

## IN SITU CHEMICAL MODIFICATION OF C-S-H INDUCED BY CO<sub>2</sub> LASER IRRADIATION

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### ABSTRACT

Fire-induced compositional changes lead to strength loss and even failure in cement and concrete. Calcium silicate hydrate (C-S-H) gel, the main product of cement hydration, dehydrates at 25 °C to 200 °C, while temperatures of 850 °C to 900 °C alter its structure. A Raman spectroscopic study of the amorphous and crystalline phases forming after CO<sub>2</sub> laser radiation of cement mortar showed that C-S-H dehydration yielded tricalcium silicate at higher, and dicalcium silicate at lower, temperatures. Post-radiation variations were identified in the position of the band generated by Si-O bond stretching vibrations.

*Keywords: Microstructure; calcium silicate hydrate; spectroscopy; degradation; Ca<sub>2</sub>SiO<sub>4</sub>; Ca<sub>2</sub>SiO<sub>5</sub>.*

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## INTRODUCTION

Concrete is a fairly non-combustible, fire-safe material that resists high temperatures well. Fire nonetheless poses a severe risk to concrete buildings and structures, inducing structural weakening [1] as well as physical changes such as spalling and colour loss [2] attributable to chemical processes governed by material composition and the temperatures reached [3].

Concrete strength declines with rising temperatures. At 100 ° to 200 °C the vapour pressure ensuing from free water evaporation prompts spalling, whereas at 300 °C non-evaporative water loss reduces strength by 15 % to 40 % [1,4,5]. Decay is most intense at 600 °C or over, when concrete compressive strength drops to 7 % to 25 % of the initial value.

The effect of heat on the composition of the primary binder in concrete, cement, is likewise temperature-dependent [6]: calcium silicate hydrate (C-S-H) dehydrates at 80 °C to 100 °C; calcium sulfoaluminate hydrate (ettringite) decomposes at 60 °C to 80 °C; calcium hydroxide dehydrates at around 400 °C; and calcium carbonate decomposes at 600 °C to 900 °C. Incipient melting is observed at 1100 °C. The change in free water from liquid to gas at that temperature varies the rate of heat transmission from the concrete surface to its interior.

C-S-H gel, the majority chemical compound in hydrated cement, precipitates as a disorderly, metastable, amorphous structure similar to tobermorite ( $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})$ ). When heated, tobermorite converts into stable, highly crystalline phases. According to Shaw et al. [6], at 840 °C to 855 °C it dehydrates and restructures into wollastonite ( $\text{CaSiO}_3$ ). In a recent study, Tajuelo-Rodríguez et al. [7] determined that the temperature at which C-S-H converts into  $\beta$ -wollastonite rises with the Ca/Si ratio in the gel.

Since the physics of the heat generated by photo-physical reactions is similar to the physics of fire, laser radiation has been used to study the effect of fire on building

materials [8, 9]. In a prior study by the authors [10], portlandite and a vitreous material were observed to form in a continuous wave CO<sub>2</sub> laser- (CW CO<sub>2</sub> laser) irradiated lime pozzolan mortar containing calcium carbonate as the main binder and a small fraction of calcium silicate. In belite cement synthesis, with high dicalcium silicate, hydrothermal procedures are applied to form hydrated phases which are subsequently calcined to extract dicalcium silicate [11]. In other words, heat is applied to hydrated phases to synthesise anhydrous calcium silicates with the same Ca/Si ratio.

Raman spectroscopy, used to analyse short-range order and local bonding in materials, is also very useful for characterising materials containing both amorphous and crystalline phases, such as cement, mortar and concrete [12-15]. Moreover, the technique requires no sample preparation and only a few milligrams of the substance to be analysed. The main drawback to Raman spectroscopy is the background noise generated by fluorescence attributable to impurities and rough surface-induced elastic scattering, which overlaps with the Raman peaks associated with cement compounds. Such fluorescence, which Newman et al. [16] suggested may be associated in portland cement with silicate phase polymerisation, can be minimised with low excitation frequency micro-Raman [10].

