A COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL Ca/Si RATIOS IN C-S-H AND C-S(A)-H GELS

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HIGHLIGHTS

- Calcium silicate hydrate, with and without Aluminium, was synthesized by double decomposition method with different nominal Ca/Si ratio.
- Ca/Si ratio ranging from 0.8 to 1.0 in the C-S-H synthesised by double decomposition method.
- C-S(A)-H gel with Ca/Si ratio less than 0.6, cannot be synthesised by double decomposition method.
- As nominal Ca/Si ratio increases, Q^1 units increases in the C-S-H gel structure.

ABSTRACT

The main component of the cement hydration, are both, the calcium silicate hydrate (C-S-H) and calcium silicate hydrate with Al (C-S(A)-H), whose composition is characterized by its calcium to silicon ratio (Ca/Si), which normally varies from 0.6 to 1.6. The theoretical Ca/Si ratios of the synthesized gels were compared with those of the experimental gels, which were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES). In addition, the microstructure of the gels was studied by spectroscopic techniques: Infrared and Raman spectroscopy and Nuclear Magnetic Resonance. By the double decomposition method used in this work (1 day at 25 °C, inert atmosphere and pH = 12,3), only C-S-H and C-S(A)-H gels with a maximum Ca/Si ratio ranging from 0.8 to 1.0 were synthesized. However, the structures of the gels are slightly different as the Ca/Si ratio increases.

Keywords: calcium silicate hydrate, calcium silicate hydrate with Al, Raman, double decomposition, Ca/Si ratio, NMR.

INTRODUCTION

Calcium silicate hydrate (C-S-H) is the main component formed in the cement hydration. Its composition is generally characterized by its calcium to silicon ratio (Ca/Si) that has been assumed to be in the interval 0.6-1.6. There are several structural models for the C-S-H gel. However, two of them are considered the most accurate [1]. One of the models considers that the C-S-H gel structure is closed to the minerals tobermorite and/or jennite depending on the Ca/Si ratio (Ca/Si ratios lower or higher than 1.3 respectively). On the other hand, the other structural model considers that the C-S-H gel is formed by tobermorite layers with portlandite bounded to these layers.

Tobermorite and jennite consist of silicon tetrahedron units connected by the vertex forming infinite linear chains, whereas in the C-S-H gel, many of the bridging tetrahedra are missing, giving rise to finite chains. Therefore, the structure of the C-S-H gel is known as the “defective tobermorite structure model”.

Several methods of laboratory synthesis have been described in the literature in order to explain structural modifications that can take place in the structure of the C-S-H gel. The main synthesis methods described in the literature, as well as the Ca/Si ratios of the C-S-H gels formed are summarized below (see supplementary material and Table 1).

The methods of synthesis of the C-S-H gel, can be summarized as follows: a) those that obtain the gel by direct reaction of the source of silicon and the source of calcium in a medium with excess water; such methods would include hydrothermal [2-5], mechanochemical [6, 7] and double decomposition methods [8,9] and b) hydration reaction of calcium silicate (C_3S or C_2S) [10-21]. Microwave synthesis is also a new approach used to synthesize the calcium silicate

hydrate [22]. In the first case, silicon is started with a structure of Q^4 units that depolymerized and give rise to hydrated calcium silicate with Q^1 and Q^2 units. In the second case, however, reaction with a Q^0 silicon structure that has to be polymerized to give rise to Q^1 and Q^2 structures. Being the connectivity factor, Q^n ($n=0, 1, 2, 3, 4$) a parameter that estimate the silicate connection, where n is defined as the number of neighboring silicate tetrahedrons connected. Q^0 is the monomer; Q^1 represents the structure of the dimer (two connected silicate tetrahedrons); Q^2 is the long chain; Q^3 is the branched structure; Q^4 is structure of the network [23].

The use of supplementary cementitious materials to reduce CO_2 emissions, causes the chemical composition of the cement to changes, resulting, after hydration, in a calcium silicate hydrate with a different Ca/Si ratio in which Al could be included. Since silicon would be replaced by aluminum the so-called C-S(A)-H gel would be formed in which the Ca/Si ratio decreases [24,25,26]. The calcium (aluminum) silicate hydrate structure is also similar to tobermorite; the main difference arises from the silicon atoms located at the bridging sites over the paired sites in the structure, which are replaced by aluminum atoms. There are several ways to prepare C-S(A)-H gel in the laboratory, i.e., by mixing SiO_2 , CaO, and $CaO \cdot Al_2O_3$ in excess of water [27]. Other authors use $AlO(OH)$ as source of aluminum [28]. As for C-S-H synthesis, double decomposition method [8] and hydrothermal [29] can also be used. Additional methods include the addition of previously synthesized C-S-H gel in freshly-filtrated C_3A solution [26].

The Ca/Si ratio of the C-S-H gel will determine its structure, but according to Grangeon et al. [30], the structure of the calcium silicate hydrate may have slight differences depending on different methods of preparation, and probably cannot be extrapolated from one method to another. In the case of direct reaction synthesis, the Ca/Si ratio is generally determined by the ratio of both, Ca and Si concentration initially added, assuming that the reaction is complete and that both calcium and silicon are fully incorporated into the gel. However, this method cannot be used to determine Ca and Si concentration when the gel comes from the hydration of C_2S and C_3S . For the C-S-H formed after hydration of calcium silicate, microscopic techniques are the most appropriate, i.e. transmission electron microscopy (TEM/EDX) and electron probe microanalyser (EMPA). Recently DTA/TG is also used as an indirect method, based on the comparison between impurities and the bulk Ca/Si ratio.

