CO₂ ADSORPTION ON CALCIUM SILICATE HYDRATE GEL SYNTHESIZED
BY DOUBLE DECOMPOSITION METHOD

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Abstract

The calcium silicate hydrate gel (C-S-H) was synthesized by the double decomposition method because of the simplicity and the quickness of the procedure. The structure of the C-S-H gels after 1 week and 4 weeks in contact with the formation solution was studied through Micro-Raman, Fourier Transformed Infrared Spectroscopy and ^{29}Si Nuclear Magnetic Resonance. Simultaneous thermodifferential-thermogravimetric analysis and mass spectrometry (DTA/TG/MS) was used to identify the amount of calcium carbonate formed due to the reaction between the calcium and atmospheric CO_2 . With DTA/TG/MS, mass loss due to CO_2 was observed to take place at temperatures below 400°C , unidentified to date, which might be associated with the CO_2 adsorbed on the C-S-H gel. Thus, in the TG analysis in the $300\text{--}430^\circ\text{C}$ range, both the loss of water due to the decomposition of the amorphous calcium carbonate (ACC) and the loss of CO_2 adsorbed on the gel must be considered. Additionally, polymerization of the gel and a decrease in the Ca/Si ratio was observed from the samples from 1 to 4 weeks.

Keywords: Calcium silicate hydrate; Thermal Analysis; Nuclear Magnetic Resonance; CO_2 adsorption.

Introduction

Calcium silicate hydrates (C-S-H) are the major reaction products of cement hydration, which may change their composition, degree of polymerization and crystallinity while maintaining the main features of the layer structure [1,2]. Thus, calcium silicate hydrates are characterized by their variability in the calcium to silicon ratio (Ca/Si), which range between 0.6 and 2.3, from pure Portland cement to blended cement with silica fume or metakaolin [3,4]. It is generally admitted that the structure of the C-S-H gel is similar to both minerals tobermorite, for C-S-H gel with low Ca/Si ratio, and jennite, for C-S-H gel with high Ca/Si ratio. Recently, Haas and Nonat [5] have described three C-S-H phases according to solubility results, $\text{Ca}_4\text{H}_4\text{Si}_5\text{O}_{16}$, $\text{Ca}_2\text{H}_2\text{Si}_2\text{O}_7$ and $\text{Ca}_6(\text{HSi}_2\text{O}_7)_2(\text{OH})_2$.

Synthetic calcium silicate hydrate phases can be prepared following various procedures: i) C_2S and C_3S hydration [6,7]; ii) lime + silica hydration [5]; iii) CaO + silica fume hydration [8]; iv) hydrothermal reaction of portlandite and amorphous silica [4,9], and v) double decomposition method [10,11]. Long-time reaction is necessary to get the full hydration of both silica and calcium compounds, with additional portlandite formation, except for the iv) and v) methods. However, in the double decomposition method, precipitation of C-S-H gel occurs immediately after mixing the starting materials, but in order to achieve the completeness of the reaction, the solution will be in contact with the reaction products for several days [11].

Experimental studies about C-S-H gel leaching in contact with deionized water leads to congruent or incongruent dissolution depending on the initial Ca/Si ratio. For Ca/Si ratios of 0.8 or higher, the C-S-H gel produces its incongruent dissolution, and if the ratio is lower than 0.8, the congruent dissolution of the gel takes place [12]. However, when the double decomposition method is used to synthesize C-S-H gel, the solution in

contact with the formed gel contains calcium and silicon ions, and it has not been studied how this solution can interact with the C-S-H gel. Additionally, the solution is in contact with air, and CO₂ can be dissolved in the water solution and interact with the forming C-S-H. Hunnicut et al., [13] established that C-S-H gel from double decomposition synthesis method is more likely to precipitate CaCO₃ than C-S-H produced by the direct reaction synthesis method. Chang and Fang [14] determined C_{0.28}SH_{0.15} as the formulae of the C-S-H after accelerated carbonation; with aragonite, calcite and vaterite formation but with no evidences of amorphous calcium carbonate.