This study explored the chemistry of calcium silicate hydrate conversion to di- and tricalcium silicate to determine whether these or other calcium silicates formed when cement samples were exposed to high temperatures. High temperatures were simulated in the samples by irradiating cement mortar with a CO<sub>2</sub> laser [17]. Micro-Raman spectroscopy was used to monitor the amorphous and crystalline phases present in the samples analysed.

## EXPERIMENTAL

### *Materials*

Type I cement and silica (SiO<sub>2</sub>) aggregate were used to prepare the mortar specimens. X-ray fluorescence showed the main cement constituents to be SiO<sub>2</sub> (18.50%), CaO

(57.75 %),  $\text{Al}_2\text{O}_3$  (4.55 %),  $\text{Fe}_2\text{O}_3$  (3.50 %) and  $\text{SO}_3$  (7.69 %). Loss on ignition at 1000 °C was 3.5 %. The  $\text{SiO}_2$  content in the siliceous sand was 98.92 %. The X-ray diffraction (XRD) patterns for the initial cement showed that the typical majority constituents, calcium silicate compounds tricalcium silicate ( $\text{C}_3\text{S}$ )<sup>2</sup> and dicalcium silicate ( $\text{C}_2\text{S}$ ) were found together with smaller amounts of calcium aluminate,  $\text{C}_3\text{A}$ ,  $\text{C}_4\text{AF}$ , gypsum and anhydrite. Quartz was used as aggregate.

The raw materials were blended at a cement/aggregate ratio of 1/3 and mixed with water at a water/cement ratio of 0.25 to prepare 1x1x6 cm mortar specimens that were cured for 50 d at 21 °C and 99 % relative humidity. After 50 days, the hydration reaction was stopped by the addition of acetone/ethanol. The diffractogram for the mortar (ground to a particle size of 45  $\mu\text{m}$ ) reproduced in Figure 1 showed portlandite and calcite to be the majority crystalline phases. An amorphous hump at  $2\theta=30^\circ\text{-}40^\circ$  was attributed to C-S-H formation. The intensity of the  $\text{C}_3\text{S}$  signals was lower than in the pattern for the dry materials as a result of hydration.

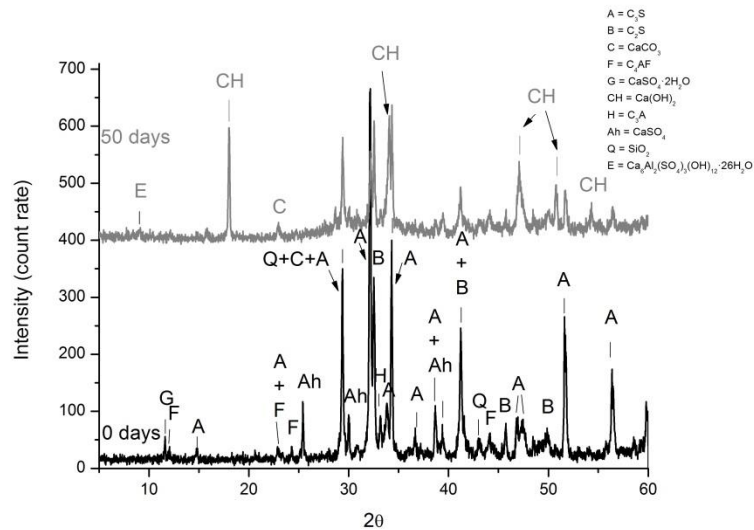


Fig. 1.- XRD patterns for anhydrous and 50 d hydrated cement

A =  $\text{C}_3\text{S}$ ; B =  $\text{C}_2\text{S}$ ; C =  $\text{CaCO}_3$ ; F =  $\text{C}_4\text{AF}$ ; G =  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; CH =  $\text{Ca}(\text{OH})_2$ ; H =  $\text{C}_3\text{A}$ ; Ah =  $\text{CaSO}_4$ ;

Q =  $\text{SiO}_2$ ; E =  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$

<sup>2</sup> Cement chemistry notation: C = CaO; S =  $\text{SiO}_2$ ; H =  $\text{H}_2\text{O}$ ; A =  $\text{Al}_2\text{O}_3$ ; F =  $\text{Fe}_2\text{O}_3$

### *CO<sub>2</sub> laser exposure*

A CW CO<sub>2</sub> laser was used to irradiate the mortar to simulate fire effect. The irradiation was carried out with a CW (Firestar t80) CO<sub>2</sub> laser operating at a wavelength of 10.591 μm, 10P(20) CO<sub>2</sub> laser line as described elsewhere [10]. This laser has a maximum power output of 80 W, but in our experiments, laser output was kept at 14, 20, 30, 50, 70, 78 and 80 W as measured with a Synrad PW-250 power meter.

