Optimization of Silica Fume, Fly Ash and Amorphous Nano-Silica in Superplasticized High-Performance Concretes

By M. Collepardi, S. Collepardi, U.Skarp and R. Troli

Synopsis*:* The influence of some pozzolanic additions – such as silica fume, fly ash and ultra-fine amorphous colloidal silica (*UFACS*) – on the performance of superplasticized concrete was studied. Superplasticized mixtures in form of flowing (slump of 230 mm) or self-compacting concretes (slump flow of 735 mm) were manufactured all with a water-cement ratio as low as 0.44, in order to produce high-performance concretes (*HPC*). They were cured at room temperature (20°C) or steam-cured at 65°C in order to simulate the manufacturing of pre-cast members. Concretes with ternary combinations of silica fume (15-20 kg/m^3), fly ash (30-40 kg/m^3) and *UFACS* (5-8 kg/m^3) perform better – in terms of strength and durability – than those with fly ash alone (60 kg/m^3) and approximately as those with silica fume alone (60 kg/m^3). Due to the reduced availability of silica fume on the market, these ternary combinations can reduce by 60-70% the needed amount of silica fume for each pre-cast *HPC* element at a given performance level. Moreover, at later ages the strength reduction in steam-cured concretes with respect to the corresponding concretes cured at room temperature, is negligible or much lower in mixtures with the ternary combinations of pozzolanic additions.

Keywords: Carbonation, Chloride Diffusion, Fly Ash, High-Performance Concrete, Self-Compacting Concrete, Silica Fume, Steam-Curing, Superplasticizer, Ultra-Fine Amorphous Colloidal Silica

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INTRODUCTION

Silica fume appears to be the best performing siliceous product among the pozzolanic materials for high-performance concretes (*HPC*). Its behavior is related to the high content (> 90%) of amorphous silica in form of spherical grains in the range of 0.01-1 μm. However, silica fume is not available in large amounts and it is also the most expensive mineral addition (about 0.25-0.50 €/kg in Europe).

On the other hand, fly ash is available in large amounts and is relatively cheap (0.02-0.03 €/kg in Europe). However, its performance is lower than that of silica fume because of the lower amount of amorphous silica (35-40%) and the larger size (0.1-40 μm) of its spherical grains.

A new pozzolanic material [1, 2] produced synthetically, in form of water emulsion of ultra-fine amorphous colloidal silica (*UFACS*), is available on the market and it appears to be potentially better than silica fume for the higher content of amorphous silica (> 99%) and the reduced size of its spherical particles (1-50 nm): due to this reduced particle size, *UFACS* is also called "nano-silica" in comparison with the term "micro-silica" sometimes used for silica fume. Presently the UFACS price in Europe is 0.45-0.90 € per kg of water emulsion depending on the dry content.

The purpose of this work was to check whether a combination of silica fume, fly ash and nano-silica could perform in the fresh and in the hardened state as approximately that of silica fume alone at a given total cost of the concrete. If so, the combination of the ternary system "silica fume-fly ash-*UFACS*" could increase the available amount of the pozzolanic material for *HPC*.

EXPERIMENTAL: MATERIALS AND METHODS

A typical blended cement with 20% of limestone interground with 75% of clinker portland cement and 5% of gypsum, widely utilized in Europe for high-strength concretes, was used in this work. This cement is indicated as CEM II A/L 42.5 R according to EN 197-1 standards.

Table 1 shows the chemical analysis and the physical properties of the blended portland cement. Three pozzolanic additions were used: fly ash, silica fume and *UFACS* in form of a water emulsion containing 25% of colloidal silica. Their XRD-patterns are shown in Fig. 1 whereas their chemical analysis with size and surface properties are shown in Table 1. SEM micrographs in Fig. 2 show the typical particle morphology of these mineral additions used in this work. In particular the Fig. 2/A indicates that silica fume was a densified type with some agglomeration of its individual grains as usually available on the market to make easier the transportation, the storage and the dosage of this material.

