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INFLUENCE OF NANO-SIZED MINERAL ADDITIONS ON PERFORMANCE OF SCC

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ABSTRACT: Superplasticizers are the most important admixtures enhancing concrete performance. The development of new superplasticizers during the last decades has determined the most important progress in the field of concrete structures in terms of higher strength, longer durability, lower shrinkage and safer placement particularly in elements with very congesteded reinforcement. The progress from sulphonated polymer to polycarboxylate has resulted in higher water reduction at a given workability and lower slump loss.
More recently poly-functional superplasticizers have been developed which are able to completely keep the initial slump for at least 1 hr without any retarding effect on the early strength. Moreover, multi-purpose and poly-functional superplasticizers have been invented which are able to reduce drying shrinkage.

Keywords: Adsorption, Polycarboxylate, Polyether, Water-reduction, Slump-loss, Shrinkage, Steric hindrance, Superplasticizer, Zeta potential.

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INTRODUCTION

Concrete performance is strongly dependent on nano-size dimensions of solid material such as C-S-H particles or voids such as the gel porosity in the cement matrix and the transition zone at the interface of cement paste with aggregates or steel reinforcements. Typical properties affected by nano-sized particles or voids are strength, durabilty, shrinkage and steel-bond. Fundamental contributions in this area of cement chemistry and concrete science are due to Bogue, Powers, Brunauer, Grudemo, Lea, Taylor, Wittmann, Mehta and many other researchers very active in this area during the second half of the previous century [1-3]: in that period of time the terms "nano-science" and "nano-technology" were not yet familiarly used as today; however they were really practicized and successfully applied to the progress in the field of concrete science and technology.

The purpose of the present work was to study some new materials in the dimension range between "micro" and "nano" size. These materials are:

- magnetite fume (MF);
- ultra-fine fly ash (FFA);
- ultra fine colloidal amorphous colloidal silica (UFACS).

EXPERIMENTAL

In the following paragraphs the materials used and the methods adopted are described.

2.1 Materials

Ordinary Portland Cement (OPC) was used (CEM I 52.5 R according to the European Standard EN 197-1). Natural sand (0-4 mm) and gravel (4-20 mm) were used for concrete mixtures.

Fly ash (FA) and silica fume (SF) were also used in order to compare the well known performance of these materials with that of the MF, FFA and UFACS. Chemical analysis of OPC, FA and SF are shown in Table 1.

Polycarboxilate-based superplasticizer (30% in aqueous solution) was used to produce Self-Compacting Concrete (SCCs) with a relatively low water-cement ratio.

The characteristics of the other three materials (MF, FFA and UFACS) are presented in the following paragraphs.

Table 1 Chemical composition of the cementitious materials.

%	OPC	FA	SF	FFA*	MF	UFACS*
SiO_2	16.8	60.0	98.2	60.1	5.1	99.1
Al_2O_3	3.7	22.7	—	22.6	2.1	—
CaO	63.1	4.5	0.2	4.5	10.7	—
MgO	1.0	1.0	—	1.0	6.7	—
Fe_2O_3	3.8	4.6	0.3	4.6	58.5	—
Na_2O	0.7	0.7	—	0.6	1.0	—
K_2O	0.6	2.0	—	2.1	1.0	—
SO_3	2.9	0.5	0.1	0.6	1.4	—
ZnO	—	—	—	—	3.7	—
PbO	—	—	—	—	2.7	—
CuO	—	—	—	—	0.2	—
L.o.i.	5.2	4.0	1.0	3.9	3.4	—