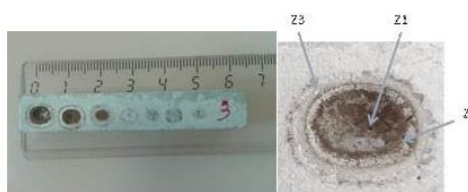


Figure 2.- Irradiated OPC mortar: a) laser power, from left to right, OPC-7 = 80 W; OPC-6 = 78 W; OPC-5 = 70 W; OPC-4 = 50 W; OPC-3 = 30 W; OPC-2 = 20 W; OPC-1 = 14 W; b) magnification of OPC-7 showing inner core (Z1); intermediate ring (Z2); and outer crown (Z3).

The unfocused laser beam was directed onto the surface of the sample by using gold coated mirrors. Irradiation time was 5 seconds. In this way, the energy delivered to the surface sample ranges between 70 and 2580 J. Irradiation of the mortar samples with the CW CO<sub>2</sub> was made in air.

After melting under laser radiation, an indication that the temperature reached was higher than its 1450 °C melting point [17], the mortar surface cooled into an amorphous mass.

The general view of the samples after laser irradiation is depicted in Figure 2, whilst exposure time, output power and spot diameter are summarised in Table 1. Spot diameter was defined as the diameter of the vitreous (brown) area of the spot measured with a precision calliper. Spot size increased with laser power, peaking in sample OPC-7, irradiated at 80 W for 5 s. Spot borders were too indistinct in the samples irradiated at less than 30 W (see Figure 2) to determine the diameter.

Table 1. CO<sub>2</sub> laser exposure conditions and spot size

Sample	Exposure time (s)	Laser power (W)	Spot dia-meter (mm)
OPC-1	5	14	N.D.
OPC-2	5	20	N.D.
OPC-3	5	30	1.8
OPC-4	5	50	2.1
OPC-5	5	70	3.9
OPC-6	5	78	5.5
OPC-7	5	80	6.4

#### *Micro-Raman spectroscopy*

A confocal Raman microscope (Renishaw Invia 2000) equipped with a Leica microscope and an electrically refrigerated CCD camera was used to collect the Raman spectra. Laser excitation lines were provided by a diode laser (785 nm) and a Renishaw Nd;YAG laser (532 nm). The 5 mW laser beam was focused on different zones of the irradiated spots. The spectra were recorded using 50x objective lenses and an integration time of 10 s. WIRE for Windows and Galactic Industries GRAMS/32™ software were used for data acquisition and Origin 8.0 for analysis. Several zones were scanned in each spot, working from core to crown, with five scans recorded in each zone to enhance the signal-to-noise ratio. Daily calibration of the wavenumber axis was achieved by recording the Raman peak of silicon at 520 cm<sup>-1</sup>. Spectra were normalized to the maximum intensity. Three spectra were analysed in z1 and z2.

#### *X-Ray diffraction*

X-ray diffraction (XRD) was conducted on a Bruker D8 Avance diffractometer fitted with a copper anode X-ray tube operating at 40 kV and 30 mA at diffraction angles ranging from 5° to 60° with a step speed of 0.038 s<sup>-1</sup>.

## RESULTS AND DISCUSSION

As high fluorescence hindered signal detection on the Raman spectra for the non-irradiated samples, they are not shown. Only one small band at  $1085\text{ cm}^{-1}$  attributed to calcium carbonate was observed on the 532 nm laser spectrum and just one signal at  $3616\text{ cm}^{-1}$  generated by portlandite on the 785 nm spectrum, whereas according to the XRD patterns the binder in the starting mortar contained  $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_4\text{AF}$ ,  $\text{C}_3\text{A}$ , gypsum, anhydrite and calcite and the aggregate, quartz.