Flowing and self-compacting concretes (*SCC*) were manufactured by using an acrylic-based superplasticizer: slump or slump flow were measured. These concretes were cured at room temperature (20°C) or steam cured at 65°C (3 hours of preliminary curing at 20°C; 3 hours from 20°C to 65°C; 7 hours at 65°C; 3 hours from 65°C to 20°C).

Compressive strength was measured at 1-90 days on all the concretes cured at 20°C or at 16 hours and 1-90 days on steam-cured concretes. The same concretes were cured 1 week (95% R.H.) and then immersed into an aqueous solution with 3.5% of NaCl or exposed to air, in order to determine the chloride diffusion or the carbonation rate respectively. The concrete thickness penetrated by Cl^- ions was determined by a colorimetric test based on the use of fluorescein and silver nitrate [3]. The concrete thickness penetrated by CO_2 was determined by the usual test based on the phenolphthalein.

RESULTS

Tables 2 and 3 show the composition of flowing and self-compacting concretes respectively. Each Table includes the composition of:

- the mix *SF* with silica fume alone (about 60 kg/m^3);
- the mix *FA* with fly ash alone (about 60 kg/m^3);
- the mix *TC1* with ternary combination containing silica fume (about 20 kg/m^3), fly ash (about 30 kg/m^3) and UFACS (about 7.5 kg/m^3 of dry colloidal silica); the cost of *TC1* was the same as that of *SF* by assuming the following prices for the pozzolanic additions: *0.50* €/kg for silica fume; 0.025 €/kg for fly ash and 0.45 €/kg for the aqueous emulsion of *UFACS* (25% of dry content);

- and the mix *TC2* containing silica fume (15 kg/m^3), fly ash (40 kg/m^3) and *UFACS* (about 5 kg/m^3 of dry colloidal silica); the cost of *TC1* was the same as that of *SF* by assuming the following prices for the pozzolanic additions: *0.25* €/kg for silica fume; *0.025* €/kg for fly ash and *0.45* €/kg for the aqueous emulsion of *UFACS* (25% of dry content).

The main differences between the flowing concretes (slump level of 230 mm) and the self-compacting concretes (slump flow of about 735 mm), both at a given *w/c* of 0.44 and with the same maximum size for the aggregate, were:

- the cement content (395 vs 425 kg/m^3), which is higher in the *SCC*;
- the aggregate grading (Fig. 3) which is richer in the sand – coarse aggregate ratio in the *SCC*;
- the amount of mixing water (175 vs 186 kg/m^3) which is higher in the *SCC*;
- the higher dosage of the acrylic superplasticizer (about 0.7 vs. 1.2% by cementitious materials) which is higher in the *SCC*.

Figures 4 and 5 show the compressive strength as a function of time for the flowing concretes and the *SCC* respectively. Both Fig. 4 and 5 show the results for concretes cured at 20°C or steam cured at 65°C and containing silica fume (mix *SF*), fly ash (mix *FA*) and the ternary two combination (*TC1* and *TC2*) of silica fume-fly ash-UFACS.

As expected, the strength development of the silica fume concrete (*SF* mix) is better than that of the fly ash concrete (*FA* mix) in both flowing (Fig. 4) and *SCC* mix (Fig. 5), regardless of the curing temperature.

On the other hand, the difference in the stregnth development between *SF* mixture and the concrete with the ternary combination (*TC1* and *TC2*) of pozzolanic mineral additions appears to be significant only for concretes cured at 20°C, specially at longer ages. However, in steam cured concretes there is no difference in the strength development between the *SF* mix and the *TC1* or *TC2* ones, regardless of the workability level of the concretes: in both flowing concretes (Fig. 4) and *SCC* (Fig. 5) the strength development of the *TC1* and *TC2* mixtures (with only 21 kg/m^3 and 15 kg/m^3 of silica fume respectively) is the same as those *SF* containing silica fume alone (about 60 kg/m^3).

Figures 6 and 7 show the penetration of chloride ions and CO_2, respectively, into the flowing concrete mixtures (Table 2). Figures 8 and 9 show the penetration of chloride ions and CO_2, respectively, into the *SCC* (Table 3). All these results deal with concretes cured at 20°C. Similar results were obtained for steam-cured concretes.

