

Early Strength Enhancement for Sustainability in The Precast Concrete Industry

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ABSTRACT

Promoting sustainability is becoming nowadays a major issue for the precast concrete industry. The challenging target may be achieved mainly by reducing the consumption of energy for concrete curing and by optimizing the mix composition. This can be done including significant amounts of Supplementary Cementitious Materials, using cements with lower clinker content or decreasing the cement content that, very often, is used only to achieve the required early strength.

At the same time, high productivity and turnaround of molds is recognized as a critical economical factor in the precast production and can be obtained only if strength development is fast enough to allow safe demolding.

Proper acceleration of the early hydration of cement could allow a cost effective and sustainable concrete production, thus combining the somehow conflicting needs mentioned above. A new accelerator, based on finely dispersed hydrated cement particles, is presented here, which fulfils the current expectations of the precast concrete industry.

INTRODUCTION

Many innovations have interested the precast concrete industry in the last decades: the introduction of the polycarboxylate-ether superplasticizers, in particular, has represented a breakthrough in concrete technology: thanks to their superior capability to make the concrete flowable at much lower water/cement ratios, they have permitted a major advancement in the quality and durability of the precast elements.

By exploiting the unique flexibility of the polycarboxylate chemistry, different polymeric structures were successively developed, which resulted over the years in different generations of polycarboxylate-based products offering, besides the water reduction, other specific benefits like early strength acceleration [Corradi et al., 2002; Khurana et al., 2002], better rheology of concrete, higher robustness in the use with diversified types of materials [Zeminian et al., 2008].

Besides the low water-to-cement ratio necessary to meet the requirements of strength and durability, concrete producers traditionally need high early strength, so as to minimize the curing time and permit a quick turnover of moulds, thus increasing and optimizing the production. In more recent times, sustainability has become a major driving force and many initiatives have been started by the precast industry in order to promote it. Sustainability may

be achieved mainly in two ways: by reducing the consumption of energy used for curing and by reducing the clinker content in the concrete mix. The reduction of clinker content, resulting in decreased CO₂ emissions, may be realized either by reducing the cement content or by switching to a lower-graded cement or, finally by partially replacing it with limestone or with the so-called Supplementary Cementitious Materials (SCM) like fly ash and ground granulated blast furnace slag. However, all these approaches would also negatively affect the early strength development, thus productivity and the economic interests of the producers. Combining the apparently conflicting properties of sustainable development and quick and efficient production process, represents the real modern challenge of the precast industry. A major advancement has been achieved, in this respect, with the introduction of the Zero Energy System, comprising very advanced PCEs which fully exploit the potential of the polycarboxylate-ether chemistry: extremely low water cement/ratios can be achieved with them, along with the minimum retardation effect on cement hydration [Corradi et al., 2002; Khurana et al., 2002].

Very often, the amount of cementitious material in the concrete mix is higher than the amount needed to achieve the required long-term strengths, just to guarantee the early strengths that are needed for a quick demolding. Having a suitable accelerator could avoid that, allowing a production efficient and economically favourable and, at the same time, sustainable. Water solutions of nitrates, thiocyanates and formates are typically used as early strengths accelerators since several decades; their use is quite widespread and effective, but not enough to win the current challenge for sustainability.

An innovative concept for hardening acceleration of concrete is presented here, that significantly exceed the performances of traditional accelerators, thus allowing to combine the apparently conflicting needs of the precast industry, i.e. high productivity and sustainability. This is based on hydrated cement finely dispersed particles (HCFDP). Experimental evidence of the performances of this admixture, as well as of its mechanism of action, will be presented in the present paper.

EXPERIMENTAL

Materials employed. Two cements, Type I 52.5 R according to EN 197/1, were employed. Their chemical analysis was carried out according to the methods reported in EN 196/2. Additionally, XRD quantitative Rietveld analysis of the cements was performed. The amounts of sulphate carriers were determined by combining XRD and DSC analysis. The chemistry of the pore solution extracted from the cements was also evaluated: soluble sulphates were measured through ionic chromatography, while soluble alkalis and calcium were evaluated by means of Inductive Coupled Plasma (ICP). Besides chemical analysis, laser granulometric analysis of the limestone, fly ash and slag was also carried out.