Three zones were distinguished in the spots generated: a central vitreous core (Z1), a thin brown ring around the core (Z2) and a wider outer crown (Z3). The differences in colour in the three zones were an indication that the peak temperature varied radially [18] (Figure 2).

The signals on the Raman spectrum for sample OPC-1, irradiated for 5 s at 14 W, varied depending on the zone (Figure 3). In Z1, where the laser impacted the surface, six bands were observed at  $356\text{ cm}^{-1}$ ,  $453\text{ cm}^{-1}$ ,  $618\text{ cm}^{-1}$ ,  $980\text{ cm}^{-1}$ ,  $1004\text{ cm}^{-1}$  and  $1070\text{ cm}^{-1}$ .

The band at  $356\text{ cm}^{-1}$  was attributed to portlandite, a phase identified in previous studies on  $\text{CO}_2$  laser-irradiated mortars and stones [8, 10]. The bands at  $1004\text{ cm}^{-1}$  and  $618\text{ cm}^{-1}$  were associated with gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), known to lose two water molecules at  $220\text{ }^\circ\text{C}$ , yielding thermodynamically metastable anhydrite III ( $\text{CaSO}_4$ ). Insoluble anhydrite II forms at approximately  $300\text{ }^\circ\text{C}$ , with a very low rehydration rate depending on the peak temperature. Anhydrite I, a high temperature variety of anhydrite, is stable at  $>1180\text{ }^\circ\text{C}$  [19], for at high temperatures and steep temperature ramping, a layer of oxides forming with  $\text{CaSO}_4$  decomposition acts as a protective coating that detains the process [20]. Sanz [20] contended that anhydrite II can be hydrated with water vapour, whereas anhydrite I hydration calls for higher concentrations of water. The presence of gypsum in Z1 attested to the formation of anhydrite II and its hydration with water vapour.

As the majority compounds in the unexposed mortar were quartz and the calcium silicates  $C_3S$  and  $C_2S$ , the bands located at  $453\text{ cm}^{-1}$ ,  $980\text{ cm}^{-1}$  and  $1070\text{ cm}^{-1}$  may be thought to have been generated by a silicate. The main  $SiO_4$  stretching bands lie at  $800\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$ , depending on the position of the tetrahedron in the network. Isolated  $SiO_4$  molecules generate signals at  $800\text{ cm}^{-1}$  to  $850\text{ cm}^{-1}$ , dimers at  $950\text{ cm}^{-1}$ , silicate chains at  $1050\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$ , silicate sheets at  $1100\text{ cm}^{-1}$  and tectosilicates at  $1150\text{ cm}^{-1}$  to  $1250\text{ cm}^{-1}$ . The broad bands peaking at  $980\text{ cm}^{-1}$  and  $1070\text{ cm}^{-1}$  on the spectra for the exposed samples were respectively attributed to non-linked Si-O antisymmetric stretching and tetrahedral Si-O symmetrical stretching vibrations. The signal at  $453\text{ cm}^{-1}$  was associated with non-crystalline  $SiO_2$ , which forms at temperatures of over  $540\text{ }^\circ\text{C}$  [22], and that can be assumed that it has been formed from the quartz may that have been melted ( $1710\text{ }^\circ\text{C}$ ).

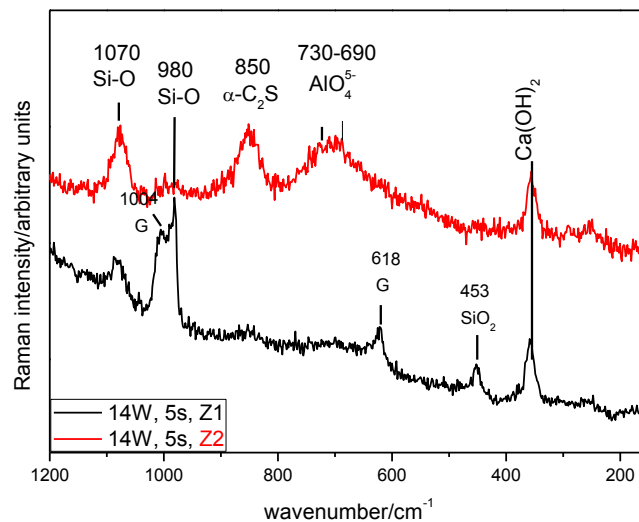


Fig. 3.- Micro-Raman spectra for zones Z1 and Z2 in the sample OPC-1 (14 W, 5 s) spot; G = gypsum

