lower than that in the corresponding normal concrete without fly ash. Therefore, there would be a potential risk of quicker carbonation in *HVFA* concrete due to the lower amount of $Ca(OH)_2$ which should be neutralized by the CO_2 ingress from the environment. However, the results shown in Fig. 6 indicate that the CO_2 penetration in *HVFA* concrete is so slow (Fig. 6) that in 1 year the carbonation depth is about 1 mm when the *SN*-based admixture is used and only 0.2 mm with the *AP*-based superplasticizer. These results confirm that carbonation does not pose any problem for corrosion of the metallic reinforcements due to the very low permeability of *HVFA* to the CO_2 penetration (1). The CO_2 penetration is so slow that is difficult to detect any difference related to the fineness of portland cement.

Chloride penetration: Figure 7 shows the chloride penetration depth with time for *HVFA* concretes. The penetration depth is lower in *HVFA* concretes with *AP*-based superplasticizer due to the lower *w/cm* with respect to those with *SN*-based superplasticizer.

The penetration depth is in general so low that any difference related to the fineness of portland cement and fly ash cannot be detected.

CONCLUSIONS

Even in *HVFA* concrete the *AP*-based superplasticizer performs significantly better than the *SN*-based admixture, in terms of higher slump level, lower slump loss and lower *w/cm*.

Consequently, *HVFA* concretes with higher compressive strength and better durability behavior (in terms of lower CO_2 and chloride penetration) can be manufactured with *AP*-based superplasticizer rather than with the *SN*-based admixture.

The retarding action of the *AP* admixture on the early portland cement hydration is beneficial for the low slump-loss of the fresh *HVFA* concrete but it does not cause any retardation in the early strength development of the hardened concrete even at low temperatures.

ACKNOWLEDGEMENT

The work in preparing the text and the Figures by Isabella Capogna is acknowledged.

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Table 1 - Chemical composition of portland cement and fly ash used to produce blended cements.

Oxyde (%)	Portland cement	Fly Ash
SiO_2	21.25	59.94
Al_2O_3	4.33	22.87
Fe_2O_3	1.85	4.67
TiO_2	0.13	0.94
CaO	64.30	3.08
MgO	1.81	1.55
So_3	3.70	0.35
K_2O	0.71	2.19
Na_2O	0.17	0.62
l.o.i	1.50	3.34

Table 2 - Composition and Blaine fineness of blended cements and individual ingredients.

Blended Cement		Portland Cement		Fly Ash		
				Un-ground. Fineness: 351 m^2/Kg	Ground. Fineness: 395 m^2/Kg	Ground. Fineness: 482 m^2/Kg
Type	Fineness: m^2/Kg	Fineness: 395 m^2/Kg	Fineness: 504 m^2/Kg			
A	368	50%	___	50%	___	___
B	388	50%	___	___	50%	___
C	415	___	50%	50%	___	___
D	487	___	50%	___	___	50%

Table 3 - Composition of concrete mixtures.

Mix	Cement		Gravel (10-25 mm)	Gravel (10-25 mm)	Sand (0-4 mm)	Water	Superpla-sticizer	w/cm	Slump
No.	Type	Kg/m^3	Kg/m^3	Kg/m^3	Kg/m^3	Kg/m^3	Type %cem.		(mm)
1	A	463	453	729	641	148	NS-1.00	0.32	200
2	B	465	455	732	643	145	NS-1.05	0.32	190
3	C	463	453	729	641	148	NS-1.05	0.32	190
4	D	465	455	732	643	145	NS-1.25	0.32	190
5	A	464	455	731	642	133	AP-0.90	0.29	230
6	B	470	460	740	650	134	AP-1.00	0.29	230
7	C	464	455	731	642	133	AP-1.00	0.29	220
8	D	473	463	745	655	135	AP-1.20	0.29	230