In both flowing mixtures (Fig. 6 and 7) and *SCC* (Fig. 8 and 9) the chloride diffusion as well as the CO_2 penetration are faster in concretes with fly ash (*FA*) with respect to those with silica fume (*SF*), independently of the curing temperature. The behavior of the concretes with ternary combinations of silica fume, fly ash and *UFACS* is very close to that of the corresponding concrete with silica fume alone (*SF*), specially in the steam-cured *SCC*.

CONCLUSIONS

As expected, concretes with silica fume alone (60 kg/m^3), perform better in terms of both strength and durability than concretes with fly ash alone (60 kg/m^3) independently of the early curing temperature (20°C or 65°C) and the workability level (flowing or self-compacted concretes).

Mixtures with ternary combinations of silica fume, fly ash and ultra-fine amorphous colloidal silica (*UFACS*), with reduced amount of silica fume (15-20 kg/m^3) perform as well as silica fume alone (60 kg/m^3) in terms of strength and durability, specially in steam-cured mixtures in both flowing and self-compacted concretes.

Moreover, these results confirm that steam-cured concretes containing silica fume or fly ash alone are much stronger than the corresponding concretes cured at room temperature only at early ages, whereas at longer ages (28-90 days) the compressive strength of the steam-cured concretes is significantly lower than that of corresponding concretes cured at room temperature. However, this strength loss at longher ages in steam-cured concretes with respect to the corresponding mixtures cured at room temperature, is negligible or much lower in the ternary combinations containing silica fume, fly ash and *UFACS*.

The results of this work indicate that for steam-cured *HPC* – such as those manufactured in precast industry – the combined use of silica fume, fly ash and *UFACS* allow two important advantages:

- the production of these concretes can occur by saving the amount of silica fume whose availability on the market is decreasing;
- the strength reduction at longer ages of the steam-cured concrete with respect to the corresponding mixtures cured at 20°C is negligible.

REFERENCES

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Table 1 – Chemical analysis and surface area properties

Composition	Cement	Silica Fume	Fly Ash	UFACS
SiO_2 (%)	16.7	98.2	60.1	99.1
Al_2O_3 (%)	3.5	—	22.8	—
Fe_2O_3 (%)	3.5	0.3	4.7	—
CaO (%)	63.0	0.2	4.6	—
MgO (%)	0.9	—	1.0	—
K_2O (%)	0.4	—	2.1	—
Na_2O (%)	0.1	—	0.6	—
SO_3 (%)	2.5	0.2	0.4	—
CO_2 (%)	8.8	—	—	—
Blaine Fineness m^2/g	0.42	18	0.36	—
Mean size (μm)	15	2	20	0.05

Table 2 – Composition of flowing concretes with cement and pozzolanic additions of silica fume, fly ash and UFACS.

Mix N°	Cementitious Materials (cm)				Aggregate (kg/m^3)	Water (kg/m^3)	Super-plasticizer (% by cm)	w/c	Slump (mm)
	Cement (kg/m^3)	Silica Fume (kg/m^3)	Fly Ash (kg/m^3)	UFACS (kg/m^3)					
SF	396	59	0	0	1800	174	0.87	0.44	230
FA	396	0	59	0	1800	175	0.61	0.44	270
TC1	393	21	29	7.8	1790	173	0.60	0.44	230
TC2	395	15	40	5.1	1800	174	0.55	0.44	230

Table 3 – Composition of SCC concretes with cement and pozzolanic additions of silica fume, fly ash and UFACS.

Mix N°	Cementitious Materials (cm)				Aggregate (kg/m^3)	Water (kg/m^3)	Super-plasticizer (% by cm)	w/c	Slump Flow (mm)
	Cement (kg/m^3)	Silica Fume (kg/m^3)	Fly Ash (kg/m^3)	UFACS (kg/m^3)					
SF	423	60	0	0	1775	186	1.30	0.44	730
FA	424	0	61	0	1780	186	1.20	0.44	740
TC1	425	21	30	7.4	1785	187	1.18	0.44	730
TC2	425	15	40	4.9	1780	187	1.10	0.44	750