In Zone 2, which would have received dissipated heat, the main vibration bands appeared at  $1070\text{ cm}^{-1}$  (broad),  $850\text{ cm}^{-1}$  (broad),  $730\text{ cm}^{-1}$  to  $690\text{ cm}^{-1}$  (very broad) and  $356\text{ cm}^{-1}$  (broad). As noted earlier, the broad band at  $1070\text{ cm}^{-1}$  might have been generated by tetrahedral Si-O symmetrical stretching. The very broad band at  $730\text{ cm}^{-1}$  to  $690\text{ cm}^{-1}$  was generated by aluminates, for according to several authors [21, 23-26],



the main Raman aluminate bands in anhydrous cement phase  $C_4AF$  lie at  $506\text{ cm}^{-1}$  ( $\nu_1$  [ $AlO_4^{5-}$ ]) and  $730\text{-}690\text{ cm}^{-1}$  ( $\nu_3$  [ $AlO_4^{5-}$ ]). The sample can consequently be assumed to have been heated to  $1200\text{ }^\circ\text{C}$  to  $1300\text{ }^\circ\text{C}$  at which these aluminate phases form [27]. The broad band peaking at  $850\text{ cm}^{-1}$  was associated with  $\alpha\text{-}C_2S^3$  [28].

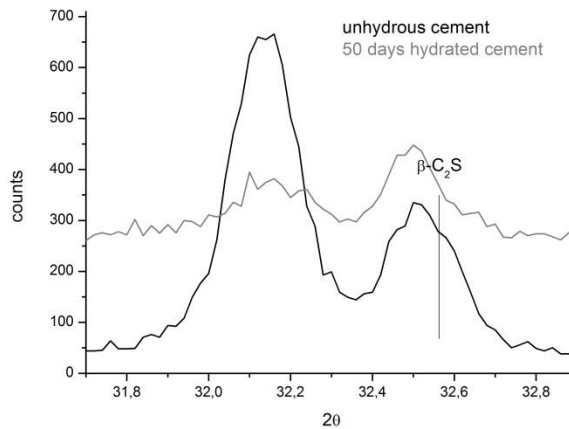
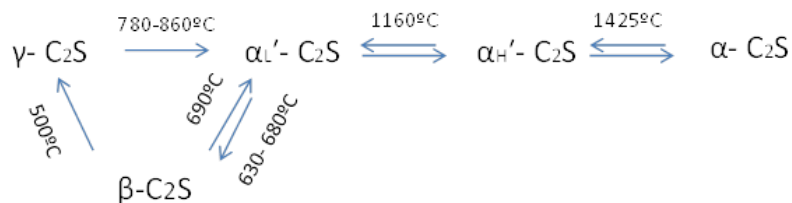


Fig. 4.- XRD patterns ( $2\theta = 31.7\text{-}32.9^\circ$ ) for anhydrous and 50 d hydrated mortar samples

Whilst initially the cement contained both  $C_3S$  and  $\beta\text{-}C_2S$ , as the hydration rate is higher in  $C_3S$ , the 50 d sample contained primarily the latter (Figures 1 and 4). After laser radiation,  $\beta\text{-}C_2S$  converted to  $\alpha\text{-}C_2S$  further to the  $Ca_2SiO_4$  phase transformation flowchart shown in Scheme 1 [27], an indication that the temperature in Z2 peaked at around  $1400\text{ }^\circ\text{C}$ .



Scheme 1.-  $Ca_2SiO_4$  transformation with temperature

<sup>3</sup> Cement chemistry notation: C = CaO; S = SiO<sub>2</sub>; H = H<sub>2</sub>O; A = Al<sub>2</sub>O<sub>3</sub>; F = Fe<sub>2</sub>O<sub>3</sub>

The presence in both Z1 and Z2 of a broad band peaking at  $350\text{ cm}^{-1}$  and a narrow band at  $3616\text{ cm}^{-1}$  (area not shown on the Raman spectrum) attested to portlandite formation in both zones. That finding was consistent with earlier reports of its presence in  $\text{CO}_2$  laser-irradiated pozzolan mortars [8, 10]. Prior research [10] showed that portlandite formed in OPC after vacuum radiation, inferring that  $\text{CaO}$  reacted with radiation-induced water vapour.

