STUDY OF C-S-H DEHYDRATION DUE TO TEMPERATURE INCREASE DURING FIRES

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ABSTRACT

Concrete is one of the most fire-resistant materials, whose resistance depends on the chemical and structural characteristics of the hydrated calcium silicate (C-S-H) formed in the hydration and hardening process. However, the structure and composition of this calcium silicate hydrate varies with the time of hydration. The effect of the composition of the calcium silicate on the anhydrous material formed has been studied after subjecting it to an accelerated study of the effect of fire, irradiating it with a CO₂ laser. Changes in the composition of C-S-H can lead to changes in the mechanical properties of the cement. Calcium silicate hydrate samples with different chemical composition (Ca/Si ratios 1 and 2) as well as different synthesis processes (double decomposition and hydrothermal) were studied. The crystalline phases obtained after heating were identified through micro-Raman spectroscopy, which confirmed the formation of anhydrous calcium silicates with the same Ca/Si ratio as the initial one. In C-S-H gels with a Ca/Si ratio of over 1.5, stable Ca(OH)₂ was formed. SEM/EDX analysis determined that in the process of heating with the laser, water is lost fast, generating porous structures. Such porosity is higher in materials with a lower Ca/Si ratio.

Keywords: C-S-H; C₂SH; micro-Raman; SEM/EDX; fire

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1 INTRODUCTION

When concrete is exposed to high temperatures, as in a fire, physical and chemical transformations take place resulting in deterioration of its mechanical properties. This deterioration varies according to the concrete mix proportions and constituents and can be determined by complex physico-chemical transformations occurring during heating^[1].

Water evaporation and chemical changes of hydrated products occur in the cementitious matrix that in turn give rise to an increase in porosity and pore size of concrete. Also, micro-cracks appear due to stress in the interface region between the cement matrix and the aggregates. Other effects relate to phase transitions or disintegration of the aggregates, as well as vapour pressure in pores and thermal stresses that give rise to spalling of concrete at high temperature. Among these changes, one of the main effects causing concrete degradation at high temperatures is the dehydration of the cement matrix.

Numerous attempts have been made to understand the complex mechanism of dehydration and the microstructural changes produced in the cement paste after heating by fire ^[2]. Especially important is the behaviour of calcium silicate hydrate (C-S-H), the major component in hydrated portland cement, is responsible of cement-based materials strength, bindability and durability.

The behaviour of concrete at high temperatures will depend on the structure and chemical composition of the cement and therefore of this calcium silicate hydrate. This depends on the chemical composition of the initial cement, temperature and time of hydration. According to the literature^[1,2], chemically bound water loosens from the calcium silicate hydrate above about 110 °C. Although the C-S-H phase maintains its molecular structure up to 300 °C, a clear change in its morphology is observed for this temperature related to an irreversible shrinkage. At 700 °C, this micro-structure is predominantly composed of globules that form upon complete breakage of C-S-H producing anhydrous silicates and losing its binding capacity.

C-S-H gel characteristics are defined, among others, by Ca/Si ratio^[3-5]. Anhydrous portland cement initially has two silicate phases with different Ca/Si ratios, tricalcium silicate (C_3S) with $Ca/Si=3$ and dicalcium silicate (C_2S), with $Ca/Si=2$ ^[6]. C_3S hydrates first, initially generating a calcium silicate hydrate with a high Ca/Si ratio, whereas C_2S hydration, which is slower, yields gels with lower Ca/Si ratios^[7,8]. As the calcium available in a cement-based matrix declines at longer hydration times, the C-S-H formed in later age materials has a lower Ca/Si ratio^[9], while the water/Si ratio in such materials also varies^[7,8].

Different methods were developed to synthesize C-S-H gels with a controlled value of the Ca/Si ratio. One of the quickest and most direct methods to achieve this control is the double decomposition method^[6]. Alternative procedures have nonetheless been prompted by the need for less polluting materials. This is the case of belite (phase β - C_2S -high) cements^[10], which with a lower calcium content and lower clinkerisation

temperature generate less CO₂ than portland cement during manufacture. That need, along with the pursuit of more sustainable processes, has placed the spotlight on the hydrothermal synthesis of belite cement from waste materials^[10-13]. The first stage of the hydrothermal β -C₂S synthesis^[14] generates a precursor, C₂SH, with a Ca/Si ratio of 2.0, the initial ratio between the calcium and silicon ions in the majority belite phase (β -C₂S) in these cements.

A number of instrumental techniques are presently used in order to determine the Ca/Si ratio of C-S-H gels, either directly or indirectly^[4-6,15-19]. The most widely used method is energy dispersive X-ray analysis (EDX), associated with transmission electron microscopy (TEM). It involves taking a large number of readings (at least 40) on a very small area of the sample to ensure accuracy and the non-inclusion of impurities in the analysis. One of the most prominent indirect techniques is ²⁹Si nuclear magnetic resonance (NMR). This method determines the area under the curve generated by the signals attributable to silicon tetrahedra with different connectivities (Qⁱ), i.e., Q¹ or Q² indicates connection with one or two adjacent tetrahedra. The Ca/Si ratio is calculated from the NMR curves with the formula proposed by various authors^[4,5]. Whilst it is one of the most widely used procedures, as it is indirect, it depends on the method applied to analyse the data.