A polycarboxylate-based superplasticizer (PCE) was used in the work, in the form of a 30% solution having pH 7 and density $1.060 \pm 0.05 \text{ g/cm}^3$. The new accelerator presented here, which will be named HCFDP (hydrated cement finely dispersed particles), is a water suspension of finely divided cement hydrates, with a total solid of 20% and density $1.135 \pm 0.005 \text{ g/cm}^3$. The traditional accelerator used is a 52% solution of nitrates and other minor components, commercially available as Glenium Activator. Its density is $1,415 \text{ g/cm}^3$.

TGA analyses. Cement pastes were prepared according to EN 196-3 with a w/c ratio of 0.33 and a PCE dosage of 0.7% bwc. The dosages of HCFDP and the traditional accelerator were respectively 4% and 2.5% bwc. This is known to be the dosage of the traditional accelerator corresponding to its maximum performances. The pastes were hydrated at 10°C in 4x4x16

cm specimens, which were tested at early ages, ranging between 4 and 24 hours, as well as after 28 days. Hydrated samples were washed with ethanol and diethyl ether in order to stop hydration and then dried at 40°C for 30 minutes. The resulting powders were analyzed by Mettler Toledo TGA SDTA 851e, increasing the temperature from 25 to 900 °C at the rate of 10°C/min in nitrogen flow.

²⁹Si Nuclear Magnetic Resonance (NMR) analyses. Cement pastes with water/cement ratio of 0.33 and PCE-based superplasticizer dosage of 0.7% by cement weight were prepared according to EN 196-3. Two of the pastes were prepared with accelerating admixtures, incorporating, respectively, 2.5% of the traditional accelerator and 4.0% of HCFDP by cement weight and were compared to a reference paste without accelerator (blank). All the cement pastes were maintained at 10°C until the age of sampling. Samples for NMR tests were obtained by grinding the hardened paste in an agate mortar followed by several rinses with ethanol and diethyl ether with the aim of preventing further hydration by removing the unbonded water.

Concrete tests. Concrete tests were made preparing 30-litre batches in a vertical axis lab mixer. The different mix proportions which were used are reported in table 1. The mixtures were prepared according to the following procedure: cement and aggregates were placed in the mixer with two thirds of the mix water and mixing was carried out for 1 minute, followed by 1 minute stop, to allow for false set, if present, to take place. One further minute mixing was done, while introducing the admixtures, PCE and accelerator; at the end, the remaining water was added. Initial slump of the concrete, as measured according to EN 12350-2, was in the range 22-24 cm in all the tests; the air content, measured by air meter (EN 12350-7) was always in the range 1.5-2.2%. Several 15 cm PVC cubes were prepared, for curing at 10°C and 95% relative humidity; 15 cm steel cubes were prepared for steam curing, that was applied with the following programme: 1h at 20°C; 2 hours increasing temperature from 20 to 60°C; 1 hour at 60°C. Compressive strengths after different curing times were measured.

Table 1. Mix Designs for Concrete Tests

| | Mix 1 | Mix 2 | Mix 3 | Mix 4 | Mix 5 | Mix 6 | Mix 7 |
|-----------------------------------|-------|-------|-------|-------|-------|-------|-------|
| CEMENT | CEM A | CEM A | CEM B | CEM B | CEM B | CEM B | CEM B |
| Cement (Kg /m ³) | 400 | 350 | 400 | 350 | 300 | 300 | 300 |
| Limestone (Kg /m ³) | | | | | 100 | | |
| Fly ash (Kg /m ³) | | | | | | 100 | |
| GGBS (Kg /m ³) | | | | | | | 100 |
| Sand 0-4 (Kg /m ³) | 990 | 1013 | 978 | 1001 | 971 | 965 | 978 |
| Gravel 8-12 (Kg /m ³) | 918 | 938 | 908 | 928 | 902 | 896 | 908 |
| Water (Kg /m ³) | 176 | 176 | 184 | 184 | 184 | 184 | 184 |
| Superplasticizer PCE (% bwc) | 0.7% | 0.7% | 0.75% | 0.75% | 0.75% | 0.75% | 0.75% |

RESULTS AND DISCUSSION

Materials characterization. Tables 2, 3 and 4 and fig.1 report all the data related to the chemical-physical characterization of the materials used. As it can be observed, the cements A and B are quite different, especially in terms of soluble alkali sulphates, which are recognized in the literature as being one decisive factor for the performances of

cements and their interaction with admixtures (Magarotto et al., 2003). Cement A is quite low in alkali and sulphates, cement B on the contrary quite high. Also the cubic to orthorhombic C₃A ratio and the type of sulphate carrier, that are also known to influence the reactivity of cement, are quite different for the two cements. As for the supplementary cementitious materials used, limestone is quite pure and very fine ($x_{50}=5.26 \mu$); fly ash can be categorized as a class F according to ASTM C-618 and has a quite low amount of unburnt carbon.