The presence of distinctly different compounds in the core and adjacent ring regions of sample OPC-1 may be an indication of different peak temperatures: higher ( $1700\text{ }^\circ\text{C}$ ) in Z1, where the laser beam impacted, and lower in Z2 ( $\sim 1400\text{ }^\circ\text{C}$ ), the heat dissipation zone.

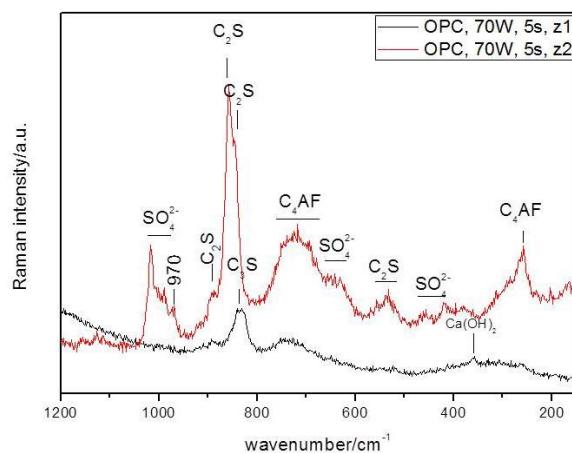


Fig. 5.- Micro-Raman spectra for zones Z1 and Z2 in the sample OPC-5 (70 W, 5 s) spot

In OPC-5, exposed to higher power (70 W, 5 s) laser radiation, the most prominent Raman signal on the spectrum for Z1, at  $850\text{ cm}^{-1}$ , was generated by Si-O stretching vibrations in  $\text{C}_3\text{S}$ , whereas that signal shifted to higher wavenumbers in Z2. The double band at  $857\text{ cm}^{-1}$  and  $845\text{ cm}^{-1}$  in the Z2 spectrum was associated with the Si-O stretching vibrations in  $\beta\text{-C}_2\text{S}$ , attesting to the formation of that calcium silicate phase [14]. Those findings may denote a high cooling rate, for  $\beta\text{-C}_2\text{S}$  formation calls for rapid

cooling to elude transformation to  $\gamma$ -C<sub>2</sub>S. Calcium sulfate-related bands in the form of anhydrite were also observed, along with the signals characteristic of the aluminoferrite (C<sub>4</sub>AF) vibrations induced at 1200 °C to 1300 °C. As noted earlier, the extent of anhydrite hydration depends on temperature and formation rate. In light of anhydrite formation in Z2, the temperature reached may be assumed to have been higher than in the Z2 in previous point with less laser power (14 W, 5 s).

Furthermore a small resonance with maximum at 970 cm<sup>-1</sup> can be an indication of another calcium silicate phase formed. When cement is exposed to temperatures of over 800 °C, C-S-H decomposes [4] into belite (C<sub>2</sub>S) and wollastonite (CS). Belite was observed in Z2 in the sample exposed to 70 W CO<sub>2</sub> laser radiation, whilst the resonance at 970 cm<sup>-1</sup> might have been generated by wollastonite [29]. Taken together, these findings would denote water loss after radiation and the formation of CS, C<sub>2</sub>S and C<sub>3</sub>S.

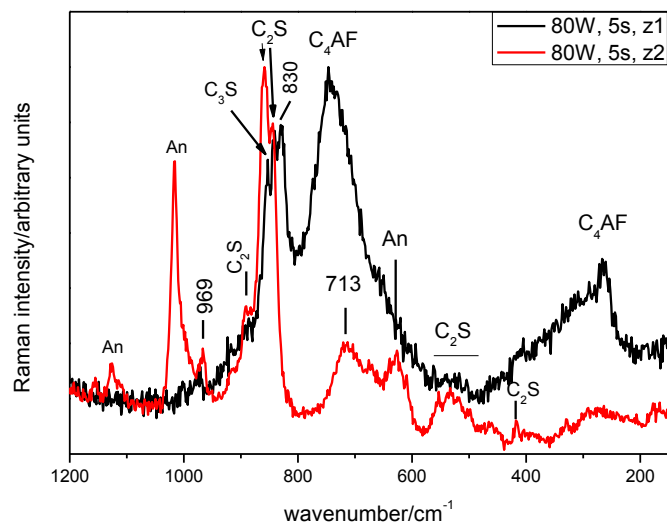


Fig. 6.- Micro-Raman spectra for zones Z1 and Z2 in the sample OPC-7 (80 W, 5 s) spot