Raman spectroscopy is a very useful technique to study amorphous and crystalline silicates^[20-22]. Both types of compounds can be formed after the heating process at high temperatures. Raman spectroscopy has been used also to study the composition of cement and concrete after heating. Vetter et al.^[23], studied the effect of fire (950°C) in a concrete structure after 28 days of hydration, finding C-S-H decomposition with the formation of gehlenite (Ca₂Al₂SiO₇) and both anhydrous silicates (C₂S and C₃S). Similar results were found by Pereskova et al.^[24], heating a cement concrete matrix with fibre reinforcement until 1200°C. In this case, in addition to gehlenite, they also identified the presence of pseudowollastonite (CS) and dicalcium silicate (C₂S) as the main phases formed.

Furnace heating has been used by several authors to investigate the thermal changes occurring in concrete at high temperature, while fire heating is usually considered in studies at a structural level^[2]. Prior studies have proposed using CO₂ laser radiation to simulate the effect of fire on cements and concretes^[25-30] as the physics of heat generated by photo-physical reactions is similar to the physics of fire. In fact, laser irradiation offers several advantages for this application, including high repeatability of experimental conditions and, most importantly, concentration of a high energy in small areas, thus allowing tests at the micro-scale on small samples^[26].

The studies on CO₂ laser irradiated cements together with Raman studies, identified the presence of crystalline or amorphous phases depending on the radiation conditions. Amorphous calcium silicate was detected in the lower radiation temperature area, while crystalline calcium silicates in the form of C₂S or C₃S were observed when higher temperatures were reached. It is expected that the final crystalline phases produced after

rapid heating would depend on the initial Ca/Si ratio of the radiated C-S-H gel. Consequently, the analysis of synthetic C-S-H gels with different nominal Ca/Si ratios after laser heating would give rise to significant information for understanding C-S-H gel and its behaviour under a fire event.

The aim of the work has been to study gels with different Ca/Si ratios exposed to high temperature processes to simulate a fire process. Then, C-S-H gels with different nominal Ca/Si ratios were synthesised using hydrothermal or double decomposition procedures and the anhydrous calcium silicates obtained after fire simulation by rapid heating with CO₂ radiation were analysed by different techniques.

2 EXPERIMENTAL PROCEDURES

Double decomposition was deployed to synthesise two C-S-H gels with nominal Ca/Si ratios of 0.5 and 2.0 (CSH^{0.5} and CSH^{2.0}). A C-S-H gel with a nominal Ca/Si ratio of 2.0 was also synthesised via hydrothermal process to obtain the calcium silicate hydrate (C₂SH) from two types of starting materials: commercial laboratory reagents (sample named C₂SH) and fly ash, as an industrial by-product (sample named FA-C₂SH). X-ray fluorescence characterisation of the used fly ash (FA) showed it to contain: 19.4 % SiO₂, 37.6 % CaO, 11.2 % Al₂O₃, 3.0 % Fe₂O₃, 3.9 % SO₃ and 22.1 % loss on ignition at 1000 °C. The samples synthesised are listed in Table 1, along with the synthesis procedure and nominal Ca/Si ratio.

Double decomposition synthesis^[31-33] was conducted in a glove box with an inert argon atmosphere. The gels were prepared from stoichiometric amounts of Na₂SiO₃·5H₂O and Ca(NO₃)₂·4H₂O with nominal Ca/Si ratios of 0.5 and 2.0. The respective amount of Ca(NO₃)₂·4H₂O was dissolved in 2 mL of decarbonated water and added to 16 mL of decarbonated water containing the respective amount of Na₂SiO₃·5H₂O. The solution pH was adjusted with NaOH to values of 12.0-12.5.

The C₂SH precursor was synthesised hydrothermally^[34]. The starting materials used as sources of silicon and calcium for the synthesis varied. Laboratory grade SiO₂ and CaO with a combined Ca/Si ratio of 2.0 were used for the C₂SH sample, whereas in the FA-C₂SH sample, the source was a fly ash (FA), to which CaO was added to adjust the initial Ca/Si ratio to 2.0. The solids and decarbonated water were mixed in a reactor at a water/solid weight ratio of 3.0. In the subsequent hydrothermal treatment the temperature of the mix was kept at 200 °C for 4 h while the solution was stirred constantly. The reactor was then cooled and the solid obtained was filtered and dried at 80 °C.

The four samples obtained were pressed into 15 mm diameter wafers and exposed to fire heating simulation by continuous CO₂ radiation for 2 s (CW CO₂ laser) sourced from a Synrad Firestar t80 CO₂ laser operating at a wavelength of 10.591 µm with a 10P(20) CO₂ laser line, as described elsewhere^[25]. Although the laser features a maximum 80 W power output, the power used was 6 W, measured with a Synrad PW-

250 power meter. The thickness of the pellets was different depending on the synthesis method of the sample. It was about 0.5 cm for the samples hydrothermally prepared and less than 0.1 cm for the samples prepared by double decomposition method. This was related with the available amount of sample in each case.

The pre-heated samples were characterised on a Bruker AXS D8 Advance X-ray diffractometer with Cu K α radiation, a step size of 0.020° and a 2 θ angle range of 5° to 60°. The diffractograms were normalised to the most intense signal (2 θ ≈29.1°). Post radiation XRD characterization was not possible since the damage was localized in a relatively small area and the considerable amount of powder necessary for XRD analysis was difficult to extract from the damaged section of the samples.

