Definition of a PCE Family that Increases Performances when a Workability Retention Agent (WRA) is Added 235

	dos.	COMPRESSIVE STRENGTH					
	%	24 h density	24 h (N/	7 d density(Kg/	7 d (N/	28 d density	28 d(N/
Additives	cem	(Kg/m ³)	mm ²)	m3)	mm2)	(Kg/m3)	mm2)
PCE 1a	0,6%	2281	24,6	2304	49,6	2320	56,4
PCE 1b	0,6%	2292	20,2	2292	44,1	2270	52,4
PCE 1c	0,6%	2289	21,8	2324	46,0	2301	55,2
PCE 2	0,6%	2257	22,8	2312	46,9	2316	55,5
PCE 3	0,6%	2246	20,0	2234	47,5	2285	57,9
PCE 4	0,6%	2308	26,2	2304	49,0	2316	58,8
PCE 5	0,60%	2250	22,1	2261	46,6	2305	54,5
PCE 6a	0,6%	2257	23,2	2316	46,0	2289	52,4
PCE 6b	0,60%	2252	22,4	2257	47,0	2307	54,6

Table 10- Compressive Strength –PCE alone (0.6% on weight of cement)

(1 N/mm²= 145 lbf/in²) (1Kg/m³=1.68 lb/yd³)

Table 11- Compressive Strength – PCE/WRA 50/50 (1.2% on weight of cement)

	dos.	COMPRESSIVE STRENGTH					
	%	24 h density 24 h 7 d density		7 d	28 d density	28 d	
Additives	cem	(Kg/m ³)	(N/mm^2)	(Kg/m3)	(N/mm2)	(Kg/m3)	(N/mm2)
PCE 1a/WRA	1,2%	2246	3,7	2261	45,0	2273	55,5
PCE 1b/WRA	1,2%	2257	11,8	2289	49,0	2281	57,9
PCE 1c/WRA	1,2%	2285	10,1	2292	48,4	2316	58,2
PCE 2/WRA	1,2%	2257	8,2	2261	48,1	2281	55,2
PCE 3/WRA	1,2%	2234	1,2	2269	45,4	2297	54,5
PCE 4/WRA	1,2%	2246	5,5	2273	42,9	2273	53,9
PCE 5/WRA	1,2%	2171	1,0	2246	43,2	2258	54,5
PCE 6a/WRA	1,2%	2277	4,5	2285	49,6	2289	58,8
PCE 6b/WRA	1,2%	2234	1,2	2261	47,2	2227	54,2

(1 N/mm²= 145 lbf/in²) (1Kg/m³=1.68 lb/yd³)

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COMPRESSIVE STRENGHT OF PCE ALONE

COMPRESSIVE STRENGTH 24h (N/mm2) COMPRESSIVE STRENGTH 7 d (N/mm2) COMPRESSIVE STRENGTH 28 d (N/mm2)





COMPRESSIVE STRENGHT-MIX PCE/WRA (50/50)

■ COMPRESSIVE STRENGTH 24h (N/mm2) ■ COMPRESSIVE STRENGTH 7 d (N/mm2) ■ COMPRESSIVE STRENGTH 28 d (N/mm2)

Fig. 7- Compressive Strength of mix PCE/WRA (50/50)

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SP-329-20

Graphite Nanoplatelets and Graphene Oxide Influence on C-S-H Formation

by P. Gronchi, S. Bianchi, L. Brambilla, and M. Goisis

Graphene, graphite nanoplatelets and graphene oxide are emerging nanomaterials for future technologies. Despite the conservative nature of the building industry, nanomaterials are already making their way into some construction applications and nanotechnologies have the potential to open a new season in this field. Recent studies reported mechanical improvements in cement-graphene oxide composites. The interaction between the carbon nanoadditives and C-S-H is not clear yet. In this paper, we investigate whether and how graphite nanoplatelets and graphene oxide affect morphology and kinetics of C-S-H formation, studying the simple reaction between calcium oxide and silica. Influence on hydration by two different types of silica having different specific surfaces was considered. Instrumental analyses of the products were performed through Infrared and Raman spectroscopy, TG and SEM analysis up to four weeks. Results indicate that GO interacts with C-S-H phase and hinders its formation while GNPs remain only dispersed in the matrix.

Keywords: Cement; graphene; graphene oxide; silica; dispersion; pozzolanic reaction; C-S-H.