* Referred to dry product

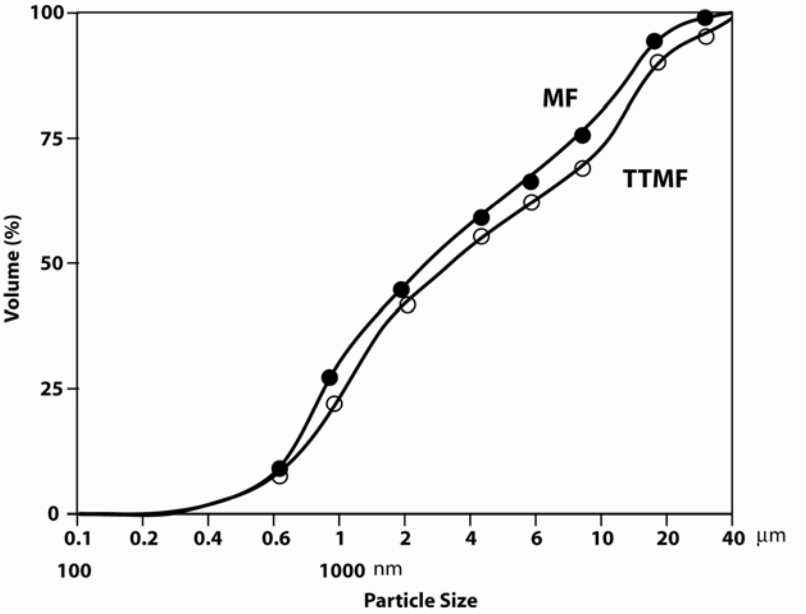

Figure 1 – Particle size distribution of MF and TTMF.

2.1.1 Magnetite Fume

MF is a very fine powder recovered as a fume from the foundry process to recycle ferrous metallic wastes. Figure 1 shows the particle size distribution: about 25 % of its volume is finer than 1000 nm. Figure 2 shows the morphology of MF by Scanning Electron Microscopy (SEM). Table 1 shows the chemical composition of magnetite fume characterized by about 60% of iron oxide and only 5% of silica; other important products are metal oxides such as ZnO, CuO and PbO acting as potentially retarders for the cement hydration. The main product, i.e. iron oxide, appears in the form of magnetite ($FeFe_2O_4$) or magnesium-hematite ($MgFe_2O_4$) in the X-Ray Diffraction (XRD) pattern shown in Figure 3. Thermal analysis of MF (Figure 4) shows that about 3.5% of this material is thermally decomposed when heated from room temperature to about 1000 °C as indicated by the thermo-gravimetric (TG) curve; this weight loss is accompanied by an exothermic effect at about 700 °C as indicated by the differential thermal analysis (DTA) curve. The TG and DTA results indicate that MF contains some organic products which are thermally destroyed, since these products are related to the organic paints coating the original ferrous materials which are not completely destroyed in the foundry process. By gas-chromatografic analysis these organic products were identified as benzaldehide and toluene based-materials. Two samples of magnetite fume were examined to study the influence of these organic products on the cement hydration and then on the strength development : MF as received and MF thermally treated at 800°C (TTMF) to completely remove the organic products. The particle size distribution (Figure 1) as well as the spherical aspect of MF (Figure 2) do not change significantly by the thermal treatment at 800°C.