After heating, the samples were analysed in three areas with different appearance: inner, intermediate and outer (Fig S3). A Renishaw inVia confocal micro-Raman spectrometer fitted with a Leica microscope. The spectra were recorded with a 785 nm diode laser. Five points were analyzed in each area. Ten scans were performed in each point with 12.5 mW of laser output power at an acquisition time of 10s. Silicon was used to calibrate the wavenumbers.

The heated samples were morphologically and chemically analysed on a Hitachi S-4800 scanning electron microscope fitted with a BRUKER 5030 energy dispersive analyser. Several points were analysed to confirm reproducibility.

3 RESULTS AND DISCUSSION

3.1 ANALYSIS OF PRE-HEATED C-S-H GELS

The XRD patterns for the pre-heated C-S-H gels are reproduced in Fig. S1 (Supporting information). The diffractograms for the CSH^{0.5} and CSH^{2.0} gel samples (Fig. S1a) (Supporting information) contain the reflections characteristic of tobermorite (PDF 00-029-0331 for 14-tobermorite, 5CaO·6SiO₂·9H₂O). The absence of [001] reflection (2 θ ≈7.4°), together with the fact that the normalised intensity of the signal at 2 θ ≈16.1° is close to 0.8, suggests that the experimental Ca/Si ratio in both gels is on the order of 0.8 to 1.0^[35,36].

Table 1.-Synthesis procedure and nominal Ca/Si ratio of the samples synthesised

Sample	Synthetic procedure	Nominal Ca/Si ratio
CSH ^{0.5}	Double decomposition	0.5
CSH ^{2.0}	Double decomposition	2.0
C ₂ SH	Hydrothermal with laboratory reagents as starting materials	2.0
FA-C ₂ SH	Hydrothermal with waste as the starting material	2.0

These values are significantly different from their nominal ratio of 0.5 and 2.0 (see Table 1). These results are in line with previous works in which it is described that the C-S-H gel obtained by the double decomposition method has Ca/Si ratios close to 1.0, independently of stoichiometric ratios^[33].

The diffractogram for the calcium silicate hydrate hydrothermally synthesized from laboratory reagents, C₂SH (Fig. S1b) (Supporting information), contains α -C₂SH (PDF 00-029-0373) as the majority phase, along with calcite, CaCO₃ (PDF 00-05-0586), and portlandite, Ca(OH)₂ (PDF 00-044-1481) as minority phases and traces of SiO₂ (PDF 00-075-1522). The pattern for the solid synthesized from fly ash (FA C₂SH) (Fig. S1b) (Supporting information) shows that it has high contents of both calcium silicoaluminate hydrate (PDF 00-032-0151/00-075-1690) and calcium silicate hydrate (PDF 00-015-0641). The formation of these compounds is consistent with the composition of the raw materials used in the hydrothermal process, namely fly ash with high silicon and aluminum oxide contents and a commercial calcium oxide to establish a Ca/Si ratio of 2.0. Portlandite and calcite are also detected. These X-ray diffraction findings are in line with those observed by other authors for synthetic dicalcium silicate hydrate^[34,37] and suggest a good agreement between the nominal and the experimental Ca/Si ratios in these gels.

C-S-H gel with nominal Ca/Si ratio 2.0 has been synthesized by two different methods (double decomposition and hydrothermal process) and different XRD diffractograms are obtained for the two products. A more crystalline solid is obtained by hydrothermal synthesis than by the double decomposition method. According to Grangeon^[36], different synthesis procedure and/or ageing of C-S-H can lead to different C-S-H structures.

Fig.1.- Micro-Raman spectra, sample in the 1200 cm⁻¹ to 100 cm⁻¹ range, for: a) double decomposition synthesis C-S-H gels (CSH^{2.0} and CSH^{0.5}); b) hydrothermally synthesised C₂SH (C₂SH and FA-C₂SH) (λ =785nm). (SS = symmetrical stretching; SB = symmetrical bending; LV = lattice vibration).

The micro-Raman spectra (Fig. 1a) of the two gels synthesized by the double decomposition method, $\text{CSH}^{0.5}$ and $\text{CSH}^{2.0}$, are quite similar. The most intense signal, at 666 cm^{-1} , is characteristic of the Si-O-Si symmetric bending vibrations in C-S-H gel. That signal shifts to lower wavenumbers at higher Ca/Si ratios, denoting a decline in silicate chain length^[38]. The wide signal observed in the $\text{CSH}^{2.0}$ gel spectrum at 850 cm^{-1} is attributed to Q^1 units, indicating lower polymerisation, i.e., shorter silicate chains than in the gel synthesised with a lower Ca/Si ratio ($\text{CSH}^{0.5}$). The spectra of the two dicalcium silicate hydrate hydrothermally synthesised (C_2SH and FA- C_2SH , Fig. 1b) exhibit high fluorescence. Consequently, the compounds present in the samples can scarcely be identified, particularly for the gel synthesised from fly ash (FA- C_2SH). Symmetric stretching (SS) vibrations characteristic of a silicate group (966 cm^{-1} ; 858 cm^{-1} and 742 cm^{-1}) and of lattice vibration (LV) SiO_4^{4-} at 425 cm^{-1} can nonetheless be identified in the C_2SH sample. A signal observed at 372 cm^{-1} in the spectrum of that sample was attributed to CaO network vibrations.

