NEW SUSTAINABLE TECHNOLOGY IN PRECAST INDUSTRY

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ABSTRACT

Nanotechnology represents one of the most promising areas of industrial activity capable of shaping the future and the economy. One example of the application of nanotechnology in the construction industry is represented by a new admixture based on nanosized silicate hydrates (MeSH) for the precast industry. This admixture is made by synthetic nanoparticles of a transition metal silicate hydrate, capable of catalyzing the hydration of the silicate phases of portland cement and strongly accelerating the early strength development of cement mixtures. MeSH also promotes the precipitation of C-S-H not only on the cement grain surface, but also in the capillary pores, with a consequent reduction of the capillary porosity of the hydrated cement paste and an improvement of the microstructure. At dosages of MeSH from 2 to 5 % by weight of cement, it is possible to completely eliminate the steam curing in the production of precast concrete elements without any adverse effect on the early strength and with a definite improvement of strength at longer ages and the durability. Furthermore, the environmental impact of the concrete produced with MeSH and without steam curing, as measured by the LCA method, is about 12% less compared with that of the normal steam cured concrete.

Keywords: Nanotechnology, Sustainability, Silicate hydrates, Precast elements, Permeability, Early strength.

INTRODUCTION

Layered metal silicate hydrates represent the essential components of novel hybrid nanocomposites, characterized by innovative characteristics and improved performances in biomedical, engineering and other advanced applications[1]. Recently, comb-polymer layered metal silicate hydrate gels were introduced in the construction industry as accelerators of Portland cement hydration[2]. In the present work, the sustainable use of such new additive in precast application is presented.

THE STRUCTURE OF THE NEW METAL SILICATE HYDRATE

Mixed Copper/Calcium Silicate Hydrate (MeSH) with molar ratios Cu/Ca = 0.1 and (Cu+Ca)/Si = 1.1 was synthesized according to a modification of the double decomposition method described by Klasse and Kühl[3] and purified according to the method described by McFarlane[4]. The structure and the characteristics of the new silicate were investigated by XRD, ^{29}Si NMR, GPC and BET techniques, and compared with a product synthesized with the same procedure without Copper (CSH). Specific surface area (SSA), as measured by BET, was 388 m^2/ g for MeSH and 320 m^2/ g for CSH, respectively. These results indicate that substitution of 10 mole per cent of calcium atoms with copper atoms considerably increases (about 20 %) the specific surface area of the silicate hydrate structure. This effect could be in relation to the progressive loss of crystallinity of the structure of the CSH, once copper atoms are introduced, as shown in Figure 1.

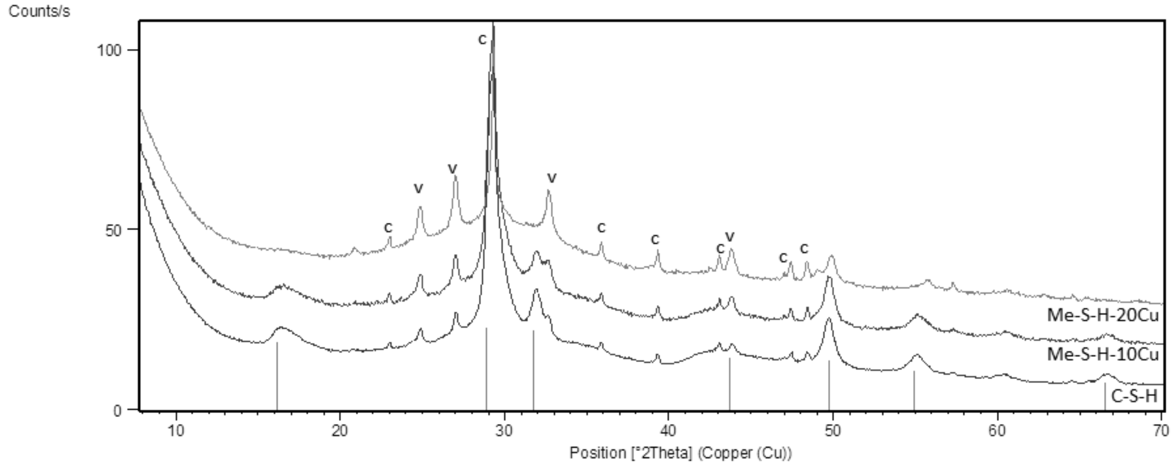

Figure 1. X-ray diffraction patterns of calcium silicate hydrate without copper (CSH) and with 10% and 20% copper substitution by mole to calcium (MeSH10Cu, MeSH20Cu). Vertical lines indicate positions of tobermorite-like CSH, v: vaterite, c: calcite.