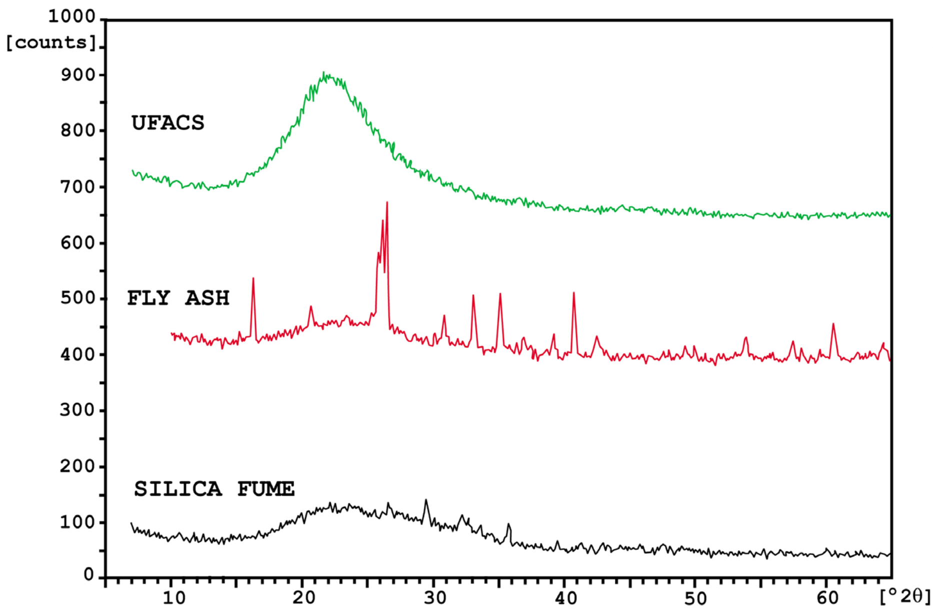

Fig. 1 – XRD patterns of silica fume, fly ash and UFACS

A **B** **C**

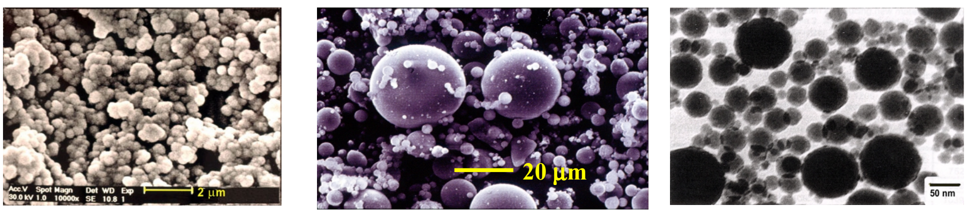

Fig. 2 – SEM micrographs showing: silica fume (A), fly ash (B) and UFACS (C). The scales of the three micrographs are significantly different.

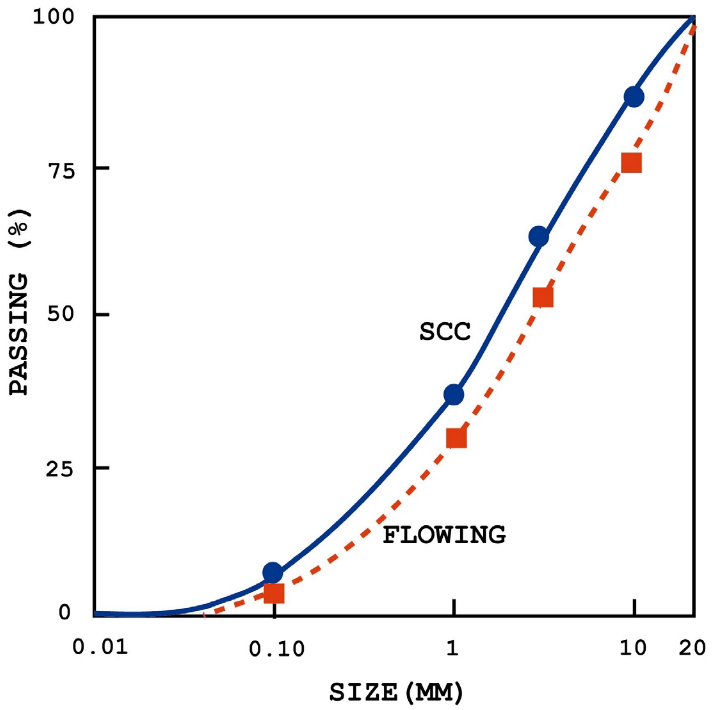

Fig. 3 – Particle size distribution of aggregates for flowing and self-compacting concretes.