Table 2. Chemical Composition of the Materials Used (% by Weight)

| | CEMENT A | CEMENT B | LIMESTONE | FLY ASH | GGBS |
|--------------------------------|----------|----------|-----------|---------|-------|
| Loss on ignition | 3.65 | 3.13 | | 1.09 | n.d. |
| SiO ₂ | 22.61 | 18.36 | 0.13 | 53.11 | 35.03 |
| CaO | 60.34 | 63.93 | | 7.13 | 39.42 |
| MgO | 0.64 | 0.60 | | 3.43 | 9.67 |
| Fe ₂ O ₃ | 3.1 | 2.75 | 0.03 | 4.26 | 0.83 |
| Al ₂ O ₃ | 5.12 | 5.04 | 0.01 | 24.69 | 12.82 |
| Na ₂ O | 0.18 | 0.42 | 0.12 | 0.21 | 0.30 |
| K ₂ O | 0.57 | 0.90 | 0.07 | 0.23 | 0.62 |
| SO ₃ | 3.35 | 3.44 | | 1.06 | <0.21 |
| Free CaO | 0.16 | 0.40 | | 1.05 | |
| R.I. | 4.55 | 1.14 | | | |
| CaCO ₃ | | | 98.61 | | |
| MgCO ₃ | | | 0.87 | | |

Table 3. XRD Quantitative Analyses (% BW.)

| | CEMENT A | CEMENT B |
|---|----------|----------|
| C ₃ S | 58.9 | 60.0 |
| β-C ₂ S | 12.5 | 8.8 |
| C ₃ A | 7.6 | 11.1 |
| C ₃ A cub.: orthor. | 60:40 | 85:15 |
| C ₄ AF | 8.0 | 6.3 |
| CaSO ₄ | 3.6 | 1.2 |
| CaSO ₄ *0.5 H ₂ O | 2.6 | 2.8 |
| CaSO ₄ *2 H ₂ O | 0.1 | 0.0 |
| K ₂ SO ₄ | 0.9 | 0.0 |

Table 4. Chemistry Of the Pore Solution of the Cements (W/C 0.50, 5')

| | CEMENT A | CEMENT B |
|--------------------------------------|----------|----------|
| Soluble SO ₄ ⁻ | 0.47 | 0.90 |
| Soluble Na ⁺ | 0.04 | 0.15 |
| Soluble K ⁺ | 0.45 | 0.61 |
| Soluble Ca ⁺⁺ | 0.14 | 0.05 |

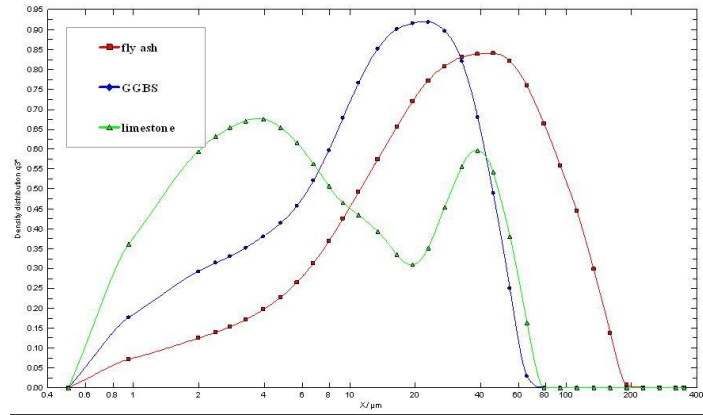


Fig.1. Particle Size Distribution of Limestone, Fly Ash and GGBS

TGA analyses. As reported in the literature (Gabrovsek et al., 2006, Tsvilis et al., 1998), four major areas can be identified in the thermogravimetric plot of hydrated cement pastes, which are related to the following compounds:

- 25–200 °C: water present in the pores, dehydration of ettringite, calcium sulfates, monosulphate and water loss from C-S-H gel layers;
- 200 – 400 °C: complex mixture of hydrated silicate- and aluminate-type compounds;
- 400-450 °C calcium hydroxide;
- 470-700 °C calcium carbonate.