The ^{29}Si NMR spectrum of MeSH confirms the typical dreierketten structure of CSH. Deconvolution of the peaks indicated the following distribution: 18.5%Q^1, 60%Q^2 and 21.5%Q^2_B. The calculated main chain length, expressed as MCL = $2\cdot(Q^1+Q^2+Q^2_B)/Q^1$ was 10.8. The degree of polymerization of MeSH was determined also by GPC, after derivatization with hexamethyldisiloxane, according to the method described by Tamas et al.[5], giving for the MeSH polysilicate a Number Average Molecular Weight of M_n = 850 g/mol, corresponding to an average polymerization degree DP = 11, in excellent agreement with the results obtained by ^{29}Si NMR.

THE CHARACTERISTICS OF MeSH-PCE GEL

When MeSH is synthesized in the presence of a PCE comb polymer superplasticizer, consisting of a copolymer between (meth)acrylic acid and methoxypolyethylene glycol methacrylate, self-assembled, highly stable nanostructured gels are easily formed, characterized by values of elastic modulus G' higher than the viscous modulus G'', as shown in the stress sweep test of Figure 2. MeSH showed a higher tendency to form structured gels compared to CSH without Cu, when synthesized in the presence of PCE superplasticizers in the same conditions, as clearly indicated by the higher viscosity values in the presence of copper, 360 cP for MeSH compared to 87 cP for CSH without Cu. These differences could be ascribed to the presence of copper ions in the lattice structure of the polysilicate, which could induce stronger interactions with the PCE anionic functionalities due to the different external electronic structure of copper ions compared to calcium ions.

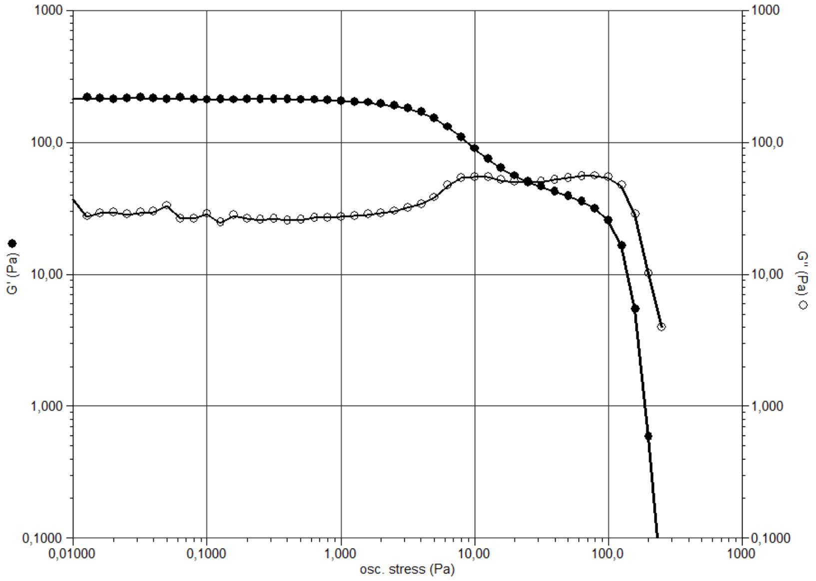

Figure 2. Stress sweep test of MeSH suspension (20 % solids) synthesized in the presence of PCE superplasticizer.

Particle size analysis of MeSH-PCE suspensions (Zetasizer Nano S, Malvern Instruments Ltd) put in evidence the predominance of particles in the range 30-60 nm, together with minor larger sub-micron agglomerates.

THE MECHANISM OF ACTION OF MeSH-PCE GEL

When MeSH-PCE gel is added to fresh cement mixtures, it catalyzes the nucleation of C-S-H from hydrating cement, not only onto the surface of cement grains, but also in the capillary pores of cement paste. The homogeneous nucleation of C-S-H in the capillary pores of cement paste has been demonstrated by synchrotron XRD-µT experiments[6] (Figure 3).