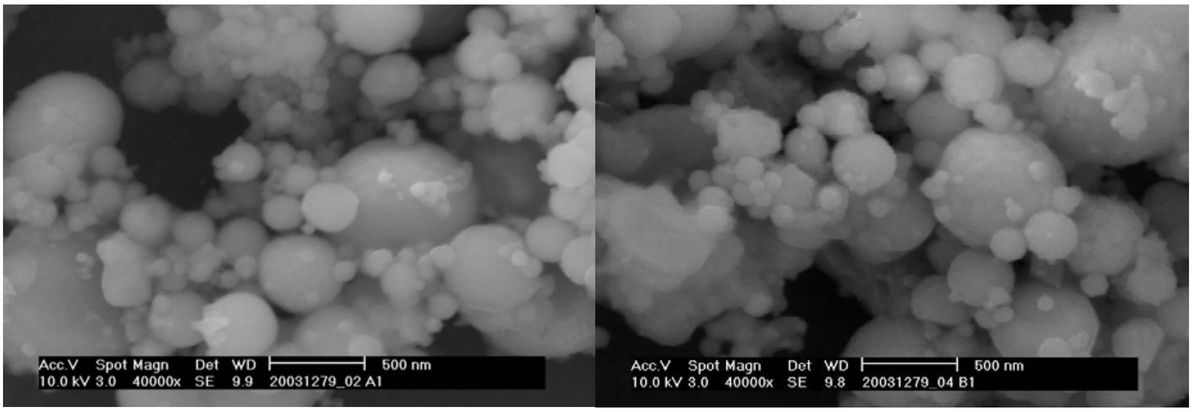

Figure 2 – SEM micrograph of MF (left) and TTMF (by courtesy of D. Salvioni - Mapei).

2.1.2 Fine Fly Ash

Fine fly-ash (FFA) is the result of a special treatment consisting in the wet grinding process of an aqueous slurry (50% of solid content). Due to this process, unburnt coal and coarse particles (>10 µm) are finely ground. This beneficiation process increases the number of spherical particles with respect of that of the un-treated fly ash, as shown in the SEM micrograph of Figure 5. The particle size distribution of FFA (Figure 6) indicates that it contains about 10% by volume of grains which are smaller than 500 nm. Figure 6 indicates that the particle size distribution of FFA is between those of silica fume and fly ash. XRD pattern indicates that the mineral composition of FFA is very similar to that of the untreated fly ash (Figure 3).

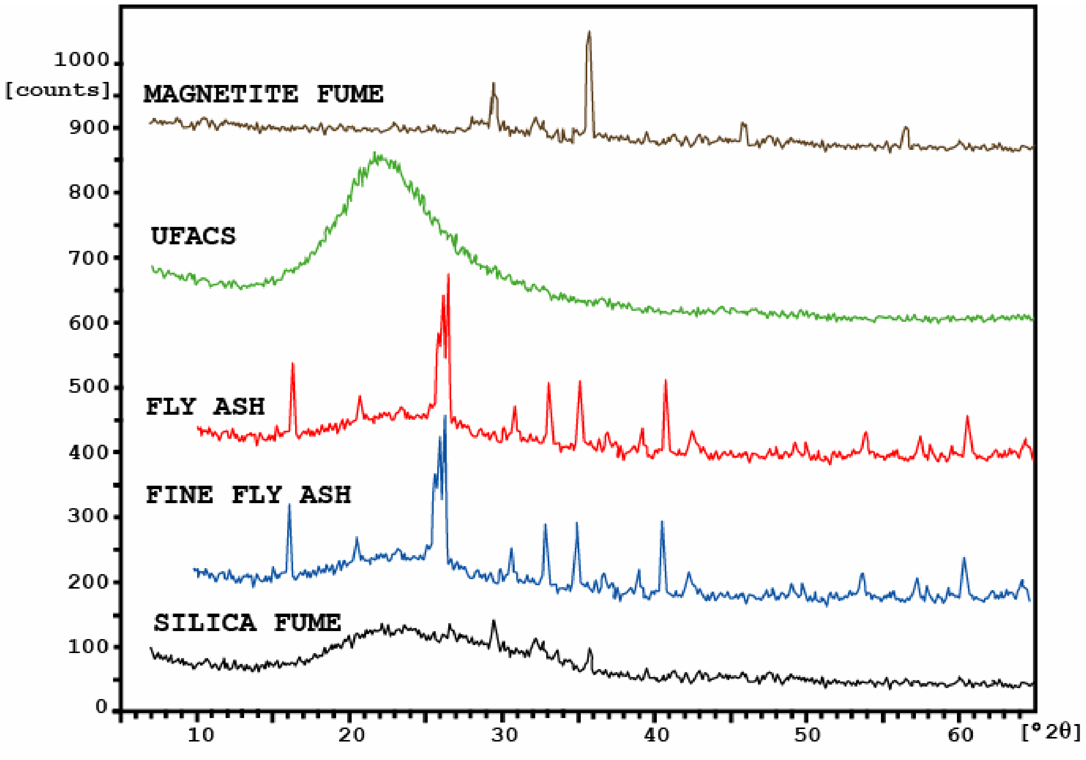

Figure 3 – XRD patterns of all the mineral additions (MF, FA, FFA, SF and UFACS).