Although most authors determine the initial Ca/Si ratios generally as stoichiometric values, the real Ca/Si ratios of the C-S-H gels formed was not always determined (Table 1). Sun et al [8] following also double decomposition method synthesized C-S-H gel with different Ca/Si ratios (0.8; 1.18 and 1.4). Although the reaction occurs immediately, they left the reaction stirring for 1 week and 4 weeks and Ca and Si were analyzed. For the samples with Ca/Si = 0.8 and 1.18 the composition was reach after 1 week, and was stable after 4 weeks; however for the sample with Ca/Si ratio 1.4, the value after 1 week was 1.14 that increases until 1.26 after 4 weeks. Garcia-Lodeiro et al [9] found also discrepancies between experimental and theoretical Ca/Si ratios for C-S-H samples synthesized by double decomposition method, at different pH values. They analyzed the Ca and Si composition of the solid samples by TEM/EDX. However, in our experiments, the pH of the solution was adjusted to 12.5, and then experimental and theoretical differences cannot be related to pH solution.

Table 1.- References of the C-S-H gel synthesis, Ca/Si nominal ratio and experimental method for Ca/Si determination.

Autor/Reference	Synthesis method	Ca/Si nominal	Ca/Si experimental*			Method of Ca/Si determination
Grangeon/Cem. Concr. Res. 52 (2013) 31-37	Soft Hydrothermal	0.82-0.87				XRD??
Marty/Miner. Magazine, 79(2), (2015) 437–458	Soft Hydrothermal	0.9 1.4 1.5	EMPA	TEM/EDX	DTA/TG	TEM and DTA/TG
			0.86	0.85	0.85	
			1.38	1.21	1.22	
			1.47	1.22	1.22	
Saito/Solid State Ionics 101-103 (1997) 37-43	Mecanochemical (CaO+SiO ₂)	0.5	n.d ^s			
		0.7	n.d			
		1.0	n.d			
		1.5	n.d			
		2.0	n.d			
		3.0	n.d			
Soyer-Uzun/J. Am. Ceram. Soc., 95 [2] (2012) 793–798	Mechanochemical+hydration (CaO + SiO ₂)	0.6	n.d			
		0.8	n.d			
		1.0	n.d			
		1.2	n.d			
		1.5	n.d			
		1.6	n.d			
		1.75	n.d			
Cappelletto/J. Phys. Chem. C, 117 (2013) 22947–22953	C ₃ S hydration	-	-			
Trapote-Barreira/Physics and Chemistry of the Earth 70–71 (2014) 17–31	C ₃ S hydration		EDX	EMPA		
			2.15	1.79		
			1.77	1.75		
			1.68	1.84		
			1.74	28.2		
			1.79	13.4		
			2.13	1.96		
			6.17	1.84		
			6.16	1.94		
			2.06	1.83		
			2.34	1.68 1.87		
Higl/Cem. Concr. Res. 88 (2016) 136–143	C ₃ S hydration	-	-			
Chen/Cem. Concr. Res. 34 (2004) 1499–1519	C ₃ S hydration	3	3			ICP (solid at 1000°C produce glass soluble in acid) ICP (initial and final Ca and Si in solution)
		3	2.99			
		3	2.64			
		3	2.42			
		3	1.87			
		3	1.81			
		3	1.75			
Chen/Cem. Concr. Res. 34 (2004) 1499–1519	Double decomposition	1.4	1.48			ICP (solid at 1000°C produce glass soluble in acid) ICP (initial and final Ca and Si in solution)
		1.4	-			
		1.4	1.44			
		1.4	1.31			
		1.4	1.20			
		1.4	-			
		1.4	1.03			
		1.4	1.05			
		1.4	0.92			
		1.4	1.03			
Hass/Cem. Concr. Res. 68 (2015) 124–138	CaO + SiO ₂	0.002				
		0.003				
		0.004				
		0.005				
		0.007				
Kim/Cem. Concr. Comp. 36 (2013) 65–70		0.9	0.7			DTA/TG
		1.2	1.0			
		1.5	1.24			
L’Hôpital/Cem. Concr. Res.	CaO +SiO ₂	0.6	>0.67			DTA/TG and XRD

85 (2016) 111–121		0.8 1.0 1.2 1.4 1.6	0.8 0.98 1.17 1.29 1.38	
Alizadeh / <i>Materials and Structures</i> 44(2011) 13–28	CaO+SiO ₂	0.8 1.0 1.2 1.5	n.d n.d n.d n.d	
Baston / <i>Mineralogical Magazine</i> , 76(8) (2012) 3045–3053	CaO + silica colloidal	0.20 0.25 0.40 0.60	0.32 0.50 n.d n.d n.d	Leaching was studied
Harris / <i>Cem. Concr. Res.</i> 32 (2002) 731–746	CaO + SiO ₂	3.0 1.8 1.5 1.2 1.0 0.90 0.85 0.80	2.7 1.6 1.4 1.1 0.90 0.81 0.76 0.72	
Sun / <i>Cem Concr Res.</i> 36 (2006) 18–29	Double decomposition	0.86 1.16 1.4	0.86 1.14 1.26	XRF
Garcia-Lodeiro / <i>J. Am. Ceram. Soc.</i> , 95 [4] 1440–1446 (2012)	Double decomposition	1 (pH = 9.2)* 1(pH=1.1)* 1 (pH=12.2)* 1.9(pH=12.3)* 1(pH=13.2) [†] 1.9 (pH=13.2) [†]	0.39 0.65 0.67 0.65 1.02 1.54	TEM/EDX
Huang / <i>J. Eur. Ceram. Soc.</i> 23 (2003) 123–126	Ca(OH) ₂ +SiO ₂ +EDTA	1 (pH=13)5h 1.25(pH=13)5h 1.5(pH=13)5h 2.0(pH=13)5h 2(pH=13) 1h 2(pH=13) 3h 2(pH=13)5h 2(pH=13)10h 2(pH=12)19h	0.71 0.72 0.73 0.74 0.67 0.68 0.71 0.74 0.64	SEM/EDS
Tränkle / <i>J. Mater. Chem. A</i> , 2013, 1, 10318	Hydrothermal	0.36 [‡] 0.36 [‡] 0.36 [§] 0.44 [§] 0.60 [§] 0.89 [§] 1.78 [§] 0.44 ^a 0.36 ^b	0.63	ICP/OES

[§]No determined; *laboratory conditions; [†]inert atmosphere; [‡]Borosilicate glass and silicic acid; ^a Quartz glass; ^bsilicic acid

Marty et al [4] showed, following the tobermorite model, that the maximum Ca/Si ratio cannot exceed 1.25 for calcium silicate hydrate hydrothermally synthesized. However, under hydrothermal synthesis, higher Ca/Si ratios can be obtained assuming the presence of nanoportlandite intermixed with the C-S-H gel, which is consistent with the tobermorite/CH model proposed by Richardson [1, 31].