3.2 ANALYSIS OF HEATED C-S-H GELS

The photographs in Fig. S2 (Supporting information) depict the wafers made from the $\text{CSH}^{0.5}$ and $\text{CSH}^{2.0}$ gels and the C_2SH and FA- C_2SH precursors after 6W CO_2 laser radiation for 2 s. Radiation broke the thinner C-S-H gel wafers ($\text{CSH}^{0.5}$ and $\text{CSH}^{2.0}$). Fig. S3 (Supporting information) shows different parts of the wafers where the Raman spectra have been measured: inner, intermediate and outer areas.

Fig.2.- Micro-Raman spectra, sample in the 1200 cm^{-1} to 100 cm^{-1} range, for three points on the $\text{CSH}^{0.5}$ sample after heating: a) outer area; b) intermediate area; c) inner area ($\lambda = 785\text{ nm}$).

The micro-Raman spectra in the three areas of the heated $\text{CSH}^{0.5}$ gel are shown in Fig. 2. When the cement is exposed to temperatures above 1000°C the sample is sintered and its chemical and physical characteristics change ^[2]. From the chemical point of view, two anhydrous calcium silicates with Ca/Si ratio of 1.0 are detected, $\alpha\text{-Ca}_3\text{Si}_3\text{O}_9$ ($\alpha\text{-CS}$) and $\beta\text{-CaSiO}_3$ ($\beta\text{-CS}$). It is known that natural calcium silicate has two polymorphs, low temperature wollastonite ($\beta\text{-CS}$), synthesising at around 800°C , and high temperature pseudowollastonite ($\alpha\text{-CS}$), at around 1200°C ^[39]. Both, alpha and beta wollastonite, are present in the three areas of the heated $\text{CSH}^{0.5}$ sample, but alpha phase is predominant in the inner area and beta phase in the outer. The formation of $\alpha\text{-CS}$ in the inner area of the sample is therefore an indication that the temperature reached there was at least 1200°C , whilst the presence of $\beta\text{-CS}$ in the outer, heat dissipation area, attests to temperatures of around 800°C . Additionally, it should be taken in account that two effects can take place when C-S-H gels are heated: a collapse of the structure or dehydration. In the case of the $\text{CSH}^{0.5}$ sample, prevalence of dehydration effect is observed with formation of dehydrated calcium silicates.

The anhydrous calcium silicate formed after heating of $\text{CSH}^{0.5}$ is wollastonite, with a Ca/Si ratio of 1.0, higher than the value used to synthesise this compound. However, as previously discussed, Ca/Si ratio of the C-S-H gel in the pre-heated $\text{CSH}^{0.5}$ sample has been identified through XRD to be in the range 0.8-1.0, since there is no shoulder in the signal at 30° , that appears from C-S-H gel with Ca/Si ratio > 1 and the band at 29° is quite broad ^[35]. If CS (wollastonite or pseudowollastonite) is formed for the samples with Ca/Si ratio < 1 , means that an excess of SiO_2 it was present in the sample ^[40]. On the other hand, an earlier study by the authors ^[33] showed experimentally that although the nominal ratio in a double decomposition synthesis was 0.5, the gel obtained exhibited a Ca/Si ratio of nearly 1.0. Formation of an anhydrous calcium silicate with a Ca/Si ratio of 1.0 after CO_2 laser radiation attests to the elimination of H_2O from the sample due to rapid localised heating and to the generation of a calcium silicate with a Ca/Si ratio of 0.8 to 1.0, as the initial hydrated phase.

The Raman spectrum of the other C-S-H gel synthesized by double decomposition ($\text{CSH}^{2.0}$) after heating is shown in Fig. 3. The spectrum confirms the predominance of the high temperature phase, $\alpha\text{-Ca}_3\text{Si}_3\text{O}_9$ ($\alpha\text{-CS}$) and also contains a double band at 860 and 845 cm^{-1} characteristic of $\beta\text{-Ca}_2\text{SiO}_4$ ($\beta\text{-C}_2\text{S}$) ^[41]. For the heated $\text{CSH}^{2.0}$ sample, no significant differences are observed with respect to the phases formed in the three zones, except for a higher intensity of the signals corresponding to the $\alpha\text{-CS}$ phase in the outermost zone of the pellet. As discussed in the aforementioned earlier paper ^[33], the C-S-H gel synthesized by double decomposition with a nominal Ca/Si ratio of 2.0 had an experimental ratio of 1.1. This behaviour might explain the identification of a majority phase with a Ca/Si ratio of 1.0 and a minority phase with a ratio of 2.0 in the heated $\text{CSH}^{2.0}$ sample. No low temperature phase ($\beta\text{-CS}$) is detected in this case, although a compound with a high Ca/Si ratio is identified. Again, the highest temperature CS phase is formed, indicating that a temperature of 1200°C was reached in the irradiation process.

Fig.3.- Micro-Raman spectra, sample in the 1200 cm^{-1} to 100 cm^{-1} range, for three points on the $\text{CSH}^{2.0}$ sample after heating :a) outer area; b) intermediate area; c) inner area ($\lambda = 785\text{ nm}$).