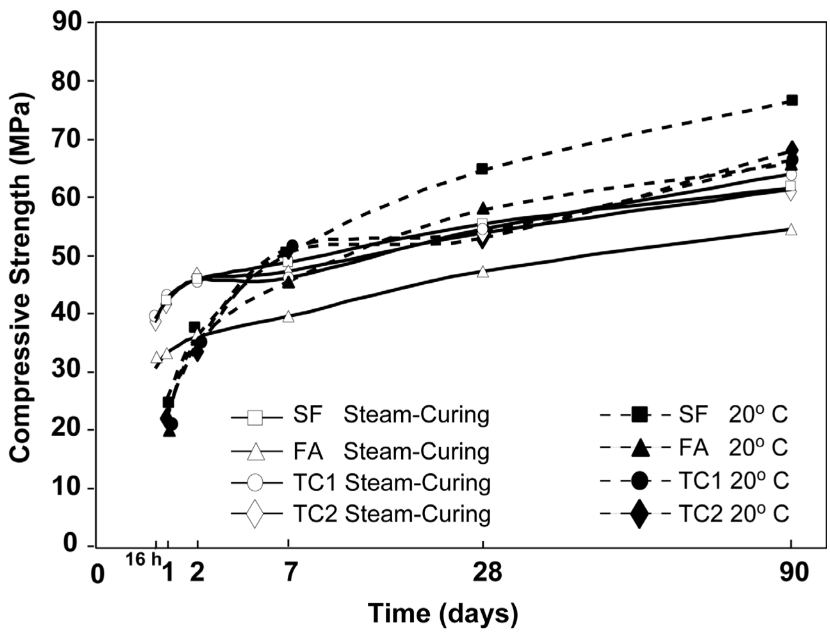

Fig. 4 – Compressive strength of flowing concretes

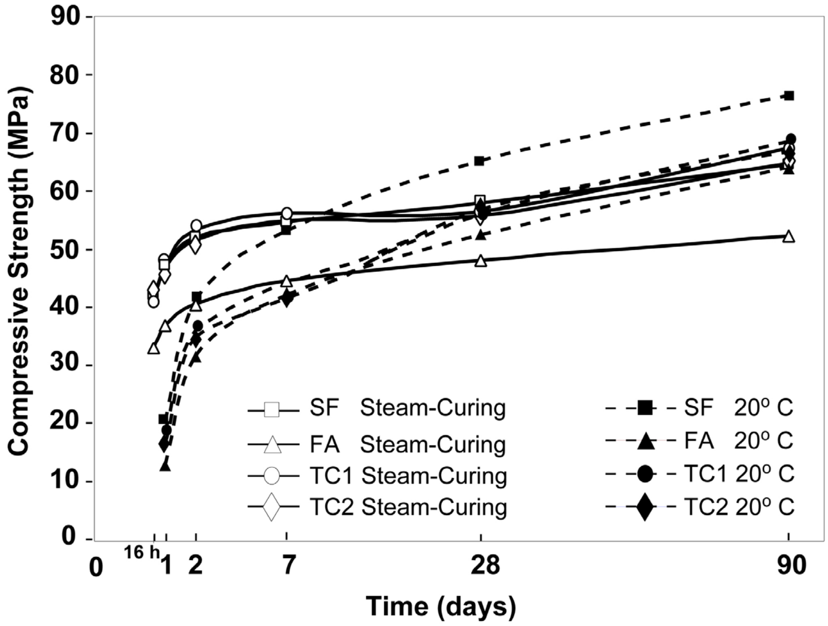

Fig. 5 – Compressive strength of SCC