From the information in Table 1, we can deduce that the greatest discrepancies in the determination of the Ca/Si ratio were for the highest Ca/Si ratios. In the present work, we have prepared C-S-H and C-S(A)-H gels with different Ca/Si ratios using the double decomposition

method as the simplest and fastest way to prepare the calcium silicate hydrate. From the double decomposition synthesis, two compounds exchange ions, typically with the precipitation of an insoluble product, in this case calcium silicate hydrate.

The experimental Ca/Si ratios of the non-reacted raw materials were determined by analyzing the liquids through ICP, in order to compare them with the initial compositions. The microstructure of the former gels was studied following their mineralogical composition by means of spectroscopic techniques such as FT-IR, Raman and NMR, which are sensitive to the vibrational modes, providing information on the local atomic structure. Our goal is to determine the maximum amount of calcium and silicon that can be incorporated into the calcium silicate gel from the double decomposition synthesis, analyzing the solution after the reaction in inert atmosphere.

EXPERIMENTAL SECTION

Under controlled argon atmosphere, in a glove-box, ten C-S-H gel samples were synthesized by the double decomposition method [8,9] using different stoichiometric mixtures of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (95% purity, Aldrich) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98% purity, Panreac). Using the same procedure, another ten aluminum-substituted C-S(A)-H gelsamples were prepared using $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98% purity, Sigma-Aldrich), $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (95% purity, Aldrich) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98% purity, Panreac) as starting materials. All reagents were dissolved in CO_2 -free deionized water. The Ca/Si atomic ratios ranged from 0.5 to 2.0 for both C-S-H and C-S(A)-H synthesis; moreover, an Al/Si atomic Al/Si ratio of 0.03 was used for the synthesis of C-S(A)-H gel samples. An Al/Si ratio of 0.03 was selected, since according to previous works [17, 32], higher Al/Si ratios can promote the incorporation of aluminum into the interlayer space of the C-S-H. The amounts of the starting materials are shown in Table 2.

Table 2. Amounts of starting materials (g), pH solution and theoretical Ca/Si ratios

Target ratio			Initial composition (C-S-H)			Initial composition (C-S(A)-H)			
Ca/Si Mol	w/s* (wt)	Water (ml)	$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (g)	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (g)	pH	$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (g)	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (g)	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (g)	pH
0.5	54	18	0,212	0,118	12.5	0,212	0,118	0,011	12.5
0.6	51	18	0,212	0,142	12.5	0,212	0,142	0,011	12.5
0.8	45	18	0,212	0,189	12.5	0,212	0,189	0,011	12.5
1.0	80	18	0,106	0,118	12.5	0,106	0,118	0,006	12.5
1.1	76	18	0,106	0,130	12.5	0,106	0,130	0,006	12.5
1.3	69	18	0,106	0,153	12.5	0,106	0,153	0,006	12.5
1.5	63	18	0,106	0,177	12.5	0,106	0,177	0,006	12.5
1.6	61	18	0,106	0,189	12.5	0,106	0,189	0,006	12.5
1.8	56	18	0,106	0,212	12.5	0,106	0,212	0,006	12.5
2.0	53	18	0,106	0,236	12.5	0,106	0,236	0,006	12.5

*w/s = water/solid ratio, solid = g of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ + g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

For C-S-H gel synthesis, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2mL) (was slowly added into the $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ solution (16mL) and a jellied precipitate was immediately formed. After this, the addition of a solution of NaOH was required in order to adjust the pH to 12.0-12.5. The synthesis of C-S(A)-H gel was performed in a similar manner, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2 mL) was added into a $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (16 mL) solution, then $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2mL) was slowly added and the precipitate formed instantly. It is important to note that for C-S(A)-H gel synthesis the addition of NaOH was unnecessary because the pH was already adjusted to 12.0-12.5.

In both synthesis (C-S-H and C-S(A)-H), the water/solid ratio was higher than 45 (Table 2).

The reactions were left one day under stirring at room temperature. The solutions were correctly filtered and hermetically stored in glass vials under a CO_2 -free atmosphere until ICP analysis. The precipitates were washed three times with CO_2 -free deionized water followed by ethanol. Finally, the samples were stored in vials inside a desiccator.

The analyses of the samples were performed in two different parts: the precipitate and the solution. First, a mineralogical characterization was carried out by Micro-Raman, FT-IR (Fourier Transform Infrared Spectroscopy) and ^{29}Si and ^{27}Al NMR in order to obtain information about the structure of the gels; and then, ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) helped us to determine the amount of calcium and silicon in the filtered liquid.

Micro-Raman analysis was performed with a Raman microscope Renishaw Invia. Laser excitation lines were 785nm wavelength (provided by a diode laser) and 532nm wavelength (from Renishaw Nd:YAG laser) with a power of 25mW in both cases. The spectra acquisition conditions were: spectral resolution of 4cm^{-1} , exposure time of 10 seconds and 20 accumulations per spectra in the range of $2000\text{-}100\text{ cm}^{-1}$ to increase signal/noise ratio. The frequencies were calibrated with silicon.

Infrared spectra were recorded using a FT-IR spectrometer Bruker IFS66. The samples were registered in the range $4000\text{-}400\text{ cm}^{-1}$ using KBr pellets with a sample/KBr ratio of 1/200. Micro-Raman and FT-IR spectra were normalized to the C-S-H gel most intense band, which were 670 and 690cm^{-1} respectively.