Comparing both samples $\text{C-S-H}^{0.5}$ and $\text{C-S-H}^{2.0}$, after fire effect, it is interesting to observe that β -CS is mainly formed after heating the $\text{C-S-H}^{0.5}$, while α -CS predominates after heating the $\text{C-S-H}^{2.0}$. There are several uncertainties about the formation of both wollastonite phases (α -CS and β -CS) from C-S-H heating, such as the effect of Ca/Si ratio, chain length, the presence of other phases, etc^[35]. In the case of $\text{C-S-H}^{0.5}$ and $\text{C-S-H}^{2.0}$ samples, probably the different chain length observed by Raman spectroscopy, with lower polymerization in the gel synthesised with a higher Ca/Si ratio, can promote the different wollastonite phase (α -CS or β -CS) formation.

Fig. 4. Micro-Raman spectra sample, in the 1200 cm^{-1} to 100 cm^{-1} range, for three points on the CO_2 laser-radiated C_2SH sample synthesised with laboratory reagents:a) outer area; b) intermediate area; c) inner area ($\lambda = 785\text{ nm}$)

When the C_2SH synthesised hydrothermally with laboratory reagents was heated, a mix of β - C_2S and γ - C_2S was formed (Fig. 4). It is known that the stable dicalcium silicate phase, α - C_2S , forms at temperature of 1450 °C, evolving towards β - C_2S if it is cooled quickly or γ - C_2S if it is cooled more slowly^[42-43].

The presence of both polymorphs denotes the existence of areas with different cooling rates: an outer, heat dissipation area where cooling was slower, generating γ - C_2S , and an inner area that cooled more quickly, generating β - C_2S . Moreover, the formation of a calcium silicate from rapidly heated C_2SH that maintains the same Ca/Si ratio as the starting material (Ca/Si = 2.0) is confirmed by the results.

At α - C_2SH dehydration temperature (450 °C), the most active phase α - C_2S forms^[44]. Having increased the temperature, the other active phases such as γ - C_2S (600 °C) and α' - C_2S (800 °C) form, yet also a small amount of inactive γ - C_2S .

The peak at 3616 cm^{-1} in the Raman spectra of the heated C_2SH samples (insert in Fig. 4) is associated with the vibrations of the OH group in portlandite. This feature might be attributed to $CaCO_3$ decarbonation and subsequent reaction with water vapour, as noted in earlier papers^[28]. Georgali and Tsakiridis^[45] also observed $Ca(OH)_2$ presence in the inner side of the cement within a reinforced 15-year-old concrete building exposed to fire. In the heating process, water is removed from the C-S-H gel and generates water vapor, which can condense due to the temperature difference between the internal and the external part of the material^[1]. Subsequent reaction with the CaO can generate the observed $Ca(OH)_2$. However, other authors^[36] contend that nanocrystalline $Ca(OH)_2$ is present in the interlayers of C-S-H gels with high Ca/Si ratios (over 1.5). Those portlandite nanocrystals can be released during rapid heating and be detected by Raman spectroscopy. Additionally, the observed $Ca(OH)_2$ must be very stable, as no calcite resulting from the reaction with atmospheric CO_2 is detected in the samples, which have not been stored in a CO_2 -free environment. According to Mendes 2012^[46], the rate of water absorption determines the growth rate and type of $Ca(OH)_2$ crystals formed. Rodriguez-Navarro et al^[47], determine that amorphous calcium hydroxide with both, smaller grain size and larger surface area than crystalline $Ca(OH)_2$, increases carbonation of portlandite. Morsy et al^[39], considered that recrystallization of amorphous portlandite after the heat treatment, produce a stable crystalline $Ca(OH)_2$ which hardly carbonates. As the portlandite observed in the heated C_2SH sample is not carbonated it can be assumed that it is crystallized in very large crystals with low surface area.

The micro-Raman spectra for FA- C_2SH (Fig. 5) after heating contain an intense signal peak at 855 cm^{-1} with a shoulder at 844 cm^{-1} . The shape of these two peaks differs from the spectra recorded for β - C_2S , where a doublet of sharp peaks at 845 and 856 cm^{-1} is observed. This behaviour suggests a possible modification of the C_2S polymorph. According to Remy *et al*^[48], the Raman spectrum of C_2S contains a signal in the 550-500 cm^{-1} range from which the polymorph formed can be identified. A wide signal with

two peaks at 550cm^{-1} and 525cm^{-1} denotes α_L' - C_2S formation. If a triple band appears with peaks at 557cm^{-1} , 539cm^{-1} and 519cm^{-1} the polymorph is dicalcium silicate (β - C_2S). The presence of three signals detected in the spectra of figure 5 denotes the formation of a mix of the two polymorphs, α_L' - C_2S and β - C_2S . The β - C_2S polymorph may have stabilised due to the uptake in its structure of minority elements present in the fly ash (FA), precluding its transformation to γ - C_2S in slower cooling. As shown in the inset of Figure 5, no clear signal from portlandite was observed in this sample.

Fig. 5.- Micro-Raman spectra for three points on the CO_2 laser-radiated FA- C_2SH sample in the 1200 cm^{-1} to 100 cm^{-1} range: a) outer area; b) intermediate area; c) inner area ($\lambda=785\text{nm}$)

The formation of $\text{Ca}(\text{OH})_2$ after heating is only observed in the C_2SH sample, which was the only one initially containing calcite. Therefore, the origin of this portlandite must be that after heating the calcium carbonate generates CaO which adsorbs ambient water and generates $\text{Ca}(\text{OH})_2$, as described previously^[28,45].