Silicate phases such as  $\beta$ -C<sub>2</sub>S as well as anhydrite were identified on the spectrum for Z2 in the samples exposed to 80 W laser radiation (Figure 6), whereas in the core region of the spot (Z1) the main phases were C<sub>3</sub>S and C<sub>4</sub>AF. An intense band at 830 cm<sup>-1</sup> on the

Raman spectra may have denoted the formation of another calcium silicate phase. The absence of a signal attributable to quartz would imply that the temperatures reached exceeded its 1710 °C melting point.

The resonance at 969 cm<sup>-1</sup> may have been generated by the very stable anhydrite [19] formed at T>1180 °C. No gypsum was detected on the 80 W, 5 s spectra.

The phases identified and the estimated surface temperature in the two zones of the irradiated samples are summarised in Table 2.

Table 2.- Phases identified in Z1 and Z2 of the irradiated samples

Sample	Raman-identified phase		Estimated surface temperature (°C)	
	z1	z2	z1	z2
OPC-1 (14 W)	gypsum, Ca(OH) <sub>2</sub> , SiO <sub>2</sub>	α-C <sub>2</sub> S*, C <sub>4</sub> AF*, Ca(OH) <sub>2</sub>	1700 (no quartz)	1400 (fast cooling)
OPC-5 (70 W)	C <sub>3</sub> S*, Ca(OH) <sub>2</sub>	β-C <sub>2</sub> S*; C <sub>4</sub> AF*; CaSO <sub>4</sub>	1700 (no quartz)	1300 (fast cooling)
OPC-7 (80 W)	C <sub>3</sub> S*, C <sub>4</sub> AF*	β-C <sub>2</sub> S*; C <sub>4</sub> AF*; CaSO <sub>4</sub>	1700 (no quartz)	1300 (fast cooling)

\*Cement chemistry notation C: CaO; S = SiO<sub>2</sub>; A = Al<sub>2</sub>O<sub>3</sub>; F = Fe<sub>2</sub>O<sub>3</sub>

A comparison of the 940 cm<sup>-1</sup> to 780 cm<sup>-1</sup> interval on the Raman spectra for Z1 and Z2 showed that the SiO<sub>4</sub> stretching band shifted with rising laser power, more visibly in Z1 (Figure 7), attesting to variations in the silicate structure. In pure β-C<sub>2</sub>S the primary symmetrical stretching bands lie at 854±5 cm<sup>-1</sup> and 841±5 cm<sup>-1</sup>, whilst in pure C<sub>3</sub>S they peak at 849±5 cm<sup>-1</sup> and 839 ±5 cm<sup>-1</sup> [14, 23, 24]; i.e., both bands lie at higher wavenumbers in the former than in the latter.

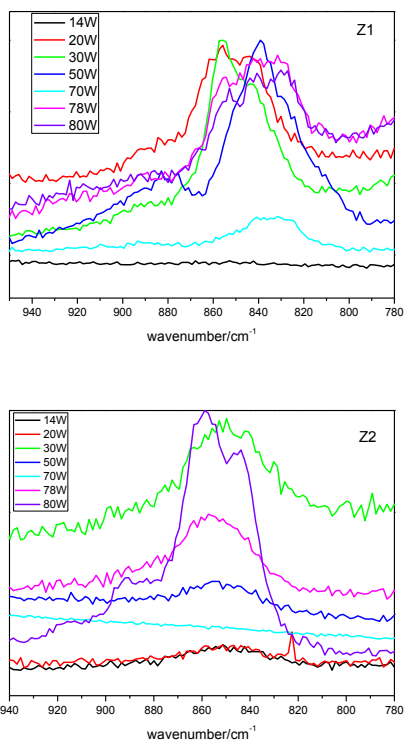


Fig. 7.- Micro-Raman spectra for Z1 (top) and Z2 (bottom) after 14 W to 80 W CO<sub>2</sub> laser radiation