Figure.2 and Figure.3 show the results of TGA analyses in the range 4 to 24 hours for cement A and B respectively. The higher weight loss for the paste with HCFDP in both ranges 200-400°C and 400-450°C confirm its superior acceleration power, also compared to the traditional accelerator. Additionally, the data at 28 days, reported in Figure 4, show that there is no impact of the new accelerator on the long term hydration of cement.

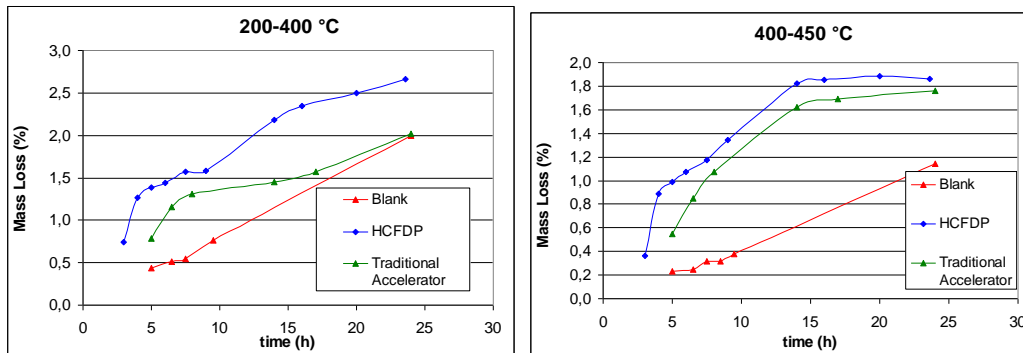


Fig.2. TGA Analyses - Cement A

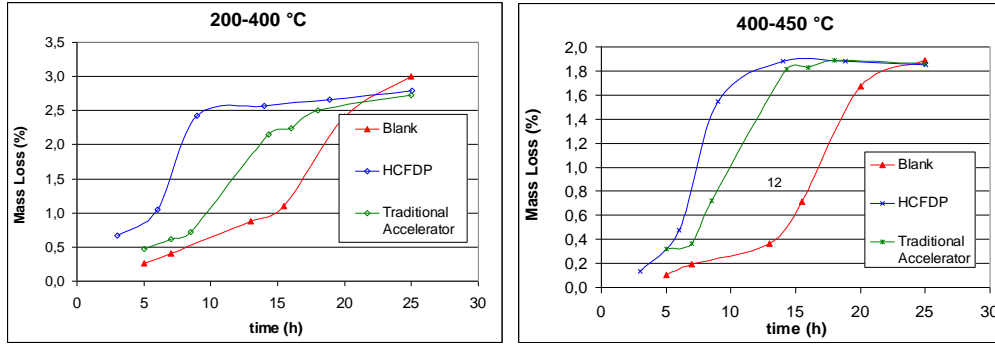


Fig.3. TGA Analyses - Cement B

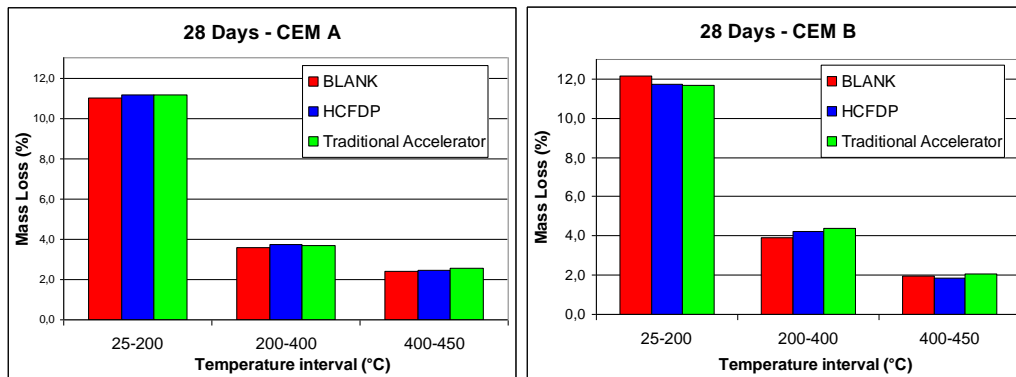


Fig.4. TGA Analyses at 28 Days (Cement A and B)