The SEM/EDX study conducted to complete the analysis of the samples behaviour when exposed to heating yielded the images shown in Fig. 6 a) to d) for the synthetic C-S-H gels ($\text{CSH}^{0.5}$ and $\text{CSH}^{2.0}$) and in Fig. 6 e) to h) for the C_2SH precursors (C_2SH and FA- C_2SH).

Table 2.-EDX-determined Ca/Si and Ca/(Si+Al) ratios in the samples studied

	Ca/Si			Ca/(Si+Al)	
	Zone 1	Zone 2	Zone 3	Zone 1	Zone 2
$\text{CSH}^{0.5}$	1.46 ± 0.05	1.27 ± 0.08		-	-
$\text{CSH}^{2.0}$	1.51 ± 0.11	1.72 ± 0.02	1.70 ± 0.05	-	-
C_2SH	2.95 ± 0.45	2.57 ± 0.19		-	-
FA- C_2SH^*	2.94 ± 0.10	2.79 ± 0.05		2.17 ± 0.08	1.20 ± 0.03

* In the FA- C_2SH sample, zone 1 was darker and zone 2 lighter

The initial structure of the C-S-H gels synthesized by double decomposition (Fig. 6a and 6b) is characteristically compact for both nominal Ca/Si ratios studied ($\text{CSH}^{0.5}$ and $\text{CSH}^{2.0}$). After heating, pores are observed in the sample with the lower nominal Ca/Si ratio (Fig. 6c), denoting rapid evaporation of the most volatile compounds, probably water. The EDX elemental analysis of the sample shows that the Ca/Si ratio in both areas of this sample fluctuates between 1.46 and 1.27. Porosity varies in the sample with a nominal Ca/Si ratio of 2.0 (Fig. 6d), while in some areas the structure appears to comprise overlapping layers. Further to the EDX findings, those areas would comprise phases with Ca/Si ratios of 1.51 to 1.72 (Table 2), which are higher than those observed in the $\text{CSH}^{0.5}$ samples.

Fig. 6.- SEM/EDX micrographs of a) $\text{CSH}^{0.5}$ before heating; b) $\text{CSH}^{2.0}$ before heating; c) $\text{CSH}^{0.5}$ after heating; d) $\text{CSH}^{2.0}$ after heating; e) C_2SH before heating; f) FA- C_2SH before heating; g) C_2SH after heating; h) FA- C_2SH after heating.

(The Ca/Si ratios found with EDX analysis of zones 1, 2 and 3 are listed in Table 2.)

Fig. 6e shows that the pre-heated C_2SH sample has a rectangular structure characteristic of this compound^[37]. After radiation and water molecule loss (Fig. 6g), the structure is laminar and $\text{Ca}(\text{OH})_2$ plates are observed. These observations are consistent with the results of Raman spectroscopy for this sample. Dehydration of the samples after heating is also associated with an increase in porosity (Fig. 6f), as described by Morsay et al.^[39] in cement samples heated to study the effect of fire.

From EDX analysis of the heated C_2SH sample, the Ca/Si ratio is determined to be higher than 2.0 (Table 1), possibly indicating that portlandite is also contributing to the signal analysed. The initial C_2SH sample also has calcite and portlandite and then, the Ca/Si ratio determined by SEM/EDX is higher than 2 (Figure 7).

The FA- C_2SH sample initially has a more or less uniform matrix resulting from wafer compaction. Radiation altered the sample substantially, however, yielding light

coloured bead-like structures in a dark matrix (Fig. 6h). EDX measurements at ten points in the two zones labelled on the post-heating micrograph of FA-C₂SH (Fig.6h) show different composition depending on the zone. From XRD analysis of the initial sample, two phases with different compositions have been identified: one with high content of Al (Ca₃Al₂SiO_{4x}(OH)_y) and an aluminium-free phase (Ca₂SiO₄·0.35H₂O). After heating two phases with different elemental composition determined by EDX are identified: the darker zones, with higher Al and lower Si and Ca signals, as well as the lighter zones in which the Al signal is less intense and the calcium and silicon signals are stronger. As the temperature increases, calcium silicate phases have been formed and something similar may have occurred in this heating process. During heating, the phase rich in Al would therefore form the matrix, over which the calcium-rich phase would then form. Micro-Raman failed to detect both phases, identifying only the latter (calcium silicate hydrate). Finally, SEM/EDX analysis confirms the absence of portlandite in this sample.

Fig. 7.-EDX-determined Ca, Si and Al in post-radiation FA-C₂SH samples (solid figures, dark zones; hollow figures, light zones)

In summary, the micro-Raman and SEM/EDX analysis confirm that diverse synthesis procedures and starting compounds result in C-S-H gels with differing composition and structure. When these gels are submitted to laser radiation to simulate the rapid temperature increase occurring in fire different calcium silicates are formed. In fact, anhydrous compounds generate with a chemical composition similar to the materials used as raw materials in the synthesis of the corresponding C-S-H gel, but in a syntered form. In the process of formation of these materials, water is lost very quickly, generating more porous structures. Such porosity is higher in materials with a lower Ca/Si ratio. On the other hand, the Ca(OH)₂ formed is less reactive, and therefore, will not carbonate and will not contribute to the increase of mechanical resistances.

4. CONCLUSIONS

Two types of gels with different nominal Ca/Si ratios were synthesised using hydrothermal or double decomposition procedures and exposed to continuous CO₂ laser radiation to simulate the temperature increase occurring in fires.

