1 *IN-SITU* REACTION OF THE VERY EARLY HYDRATION OF C₃A-GYPSUM-SUCROSE SYSTEM BY
2 MICRO-RAMAN SPECTROSCOPY.

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4 Sagrario Martínez-Ramírez^{*,1}, Rocio Gutierrez-Contreras¹, Nuria Husillos-Rodriguez², Lucia
5 Fernández-Carrasco³

6 ¹Instituto de Estructura de la Materia (IEM-CSIC), C/Serrano 121, 28006 Madrid, Spain

7 sagrario.martinez@csic.es (S. Martinez-Ramirez); rocio.gutierrez@io.cfmac.csic.es (R. Gutierrez-
8 Contreras)

9 ²Instituto de Ciencias de la Construcción Eduardo Torroja (IETCC-CSIC), C/Serrano Galvache 4,
10 28033 Madrid, Spain

11 nuriashr@hotmail.es

12 ³Universidad Politécnica de Catalunya, Departament de Construccions Arquitectòniques I,
13 08028 Barcelona

14 lucia.fernandez@upc.edu

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16 ABSTRACT

17 This paper studied *in situ*, by Micro-Raman spectroscopy, the very early hydration of C₃A in the
18 presence and absence of sulphates and with sucrose as an additive. For C₃A hydration in the
19 absence of gypsum, when carbonation is not avoided, carbonate-AFm phases are formed, but in
20 the presence of gypsum, hydroxi-AFm are the main phases. Ettringite is the AFm stable phase
21 developed initially at 70 minutes of hydration with gypsum and no monosulphate is formed. In
22 the presence of sucrose, this salt, instead of sulphate, is adsorbed over the surface of the C₃A,
23 avoiding its reaction with sulphates until sucrose desorption. Three hours are necessary to
24 lead to ettringite formation. A nucleation poisoning/adsorption surface mechanism is proposed
25 for added sucrose systems.

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*Corresponding author: Instituto de Estructura de la Materia, C/Serrano 121, 28006 Madrid, Spain; Tel.: +34 915656800; Fax.: +34 915645557; e-mail: sagrario.martinez@csic.es

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1INTRODUCTION

The characterization of the very early hydration of cement is difficult, since fresh cement pastes are highly reactive and most materials characterization techniques (i.e. XRD, SEM, etc.) present some difficulties with the analysis of humid samples; moreover, the early developed phases must be altered when removing the free water. Drying of the cement samples, removes free water but also can degrade ettringite, monosulphate and carboaluminate phases. In addition, solvent exchange methods produce replacement of free water by an organic solvent that also can be absorbed into the surface of the phases [1-4]. Thus, alternative procedures should be proposed in order to avoid any change in the sample composition. In this context, Micro-Raman spectroscopy is a very useful technique since no sample preparation is needed and *insitu* experiments can be performed without sample transformation.

Tri-calcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$, C_3A) is the most reactive phase of Portland cement (PC) that reacts with water, producing a rapid setting due to formation of metastable hexagonal hydrates (C_4AH_{13} and C_2AH_8), that evolves towards a stable phase, cubic hydrogarnet [5], C_3AH_6 . A setting regulator, usually gypsum, is added to cement in order to control the rapid setting, the C_3A reaction with calcium sulphate leading to ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) formation. The mechanism controlling the first stage of the C_3A -gypsum reaction is the adsorption of calcium and sulphate ions on active dissolution sites of C_3A . That slows down the rate gradually due to the reduction of the surface area of C_3A as the particles dissolve [6-9].

Admixtures can be added to cement in order to modify normal properties; in particular retarders inhibit the setting and hardening of concrete. Sucrose, one of the most commonly used retarders, is an effective hydration inhibitor because it selectively adsorbs at C_3A surfaces, with its ring structure intact, resulting in higher local surface coverage [10].

However, it has been reported that in the presence of gypsum, the sucrose accelerates ettringite formation[11].

Additives and sulphates, both, can be absorbed in the active sites of C_3A avoiding or promoting the retarding effect or ettringite formation. It is not clear the effect of both sucrose and gypsum in the hydration of C_3A . In the present paper, Micro-Raman spectroscopy has been used to study *in situ*, in real time, the very early hydration of C_3A , with and without gypsum, in a sucrose solution, without removing the free water from the sample. In this way the introduction of possible changes in the early age hydration products such as ettringite and monosulfate due to sample preparation can be avoided. This research investigates the mechanism in which the sulphates compete with sucrose for C_3A active points, in the early stages of hydration.

2 EXPERIMENTAL

C_3A was synthesized using stoichiometric proportions of aluminum oxide and calcium oxide. The obtained powder was ground by hand, pressure-pelletized, and heated in a platinum crucible at temperatures ranging from 1200 to 1400°C, as explained by Torrns-Martn et al.[12]. Differential Thermal Analysis combined with Thermogravimetric analysis (DTA/TG)(Q600 TA Instruments) of the initial C_3A was done in order to determine the purity, which means the amount of portlandite and/or calcite present in the samples.