Samples were analyzed on a Bruker AV-400 (9.4T) NMR spectrometer with these settings for the ^{29}Si NMR experiments: $\nu_R = 4\text{kHz}$ (20kHz for ^{27}Al NMR); pulse width = $7\mu\text{s}$ ($1\mu\text{s}$ for ^{27}Al NMR); relaxation delay = 60s (2s for ^{27}Al NMR). Typically, 3000 scans were run and the ^{29}Si and ^{27}Al chemical shifts were determined relative to tetramethylsilane and an aluminum trichloride solution, respectively. The spectra were deconvoluted into Gaussian peaks and fitted using Origin 8.0.

The experimental Ca/Si ratios of the C-S-H and C-S(A)-H gels samples were determined by difference between the added amount of reactants and the remaining calcium and silicon quantity determined in the solutions.

RESULTS AND DISCUSSION

Solution analyses

Samples were filtrated in the glove-box and the collected liquids were placed in a 30-mL glass bottles provided with airtight caps before removing them from the glove-box. Then, the calcium and silicon in solution were determined by ICP (Table 3), those are the amounts that have not become part of the C-S-H or C-S(A)-H gels structures. The calculation was made according to Haas and Nonat [14], so the experimental Ca/Si ratio was calculated as following: the initial amount of calcium minus the calcium determined by ICP (expressed by Ca_{ICP}) divided by the subtraction of the initial amount of Si minus the amount determined in the liquid by ICP (named Si_{ICP}). Within this calculation it is considered that this is the Ca/Si ratio that can be in the calcium silicate hydrate formed phase, which will be referred to Ca/Si_{exp} .

Table 3. ICP determination of calcium (ppm) and silicon (ppm) in solution after C-S-H precipitation, theoretical and experimental Ca/Si molar ratios

Ca/Si _{th}	C-S-H gel			C-S(A)-H gel			
	Ca _{ICP}	Si _{ICP}	Ca/Si _{exp}	Ca _{ICP}	Si _{ICP}	Ca/Si _{exp}	Ca/(Si+Al) _{exp}
0.5	1.6	455.0	0.74	2.7	581.2	0.70	0.76
0.6	1.3	250.6	0.74	49.1	374.9	0.65	0.74
0.8	1.2	40.8	0.83	36.5	94.1	0.79	0.81
1.0	49.3	19.0	0.98	184.0	21.1	0.74	0.84
1.1	96.4	9.2	1.01	253.1	13.5	0.81	0.85
1.3	328.9	4.0	0.98	509.3	13.5	0.86	0.84
1.5	517.8	2.2	1.00	791.1	15.4	0.85	0.79
1.6	624.3	2.0	0.98	830.7	12.4	0.84	0.84
1.8	837.3	1.5	0.96	1157.4	11.2	0.80	0.75
2.0	1171.6	1.6	0.83	1314.8	11.9	0.86	0.80

Figure 1 shows the theoretical Ca/Si ratio versus the experimental one with some differences between the theoretical and the experimental values. The Ca/Si experimental value, ranging from 0.74 to 1.01 for C-S-H gel while, that of the C-S(A)-H gel shortens its range, and varies from 0.65 to 0.86. When Ca/(Si+Al) ratio is calculated increases until 0.74 to 0.85. In the same way, the experimental ratio rarely matches with the theoretical one. Only in cases in which the experimental ratio is 1.0 or close to 1.0, both ratios match.

Fig 1 Representation of the theoretical and experimental Ca/Si ratios

Taking into account that in the double decomposition method, both salts used as starting materials, are very soluble and fully dissolve before mixing and also that the samples were prepared in an argon atmosphere glove box, we can assume that calcium and silicon react to form, only, C-S-H and C-S(A)-H gel. As it can be seen, most of the experimental Ca/Si ratios were closed to 1.0, so this can be an indication that by the double decomposition method, with the experimental conditions we prepare, only C-S-H and C-S(A)-H gels with an experimental Ca/Si ratio ranging from 0.8 to 1.0 can be synthesized.

Other authors also found discrepancies between experimental and theoretical Ca/Si ratios [9] of C-S-H gels synthesized by the double decomposition method, obtaining the highest discrepancies for Ca/Si ratios greater than 1.2 [8]. If the gel is synthesized under the hydrothermal method, Ca/Si values higher than 1.2 are not obtained either, unless the presence of nanoportlandite intermixed with the C-S-H gel [4] predicted in Richardson's model [1, 31] is considered.

It is noticeable that the amount of calcium and silicon determined by ICP-OES, is always higher in the solution of the C-S(A)-H gel than in the C-S-H gel one. This fact can be an indication of the replacement of silicon with aluminium in the bridging tetrahedra of the chain structure. Therefore, if the amount of silicon in the gel structure decreases, the Ca/Si ratio will necessarily increase.

Micro-Raman and FTIR

A spectroscopic study was done in order to study if any microstructural modifications were effectively produced in both C-S-H and C-S(A)-H gels. Spectroscopically, there were differences between the spectra of a crystalline and an amorphous material. While the former presents sharp, well-defined bands, those of the latter, are wide and poorly defined. The reason for these differences was essentially structural. Figure 2 shows the Raman spectra of the C-S-H gel prepared with different Ca/Si ratios. If the spectrum of calcium silicate hydrate gel is

meticulously observed, it is deduced that the nature of this compound is clearly a mixture of both amorphous and crystalline phases, as it has short-range order. The number of accumulations performed in Micro-Raman spectra was great enough so as to be obtained with a fine resolution, and able to be compared to those spectra that appear in literature.