Raman band shifts may be attributed to changes in compound microstructure, in the form of either impurity uptake, which is known to stabilise calcium silicate polymorphs, or variations in the Ca/Si ratio [28]. The latter would infer the existence of two distinct compounds, such as C<sub>3</sub>S and C<sub>2</sub>S. Inasmuch as one or the other formed when the mortar was laser irradiated, the band shifts observed here should be attributed such differences in the Ca/Si ratio. The Si-O bond stretching bands (at 854 cm<sup>-1</sup> and 839 cm<sup>-1</sup>) depicted in Figure 8, resulting from the deconvolution of the Raman spectra in the interval 920 cm<sup>-1</sup> to 820 cm<sup>-1</sup>, shifted with rising laser power, downward in Z1 and upward in Z2. The conclusion drawn is that in the inner core of the irradiated sample C<sub>3</sub>S formed at higher and C<sub>2</sub>S at lower laser output. The opposite pattern was observed in the intermediate ring, where C<sub>3</sub>S formed when laser radiation was applied at lower power.

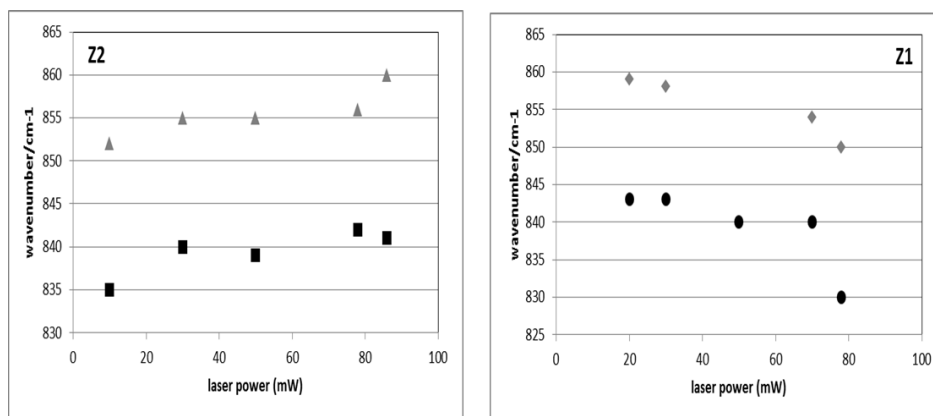


Fig. 8.- Variations in stretching band position vs laser power in exposure zones Z1 and Z2

## CONCLUSIONS

This study showed that the composition of the anhydrous calcium silicate resulting from calcium silicate hydrate in laser irradiated cement depends on the laser power used.  $C_3S$  was identified in the inner core of irradiated spots, where the temperatures reached were higher, and  $C_2S$  in the Z2 zone, where the temperatures were lower. With rising laser power, the position of the Si-O bond stretching band shifted to higher values in the intermediate ring and lower values in the inner zone. The inference is that as power was raised,  $C_3S$  converted to  $C_2S$  in the core, and vice-versa in the ring. Tri- and dicalcium were consequently synthesised from calcium silicate hydrate along other than the usual pathway when CaO and  $SiO_2$  are heated to 1200 °C- 1500 °C or hydrothermal procedures are deployed.

Calcium sulfate and  $C_4AF$ , other anhydrous phases, were also identified in the  $CO_2$  laser-irradiated samples. The lowest power used, 14 W, induced the formation of anhydrite II. Stable at temperatures of under 1180 °C, this compound was subsequently hydrated with water vapour to yield gypsum. In contrast, anhydrite I, which is stable at temperatures over 1180 °C, formed at the highest power applied, 80 W. Hydration of the CaO present in the cement with the water vapour released in hydrated compound dehydration gave rise to  $Ca(OH)_2$ .

On the grounds of the phases formed and given the absence of quartz, the temperature in the inner zone was estimated to peak at around 1700 °C. The non-detection of  $\gamma$ -C<sub>2</sub>S was indicative of rapid cooling from core to adjacent ring.

The authors declare that there is no conflict of interest.

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