²⁹Si Nuclear Magnetic Resonance analyses. A Bruker AMX-300 MHz solid-state high-resolution spectrometer with thick-walled zirconia rotors, rotating at 3800 Hz, was used to perform the ²⁹Si MAS (magic angle spinning) Nuclear Magnetic Resonance (NMR) analyses of the pastes. The spectra were performed at 59.6 MHz. This technique provides useful information about the state of the tetrahedral SiO₄⁴⁻ in the paste (Zanni et al., 1995), which is indicative of the formation of *C-S-H* due to hydration. In the process of silicate polymerization, the individual tetrahedrons (called monomers, whose state is designated as Q⁰) of the anhydrous silicate phases (C₃S, C₂S) of the cement are transformed through hydration in dimers (Q¹) and polymeric chains (Q²) of tetrahedrons by means of connections through oxygen atoms. Each of these states, which reflect the degree of polymerization of the silicates in the paste due to the *C-S-H* formation, is represented by a peak in the NMR spectrum (given as a function of the chemical displacement).

Figure 5 shows the ²⁹Si NMR spectrum of the blank paste along with that of the paste incorporating the traditional accelerator and the paste incorporating HCFDP, at different early ages. Two peaks can be identified in the plots: that of Q⁰ in the chemical displacement range of -66 to -74 ppm, and that due to the formation of *C-S-H* corresponding to Q¹ and Q² signals, in the range of -75 to -82 ppm and -85 to -89 ppm, respectively.

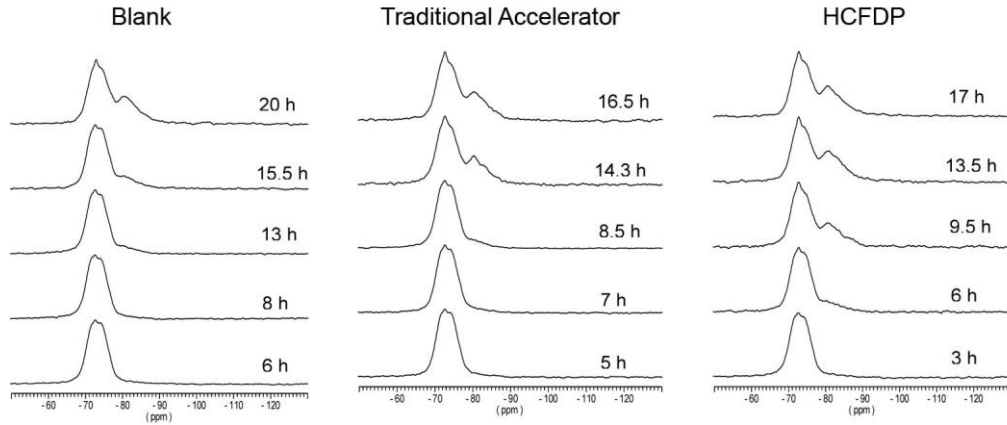


Fig. 5. ^{29}Si NMR Spectra of the Blank Paste Along With That of the Pastes Incorporating the Traditional Accelerator and HCFDP.

Since the peaks in the NMR spectra overlap, a semi-quantitative method is used to compare the curves obtained at different ages. The areas of the anhydrous silicates (Q^0) and those of the $C-S-H$ (Q^1 and Q^2), denoted respectively as A_0 and A_{C-S-H} , are obtained for each spectrum as in Figure 6, and shown in Table 5 and Figure 7. It can be observed that the new and innovative accelerator HCFDP has significant effect on the polymerization of the silicates at early ages, in comparison to the blank paste and the paste with the traditional accelerator. Along these lines, at 6 hours, the formation of $C-S-H$ in the paste with HCFDP is similar to that obtained in the blank paste after 15.5 hours. The table also shows the significant increase in $C-S-H$ formation of the paste incorporating HCFDP in comparison to the paste with the traditional accelerator, confirming the trends observed in the TGA analysis and thus demonstrating the effectiveness of the crystal seeding mechanism.