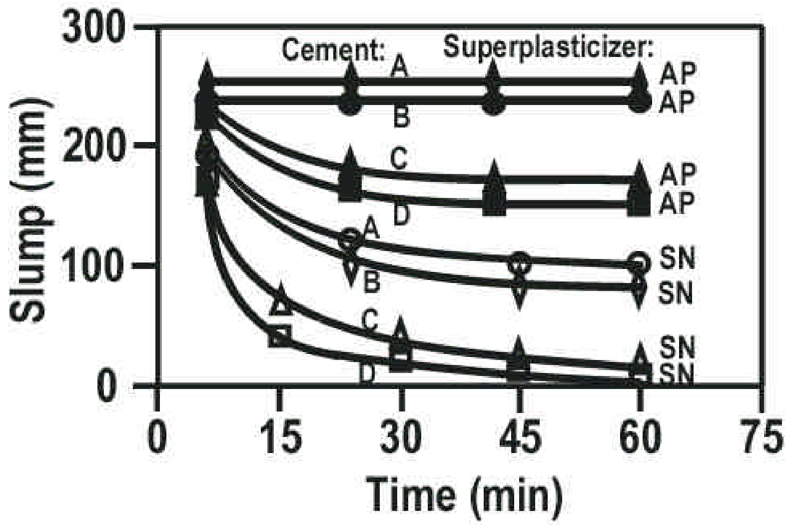

Fig. 1 - Slump-loss of concrete mixture with AP or SN superplasticizer (cements A, B, C and D in Table 2).

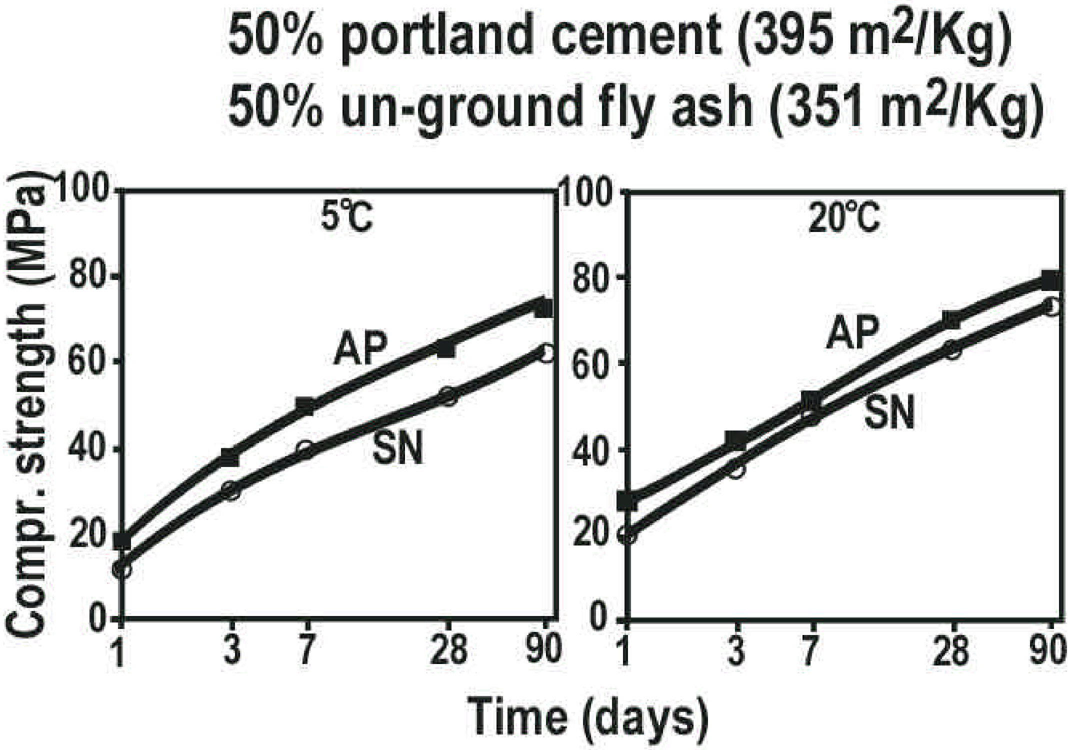

Fig. 2 - Influence of temperature and superplasticizer type on compressive strength versus time (cement A).