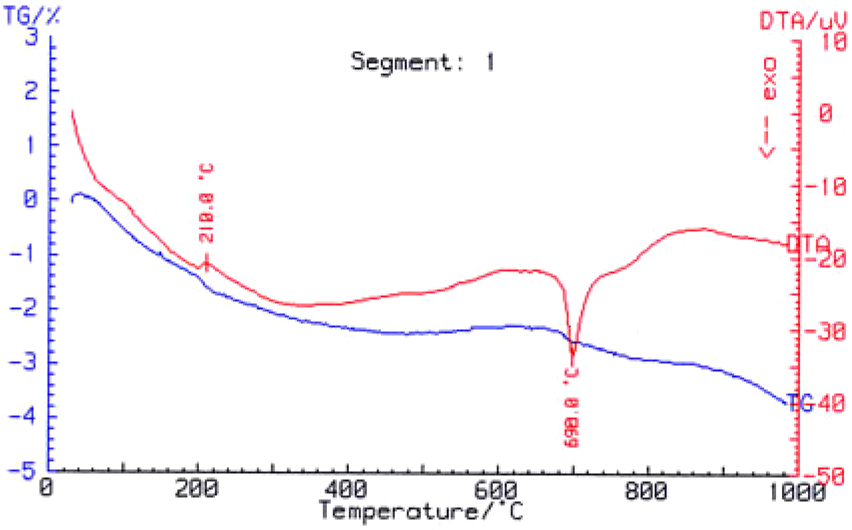

Figure 4 – Thermal analysis of MF.

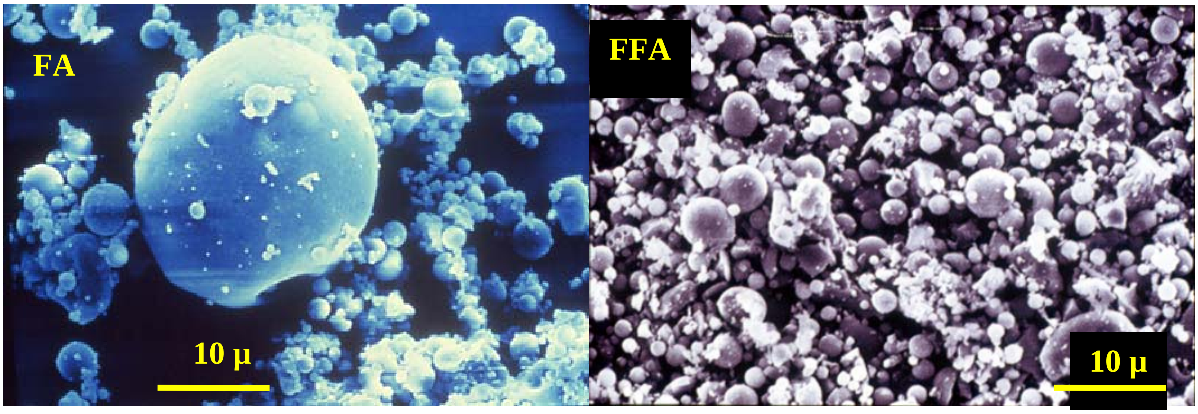

Figure 5 – SEM micrograph of FA and FFA.