The micro-Raman and SEM/EDX analysis of the compounds obtained after heating draw the following conclusions.

- The silicate formed in each sample depends on the initial Ca/Si ratio of the heated C-S-H gel and appears in a different polymorphic phase, depending on the temperature reached in each area of the sample. In the area impacted by the laser, where the highest temperature is reached (1200-1400 °C) two varieties of calcium silicates are formed depending on the initial Ca/Si ratio: α -CS for the samples with Ca/Si ratio around 1 and α -C₂S when the Ca/Si ratio is 2. In the more distant heat dissipation areas, one of two low temperature anhydrous calcium silicates are formed: β -CS for lower Ca/Si ratios and γ -C₂S for higher Ca/Si ratios.
- After heating the C-S-H gel hydrothermally synthesised with laboratory reagents and an initial Ca/Si ratio of 2.0 (sample C₂SH) the anhydrous dicalcium silicate with different polymorphs is formed. The two polymorphs, β -C₂S and γ -C₂S, are formed, due to the existence of areas with different cooling rates: an outer, heat dissipation area where cooling is slower, generating γ -C₂S, and an inner area that cools more quickly, generating β -C₂S. Additionally, in this samples highly stable Ca(OH)₂ is formed.
- In the case of radiation of the gel synthesised from a calcium silico-aluminate hydrate, FA-C₂SH, low temperature phase β -C₂SH formation stabilised. Two clearly distinct phases formed in these samples, one Ca and Si-high and the other Ca and Al-high. Continuous CO₂ laser radiation of synthetic C-S-H gels with different Ca/Si ratios yielded an anhydrous calcium silicate that maintained the Ca/Si ratio present in the initial gel.

The results of the present work confirm that analysis of laser radiated samples by Micro-Raman spectroscopy is a powerful tool for understanding C-S-H gel composition and structure after heating at high temperatures. Moreover, it allows evaluating the gel Ca/Si ratio, separating contributions from silicates and from other phases, like portlandite. This could be an apt method for determining the ratio in C-S-H gels featuring advantages such as the need for only small amounts of sample as well as to evaluate the effect of the fire over the cement composition. Further testing with other types of samples and less aggressive radiation would be required for its optimisation.

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REFERENCES

- [1] S. Lim and P. Mondal, *Mater. Charac.* **2014**, 92, 15
- [2] Q. Ma, R. Guo, Z. Zhao, Z. Lin, K. He. *Constr. Build. Mater* 2015, 93, 371.
- [3] H. Taylor, *J. Am. Ceram.Soc.* **1986**; 69, 464.
- [4] I. Richardson, G. Groves, *Cem. Concr.Res.* **1992**; 22, 1001.
- [5] I. Richardson, G. Groves, *Cem. Concr.Res.* **1993**; 23, 131.
- [6] J. Chen, J. Thomas, H. Taylor, H. Jennings, *Cem.Concr.Res.* **2004**; 34, 1499.
- [7] S. Garrault, A.Nonat, *Langmuir* **2001**; 17, 8131.
- [8] V. Walker, S. Sutou, C. Oda, M. Mihara, A. Honda, *Cem.Concr.Res.* **2016**; 79, 1.
- [9] H. Taylor, *Cement Chemistry*, Thomas Telford, London, 1997.
- [10] I. Jiménez, G. Pérez, A. Guerrero, B. Ruiz, *Int. J. Miner. Process.* **2017**; 158, 8.
- [11] K. Pimraksa, S. Hanjitsuwan, P. Chindaprasirt, *Ceram. Int.* **2009**; 35, 2415.
- [12] A. Guerrero, S. Goñi, A. Moragues, J. Dolado, *J. Am. Ceram.Soc.* **2005**; 88, 1845.
- [13] S. Maheswaran, S. Kalaiselvam, G. S. Palani, S. Sasma, *J. Therm. Anal. Calorim.* **2016**; 125, 53.
- [14] M. Georgescu, J. Tipan, A. Badanoiu, D. Crisan, I. Dragan, *Cem.Concr.Compos.* **2000**; 22, 315.
- [15] E. Cappelletto, S. Borsacchi, M. Geppi, F. Ridi, E. Fratini, P. Baglioni, *J. Phys. Chem. C* **2013**; 117, 22947.
- [16] A. Trapote-Barreira, J. Cama, J. Soler, *Phys.Chem. Earth* **2014**; 70-71, 17.
- [17] J. Higl, M. Köhler, M. Lindén, *Cem.Concr.Res.* **2016**; 88,136.