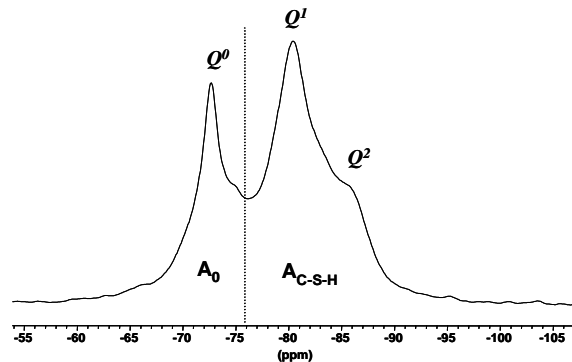


Fig.6. Integration Method Used for Evaluating the ^{29}Si NMR Spectra.

Table 5. Relative Area Corresponding to the Formation of $C-S-H$ (A_{C-S-H}/A_0) for Blank Paste and Pastes with Traditional Accelerator and HCFDP, at Different Ages.

| Blank | | Traditional Accelerator | | HCFDP | |
|-------|-------------------|-------------------------|-------------------|-------|-------------------|
| Age | $(A_{C-S-H})/A_0$ | Age | $(A_{C-S-H})/A_0$ | Age | $(A_{C-S-H})/A_0$ |
| 6 h | 0 | 5 h | 0 | 3 h | 0 |

Fig.8. Cement Reduction with CEMENT A, Curing at 10°C (Mix 1 and 2)

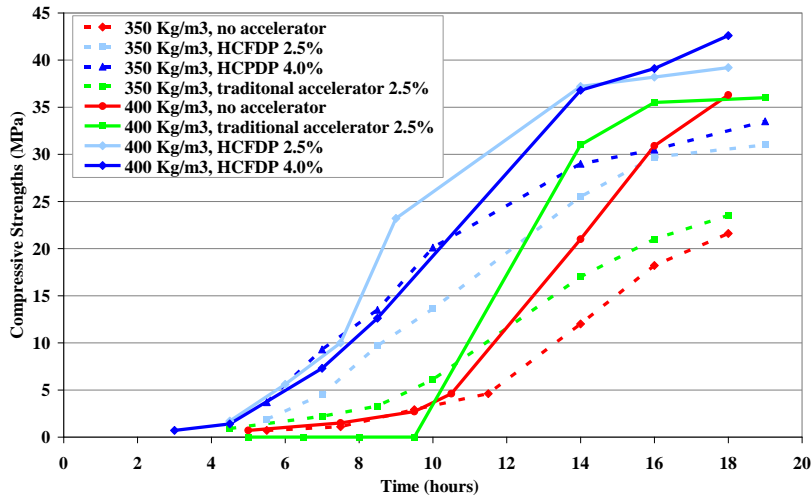


Fig.9. Cement Reduction with CEMENT B, Curing at 10°C (Mix 3 and 4)

Figure 10 and 11 report the compressive strengths results for cement A and B in the case of heat curing: in both cases, 1.5 hours of steam, out of 6, can be saved, which mean a significant saving of energy.

In Figure 12, the 28 days strengths for both cement A and B are presented, showing that HCFDP, though strongly accelerating the early hydration of cement, do not impact the ultimate strengths of concrete. That is also in line with the results of the thermogravimetric analyses.

Figure 13, 14 and 15 report the results obtained in concrete tests exploring the possibility to partially replace cement with SCM: 100 kg out of 400 kg of cement B were replaced with limestone filler, fly ash and GGBS respectively. The results confirm that the acceleration of early strengths provided by HCFDP allows to partially replace cement with supplementary cementitious materials.