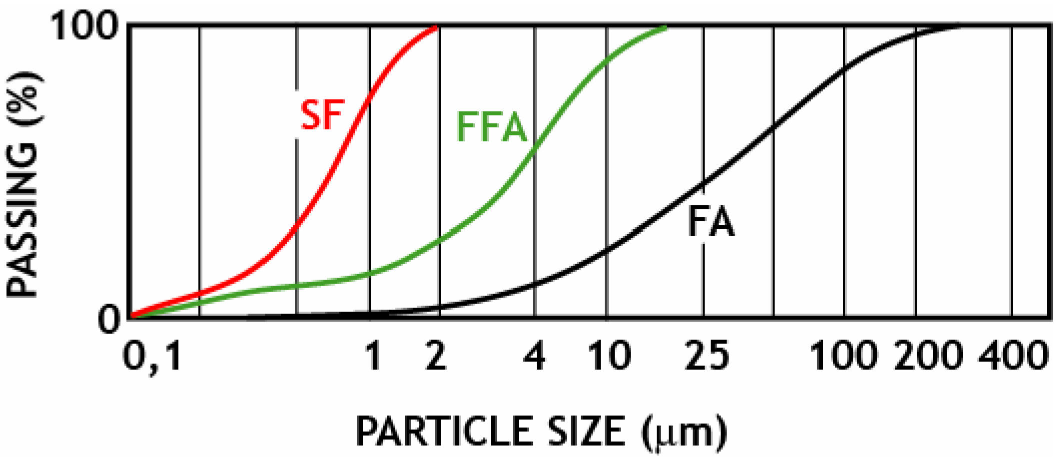

Figure 6 – Particle size distribution of SF, FA and FFA.

2.1.3 Ultra-Fine Amorphous Colloidal Silica

UFACSs are synthetic products with spherical particles in the range of 1-50 nanometers. They have already been studied as viscosity modifying agents (VMA) in combination superplasticizers in order to produce SCC: the product used in this work is a colloidal silica water emulsion (35% of dry solid) with particle size distribution of the solid material in the range of 5-15 µm. The chemical analysis shows that it consists mainly of pure silica (>99%) dispersed in an aqueous phase as shown in Table 1. Figure 3 shows the XRD pattern of UFACS in comparison with the other materials studied in the present work and confirms that is a completely amorphous silica without any form of crystallized products.

2.2 Methods

Self-Compacting Concretes have been manufactured and characterized in the fresh state by slump-flow test and/or other rheological measurements such as V-funnel and L-box tests. They were cured at room temperature (20°C) or steam cured for 6 hours at 65°C after a preliminary curing at room temperature of 2 hours and a heating process at 10°C/hours at 18 hours the steam treated specimens were cured at room temperature. Compressive strength were generally measured at 1-60 days, and in some cases up to 90 days.

RESULTS

In the following paragraphs the properties of the self-compacting concretes containing the three "nano-size" mineral materials are discussed in terms of rheological performance in the fresh state and compressive strength in the hardened one.

3.1 MF-SCC

The composition of self-compacting concretes with magnetite fume (MF-SCC) is shown in Table 2: MF as received or thermally treated at 800°C (TTMF) have been used to replace 100 kg/m^3 of limestone of the control SCC mix. The control mix without MF or TTMF shows some segregation and bleeding water, whereas both the MF-SCC and TTMF-SCC mixtures are much more cohesive and without any significant bleeding (Table 2). So both MF and TTMF act as excellent viscosity modifying agents due to the presence of nano-sized MF particles (Fig. 1). On the other hand, due to the favourable spherical particles there is no significant change in the slump flow at a given water-binder ratio and dosage of superplasticizer.

Table 2 Composition and properties of SCCs in the fresh state with and without MF or TTMF.

kg/m^3	CONTROL SCC	MF-SCC	TTMF-SCC
OPC (CEM I 52.5R)	320	318	322
Filler ($CaCO_3$)	230	130	130
Water	180	179	181
MF	—	100	—
TTMF	—	—	100
Sand (0-4 mm)	785	784	786
Gravel (4-16 mm)	820	819	821
SP	6	6	6
VMA	0.5	0.1	0.1
Slump-flow (mm)	700	705	700
Bleeding capacity (%)	1	0.1	0.0

Compressive strength as a function of the curing time at room temperature is shown in Figure 7. The replacement of 100 kg/m^3 of limestone by MF significantly retards the strength development at early ages (1-7 days). At longer ages (28-60 days) there is still a strength deficiency of about 25 %.