- [18] L. Zhang, X. Cheng, D. Hou, S. Guo, *Constr. Build. Mater.* **2017**; 155, 413.
- [19] A. Harris, M. Manning, W. Tearle, C. Tweed, *Cem. Concr. Res.* **2002**; 32, 731.
- [20] C. García-Florentino, M. Maguregui, H. Morillas, U. Balziskueta, A. Azcarate, Gorka Arana, J.M. Madariaga, *J. Raman Spectrosc.* **2016**; 47, 1458.
- [21] L. Robinet, C. Couprie, K. Eremin, C. Hall, *J. Raman Spectrosc.* **2006**; 37, 789.
- [22] M. Torres-Carrasco, A. del Campo, M. A. de la Rubia, E. Reyes, A. Moragues, J. F. Fernández, *J. Raman Spectrosc.* **2019**; 50, 720.
- [23] M. Vetter, J. Gonzalez-Rodriguez, E. Nauha, T. Kerr, *Constr. Build. Mater.* **2019**; 204, 450.
- [24] Š. Pešková, V. Machovič, P. Procházka, *Ceramics – Silikáty* **2011**; 55, 410.
- [25] S. Martinez-Ramirez, L. Diaz, J. J. Camacho, *J. Am. Ceram. Soc.* **2013**; 96, 2824.
- [26] M. Gomez-Heras, R. Fort, M. Morcillo, C. Molpeceres, J.L. Ocaña, *Mater. Construcc.* **2008**; 58, 217.
- [27] K. Kawaka, N. Idris, M. Wada, H. Kurniawan, K. Tsuyuki, S. Miura, *Appl. Spectrosc.* **2004**; 58, 887.
- [28] R. Moreno-Virgen, J.J. Soto-Bernal, J. A. Ortiz-Lozano, J. T. Bonilla-Petriciolet, J. T. Vega-Duran, R. Gonzalez-Mota, J. Pineda-Piñón, *Mater. Construcc.* **2011**; 61, 77.
- [29] J.A. Lawrence, *Wear* **2004**; 257, 590.
- [30] J.A. Lawrence, L. Li, *Mater. Sci. Eng. A*, **2000**; 284, 93.
- [31] G. K. Sun, F. J. Young, R. J. Kirkpatrick, *Cem. Concr. Res.* **2006**; 36, 18.
- [32] I. García-Lodeiro, A. Fernández-Jiménez, I. Sobrados, J. Sanz, A. Palomo, *J. Am. Ceram. Soc.* **2012**; 95, 1440.
- [33] M. Martín-Garrido, M. T. Molina-Delgado, S. Martínez-Ramírez, *J. Sol-Gel Sci. Technol.* **2020**; 94, 11.
- [34] A. Guerrero, S. Goñi, I. Campillo, A. Moragues, *Environ. Sci. Technol.* **2004**; 38, 3209.
- [35] E. Tajuelo-Rodríguez, K. Garbev, D. Merz, L. Black, I. G. Richardson, *Cem. Concr. Res.* **2017**; 93, 45.
- [36] S. Grangeon, F. Claret, C. Roos, T. Sato, S. Gaboreau, Y. Linard, *J. Appl. Cryst.* **2016**; 49, 771.
- [37] K. Garbev, G. Beuchle, M. Bornefeld, L. Black, P. Stemmermann, *J. Am. Ceram. Soc.* **2008**; 91, 3005.

- [38] K. Garbev, P. Stemmermann, L. Black, C. Breen, J. Yarwood, B. Gasharova, *J. Am. Ceram. Soc.* **2007**; 90, 900.
- [39] M. M. Morsy, S. S. Shebla, A. M. Rashad, *Asian J. Civil Eng. (Building and Housing)* **2008**; 9, 93.
- [40] K. Garbev, M. Bornefeld, G. Beuchle, P. Stemmermann, *J. Am. Ceram. Soc.* **2009**; 91, 3015.
- [41] M. Handke, *Appl. Spectrosc.* **1986**; 40, 871.
- [42] C. J. Chan, W. M. Kriven, J. F. Young, *J. Am. Ceram. Soc* **1992**, 75, 1621.
- [43] N. Ghosh, P. Bhaskara Rao, A. K. Paul, K. Raina, *J. Mater Scienc.* **1979**, 14, 1554.
- [44] M. Stankeviciute, R. Siauciunas, A. Miachai, *J. Therm. Anal. Calorim.* **2018**; 134, 101.
- [45] B. Georgali, P. E. Tsakiridis, *Cem. Concr. Compos.* **2005**, 27, 255.
- [46] A. Mendes, J. G. Sanjayan, W. P. Gates, F. Collins, *Cem. Concr. Compos.* **2012**; 34, 1067.
- [47] C. Rodriguez-Navarro, E. Hansen, W. S. Ginell, *J. Am. Ceram. Soc.* **1998**; 81, 3032.
- [48] C. Remy, B. Reynard, M. Madon, *J. Am. Ceram. Soc.* **1997**; 80, 413.

SUPPORTING INFORMATION

Figure S1. Fig. S1.-XRD patterns for: a) $\text{CSH}^{0.5}$ and $\text{CSH}^{2.0}$; b) C_2SH and $\text{FA-C}_2\text{SH}$ (T = $5\text{CaO} \cdot 6\text{SiO}_2 \cdot 9\text{H}_2\text{O}$; H = $\text{Ca}_2\text{SiO}_4 \cdot 0.35\text{H}_2\text{O}$; A = $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_x(\text{OH})_y$; C = CaCO_3 ; P = $\text{Ca}(\text{OH})_2$; α = $\alpha\text{-C}_2\text{SH}$).

Figure S2.- Wafers after radiation: a) $\text{CSH}^{0.5}$; b) $\text{CSH}^{2.0}$; c) C_2SH ; d) $\text{FA-C}_2\text{SH}$

Fig. S3.- Wafers after radiation showing inner, intermediate and outer parts: a) $\text{CSH}^{0.5}$; b) $\text{CSH}^{2.0}$; c) C_2SH ; d) $\text{FA-C}_2\text{SH}$