The fastest method of synthesis of C-S-H gel is the double decomposition method [10, 11]. If this method is performed in a laboratory environment, it is possible for the atmospheric CO₂ to dissolve in the reaction medium, modifying the composition of the C-S-H gel formed [14] and/or precipitating different polymorphs of calcium carbonate [14]. Some authors have indicated the possibility of the CO₂ being adsorbed into the C-S-H gel [15].

The objective of this paper was to synthesize C-S-H gel following the double decomposition method and to study how the extra time that the gel is in contact with the solution can influence in the structure of the formed gel and how the CO₂ affects the C-S-H formation as well as the calcium carbonates. The possibility of adsorption of atmospheric CO₂ on the C-S-H gel will also be studied. Due to the low crystallinity of the C-S-H gel, spectroscopic techniques such as Micro-Raman [16, 17]; Fourier Transform Infrared Spectroscopy (FT-IR) [18, 19] and ²⁹Si Nuclear Magnetic Resonance (NMR) [20] are the most suitable for characterizing the structure of the amorphous compound. Differential thermogravimetric analysis (DTG) was used to determine the amount of calcium carbonate formed by the reaction with the atmospheric CO₂. By coupling a mass spectrometer to a thermogravimetric instrument

(DTA/TG/MS), it is possible to correlate mass losses resulting from the progressive thermal decomposition of the C-S-H gel with water and CO₂ releases. This approach enables to determine in a more consistent view the possible adsorption/absorption of CO₂ by the gel.

Experimental Section

Four C-S-H samples were prepared by the double decomposition method [10,11,21] using stoichiometric mixtures of Na₂SiO₃·5H₂O and Ca(NO₃)₂·4H₂O dissolved in CO₂-free deionized water, in order to obtain a C-S-H gel with an atomic Ca/Si ratio of 2.0. Before use, the deionizer water (<30 ppb of CO₂) was boiled at 100°C for 1 hour, covered with a plastic cap and cooled until room temperature. CO₂-free water was used to avoid the initial reaction of calcium with atmospheric CO₂ in order to promote the calcium and silicon reaction. The amounts of the starting materials were 0.5mol and 1mol respectively, thus the water/solid ratio was 52 (by weight). That means that once Ca(NO₃)₂·4H₂O was slowly added into the Na₂SiO₃·5H₂O solution, a jellied precipitate immediately formed and, after that a solution of NaOH was added in order to adjust the pH to 12.0-12.5. The reactions were kept one day under stirring at room temperature, but the precipitates were maintained in their own solutions (without stirring) during one (CSH^{1w}), two (CSH^{2w}), three (CSH^{3w}) and four (CSH^{4w}) weeks respectively. The samples were maintained in glass bottles with plastic tight lid during 1 or 4 weeks. The solutions were filtered, and the precipitates were washed three times with CO₂-free deionized water followed by ethanol. Finally, the samples were stored in vials inside a desiccator.

Each sample was analysed in three different ways. First, Micro-Raman and FT-IR were used in order to obtain a mineralogical characterization. After that DTG helped us to

quantify the amount of carbonates. Finally, ^{29}Si NMR, was used to carry out a microstructural analysis in both samples CSH^{1w} and CSH^{4w}.

Micro-Raman analysis was performed with a confocal Raman microscope Renishaw InVia (Renishaw, Wotton-under-Edge, UK) equipped with a Leica microscope and an electrically refrigerated CCD camera. Laser excitation lines were provided by a diode laser (785nm wavelength, 25mW power) and a Renishaw Nd:YAG laser (532nm wavelength, 25mW power). The spectra were obtained using a 50x magnification objective, a spectral resolution of 4cm^{-1} , a 10-s exposure time and 20 accumulations per spectra in the range of $100\text{-}1200\text{cm}^{-1}$ in order to increase signal/noise ratio. The frequencies were calibrated with silicon.