Fig 2 Micro-Raman spectra of C-S-H gels with different Ca/Si ratio. The curves have been vertically shifted for clarity.*see text for explanation

The most intense, narrow band in the Raman spectra of the C-S-H gel is centered at about 667 cm^{-1} (Symmetrical Bending Si-O-Si). Furthermore, there are other wider and poorly defined bands which confirm the presence of this calcium silicate hydrate (C-S-H gel), such as 1009 cm^{-1} ($\nu_1 \text{SiO}_4$ Symmetrical Stretching of Q^2), 850 cm^{-1} ($\nu_1 \text{SiO}_4$ Symmetrical Stretching of Q^1), 488 cm^{-1} ($\nu_4 \text{SiO}_4$), 444 cm^{-1} ($\nu_2 \text{SiO}_4$ non-bridging oxygen atoms attached to silicon ($\text{O}_{\text{non}}\text{-Si-O}_{\text{non}}$)) and 320 cm^{-1} (Lattice vibrations Ca-O). Raman spectra of C-S-H gel with different Ca/Si ratio exhibit two main changes related to Si-O bands. The first one is related to the most intense peak, generated by Si-O-Si symmetric bending (SB) vibrations [33, 34], which slightly shifts to lower wavenumbers. For nominal values Ca/Si lower than 0.8 the signal appears at 674 cm^{-1} that shifts to 670 cm^{-1} , for Ca/Si ratio higher than 0.8, indicating a decrease in the Ca/Si ratio [33] in accordance with experimental values (Table 2) [33, 34].

The second difference is associated with an increase in the intensity of the $\nu_1 \text{SiO}_4$ SS of Q^1 band as the nominal Ca/Si ratio increases; it is attributed to the presence of dimer units with a lower polymerization degree in the C-S-H gel, as Ca/Si increases.

The C-S-H gels with lower Ca/Si ratios (0.5 and 0.6) present two bands at 606 and 490 cm^{-1} (marked with asterisk in Figure 2), which some authors[33] indicate are due to Q^3 units. Other authors [35] indicate that crystalline tobermorite can be formed when C-S-H has been formed at low Ca/Si ratio.

Raman spectra of C-S(A)-H gel with different Ca/Si ratios are presented in Figure 3. It is observed that in the samples with a Ca/Si ratio of 0.5 and 0.6, the main vibration band (SB Si-O-Si) is broad and quite small, so we can assume that the expected C-S(A)-H was not formed with such a low Ca/Si ratio. In these samples the 850 cm^{-1} signal is not observed, Ortaboy [36], indicates that this signal only appears in Raman at high Ca/Si ratios, which confirms that the

samples synthesized in this work have Ca/Si ratio ≤ 1 . It is also interesting to remark the appearance of two broad bands located at 580 and 530 cm^{-1} , which are assigned to Al-O linkages [37].

Fig 3 Micro-Raman spectra of C-S(A)-H with different Ca/Si ratio. The arrows point to the broad bands at the interval 580-530 cm^{-1} .

Furthermore, bands at 1090; 1086 and 1075 cm^{-1} enable us to determine in both gels, C-S-H and C-S(A)-H, the presence of crystalline (vaterite, calcite) and amorphous calcium carbonate (ACC) respectively [38]. In this way, for the samples with low Ca/Si ratio (0.6-08) ACC has been formed; as the Ca/Si ratio increases (1.0-1.6) calcite and for the samples with the highest Ca/Si ratio (1.8-2.0) vaterite and calcite are both present. From a thermodynamic point of view the ACC is unstable and will transform into calcite via vaterite at room temperatures. In addition, the ACC can also be formed from oversaturated solutions. In the case of the C-S-H with low initial Ca/Si ratios, the starting solution contains a high concentration of calcium (Table 2) and therefore the formation of ACC will be more favourable. In the case of gels with higher Ca/Si ratios, there is less initial calcium in the solution and the possible formed ACC evolves rapidly to the more stable forms, calcite and vaterite.

In the case of the samples with aluminum (C-S(A)-H), for all the Ca/Si ratios ACC and vaterite are formed, and no calcite is identified, since the presence of impurities (in this case Al) modifies the crystallization of the calcium carbonate avoiding the formation of calcite [39]. For the C-S(A)-H samples with the high Ca/Si ratio (1.6-2.0) the Raman spectra shows a small band at 735 cm^{-1} from symmetric flexion of Ca-O (ν_4) in vaterite.

Ortaboy et al [36] have synthesized C-S(A)-H gels and through Raman have identified one signal at 756 due to O-Al-O symmetrical flexions and another at 980 cm^{-1} generated by the symmetrical flexion of the Al-O-H link. However, they have not been observed in this work since the amount of aluminum used in this work for the synthesis of C-S(A)-H was lower.

Nevertheless, in the C-S-H gel with a Ca/Si ratio of 0.5, the bands which correspond to calcite are better defined and it is possible to distinguish small bands such as 712, 282 and 154 cm^{-1} . Since no C-S-H is formed, calcium reacts with atmospheric CO_2 to produce amorphous and crystalline calcium carbonate.

Figure S1 shows the FTIR spectra of C-S-H and C-S(A)-H gels with the Ca/Si ratio of 0.5; 1 and 2 in the interval 2000-400 cm^{-1} . The Ca/Si ratios selected were those that present the more significant differences. No portlandite band at 3641 cm^{-1} was identified in any of the samples in agreement with Raman results. Several authors [30, 33, 40] found portlandite in the C-S-H gel synthesized with Ca/Si ratios higher than 1.5; since we have not detected Ca(OH)_2 this can be one more evidence that the C-S-H gel synthesized has Ca/Si <1.1. For both gels with Ca/Si ratio 0.5, the FTIR presents a broad band in the interval 800-1300 cm^{-1} confirming the Raman results, in which it was observed that a very low amount of gel was formed. The main difference between FT-IR spectra of both gels arise out of the strongest band previously mentioned, as it is possible to distinguish a doublet at 974 and 966 cm^{-1} in the C-S(A)-H gel (Figure S2, enlarged view). Kapeluszna et al., [40] study C-S(A)-H gel, concluding that the increases in aluminum content leads to the bands shift towards the lower wavenumbers due to Si-O- terminal bonds formed. Additionally Mozgawa et al. [42] refers a split of the previous band as the AlO_4 increases in the SiO_4 structure, which confirms the substitution of the Si by Al.