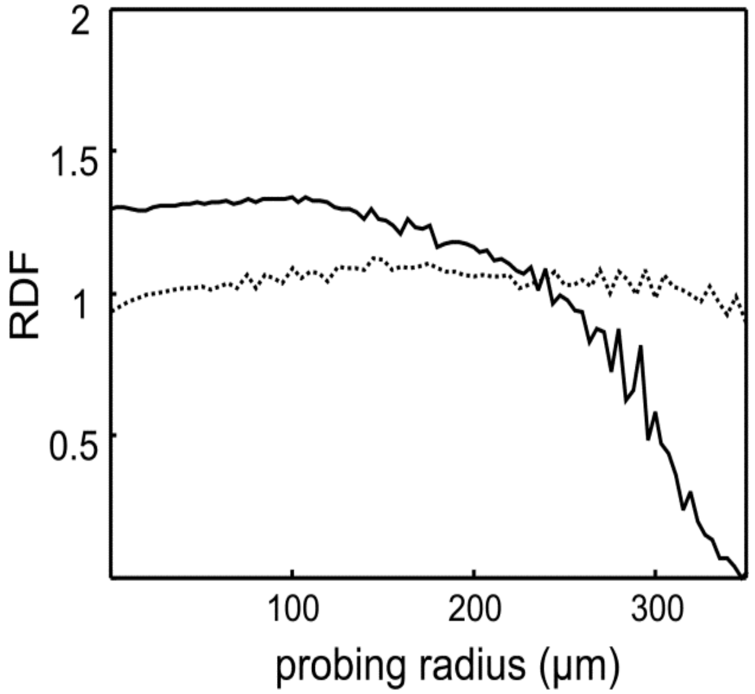

Figure 3. Radial Distribution Frequency (RDF) of C-S-H from the surface of hydrating cement grains, without MeSH-PCE gel (solid line) and with 3% MeSH-PCE gel (dotted line).

The curves of Figure 3 display the variation of the average C-S-H concentration within the specimen, as a function of the distance from the clinker surfaces. Values larger or smaller than unity, respectively, indicate that the local C-S-H concentration, at a given distance from the clinker surfaces, is larger or smaller compared with the average concentration. In the absence of MeSH-PCE gel, the value of the RDF tends to decrease with the distance from the clinker surfaces, suggesting that C-S-H precipitates in proximity of the clinker grains. On the other hand, in the presence of MeSH-PCE gel, the value of the RDF is close to unity at any distance from the clinker surface, confirming that C-S-H is homogeneously distributed throughout the available pore space. This result is possible only if the formation of C-S-H occurs in the capillary spaces of cement paste, through nucleation induced by the presence of MeSH-PCE gel.

As a result of the catalyzed nucleation and growth of C-S-H crystals in the capillary pores, the hydration of cement is greatly accelerated and high early compressive strength is promoted, even in the absence of steam curing. At the same time and for the same reasons, the capillary porosity of cement materials is reduced compared to an equivalent (same W/C) cement paste not containing MeSH-PCE gel. This reflects on a reduced permeability of water of concrete under hydrostatic pressure. For both these reasons, MeSH-PCE gel can be particularly applicable in the precast industry, as an alternative to steam curing.

In the present work, the results of early and long term compressive strength and water permeability of two different concretes, one produced by steam curing and without MeSH-PCE gel (Concrete 1), with lower W/C, and the second without steam curing and with MeSH-PCE gel (Concrete 2), are compared. Both concretes were produced at a concrete plant producing precast piles for winery. Environmental impact of the different concretes was also calculated by the Life Cycle Assessment LCA method.

MATERIALS AND METHODS

Portland cement type CEMI 52.5R according to European norm EN197-1 was used for both concretes. Maximum aggregate diameter was 20 mm. Polycarboxylate superplasticizer NRG1022, supplied by Mapei, was used to obtain a slump value of 19 mm ± 2 mm for both concretes. Concrete 1 was the mix design used at the precast plant for the piles production. This recipe was designed to give compressive strength of about 30 MPa after 15 hours of curing, with a steam curing treatment at 65 °C for 8 hours. Concrete 2 had a different mix design, to give approximately the same compressive strength as Concrete 1 after 15 hours, but without steam curing and with the addition of the new accelerating additive (MeSH-PCE gel). Curing temperature of Concrete 2 was 22 °C. After demolding, both concretes were cured at 20 °C and 95% R.H. The characteristics of the two concretes are reported in the following Table 1.

Table 1. Mix Design and Characteristics of the Two Different Concretes.

Concrete	**Curing**		**Dosages**			**W/C**	**Slump**	**Entrapped air**
			Cement	**NRG1022**	**MeSH**		**(mm)**	**(%)**
			Kg/m^3	**% bmc***	**% bmc***			
1	Steam curing	65 °C for 8 hours	370	0.54	-	0.47	19	3.1
2	Normal curing	22 °C	330	0.61	2.12	0.53	19	2.7

*bmc = by mass of cement.

Water permeability tests were made according to the UNI-EN 12390-8 standard, by measuring the water penetration under pressure of 150x150x150 mm specimens of the 2 concretes, cured at 20 °C and 95% R.H. for 28 days after demolding, by the application of a water load of 500 kPa for 72 hours.