Infrared spectra were recorded in the range of $400\text{-}4000\text{cm}^{-1}$ using a FT-IR spectrometer Bruker IFS66 (Bruker, Germany), a Globar source and a DTGS detector. The samples were mixed with KBr with a sample/KBr ratio of 1/200 and compressed to give pellets. The range of $900\text{-}1200\text{cm}^{-1}$ was deconvoluted into gaussian peaks and fitted using Origin 8.0. Micro-Raman and FT-IR spectra were normalized to the C-S-H gel most intense band, which were 670 and 690cm^{-1} respectively.

The DTG analysis were conducted on a Q600TA Instruments thermal analyzer (TA Instruments, USA) in air atmosphere. The samples were heated at a rate of $10^\circ\text{C}/\text{min}$, from the ambient temperature to 1000°C .

For the ^{29}Si NMR analysis a Bruker AV-400 (9.4 T and $\nu\text{R} = 4\text{ kHz}$) (Bruker, Germany) NMR spectrometer was used in the following conditions: pulse width = $7\mu\text{s}$ and relaxation delay = 60 s with a typically 3000 scans. The ^{29}Si chemical shifts were determined relative to tetramethylsilane. The spectra were deconvoluted into Gaussian peaks and fitted using Origin 8.0.

Results and Discussion

Micro-Raman characterization

The Micro-Raman spectrum (Figure 1) of the sample CSH^{1w} reveal the presence of an amorphous compound which is identified as C-S-H gel due to a strong band centered at 667cm^{-1} (symmetrical bending (SB) Si-O-Si) [16, 17]. Additionally, there are other wide and poorly defined bands which confirm the formation of this compound, such as 1006cm^{-1} (ν_1 SiO_4 symmetrical stretching (SS) of Q^2), 856cm^{-1} (ν_1 SiO_4 SS of Q^1), 485cm^{-1} (ν_4 SiO_4), 444cm^{-1} (ν_2 SiO_4 $\text{O}_{\text{non}}\text{-Si-O}_{\text{non}}$) and 318cm^{-1} (lattice vibrations (LV) Ca-O). Nevertheless, another compound can be identified in all samples as amorphous calcium carbonate (ACC), owing to a broad band at 1078cm^{-1} [22].

Similar spectra for the samples CSH^{2w} , CSH^{3w} and CSH^{4w} were obtained with the main differences arising from the carbonate signals. A very narrow band appears for the first time in sample CSH^{2w} and its intensity increases in samples CSH^{3w} and CSH^{4w} as the gels are maintained in their aqueous solutions. This band appears at 1086cm^{-1} and can be identified as calcite through the presence of other bands at 712 , 282 and 154cm^{-1} . Furthermore, in the sample CSH^{3w} , there is calcite and another crystalline carbonate, which is aragonite due to a doublet at 706 and 700cm^{-1} , and a band at 206cm^{-1} [23].

Figure 1. Micro-Raman spectra of C-S-H samples ($\lambda = 532\text{ nm}$).

The samples were carbonated despite been covered.

FTIR Characterization

The FT-IR spectra of C-S-H gels showed in Figure 2 presented some differences that appear as the compounds are maintained in their own solutions. The main variances arise in the range of 900-1200 cm^{-1} owing to a complex group of bands [18, 19, 24]. The mid-IR spectrum of the sample $\text{CSH}^{1\text{w}}$ shows a strong band at 970 cm^{-1} which is in fact, a convoluted group of bands related to the symmetric and asymmetric stretching vibrations (Si-O) of Q^2 tetrahedra [18, 25]. There are other bands associated to C-S-H gel such as 837 cm^{-1} (stretching SiCa-O of Q^2_{B}), 811 cm^{-1} (Si-O SS of Q^1), 663 cm^{-1} (bending Si-O-Si), 488 cm^{-1} and 449 cm^{-1} (internal deformations SiO_4). The band at 1640 cm^{-1} (bending H-O-H) and the broad bands at 3440 and 3230 cm^{-1} (stretching H-O) correspond to water and hydroxyl groups in the C-S-H gel structure.