INTRODUCTION

Carbon nanomaterials have proven to be very promising tools for the improvement of composite materials in various industrial and academic fields. For what concerns the construction industry, several studies have been reported about the possibility of introducing carbon micro and nanofillers in cement thus increasing its resistance, in particular its flexural strength.¹ Li et al.² found that carbon nanotubes functionalized with carboxylic groups interact strongly with the cement matrix. Improvements of compressive and flexural strength by up to 19% and 25% with respect to the control were found. A carbon nanomaterial with excellent mechanical properties is graphene. In simple terms, graphene is a single layer of graphite that is a two-dimensional atomic crystal made up of carbon atoms arranged in a hexagonal lattice. Graphene oxide (GO) is the product of the strong oxidation of graphite through Hummer's method³ and it is made of a layer of graphene with epoxy and hydroxyl groups attached on its surface and carboxyl groups attached on the edges. These moieties make GO polar and dispersible in water. The patent WO2013096990 A1,

published in 2013 by the Monash University⁴ is related to the addition of GO in cement mortar. The patent claims that small amounts of GO are able to produce remarkable improvement of mechanical properties of the composite. Lv et al.^{5,6} found a compressive/ flexural strength increase of more than 45/60% respectively at 28 days with the addition of 0.03% GO bwc. The authors related these results to the effect of GO on the microstructure of the cementitious matrix, which appeared denser and modified with respect to the control. Moreover, they suggested that GO can have a template effect and that GO promotes the assembly of flower-like and polyhedral structures from rod-like crystals, with the ultimate formation of a dense structure.

Pan et al.⁷ found that the addition of GO increases the compressive/flexural strength by 15-33/41-59% respectively. This is ascribed to two reasons: the high load transfer efficiency of the strong covalent bonds between GO (thanks to its functionalities) and the products of hydration and the capacity of GO sheets to deflect cracks and change the fracture behaviour. It was found that the addition of GO produced an increase of the amount of small and medium pores (1-45 nm/3,937e-8-1,7717e-6 in) with the surface area rising from 27.3 m²/g (8330.6 ft²/oz) to 64.9 m²/g (19804.4 ft²/oz). The reasons were attributed to the high degree of hydration promoted by GO.

Probably the main issue of the use of graphene-related material (GRM) is the good dispersion of the nanoparticles in the cementitious matrix. Babak et al.⁸ used a polycarboxylate superplasticizer and an ultrasonication process in order to disperse adequately GO in water. Moreover, Li et al.⁹ found that, in presence of Ca^{2+} ions, the aggregation of GO platelets is facilitated and that the addition of a proper amount of silica fume (SF) is able to tackle it.

In this paper, we investigate the effects of graphite nanoplatelets (GNPs) and GO addition on C-S-H formation. It is the main product of the hydration of Portland cement and is primarily responsible for the strength in cement-based materials.¹⁰ C–S–H makes up about 50% of the hardened paste volume and plays an essential role in controlling its engineering behaviour.

In this study, we adopt a simple model by exploiting the pozzolanic reaction between calcium oxide and silica to produce the C-S-H phase and by using a high water-to-solid ratio, according to the fundamental studies on the subject.^{12,13} We also investigate the effects of two different kinds of silica, silica fume and pyrogenic silica, characterized by two very different specific surface areas. Previous preliminary studies performed in Politecnico di Milano, CMIC laboratory,¹⁴ have attained the optimisation of instrumental analysis on cement–GO composites by Raman and SEM methods. The relevance of particle dimensions was there underlined.

RESEARCH SIGNIFICANCE

This paper studies the influence of graphene-related nanomaterials like GNPs and GO on C-S-H, the main phase of hydrated cement. By confining the investigation to the simple CaO/SiO₂/H₂O system, we intend to get results on the interaction of C-S-H with GRM, for both kinetics and morphology. The capability of controlling the cement core is considered a fundamental key to produce improved binders and superior concrete.¹⁰ Fundamental understanding at the nanoscale of the hydration process and cementitious matrix structure

	Silica fume	Aerosil© 200 (pyrogenic silica)	
specific surface area	15-30 m ² /g (4577- 9155 ft ² /oz)	200 m ² /g (61030 ft ² /oz)	
average particle diameter	150 nm (5.9e-6 in)	12 nm (4.7e-7 in)	

Table 1–Raw materials. Characteristics of silica.



Fig. 1- SEM image of Aerosil© 200 at 25000x

and its interaction with other constituents is still limited and C-S-H is not yet completely resolved. The goal of making nanotechnology on the hydrated products is even farther.¹¹

EXPERIMENTAL PROCEDURE

Materials

CaO was prepared through decarbonation of CaCO₃ (VWR International, Lutterworth, Leicestershire UK; reagent grade) at 950°C (1742°F) for 3 hours and maintained under anhydrous dried atmosphere. Two different types of SiO₂ have been used: commercial silica fume (Globe Metallurgical, Inc., Selma, Alabama, USA) and Aerosil©200 by Evonik (Evonik Industries, Essen, Germany). Differences in dimension and morphology are shown in **Table 1** and **Figs. 1-2**.