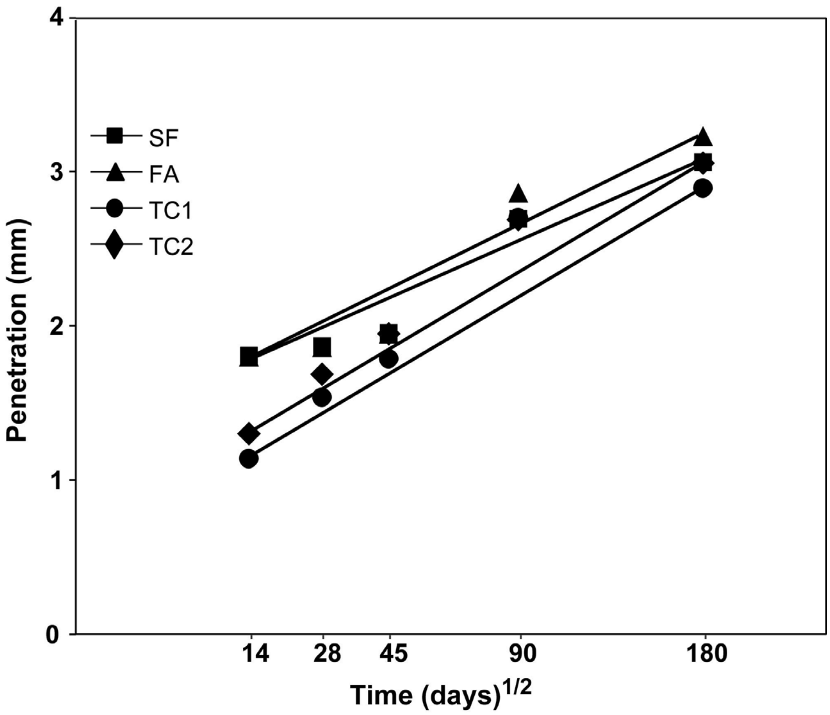

Fig. 6 – Penetration of Cl^- in flowing concretes cured at 20°C

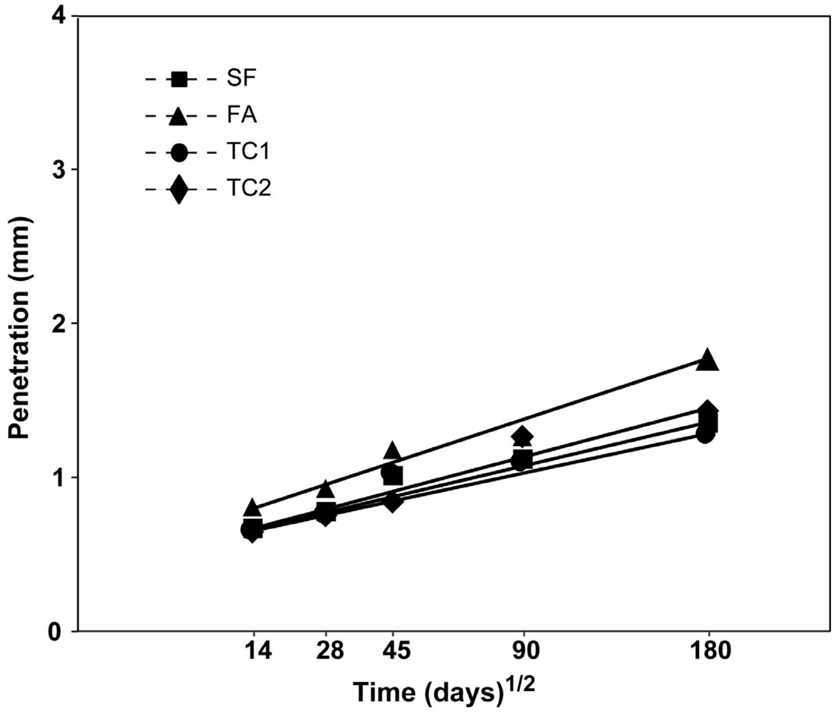

Fig. 7 – Penetration of CO_2 in flowing concretes cured at 20°C