Figure 2.- FT-IR spectra of C-S-H samples

Moreover, another compound can be identified in all samples as amorphous calcium carbonate due to bands at 1479, 1418 and 866 cm^{-1} [26] confirming natural carbonation of the samples. Similar spectra for the samples $\text{CSH}^{2\text{w}}$, $\text{CSH}^{3\text{w}}$ and $\text{CSH}^{4\text{w}}$ were obtained with the main difference arising from the carbonate signals. These samples show, besides amorphous calcium carbonate, other peaks at 1420 and 875 cm^{-1} which

enables us to identify calcite in samples $\text{CSH}^{2\text{w}}$, $\text{CSH}^{3\text{w}}$ and $\text{CSH}^{4\text{w}}$. The presence of aragonite can be noticed because of bands at 1490, 856 and 713cm^{-1} in the sample $\text{CSH}^{3\text{w}}$ [26]. This is in line with Raman results. No significant differences can be observed in the C-S-H gel signals.

A calcium carbonate has been formed in all samples since the first week. Hunnicut et al., [13] considered that from double decomposition synthesis method is more likely to precipitate CaCO_3 than by the direct reaction synthesis method. However, as the reaction is very fast, we could consider that the atmospheric CO_2 has been dissolved in the solution and has reacted with the formed gel.

The phenomenon of carbonation is reflected in both, Micro-Raman and FT-IR spectrum considering that the more time the C-S-H gel is maintained in its solution, the more carbonation is noticed, due to the increase of the bands associated to amorphous and/or crystalline calcium carbonate. This carbonation is correlated with the C-S-H gel decalcification; atmospheric CO_2 dissolve in water solution, producing decalcification of C-S-H [16, 17]. Several authors [13, 27] concluded that calcium carbonate formed in the C-S-H synthesis produce ACC that evolves to aragonite and calcite. However, those studies [13, 27] determined carbonation of the C-S-H in solid phase, after filtration of the formed C-S-H. However, in our experiments, natural carbonation is produced in the samples immersed in the formation solution, before filtration.

DTA/TG/MS Characterization

DTG analysis was performed in order to quantify the amount of carbonates the samples had. The TG curves for all the samples in Figure 3 exhibited a mass loss in four distinct temperature intervals. The first, between 25 °C and 300 °C, was associated with the loss of adsorbed water and the C-S-H gel itself [28, 29]. Some authors [27, 30], extend this

interval up to 400°C since they consider the presence of other phases as hydrated calcium sulphotoaluminates; however, we consider only 300°C, based on the work of loss of mass of samples of only hydrated calcium silicates [28]; the second one, at 300 °C-430 °C, with the loss of water from the amorphous calcium carbonate [26, 31, 32]; the third one, at 430 °C-800 °C, with the loss of CO₂ from calcium carbonate in different forms [33]. In this interval there are three losses of mass, the first mass loss around 680° C is attributed to the decomposition of CaCO₃ in its unstable forms, vaterite and aragonite. The loss of mass at a higher temperature, 750 °C, is due to the decomposition of CaCO₃ in a stable form of calcite. And the last one, at 800 °C-1000 °C, with the loss of hydroxyl groups in C-S-H gel [28].

Figure 3.- TG of the C-S-H after 1, 2, 3 and four weeks in solution.

These losses together with the losses due to ACC and the water adsorbed in the sample are shown in Table 1.

The amount of ACC decreases with time, as there is an evolution to aragonite and vaterite, both unstable phases that evolve to calcite, the stable calcium carbonate.

However, there is no clear increase in stable phases over time. In order to study this process, a DTA/TG/MS study was conducted.

Table 1.- Percentages of adsorbed H₂O, ACC, calcite, vaterite and aragonite from TG values

	CSH ^{1w}	CSH ^{2w}	CSH ^{3w}	CSH ^{4w}
H ₂ O adsorbed (%) (25-270°C)	16.0	18.8	21.5	19.1
ACC (%) (270-430°C)	36.7	31.5	28.8	17.7
Aragonite + vaterite (%) (430-650°C)	2.2	1.4	2.4	5.6
Calcite (%) (650-850°C)	1.1	0.9	0.8	2.4

A study was conducted for the samples CSH^{1w} and CSH^{4w}, with DTA/TG/MS at the interval 25 °C-1000 °C (ramping at 15 °C/min) in an N₂ atmosphere. The TG curves for the two samples have been reproduced in Figures 4 and 5, showing the aforementioned four-interval pattern mass loss (Figure 3).