The infrared spectra are similar and present the two characteristic peaks of silica at 1105 cm^{-1} (strong, large) and 814 cm^{-1} (weak).

The graphite nanoplatelets (GNPs) were supplied by Nanesa Srl (Nanesa Srl, Arezzo, Italy) with the commercial name of G2Nan. It is a water-based paste with a GNPs concentration of 5%. The exfoliated graphene oxide (GO) was supplied by Graphenea S.A. (Graphenea S.A., Donostia-San Sebastian, Spain) at a concentration of 4 mg/ml (0.53 oz/gal (US)) in aqueous dispersion. The reported carbon content is 49–56% on dry base; the oxygen content is 41-50%.

Further information is available in Tables 2-3 and Fig. 3.



Fig. 2-SEM image of silica fume at 25000x

Table 2–G2Nan features	(after Nanesa	technical	documentation)
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Parameter	G2nan		
Concentration	5% graphite GNPs in water		
Colour	Black		
Appearance	Powder		
Carbon content	> 98%		
Average flake thickness	~ 10 nm / 3.9e-7 in (30 layers)		
Average Particle (lateral) size	5 – 50 µm (2.0e-4 – 2.0e-3 in)		
Bulk density	$0.042 - 0.020 \text{ g/cm}^3 (56.08 - 26.71 \text{ oz/gal})$		
Residual acid content	< 1%		
Specific surface area	$> 30 \text{ m}^2/\text{g} (9155 \text{ ft}^2/\text{oz})$		

A very small amount of polycarboxylate-based dispersant (PCP) was added to water to facilitate the dispersion of GO and GNPs. The PCP is a comb-polymer polyethylene oxide (PEO) branched polyacrylic acid synthesized in our laboratories having about 70% of free carboxylic functionalities on the backbone, with the remaining part substituted by PEO 1000 methoxy-terminated. The molecular weight is approximately 30000 g/mol (66.139 lb/mol).

Preparation of specimens

An aqueous dispersion of CaO and SiO₂ was stirred up to 4 weeks to synthesize C-S-H. We followed the procedure by Haas and Nonat.¹² The Ca/Si ratio was 3:1 to resemble the stoichiometric proportion of un-hydrated C₃S and the water/solid ratio was 50:1 to dilute the heat produced by CaO hydration. The percentages of addition for both the GO and the GNP were 0.05%, 0.10% and 0.20% by weight of solid part, while the dispersant was added at 0.008% by weight of water. The samples are listed in **Table 4**.

Parameter	Graphene Oxide		
Concentration	4 mg/ml (0.53 oz/gal)		
Colour	Black		
Appearance	Liquid		
Odour	Odourless		
Dispersibility	Polar solvents		
Solvent	Water		
рН	2.2-2.5		
Monolayer content (0.05 wt%)	>95%		
Carbon content	49-56% on dry base		
Oxygen content	41-50%		
Hydrogen content	0-1%		
Nitrogen content	0-1%		
Sulphur content	0-2%		

Table 3–GO features (after Graphenea S.A.)

The GO and the GNPs were added to the water together with the dispersant and the mixture was sonicated for 30 minutes to improve the dispersion. Then, the CaO and the SiO_2 were added to the aqueous bath and kept under mechanical stirring in a closed reactor for 4 weeks. The samples were also kept under thermostatic control at 23°C (73.4°F).

After taking samples from the mixtures, we centrifuged them, in order to remove most of the water, then we added methanol and acetone to stop the reaction and eliminate the remaining water and finally we let them dry under mild vacuum at room temperature.

Analytical investigation

Infrared and Raman analyses

IR spectra were recorded in transmission mode using a Nexus Nicolet FT-IR spectrometer (Nicolet Instrument. Inc., Madison, WI 53711, USA) coupled with an infrared microscope Continuµm Thermo Electron Corporation (GMI, Inc, Ramsey, Minnesota, USA). Spectra were acquired in a diamond anvil cell (DAC) (resolution, 4 cm^{-1} (10.2 in⁻¹); scans 128). Raman analyses were performed with a Horiba Jobin Yvon Labram HR800 (HORIBA Jobin Yvon IBH Ltd., Glasgow, UK) dispersive Raman spectrometer equipped with Olympus BX41 microscope and a 50X objective (resolution, 2 cm^{-1} (5.1 in⁻¹); acquisition time, 30 s; 4 accumulations). We used the 785 nm (3.0906e-5 in) excitation laser line with a power of 0.4 mW in order to prevent possible photo-induced thermal degradation of the samples.