Microstructure investigation of a polished section of the different concretes was performed by reflection optical microscope analysis, in order to compare the microstructure of different concretes.

Environmental impact of both concretes was calculated by LCA method, by using GaBi software, capable of calculating the carbon footprint associated with concrete, along its supply chain, using indicators such as the Global Warming Potential (GWP), expressed as kg of CO_2/m^3 of concrete.

RESULTS AND DISCUSSION

Compressive strength of both concretes at early age (after 15 hours) and at longer age (after 80 days) were measured on 150x150x150 mm cubes cured at 20 °C and 95% R.H. Compressive strength was expressed as the average of 2 specimens for each concrete. Results are shown in Table 2.

Table 2. Compressive Strength at Early (15 hours) and Longer Ages (80 days) of the Different Concretes.

Concrete	**Curing**		**Dosages**			**W/C**	**Compressive strength (MPa)**	
			Cement	**NRG1022**	**MeSH**		**15 hours**	**80 days**
			Kg/m^3	**% bmc***	**% bmc***			
1	Steam curing	65 °C for 8 hours	370	0.54	-	0.47	35.6	56.8
2	Normal curing	22 °C	330	0.61	2.12	0.53	32.6	72.6

*bmc = by mass of cement

Results from Table 2 indicate that Concrete 1, characterized by lower W/C compared to Concrete 2, exhibited similar compressive strength after 15 hours and lower compressive strength at longer ages (80 days). The reason for these unexpected results could be the deterioration of the cement paste microstructure of Concrete 1, caused by the steam curing. In fact, if the thermal expansion of the water in the capillary pores of cement paste occurs when the cement paste does not have sufficient mechanical strength, micro-cracks can be produced, with the deterioration of the cement microstructure and the consequent reduction of mechanical performance. This effect is quite evident by observing Figure 4, which shows the thin section reflection optical microscope images of two samples of Concrete 1 and Concrete 2, after polishing and resin impregnation.