Figures 4 and 5 also show the loss of mass loss of the two compounds, with m/z 18 (H₂O) and 44 (CO₂) versus temperature. While water was released throughout the temperature interval in the two gels, most of it was lost between 25 °C and 225 °C associated with the loss of adsorbed water and the C-S-H gel itself. There is no portlandite present in either CSH^{1w} or CSH^{4w} as no water release at about 400°C is observed. There were observed two exothermic effects at 814 and 887° C that are characteristic of C-S-H(I) and C-S-H(II) respectively, indicating their recrystallization to wollastonite [34].

Figure 4. TG/MS curves of CSH^{1w} samples in N₂ atmosphere

Figure 5. TG/MS curves of CSH^{4w} samples in N₂ atmosphere

According to CO₂ release ($m/z = 44$) several peaks have been observed. The peaks at 450 °C-600 °C have been identified, to date, in the literature as associated to aragonite and vaterite decomposition, both salts are an unstable type of calcium carbonate which decomposes typically at a lower temperature than calcite [14, 35, 36]. Additionally, calcite decomposition is produced in the interval 600-800°C [35]. Different decomposition temperatures may indicate various calcium polymorphs, such as amorphous calcium carbonate, aragonite, vaterite and calcite, all of them have been identified by Raman and FTIR. Stepkowska [37, 38] established, at least 4 different steps as gradual transformation from calcium carbonate hydroxy hydrates (amorphous) to rhombohedral calcite in cement carbonation. According to Sauman [39], the carbonation of tobermorite in environments with low CO₂ concentration, produces firstly vaterite that gradually evolves to calcite. Several papers describe TG/MS from C-S-H decomposition [40-42], however none of them show a peak before 400°C as we saw in both of the samples. This is the main finding of our research, to identify CO₂ adsorbed in the C-S-H gel.

The premise put forward here is that the peaks in the interval 300-400°C were due to carbonates or atmospheric CO₂ adsorbed onto the gel, since CO₂ release temperature is very low and no chemical bond will be expected; then physically CO₂ jointed to the C-S-H is considered. The presence of adsorbed CO₂ over the C-S-H gel has been postulated previously [15] but this is the first time that is determined by TG/MS. The signal at 350-380°C, and assigned to adsorbed CO₂, decreases as the time in solution increases, in agreement with higher calcium carbonate formation for the sample CSH^{4w}. Therefore, the values of the TG losses should be reconsidered, since at 390°C adsorbed CO₂ is lost, previously not considered. Thus, in the 300-430°C range, the loss of water due to ACC decomposition and the loss of adsorbed CO₂ must be considered. This may

justify the discrepancies in the literature regarding the mass loss range of C-S-H, in which some authors consider 300°C [28, 29] and others consider 400°C [27, 30] since adsorbed CO₂ is included in this interval. Therefore, the best way to quantify the different mass losses is to perform a TG/MS.

Then, we recalculate the values of the losses of the CSH^{1w} and CSH^{4w} samples. To do so, we deconvolute the values of MS of $m/z = 44$ (Figure 6). The amount of CO₂ adsorbed decreases from 1 to 4 weeks, increasing the amount of unstable phases (aragonite and vaterite) that slowly evolve towards calcite. Therefore, we consider that in order to be able to determine more accurately the amount of ACC and different calcium carbonate polymorphs, the most suitable technique is ATD/TG/MS.