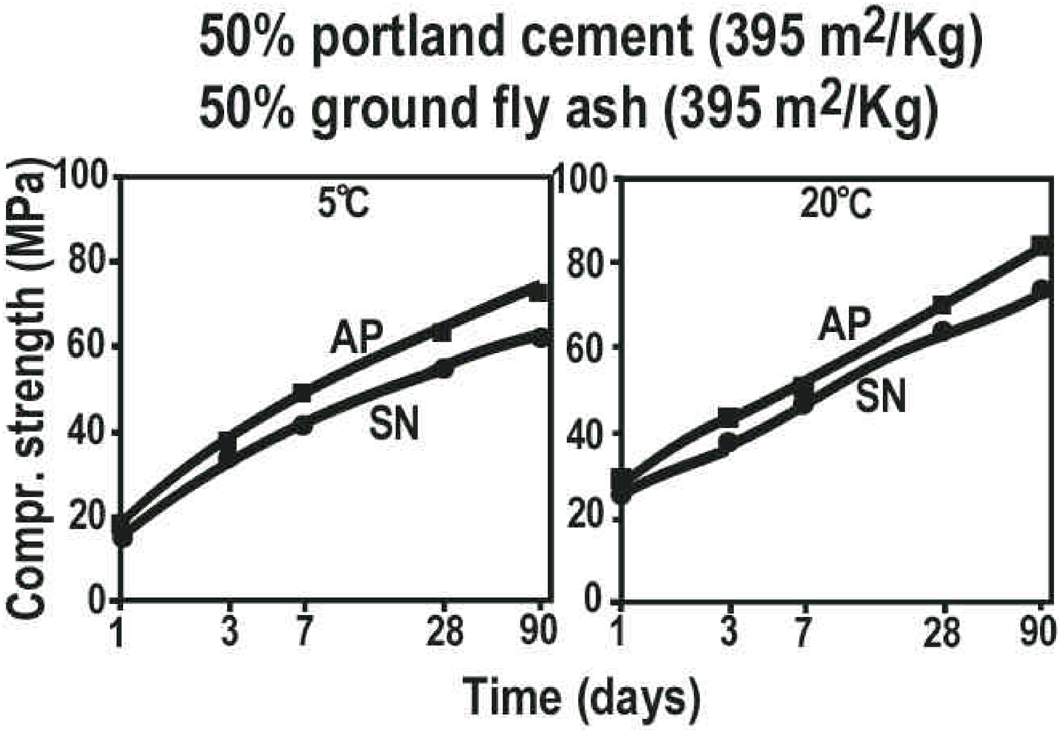

Fig. 3 - Influence of temperature and superplasticizer type on compressive strength versus time (cement B).