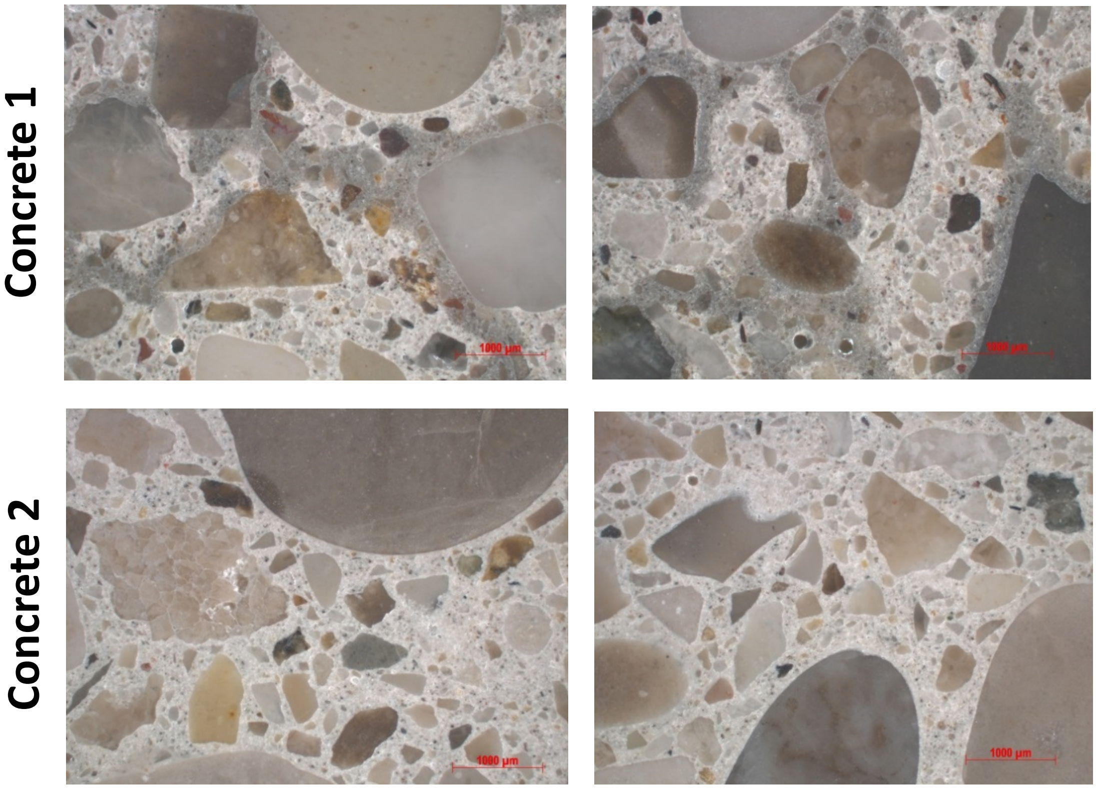

Figure 4. Polished sections of Concrete 1, steam cured without MeSH-PCE gel, and that of Concrete 2, containing MeSH-PCE gel and cured in normal conditions. The gray areas around the aggregates of Concrete 1 samples represent microcracks filled by impregnation resin, originated by the thermal stress caused by the steam curing process.

Figure 4 indicates the presence of many deteriorated zones - the gray areas in the two polished section of Concrete 1 – mainly localized at the interface between the cement paste and the aggregates, due to the thermal stress caused by steam curing. On the other hand, no deterioration was observed in Concrete 2, cured in normal conditions and containing MeSH-PCE gel as accelerating admixture. This difference in the microstructure is responsible for the lower compressive strength of Concrete 1 at longer age, even if the W/C is lower compared to Concrete 2.

As a result of the better microstructure, Concrete 2, even if its W/C is higher than Concrete 1, is impermeable to water under pressure and durable, as confirmed by the water permeability tests of Figure 5.

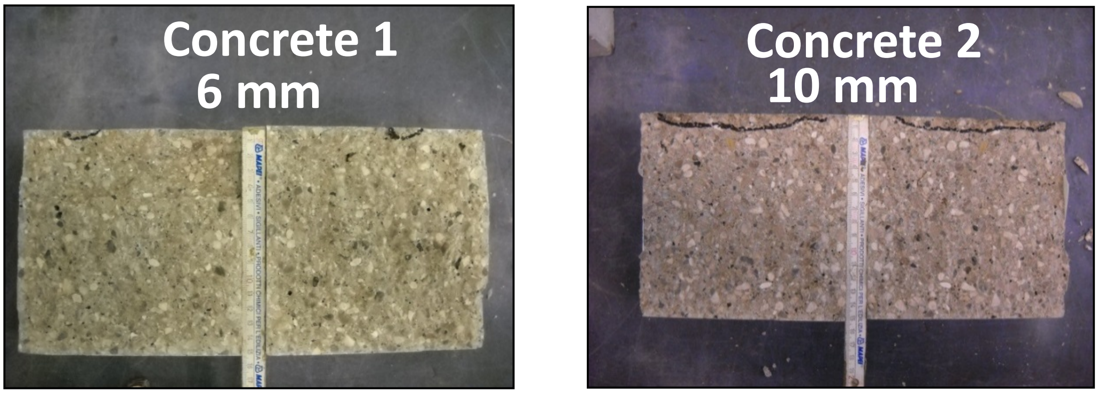

Figure 5. Water penetration depth on split specimens of Concrete 1 (steam cured) and of Concrete 2 (normal curing containing MeSH-PCE gel). Even if the water permeability of Concrete 2 is slightly higher than Concrete 1 due to the higher W/C (W/C = 0.61 for Concrete 2 compared to W/C = 0.54 for Concrete 1), it is still impermeable to water under pressure.

Concrete 2 is also less environmental impacting and, therefore, more sustainable than Concrete 1. In fact, for its production, no steam was necessary and a lower dosage of cement was used. By using Life Cycle Assessment LCA method, it was possible to calculate the overall contribution to CO_2 emission for the different concrete, which resulted 360 kg CO_2/m^3 for Concrete 1 and 315 kg CO_2/m^3 for Concrete 2, with a reduction of about 12 per cent for the latter, indicating that Concrete 2 is more sustainable than Concrete 1.

CONCLUSIONS

The results of the present paper indicated that the addition of MeSH-PCE gel catalyzes the homogeneous nucleation and growth of C-S-H in the capillary pores of cement paste. This new admixture offers the possibility to the concrete industry to improve early compressive strength and to reduce the penetration of water under pressure in concrete structures. The preliminary results of the present work indicated that MeSH-PCE gel could find important applications in the precast industry, including production of large-scale structural elements as well as non-structural products, because it could allow the production of concrete with outstanding performance and durability and lower the environmental impact compared to traditional steam cured concrete. Furthermore, the replacement of steam curing processes could bring considerable economic savings. Finally, the use of nanoparticles diluted in aqueous solutions would not pose any health hazard issue for the operators, as this particular application requires at no point the particles becoming airborne.

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