Figure 6.- Percentage of CO₂ adsorbed, aragonite + vaterite and calcite determined by TG/MS

²⁹Si NMR Characterization

Finally, the samples CSH^{1w} and CSH^{4w} were analysed by ²⁹Si NMR in order to perform a microstructural analysis of C-S-H gel. This technique allows us to distinguish among

the different linkages with other atoms depending on their chemical shift, and consequently understand the connectivity between the atoms and the structure of C-S-H gel [43]. The ^{29}Si NMR spectra (Figure 7) of both samples exhibit two groups of signals at different shifts depending on the environments in which silicon is involved. These signals appear at -80 and -85 ppm, due to the presence of Q^1 and Q^2 units respectively.

Figure 7.- ^{29}Si NMR spectra of C-S-H samples.

The ^{29}Si NMR profile of both samples CSH^{1w} and CSH^{4w} agrees with results from Chen et al [10] for C-S-H prepared by double decomposition method with different Ca/Si ratio. In ^{29}Si NMR spectroscopy, Q^n nomenclature makes reference to SiO_4^{4-} tetrahedra connectivity, thereby Q^1 tetrahedra means that one oxygen atom is shared with other silicon atom, Q^2 tetrahedra signify that two oxygen atoms are shared, and so on. Moreover, Q^2 units can be classified in Q^2_P and Q^2_B tetrahedra, depending on whether they are pairing or bridging in the dreierkette structure of the C-S-H gel [44, 45].

In a more accurate analysis, sample CSH^{1w} shows two bands located at -85.9 and -79.8 ppm, while in sample CSH^{4w} the last one shifted to -79.6 ppm and another one appeared at -83.7 ppm [25]. The intensity of Q^1 bands decreases as the C-S-H gel is maintained in

its solution, whilst the Q^2 band experiences a large increase, which leads us to think that the microstructure of C-S-H gel is changing. This alteration consists in the polymerization of short chains of gel into longer ones, which can explain the increase of Q^2 units linked to the reduction of Q^1 tetrahedra. A small shoulder it is also observed at -104 ppm that can be due to the presence of Q^3 units. As mentioned above, deconvolution of ^{29}Si NMR analyses was necessary in order to determine more precisely the microstructural changes produced in the C-S-H gel.

The range from -78 to -88 ppm, in which there is all the information related to Q^1 and Q^2 tetrahedra, was deconvoluted (Figure S1) in order to perform a more precise interpretation of the obtained results. The chemical shift, area and full width at half maximum (FWHM) were the parameters optimized in the fit, and the values are shown in Table 3.

Table 3. Value of the parameters optimized in the ^{29}Si NMR spectra deconvolution and their assignment.

CSH^{Iw}			CSH^{4w}			Assignment ^{23,38}
ppm	Area	FWHM	ppm	Area	FWHM	
-79.8	37.1	1.4	-79.6	12.01	1.1	Q^1
-81.1	-	-	-81.7	9.65	1.4	
-82.9	30.4	2.0	-83.7	31.57	1.8	Q^2_{B}
-85.8	32.6	1.5	-85.9	46.77	1.3	Q^2_{P}
<i>MCL</i>	5.39		<i>MCL</i>	9.23		

An important characteristic of C-S-H is their ability to vary in composition and degree of polymerization, while maintaining the essential features of the composite layer

structure. The degree of polymerization of silicate monomers can be determined by the medium chain length (MCL), with the following equation [43]:

$$MCL = \frac{2(Q^1 + Q^2)}{Q^1}$$

The data obtained in ^{29}Si NMR deconvolution confirm that the more time the C-S-H gel is maintained in its aqueous solution, the more polymerization takes place. This fact is reinforced due to the calculated value of the MCL, which increases considerably.

The area of the deconvoluted peaks Q^1 ; Q^2_P and Q^2_B are represented in Figure 8. In this way, both Q^2 units, pairing and bridging, increase at the same time Q^1 tetrahedra diminish.

Figure 8. Area percentage from ^{29}Si NMR deconvolution. Sample (1) = CSH^{1w} and Sample (2) = CSH^{4w} .