In the literature there are not results of experimental Ca/Si ratio determined for C-S-H and C-S(A)-H gels synthesized by precipitation from soluble precursor. Present results put a new insight on real Ca/Si ratio of the gels.

Deepening in the microstructure of both C-S-H and C-S(A)-H ^{29}Si and ^{27}Al NMR studies were performance in the samples with Ca/Si ratio 0.5; 1 and 2.

Figure 6 shows ^{29}Si NMR of the samples synthesized under double decomposition method with Ca/Si ratios 0.5; 1 and 2 with and without Al. Table 4, shows the Q^n units and the medium chain length (MCL) [9] of both C-S-H and C-S(A)-H, determined after spectra deconvolution (Figure S3 and S4).

Fig 6 ^{29}Si NMR of C-S-H (left) and C-S(A)-H (right) with Ca/Si ratios 0.5; 1 and 2

The ^{29}Si NMR spectra shows different silica environments, previously assigned as Q^1 from the end of chain at -79.4 ppm, silica Q^2_b from the bridging tetrahedron at -83.4 ppm, Q^2_p assigned

of the pairing site at -85.3 ppm. The signal at -88.5 ppm can be attributed to a bridging tetrahedra connected to another bridging silica and is called Q^2_u [43, 44]. However another authors considered this signal due to Q^3 units [9, 45]. Raman results, where Q^3 units were identified, allow us to conclude that in the C-S-H and C-S(A)-H with Ca/Si ratio 0.5 the peak at -89 ppm is attributed to Q^3 units. The relative low intensity of the end of chain silicate Q^1 units, in both samples with Ca/Si ratio 0.5, leads to a higher MCL value, supporting the fact of the elevated degree of polymerization.

Table 4.- Main chain length (MCL) and Q^n units from deconvolution of ^{29}Si MAS NMR spectra into Gaussian components

CSH05			CSH1			CSH2		
δ (ppm)	units	%	δ (ppm)	units	%	δ (ppm)	units	%
-79.9	Q^1	12.0	-79.9	Q^1	33.3	-79.9	Q^1	48.0
-82.8	Q^2_b	22.9	-82.3	Q^2_b	9.3	-81.5	Q^2_b	3.0
			-83.4	Q^2_b	3.6	-82.5	Q^2_b	12.2
			-84.3	Q^2_p	9.8			
-85.6	Q^2_p	51.6	-85.9	Q^2_p	44.0	-85.6	Q^2_p	36.8
-89.0	Q^3/Q^2_u	13.5						
MCL*								
14.4			6.0			4.2		
CS(A)H05			CS(A)H1			CS(A)H2		
δ (ppm)	units	%	δ (ppm)	units	%	δ (ppm)	units	%
						-77.5	Q^1	9.1
			-78.8	Q^1	27.9	-78.5	Q^1	6.1
-80.0	Q^1	15.0	-79.9	Q^1	29.0	-79.7	Q^1	53.2
			-82.2	$Q^2(1Al)$	16.4	-82.3	$Q^2(1Al)$	2.5
-83.0	Q^2_b	21.5						
			-84.5	Q^2_p	4.3	-84.6	Q^2_p	0.3
-85.6	Q^2_p	36.2	-85.3	Q^2_p	22.4	-85.4	Q^2_p	28.9
-89.1	Q^3/Q^2_u	27.3						
MCL*								
9.7			3.3			2.9		

*MCL has been calculated considering that the signal at -89 ppm is due to Q^3 , see text for more explanation

As the nominal Ca/Si ratio increases the fraction of the Q^1 unit increases leading to a decrease in the fraction of pairing and bridging tetrahedra, Q^2_p , Q^2_b and a shortening of the mean chain length, which agrees with previous observations [13, 8].

Both samples with nominal Ca/Si ratio 0.5 present a peak at -83.1 ppm from Q^2_b that decreases in intensity as the Ca/Si ratio increases.

The presence of aluminum in the C-S-H introduces an additional peak, between -82.0 and -80.5 ppm assigned to $Q^2_p(1Al)$ [8, 25, 46, 47, 48], as confirmed by ^{27}Al NMR results (Figure 7) [49]. As the Ca/Si increases, the fraction of Al in bridging position (Q^2_b), decreases, leading to a lower degree of polymerization and therefore a smaller MCL value.

^{27}Al NMR of the samples has the main signals in the interval assigned to tetrahedrally coordinated Al. The sample with Ca/Si ratio 0.5 presents a broad band with the maximum at 56.9 ppm attributed to a bridging Al Q^3 [49] whose presence has been discussed previously. As the

Ca/Si ratio increases, the signal shifts to a higher ppm values (65.7 and 71.8 ppm), in agreement with the presence of Al as part of the C-S-H gel structural skeleton [49].

Fig 7 ^{27}Al NMR of C-S(A)-H with Ca/Si ratios 0.5; 1 and 2

CONCLUSIONS

Double decomposition method was followed to synthesize ten C-S-H and ten C-S(A)-H gel samples with different Ca/Si ratios (from 0.5 to 2.0) and a Al/Si ratio of 0.03. The analyses of the solutions after 24 hours of reaction in inert atmosphere were necessary in order to determine the maximum experimental Ca/Si ratios in both gels. This information revealed that only C-S-H and C-S(A)-H gels with a Ca/Si ratio ranging from 0.8 to 1.0 can be synthesized (following 1 day stirring double decomposition method at pH =12.3), because in this interval both theoretical and experimental Ca/Si ratios match. Additionally, it can be observed that the amounts of calcium and silicon are always higher in the C-S(A)-H solutions than in the C-S-H gels ones. This fact can be an indication of the replacement of silicon with aluminium in the bridging tetrahedra of the chain structure.