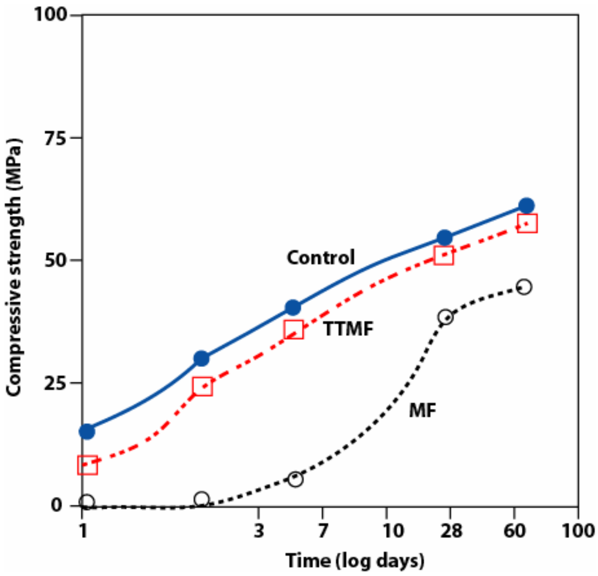

Figure 7 – Concrete compressive strenth as a function of time at 20°C with and without MF or TTMF.

On the other hand, in the presence of TTMF, the retarding effect on the strength development at early ages is significantly reduced and completely disappears at longer ages (60 days). This behaviour indicates that the retarding effect in cement hydration responsible for the early strength reduction, is primarily due to the organic products destroyed by the thermal treatment at 800°C. Moreover, the slight strength reduction at early ages in TTMF-SCC with respect to the reference mix may be related with the retarding effect of the metallic elements (Zn, Pb, Cu) and/or with the replacement of OPC by TTMF: however, since this effect completely disappears at longer ages (60 days) and since TTMF is not a pozzolanic material it may contribute to improve the nano-structure of the cement paste (by reducing the capillary porosity) or that of the transition zone by filling the micro-voids at the interface of the cement matrix with the coarse aggregate.

3.2 FFA-SCC

The compositions and the rheological properties of self-compacting concretes with 20% replacement of OPC by fine fly ash (FFA-SCC) or by ordinary fly ash (FA-SCC) are shown in Table 3 in comparison with the self-compacting concrete containing 10% of silica fume (SF-SCC) and the reference SCC mix without any mineral addition and containing 530 kg/m^3 of OPC.

In the fresh state, at a given slump flow (about 700 mm) the FFA-SCC mix is much better than the corresponding FA-SCC mix or the reference SCC mix without any ash addition, in terms of a better mobility measured by the V-funnel or L-box tests. Moreover, the amount of superplasicizer needed to reach a given value of the slump flow for the FFA-SCC is slightly lower (about 10%) than that required for the corresponding FA-SCC, lower (about 20% less) than that necessary for the SF-SCC, and much lower (about 30% less) than that needed for the reference SCC mix.

Table 3 Composition and properties of SCCs in the fresh state with and without SF, FA and FFA.

kg/m^3	CONTROL SCC	SF-SCC	FA-SCC	FFA-SCC
OPC (CEM I 52.5R)	530	477	425	424
Filler ($CaCO_3$)	205	200	195	195*
Sand (0-4 mm)	860	850	840	840
Gravel (4-16 mm)	780	781	770	780
SF	—	53	—	—
FA	—	—	106	—
FFA	—	—	—	110**
Water	238	239	239	237
SP	8.0	7.0	6.2	5.6
VMA	0.6	0.4	0.6	0.5
Slump-flow (mm)	700	690	700	710
V-Funnel (sec)	21	31	28	16
L-Box (sec)	47	56	50	40

* including the water of the FFA Slurry ** referred to dry FFA

Figure 8 shows the compresssive strength development at 1-90 days. FFA-SCC performs much better than the corresponding FA-SCC at both early and longer ages, better than the reference SCC mix at ages longer than 7 days, and very close to the SF-SCC particularly at 90 days. Other results, not shown in this paper, indicate that - when manufactured at the same superplasticizer dosage (1.3 % by binder weight) - FFA-SCC performs better than SF-SCC due to the lower w/c adopted in the former with respect to the latter. Moreover, due to the lower cost of FFA with respect to the SF, FFA-SCC with 20% of OPC replacement is cheaper than FS-SCC with 10% of OPC replacement.