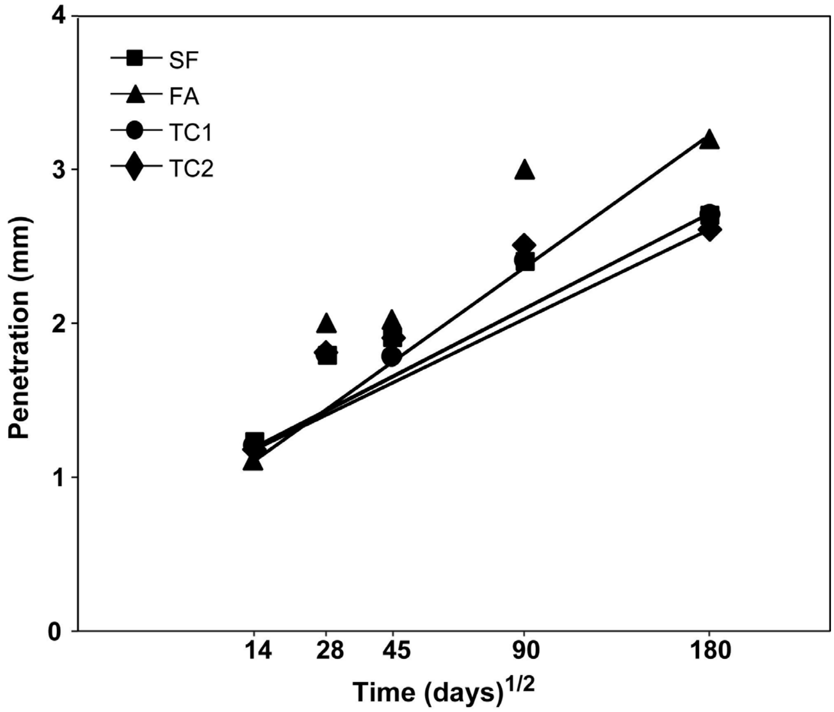

Fig. 8 – Penetration of Cl^- in SCC cured at 20°C

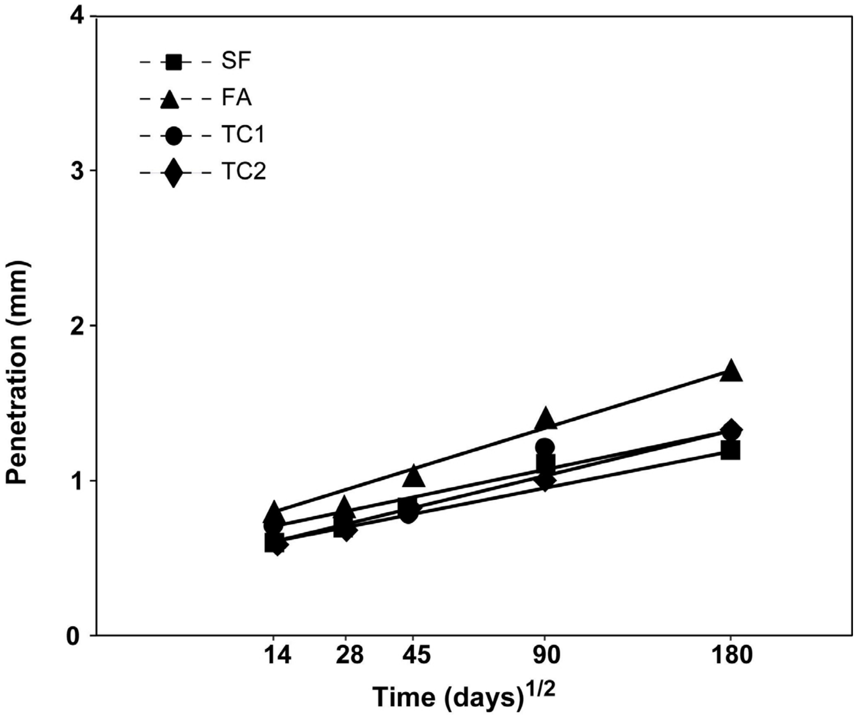

Fig. 9 – Penetration of CO_2 in SCC cured at 20°C