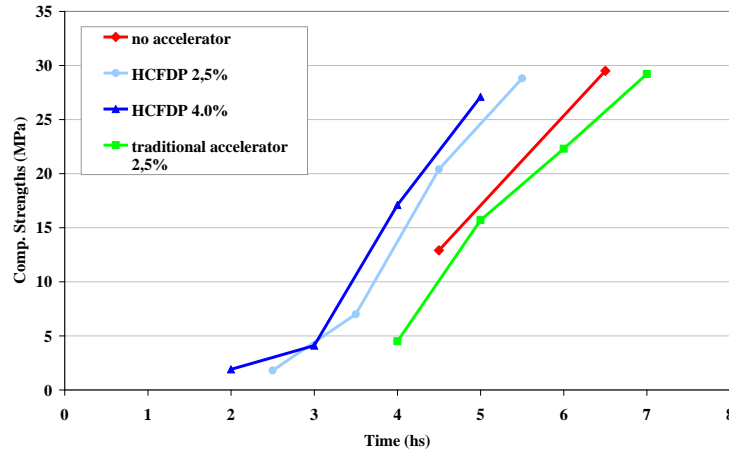


Fig.10. Energy Saving with CEMENT A, Steam Curing (Mix 1)

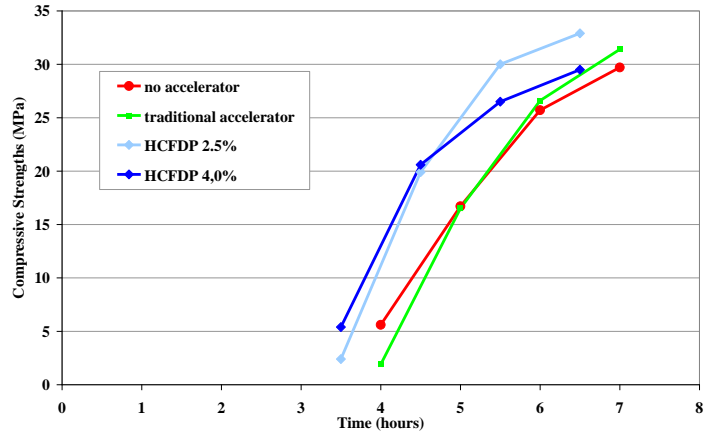


Fig.11. Energy Saving with CEMENT B, Team Curing (Mix 3)

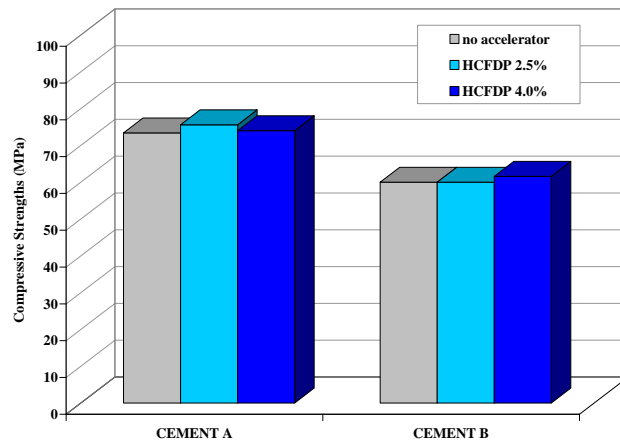


Fig.12. Strengths at 28 Days

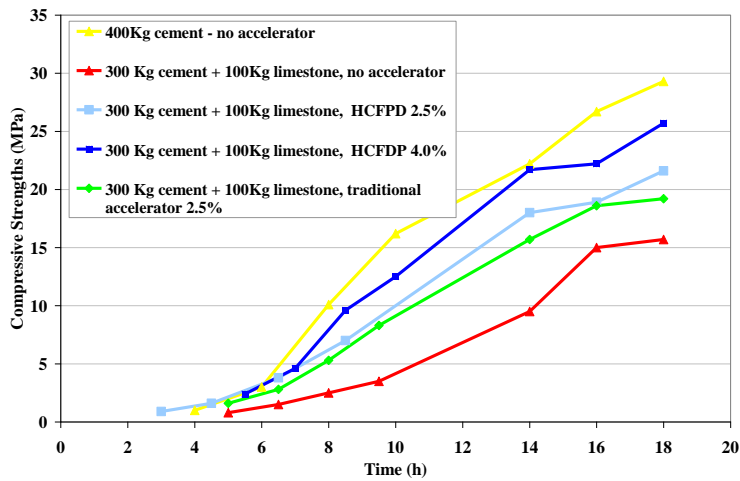


Fig.13. Cement B + Limestone – Curing at 10°C (Mix 5)