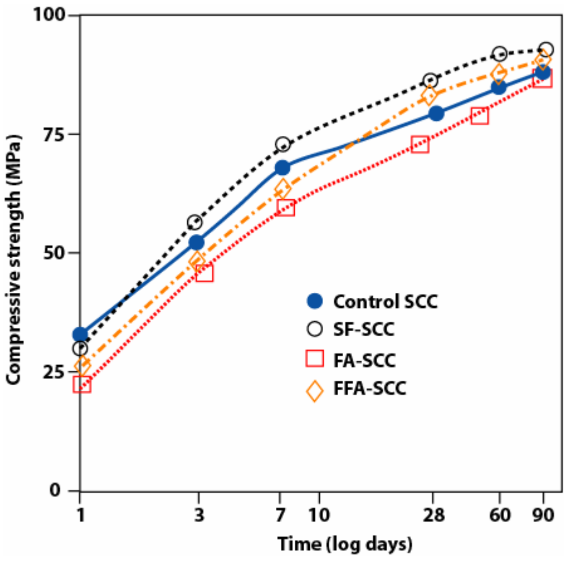

Figure 8 – Concrete compressive strength as a function of time at 20°C with and without SF, FA or FFA.

3.3 UFACS-SCC

Figure 8 shows that 100 kg/m^3 of fine fly ash, corresponding to a 20% replacement of OPC in FFA-SCC, perform as well as 50 kg/m^3 of silica fume, corresponding to a 10% replacement of OPC in the SF-SCC only at longer ages (90 days). In order to further improve the performance even at early ages of FFA - potentially available in very large amounts - with respect to that of silica fume, which is very espensive because it is available in very small amounts [4], a combination of FFA and UFACS, in the form of an aqueous slurry, was studied in comparison with silica fume for SCC cured at room temperature or steam cured at 65°C.

Self-compacting concretes with a binder content of 530 kg/m^3 were manufactured (Table 4): the SF-SCC mix contains 477 kg/m^3 of OPC and 53 kg/m^3 of silica fume; the UFACS-SCC mix based on the combination of FFA and UFACS contains 200 kg/m^3 of the FFA-based slurry (corresponding to 100 kg/m^3 of dry fine fly ash) and 10 kg/m^3 of the UFACS aqueous emulsion, corresponding to 3.5 kg/m^3 of dry colloidal silica. By taking into account the typical cost of these materials in Europe (0.5 €/kg for SF; 0.8 €/kg for UFACS in the form of a water emulsion with a solid content of 35%; 0.05 €/kg for FFA in the form of an aqueous slurry with 50% of solid material) the combination of 100 kg of dry FFA and 3.5 kg of dry UFACS is cheaper than 50 kg of SF. These amounts for these ingredients were used in the two SCC shown in Table 4. The water-binder ratio was the same for the two SCCs (0.38) and the same slump flow (about 700 mm) was obtained by using a proper dosage of superplasticizer (6 vs. 7 kg/m^3) was needed with respect to the SF-SCC mix to obtain the same workability level. Moreover, due to the improvement in the cohesiveness of the mix produced by the presence of UFACS, no viscosity modifying agent (VMA) was needed in the UFACS-SCC mix.