For the experiments, four samples were prepared. Two of them had pure C_3A , and the other two had a prepared mixture of C_3A and gypsum from Merck (9:1). The samples were prepared following the procedure proposed by Black et al.[13]. They were hydrated with either decarbonated water or a 0.05% sucrose solution. The selected liquid/solid ratio was 0.3 (simulating the w/c ratio in a cement mixture). In these systems, the changes produced upon hydration were studied by Raman spectroscopy, using a confocal Raman microscope (Renishaw Invia), that had a Renishaw Nd:YAG 532 nm laser, a Leica microscope, and a thermoelectrically cooled CCD camera. The spectra were obtained using a 50x0.75 objective lens resulting in a laser beam size at the sample of the order of 2 μm . The laser output was 5

mW, and the exposure time 10s. All the spectra were normalized to their maximum. In order to analyse the spectra obtained, two software applications were used: WIRE for Windows for data collection and OriginPro 8 for spectra analysis. The spectral region scanned was 4000-100 cm^{-1} . Spectra were taken at two different points for each sample to minimize any lack of sample uniformity. Raman spectra of the samples were recorded over a period of 3 hours maximum (5 seconds, 10, 20, 30, 40, 50, 60, 70 minutes and 3 hours). However, only certain time intervals were selected for inclusion in this paper.

The possibility of carbonation was not controlled during the experiments in order to follow the real hydration conditions.

During the experimental analysis it was proved that the reproducibility of the spectra was good for hydrated samples with water; however, more variability was achieved for samples in presence of sucrose. For this reason, in these cases the spectra were recorded on two different days. As supplementary material all the acquired spectra are present (Figures S1-S20).

The samples $\text{C}_3\text{A} + \text{gypsum} + \text{H}_2\text{O}$ and $\text{C}_3\text{A} + \text{gypsum} + \text{sucrose}$, were mixed and examined under environmental scanning electronic microscopy with energy dispersive spectrometer (ESEM/EDS, QUANTA-2000) at 28KV using low vacuum mode (9.2 Torr) with a peltier temperature of 10°C in order to maintain 100% R.H. Under these conditions, we expect to study the reaction *in situ* in similar conditions as those in the Micro-Raman studies.

3 RESULTS AND DISCUSSION

The most representative bands of the different phases found in this study, as well as the spectra of synthetic phases, are collected in Table 1.

3.1 C_3A hydration

The assignment of the spectra of the anhydrous cubic C_3A (Figure 1) is based on isolated six-membered rings of AlO_4 tetrahedra [15]. The Raman spectrum exhibits several modes in the range of 150–1000 cm^{-1} , which are assigned to Al–O framework vibrations. The most dominating modes at 506 cm^{-1} and 754 cm^{-1} are attributed to a ν_3 and ν_1 [AlO_4^{5-}] respectively.

The group of weaker bands, which appears between 150 cm^{-1} and 400 cm^{-1} , are assigned to doubly and triply degenerated oxygen frameworks. Small amount of impurities of CaCO_3 (0.46%wt) and Ca(OH)_2 (0.84%) have been determined by DTA/TG (Figure 2), however CaCO_3 signals were not identified in the Raman spectra of the initial sample due to its low concentration. Immediately upon hydration of C_3A with water, several changes can be observed in the $4000\text{--}3000\text{ cm}^{-1}$ interval with two bands growing in intensity (Figure 3). The sharp peak at 3617 cm^{-1} due to OH present in portlandite [13] (impurity) disappears upon hydration and a broad band with two maximums at 3676 and 3683 cm^{-1} that can be associated to carbonated phases monocarboaluminate and/or hemicarboaluminate, respectively appears [12]. Carbonation is produced because of the atmospheric CO_2 . These peaks were found to shift to higher frequencies with time. In the interval $1100\text{--}100\text{ cm}^{-1}$ all the spectra contain the main bands from un-hydrated C_3A . A band at 1067 cm^{-1} that is caused by C-O-C bending for the carbonate groups present in the carboaluminate phase [12, 13] is also found in the spectra (Supplementary Material Figure S21). No evidences of C_3AH_6 are detected at this early stage of hydration (70 minutes). The vibrational modes of OH for C_3AH_6 appear at 3650 cm^{-1} [12] and for hydroxi-AFm phases at 3620 and/or 3610 cm^{-1} , [12]. Neither katoite nor hydroxi-AFm phases (C_4AH_{13} or C_2AH_8) have been observed in the very early hydration of the C_3A . However, only carbonate-AFm phases were detected due to atmospheric CO_2 absorption during hydration. Similar carbonation was previously described after 24 hours of hydration of 80% (wt) C_3A + 20% (wt) CaCO_3 at room temperature [16]. In the same way, Black et al. [13] studied for 24 hours C_3A hydration either in the presence or in the absence of gypsum, and C_4AH_{19} was identified in the sample hydrated in the absence of sulphates while the samples hydrated with gypsum presented monocarboaluminate and/or hemicarboaluminate phases. In the same manner and according to experimental results, Matschei et al. [17] concluded that, phases like hemicarboaluminate can precipitate in the C_3A hydration when the stoichiometry follows a

carbonate molar ratio of $0.2 < (\text{CO}_3/\text{CO}_3+2\text{OH}) < 0.8$. Then in these samples, atmospheric CO_2 will promote CO_3 -AFm formation against hydroxi-AFm phases.