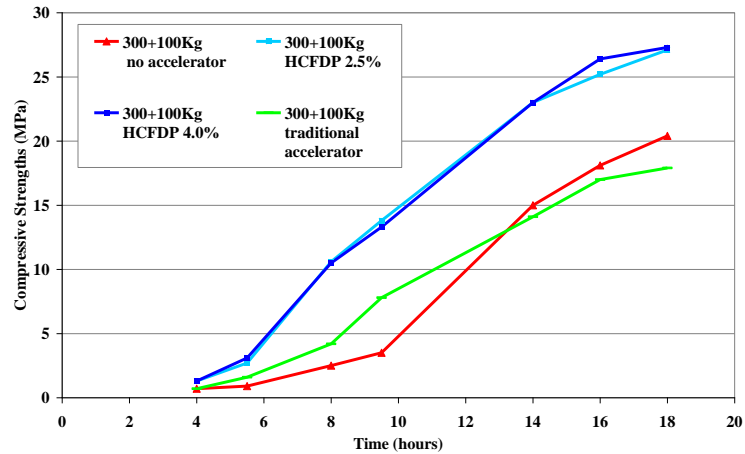


Fig.14. Cement B + Fly Ash – Curing at 10°C (Mix 6)

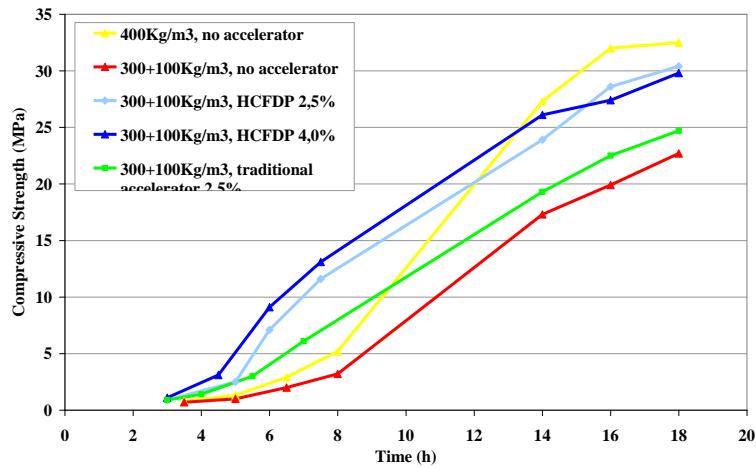


Fig.15. Cement B + GGBS – Curing at 10°C (Mix 7)

In standard cement hydration many and complex are the parallel reactions occurring during the set and hardening of cement. However, in general, before the strength development produced by the acceleration and deceleration period of the hydration process, an induction period is always observed during which nucleation and growth of hydrated cement crystals occurs. During the induction period, the slow dissolution of cement particles occurs, forming clusters. Only when the clusters can be aggregated through weak attraction forces small nuclei are formed and therefore, when the system can overcome a certain energy barrier, the CSH growth can proceed, providing strength to the system.

In addition, in standard conditions, the hydration occurs close to the surface or onto the surface itself creating a dense layer which slows down the diffusion of products and delay further crystal formation thus the strength development.

In the presented innovative system, synthetically produced extra fine cement hydration products can be added in suspension and used as seeding material in the pore solution between the grains.

The active cement hydration crystals can virtually grow without energy barrier. The crystal seeding method presumably provides a preferential growth behavior in between and not on the surface of the cement grains, which can be beneficial avoiding high densification of the surface layer and slow down of the diffusion of products and reactants.

CONCLUSIONS

Based on the data presented, the following conclusions can be drawn:

- 1) Hydrated cement particles, very finely dispersed (HCFDP), represent a powerful hardening accelerator for concrete, showing superior performances as compared to traditional salt-based, accelerators.
- 2) HCFDP act as crystal seeds in the concrete pore solution, allowing to overcome the energy barrier that otherwise characterizes the end of the dormant period and the beginning of C-S-H nucleation on the surface of cement particles.
- 3) These performances were observed in concrete tests and validated through TGA and NMR investigations.
- 4) Thanks to the increase of early strengths, the concrete mix can be optimized by either reducing the cement content or partially replacing cement with supplementary cementitious materials (SCMs).
- 5) The accelerating power of HCFDP was observed both in high and in low alkali cements.
- 6) In conclusion, the accelerator presented here can help the precast concrete industry to win the current challenges related to sustainability.

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