TGA analysis

The instrument is a Seiko Exstar 6000 TG/DTA 6300 thermal analyser (Seiko Instruments Inc., Chiba, Japan). We performed the analysis in air from room temperature to 800°C (1472°F) with a constant heating rate of 10°C/min (18°F/min).

SEM analysis

We performed SEM analysis through two scanning electron microscopes: i. Zeiss Evo 50 EP instrumentation (Carl Zeiss AG, Oberkochen, Germany) equipped with a lanthanum



Fig. 3–SEM images of GNPs (left) and GO (right) at (a) and (b) 500x; (c) and (d) 3000x; and (e) and (f) 7500x from the top.

hexaboride (LaB6) thermionic source, at 20 kV; ii. Zeiss Evo MA15 instrumentation (Carl Zeiss AG, Oberkochen, Germany), equipped with an Oxford X-Max EDX.

SAMPLE NAME	CaO g (oz)	SiO2 g (oz)	GNP g (oz)	GO g (oz)
CONTROL_A	2.0 (0.07)	0.714 (0.0252) Silica fume	0	0
CONTROL_B	2.0 (0.07)	0.714 (0.0252) Aerosil© 200	0	0
CONTROL_C*	2.0 (0.07)	0.714 (0.0252) Silica fume	0	0
G_0.05_A	2.0 (0.07)	0.714 (0.0252) Silica fume	0.027 (0.00095)	0
G_0.05_B	2.0 (0.07)	0.714 (0.0252) Aerosil© 200	0.027 (0.00095)	0
G_0.10	2.0 (0.07)	0.714 (0.0252) Silica fume	0.054 (0.00190)	0
G_0.20	2.0 (0.07)	0.714 (0.0252) Silica fume	0.108 (0.00381)	0
GO_0.05_A	2.0 (0.07)	0.714 (0.0252) Silica fume	0	0.371 (0.0131)
GO_0.05_B	4.0 (0.14)	0.714 (0.0252) Aerosil© 200	0	0.371 (0.0131)
GO_0.10_A	2.0 (0.07)	0.714 (0.0252) Aerosil© 200	0	0.743 (0.0262)
GO_0.10_B	2.0 (0.07)	0.714 (0.0252) Silica fume	0	0.743 (0.0262)
GO_0.20_A	2.0 (0.07)	0.714 (0.0252) Silica fume	0	1.485 (0.0524)
GO_0.20_B	2.0 (0.07)	0.714 (0.0252) Aerosil© 200	0	1.485 (0.0524)

Table 4–S	ynoptic	Table of	of prep	bared s	pecimens
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* With PCP



Fig. 4–Raman spectra of: $G_{0.20}$ dispersion inorganic matrix (upper), GNP flake in $G_{0.20}$ (middle), and bare GNP (lower).

EXPERIMENTAL RESULTS AND DISCUSSION Raman spectroscopy

Figs. 4 and 5 report the Raman spectra of GNP and GO respectively, when dispersed on C-S-H matrix obtained by the $CaO/SiO_2/H_2O$ reaction.

The following peaks have been identified^{15,16}:



Fig. 5–Raman spectra of GO_0.20 dispersion recorded in two different positions of the laser beam, GO_0.20 A (middle) and GO_0.20 B (upper) compared with the spectrum of bare GO (lower).

- D peak (≈1320 cm⁻¹ (3350 in⁻¹)), associated to breathing ring vibrations of sp² carbon atoms that can be observed in Raman scattering in the presence of either chemical/ structural disorder or confinement (e.g., by the edges) of the graphitic layers;
- G peak (≈1580 cm⁻¹ (4013 in⁻¹)), associated to the collective C=C stretching vibration of the graphitic layers;
- 2D peak (≈2640 cm⁻¹ (6706 in⁻¹)), due to second order vibrations of the D peak observed only in the presence of extended sp² carbons domains.

The peaks of G_0.20 in the spectrum in the middle in **Fig. 4**, were detected pointing the laser on a GNP flake. When we moved the laser randomly, away from any flakes (see upper spectrum in **Fig. 4**), we did not observe any G and D features associated with GNPs anymore. The broad and low features observed in this spectrum are due to trace of carbonaceous structures observed in the silica fume sample.

On the contrary, in the Raman spectra of samples containing GO, we always saw the very strong and broad peaks in the G and D regions associated with GO, independently from the analysed area (see **Fig. 5**).

FTIR spectroscopy

The spectra obtained by reacting CaO with: *i*. SiO₂ fume, without any carbon additives, after 1 and 4 weeks and *ii*. with Aerosil after 1 week are characterised by several peaks whose interpretation is given in the **Table 5**.^{17,18}

The evolution of SiO₂ to C-S-H is well evident from the two peaks related to the Si-O stretching (1105 and 905 cm⁻¹ / 2806 and 2299 in⁻¹).