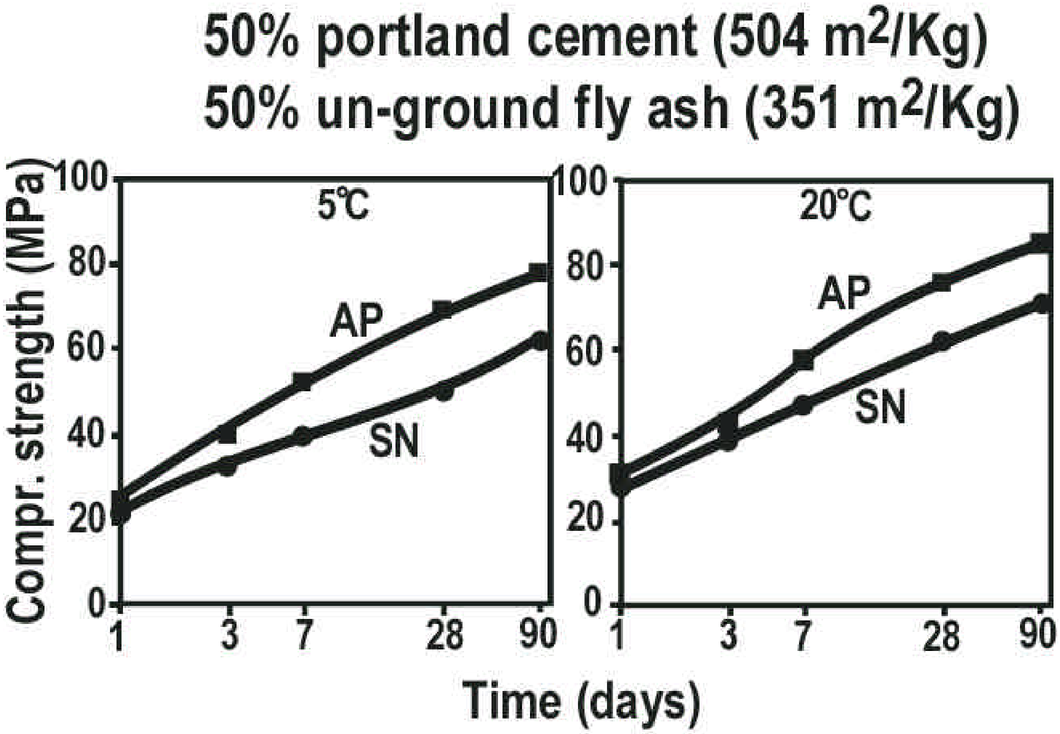

Fig. 4 - Influence of temperature and superplasticizer type on compressive strength versus time (cement C).

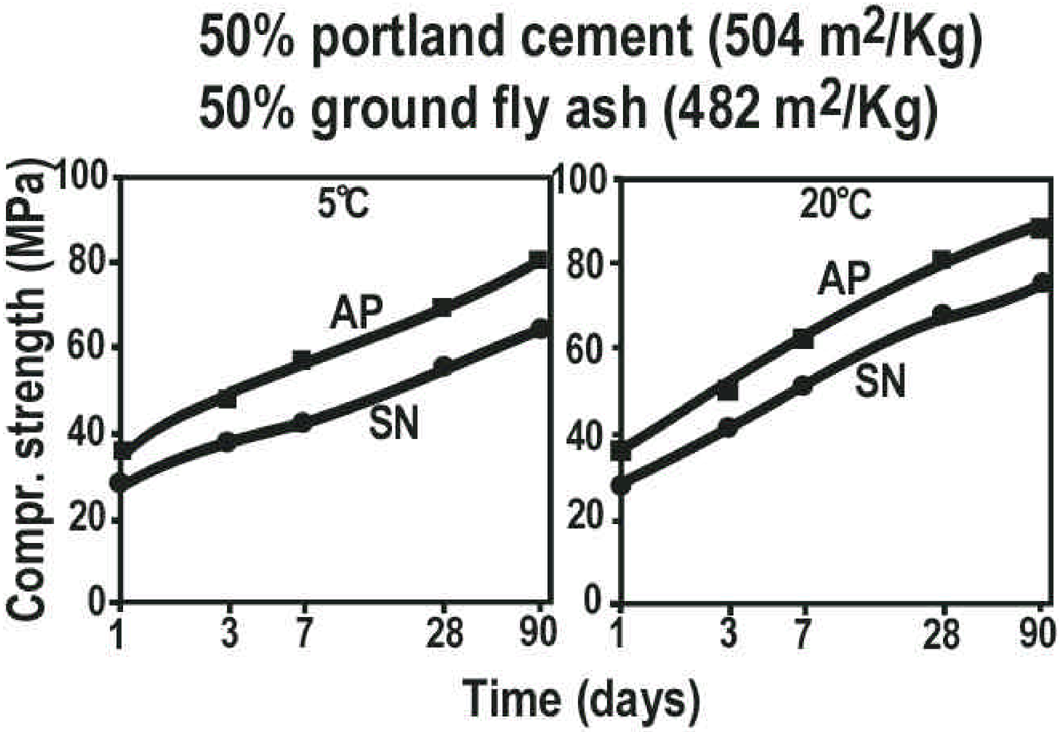

Fig. 5 - Influence of temperature and superplasticizer type on compressive strength versus time (cement D).