We also investigated the structure of the C-S-H and C-S(A)-H gels by Micro-Raman and FT-IR that confirms Ca/Si ratio close to 1 for all the samples. NMR, Raman and FTIR of the gels with a Ca/Si ratio less than 0.6 indicate that the degree of polymerization of the gel is very low. So more time is needed for C-S-H and C-S(A)-H gels formation with Ca/Si ratio ≤ 0.6 under double decomposition method.

The main fact we can show is, although their Ca/Si are quite similar, as it can be seen by micro-Raman, FT-IR and NMR spectra, that there are differences in their structures. The structures are slightly different as the Ca/Si ratio increases; there is an enhancement of the intensity of Q^1 band, attributed to dimers formation. Medium chain length decreases with an increase of the Q^2 units and diminution of Q^1 units presents in the formed calcium silicate hydrate. Additionally, in both C-S-H and C-S(A)-H with Ca/Si ratio 0.5 the peak at -89 ppm is attributed to Q^3 units.

As the Ca/Si ratio increases, the ^{27}Al NMR signal shifts to a higher ppm values (65.7 and 71.8 ppm), in agreement with the presence of Al as part of the C-S-H gel structural skeleton.

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COMPLIANCE WITH ETHICAL STANDARDS

Conflict of interest. The authors declare that they have no conflict of interest.

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SUPPLEMENTARY MATERIAL

There are several ways to prepare C-S-H in the laboratory; following it is a summary of them with the references and characteristics of the synthesis process as well as the theoretical and experimental Ca/Si ratio.

i) Hydrothermally: mixing quartz and CaO at different temperatures (150°C, 80°C) and times (2, 133 days). Grangeon et al [*Cem Concr Res* 52 (2013) 31-37] prepared C-S-H gel with the tobermorite Ca/Si ratio. However, Marty et al [*Miner Magazine*, 79(2), (2015) 437–458] synthesized the samples with nominal Ca/Si ratios of 0.9, 1.4 and 1.5, but TEM and ATD/TG results show Ca/Si ratios of 0.8, 1.2 and 1.2 respectively.

ii) Mechanochemically: grinding stoichiometric mixtures of Ca(OH)_2 and SiO_2 (silicagel) in a planetary mill from minutes to hours according to the method of Saito et al. [*Solid State Ionics* 101-103 (1997) 37-43]. The Ca/Si ratio was 1.5 to synthesize afwillite or in the range 0.5-3.0 to synthesize tobermorite.

iii) A modification of the previous one which consist in grinding stoichiometric mixtures of CaO and amorphous silica in a rotating mill for two weeks followed by 20 months of hydration [*J. Am. Ceram. Soc.*, 95 [2] (2012) 793–798]. The nominal Ca/Si ratio varied between 0.6 and 1.75 and no information about the real composition of the C-S-H gel formed was included.

iv) Tri-calcium silicate hydration [*J. Phys. Chem. C*, 117 (2013) 22947–22953; *Physics and Chemistry of the Earth* 70–71 (2014) 17–31; *Cem Concr Res* 88 (2016) 136–143] at different ages from 7 to 120 days, or even 8 months [*Cem. Concr. Res.* 34 (2004) 1499–1519]. In this case, the determination of the initial Ca/Si ratio is impossible.

v) Tri-calcium silicate hydration with a lime-saturated solution and C-S-H gel seeds [*Cem. Concr. Res.* 68 (2015) 124–138] in order to get full C_3S hydration in a few days. The initial Ca/Si ratio was not determined.

vi) Hydration of stoichiometric mixtures of silica fume and CaO during 7 days [*Cem. Concr. Comp.* 36 (2013) 65–70] with initial Ca/Si values of 0.9, 1.2 and 1.5, that after TG results showed Ca/Si ratios of 0.7, 1.0 and 1.2 respectively. L'Hôpital et al [*Cem Concr Res* 85 (2016) 111–121] prepared C-S-H gels with initial Ca/Si ratios of 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6, which after 182 days of hydration were identified as >0.67, 0.8, 0.98, 1.17, 1.29 and 1.38 respectively.

vii) Pozzolanic reaction between amorphous SiO_2 and CaO in excess of water in a rotating rack for 1 week [*Materials and Structures* 44(2011) 13–28] or hydrating during four months [*Cem. Concr. Res.* 42(2012) 1534-1548]. The nominal Ca/Si ratios ranged between 0.8 and 1.5, while the stoichiometric ratios were 1.0 and 1.5 for both authors. None of the authors previously mentioned determined the real composition of the C-S-H gel formed.

viii) Dispersion of CaO in mineralized water and subsequent addition of colloidal silica dispersion to give the required Ca/Si ratio. The containers were sealed and shaken vigorously [*Mineralogical Magazine*, 76(8) (2012) 3045–3053] one month or non-determined [*Cem. Concr. Res.* 32 (2002) 731–746] until the gels begins to form. The target Ca/Si ratios ranged

from 0.2 to 0.6 for the first author and varied between 0.42 and 2.7 for the second one. The real Ca/Si ratios of the gels were not given in the papers.

ix) Double decomposition method: using sodium silicate and calcium nitrate solutions where the C-S-H gel precipitates immediately after mixing. The Ca/Si ratios for the initial solutions determined by Sun et al [*Cem Concr Res.* 36 (2006) 18–29] were 0.86, 1.16 and 1.4 but the analyses indicate compositions of 0.86, 1.14 and 1.26 respectively. However, García-Lodeiro et al [*J. Am. Ceram. Soc.*, 95 [4](2012)1440–1446] show larger discrepancies between the theoretical and the experimental values depending on the laboratory conditions. Therefore, they are more accurate for Ca/Si ratios of 1.0 and higher pH values (13) in inert atmosphere.

x) Hydrothermally: using CaO and amorphous SiO₂ with a chelating agent (EDTA) [*J. Eur. Ceram. Soc.* 23 (2003) 123–126] from 1 to 10 hours. The initial Ca/Si ratios ranged from 1.0 to 2.0 and the final ones were lower in all cases, from 0.64 to 0.84.

xi) Microwave synthesis: mixing a Ca(OH)₂ solution (pH adjusted to 13 with KOH) with silicic acid and another additional silicon source to adjust the Ca/Si ratio; i.e. borosilicate glass, quartz [*J. Mater. Chem. A*, 1(2013)10318] with and without EDTA during 7 days. The initial Ca/Si ratios ranged from 0.36 to 1.78 but in these conditions the Ca/Si ratio determined was higher than the initial one.