Table 4 Composition and properties of SCCs in the fresh state with SF or FFA and UFACS.

kg/m^3	**SF-SCC**	**FFA-UFACS SCC**
OPC (CEM I 52.5R)	477	427
Water	200	190
Sand (0-4 mm)	850	855
Gravel (4-16 mm)	781	780
SF	53	—
FFA	—	100*
UFACS	—	3.5*
SP	7.0	6.0
VMA	0.4	—
Slump-flow (mm)	690	700

* Referred to dry product

Compressive strength values of the concretes cured at room temperature (20°C) or steam cured at 65°C are shown in Figure 9 or Figure 10, respectively. The performance of silica fume is slighty better than that of the combination FFA-UFACS only for concretes cured at room temperature at early ages (1-7 days). The opposite is true for concretes steam cured at early or later ages. The combination of FFA and UFACS is better than that of SF at longer ages (28-69 days) independently of the curing temperature. Moreover, it is confirmed [4] that, in the presence of UFACS, there is no usual strength reduction at longer ages in steam cured concretes with respect to the corresponding concretes cured at 20°C.

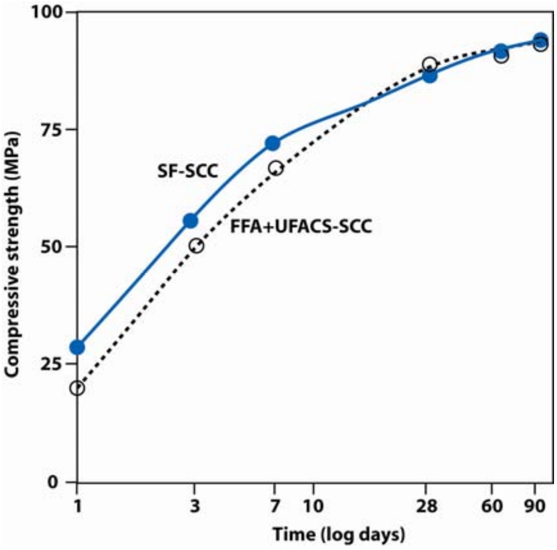

Figure 9 – Concrete Compressive strength as a function of time at 20°C with SF or FFA+UFACS.

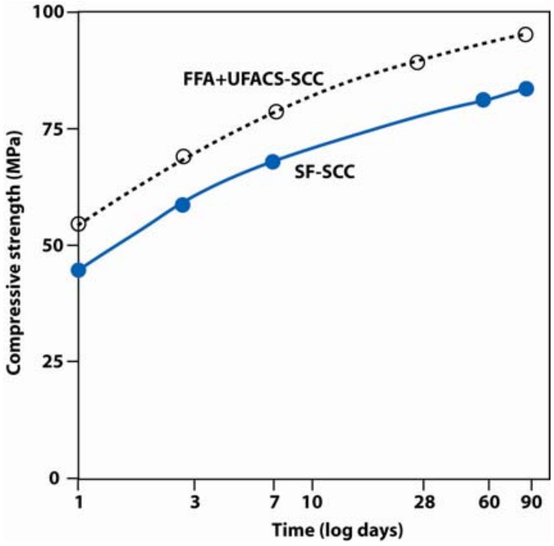

Figure 10 – Compressive strength of steam cured SCCs with SF or FFA + UFACS.

CONCLUSIONS

Three materials with their particle size completely or partially in the range of 0-1000 µm have been studied to manufacture SCCs:

- UFACS (ultra-fine amorphous colloidal silica) in the form of a sinthetic water emulsion, with spherical particles in the range of 5-15 µm.
- FFA (fine fly ash), from a wet-grinding process of coal fly ash, with 10 % of particles smaller than 500 nm.
- MF (magnetite fume),recovered from the foundry process to recycle ferrous metallic wastes, with 25 % of spherical particles smaller than 1000 nm.

The combined action of FFA with UFACS, in the form of an aqueous slurry, appear to perform better than silica fume alone, particularly in steam cured SCCs, with an economic advantage with respect to the very expensive silica fume.

SCC with fine fly ash performs much better, in terms of both rheological properties and compressive strength, than the corresponding concrete with fly ash.

Magnetite fume could be advantageously used as an effective filler in manufacturing SCC, provided that the unburnt organic products are completely removed by heating MF at 800°C. In the absence of this thermal treatment, a strong retarding effect on the cement hydration occurs and then also the hardening process too is significantly retarded.

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