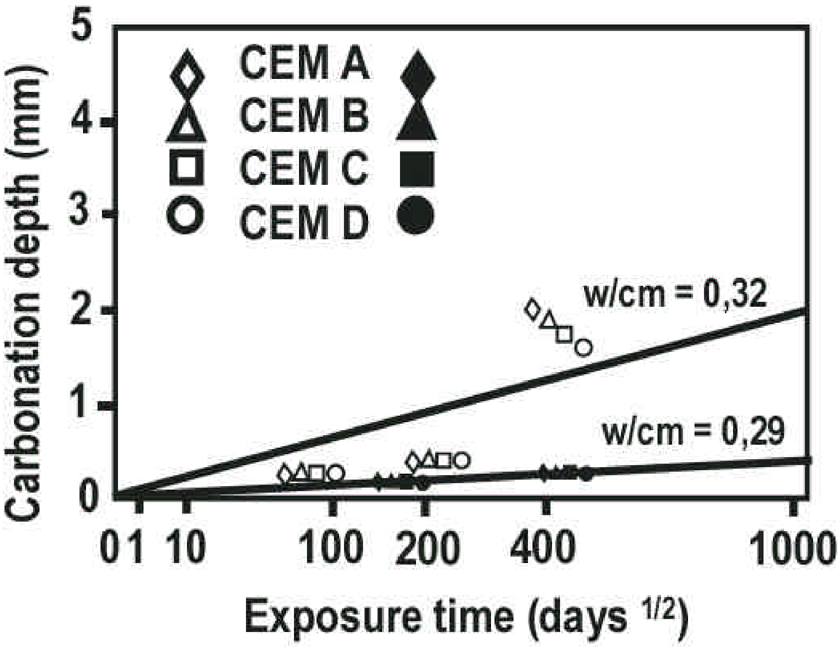

Fig. 6 - Carbonation of HVFA concretes as a function of cement fineness (Table 2) and superplasticizer type (SN or AP).

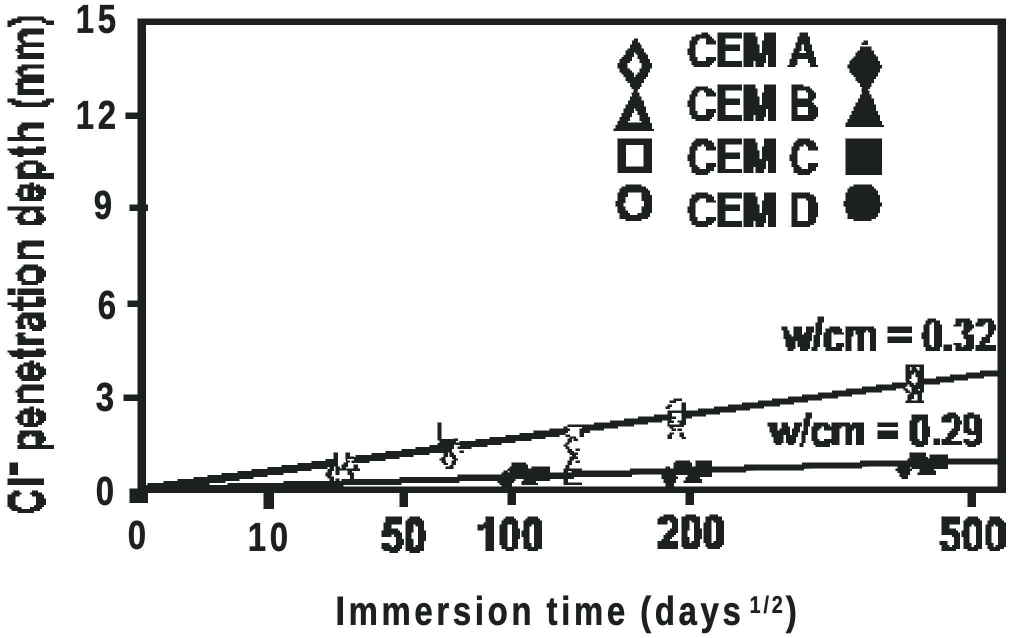

Fig. 7 - Chloride penetration in HVFA concretes as a function as the cement fineness (Table 2) and superplasticizer type (SN or AP).