Experimental procedure to synthesis C-S(A)-H

i') Mixing SiO₂, CaO, and CaO·Al₂O₃ in excess of water, shaking twice per week until equilibrium was achieved and leaving 182 days at 25°C [*Cement and Concrete Research* 75(2015)91-103; *Cement and Concrete Research* 68(2015)83-93]. The Ca/Si ratio was 1.0 and the Al/Si ratio ranged from 0.05 to 0.15.

ii') Other authors used AlO(OH) as source of aluminium [*Cement and Concrete Research* 71 (2015)56-65]. The initial Ca/Si ratios were 0.6, 1.0 and 1.5 and the Al/Si ratio was 0.05. The samples were carbonated and the Ca/Si ratio was calculated under carbonation. No information was supplied for a reference sample without carbonation.

iii') Double decomposition method [*J. Am. Ceram. Soc.*, 95 [4](2012)1440–1446]: The initial Ca/Si ratios were 0.86, 1.18 and 1.40, and the silicon was replaced by aluminium in the following amounts: 7.5, 15 and 30%, keeping the Ca/(Al+Si) ratios in 0.86, 1.18 and 1.4. After 4 weeks, the Ca/(Al+Si) ratio decreased until 1.2 for the last sample, keeping the initial value for the other two samples.

iv') Previously synthesized C-S-H gel was added into solutions of freshly-filtrated C₃A [*Cement and Concrete Research* 39(2009)637-643]. The authors determined with this procedure that, pure C-S(A)-H can be synthesized only if the initial C-S-H gel has a Ca/Si ratio of 1.0.

v') Hydrothermally: mixing SiO₂, CaO and Al₂O₃ at 150°C. After heating during 3 hours or 4 days, the mixtures were quickly quenched within 30 minutes [*Geochemical Transactions* (2009)10]. The initial Ca/(Al+Si) and Al/(Al+Si) ratio were 0.83 and 0.15 respectively.

Table 1 in the main text shows the main references for C-S-H gel synthesis and the Ca/Si ratio determination as well as the experimental procedure followed for those determinations.

Table S1. Amounts of starting materials (mol), pH solution and theoretical Ca/Si ratios.

C-S-H gel		C-S(A)-H gel			Ca/Si _{th}
Ca(NO ₃) ₂ ·4H ₂ O	Na ₂ SiO ₃ ·5H ₂ O	Ca(NO ₃) ₂ ·4H ₂ O	Na ₂ SiO ₃ ·5H ₂ O	Al(NO ₃) ₃ ·9H ₂ O	
0.50	1.00	0.50	1.00	0.030	0.5
0.60	1.00	0.60	1.00	0.030	0.6
0.80	1.00	0.80	1.00	0.030	0.8
0.50	0.50	0.50	0.50	0.015	1.0
0.55	0.50	0.55	0.50	0.015	1.1
0.65	0.50	0.65	0.50	0.015	1.3
0.75	0.50	0.75	0.50	0.015	1.5
0.80	0.50	0.80	0.50	0.015	1.6
0.90	0.50	0.90	0.50	0.015	1.8
1.00	0.50	1.00	0.50	0.015	2.0

Figure S1 shows the FTIR spectra of C-S-H and C-S(A)-H gels with the Ca/Si ratio of 0.5; 1 and 2 in the interval 2000-400 cm⁻¹.

Figure S1 FT-IR spectra of C-S-H (top) and C-S(A)-H (bottom) with different Ca/Si ratio

The mid-IR spectra (Figure S1) of both C-S-H and C-S(A)-H gels with Ca/Si ratio 1, are comparable to those that appear in the literature [40-41]. The most intense band for both gels appears at 900-1200 cm^{-1} . This strong band is a convoluted group of bands related to the symmetric and asymmetric stretching vibrations (Si-O) of Q^2 tetrahedra [41].

Besides, there are other bands that enable us to determine the presence of both gels such as 838 cm^{-1} (stretching SiCa-O of Q_B^2), 811 cm^{-1} (Si-O SS of Q^1), and 665 cm^{-1} (bending Si-O-Si). According to Yu [41] the Si-O-Si bending band decreases in intensity for samples with Ca/Si higher than 1.19. This cannot be observed in our samples, as the nominal Ca/Si ratio is similar and always lower than 1.1.

As the nominal Ca/Si ratio increases, for both C-S-H and C-S(A)-H, a small band at 811 cm^{-1} appears due to Q^1 units formation in agreement with Raman results where Q^1 units increases with the Ca/Si ratio.

Besides, there are other subtle modifications in the zone of SiO_4 internal deformations. The most important is the shift to lower frequencies of the band located at 446 cm^{-1} in the C-S-H gel, which is centered at 440 cm^{-1} in the C-S(A)-H gel. Another minor difference is associated to a shoulder that appears in both gels at 459 cm^{-1} , which is better defined in the C-S-H gel.

In addition, the identification of crystalline (calcite) and amorphous calcium carbonate is possible because of the bands located at 1486 , 1419 and 872 cm^{-1} [39]. This information is in line with Micro-Raman results.

Fig S2 FT-IR spectra of C-S-H and C-S(A)-H gels with Ca/Si ratio of 1.0. On the top left hand corner, enlarged view of the zone $900\text{--}1100 \text{ cm}^{-1}$

Figure S3.- Deconvolution of the ^{29}Si NMR spectra of the C-S-H with Ca/Si ratios 0.5; 1 and 2

Figure S4.- Deconvolution of the ^{29}Si NMR spectra of the C-S(A)-H with Ca/Si ratios 0.5; 1 and 2