The Ca/Si ratio of the samples CSH^{1w} and CSH^{4w} was determined by SEM/EDX as 1.28 ± 0.07 and 1.06 ± 0.02 . This indicates that this ratio decreases, as the time that the gel is

in dissolution increases. This may be due to the decalcification of the gel caused by the adsorption of CO₂, as well as the increase in the length of the chain. The fact that the CSH^{4w} sample presents aragonite and vaterite is due to the fact that the carbonation of the C-S-H gel generates these compounds [39].

The SiO₂ formation attendant upon gel decalcification would justify the small Q³ signal on the ²⁹Si NMR spectrum for sample CSH^{4w}, also in agreement with higher calcium carbonate formation.

As it can be seen from ²⁹Si NMR results, the C-S-H gel polymerizes as it spends more time in its solution. The polymerization is endorsed by the increase and the decrease of Q² and Q¹ units respectively, the presence of Q³ in the sample CSH^{4w} and the MCL values. In the same way, FT-IR data imply a series of structural modifications in the gels because there is an alteration in the intensity of the bands located at 900-1200 cm⁻¹. From TG results, carbonation is associated with a release of calcium from the C-S-H gel to the aqueous solution; and during the first three weeks is quite continuous but in the last week the percentage of carbonate doubles. Additionally, for the first time, the adsorption of CO₂ in the C-S-H gel is demonstrated. Micro-Raman and FT-IR results support the decalcification of C-S-H gel, and consequently the formation of calcium carbonates, because these signals enlarge as the C-S-H gel is maintained more time in the aqueous solution.

Conclusions

By means of the double decomposition method, C-S-H gel is synthesized suitably. Micro-Raman and FT-IR are convenient techniques for carrying out the mineralogical characterization of the samples, thereby structural modifications of the gel can be

noticed, and they can be explained as the C-S-H gel decalcification. This fact is ratified because the bands in which calcium is implied in the bond ($964\text{-}966\text{ cm}^{-1}$ and $987\text{-}992\text{ cm}^{-1}$ in the FT-IR deconvolution) decrease while C-S-H gels pass more time in their solution.

The uptake of atmospheric CO_2 produce C-S-H gel decalcification and carbonation takes place; the more time the gel passes in contact with the solution, the sharper are the bands related to different types of calcium carbonates (1086 and 1420 cm^{-1} in Micro-Raman and FT-IR respectively). Amorphous calcium carbonate, calcite, aragonite, vaterite as well as adsorbed CO_2 were identified after natural carbonation of the C-S-H gel. The study of the carbonate phases formed by the reaction of CO_2 with C-S-H gel has been studied through DTA/TG/MS, determining for the first time the loss of CO_2 at temperatures below 400°C is associated with CO_2 adsorbed on C-S-H gel. Thus, in the $300\text{-}430^\circ\text{C}$ range, the loss of water due to the decomposition of the ACC and the loss of the CO_2 adsorbed on the gel must be considered. This is the first study to identify desorption of CO_2 adsorbed onto C-S-H gel exposed to natural carbonation.

The adsorbed CO_2 reacts with the calcium in the C-S-H gel to form calcium carbonates. This generates a loss of calcium in the above mentioned gel, going from Ca/Si ratio values of 1.28 to 1.06. This is also associated with a change in the polymerization of the gel, increasing the Q^1 units and decreasing the Q^2 units.

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Figure 1. Micro-Raman spectra of C-S-H samples ($\lambda = 532$ nm).

Figure 2.- FT-IR spectra of C-S-H samples

Figure 3.- TG of the C-S-H after 1, 2, 3 and four weeks in solution.

Figure 4. TG/MS curves of CSH^{1w} samples in N₂ atmosphere

Figure 5. TG/MS curves of CSH^{4w} samples in N₂ atmosphere

Figure 6.- Percentage of CO₂ adsorbed, aragonite+vaterite and calcite determined by TG/MS

Figure 7.- ²⁹Si NMR spectra of C-S-H samples.

Figure 8. Area percentage from ²⁹Si NMR deconvolution. Sample (1) = CSH^{1w} and Sample (2) = CSH^{4w}.