The Micro-Raman spectra of the OH stretching region of the C_3A hydrated in sucrose solution (0.05% w/w) for the first 70 minutes are shown in Figure 4 (3800-3450 cm^{-1} interval) (interval 1200-400 cm^{-1} is shown in supplementary material S22). Raman bands are observed at 3540 cm^{-1} (broad and weak), 3618 cm^{-1} (sharp and weak, from impurity of $\text{Ca}(\text{OH})_2$), 3625 cm^{-1} (shoulder), 3675 cm^{-1} (medium and broad) and 3680 cm^{-1} (shoulder) (Figure 4). The low amount of portlandite must be due to its complexation with sucrose [18]. The main difference between samples of C_3A with water or sucrose solution is that the evolution from monocarboaluminate to hemicarboaluminate is low in sucrose solution. After 70 minutes of hydration, the broad peak, for the sample hydrated in sucrose solution, has the maximum at 3679 cm^{-1} with a shoulder at 3680 cm^{-1} ; however the sample hydrated with water has a broad band with the maximum at 3683 cm^{-1} indicating that monocarboaluminate formation is higher than hemicarboaluminate (Supplementary Material Figure S23). From Torrns-Martn et al [12] as was the case for the samples hydrated with water, neither of the peaks related to katoite (C_3AH_6) (3650 cm^{-1}) [12] nor hydroxi-AFm phases (3620 and/or 3610 cm^{-1}) [12] were detected. Sucrose is stable in alkaline cement solutions and is selectively adsorbed at C_3A surfaces delaying its hydration [10, 19]. This selective adsorption can also modify the reaction of C_3A with atmospheric CO_2 and lead to more monocarboaluminate formation.

3.2 C_3A + gypsum hydration

The evolution of the Micro-Raman spectra of very early hydration of C_3A + 10% gypsum shows that upon the first 5 seconds of contact (Figure 5), a new weak band at 1007 cm^{-1} , associated to the $\nu_1[\text{SO}_4^{2-}]$ symmetric stretching mode in gypsum appears. Additionally, two new signals as broad bands appear, the first one at 988 cm^{-1} associated to $\nu_1[\text{SO}_4^{2-}]$ in ettringite, which appears after 5 s, and the second one at 530-520 cm^{-1} . The second one is a broad band ranging from 530 to 520 cm^{-1} . Assignment of this broad band is more difficult since no bands in the

4000-3000 cm^{-1} interval are observed (Figure S15 in Supplementary Material). We can postulate an intermediate phase or a non-crystalline ettringite formation coming from the absorption of sulphates over the C_3A . This metastable phase together with gypsum depletion and a very low amount of ettringite formation can be in agreement with Quenoz[6] who suggested that the hydration rate during the first stage of the C_3A + gypsum reaction is controlled by the absorption of sulphate and calcium ions on active sites over the surface of the C_3A .

The microstructure of the sample C_3A + gypsum hydrated with water (ESEM), shows, the presence of small needles (Figure 7a), the EDS analysis over 10 points indicates a Ca/Al ratio of 4.3 and Al/S of 1.1 (Table 2). For ettringite, Ca/Al ratio is similar, but Al/S ratio is lower, then it can be confirmed as a metastable phase formation.

Comparing C_3A at very early hydration in presence and absence of gypsum it is clear that when no sulphates are present (but carbonation is not avoided), carbonate-AFm phases are formed, but in the presence of gypsum, AFt are the main phases. Ettringite is the AFt stable phase for the 70 minutes of hydration with gypsum and no monosulphate is formed.

The effect of the sucrose addition to the C_3A + gypsum system can be followed in Figure 6. The main difference arises from the fact that the gypsum signal is present in all the samples, with a weak intensity peak associated to ettringite formation observed by the $\nu_1[\text{SO}_4]$ band. No bands from the formation of C_3AH_6 are observed. A relatively high signal of $[\text{SO}_4]$ in gypsum, indicates that sucrose decreases the hydration of C_3A as well as its reaction with gypsum. The spectra have been normalized to the maximum, so intensity of the peaks can give us semi-quantitative information about the relative amount of the phases present in the sample.

For the samples C_3A + gypsum in 0.05% sucrose solution, peaks from C_3A decrease with time, however no new crystalline phase formation is observed. After 3 hours of reaction, the gypsum band decreases dramatically and ettringite starts to be formed (Figure 6b). In the presence of sucrose, this compound, instead of sulphate, is selectively adsorbed over the surface of the

C₃A[10, 19], avoiding its reaction with sulphates until sucrose desorption. Three hours are necessary for ettringite formation and this is a possible explanation for the delayed hydration in the presence of sucrose.

Bishop et al.[11] had some doubts about the mechanism of sucrose acting as a retarder since they considered that potentially either a nucleation poisoning/surface adsorption or calcium chelating mechanism may explain the inhibition of hydration. From our results we can propose a nucleation poisoning /adsorption surface mechanism.

Microstructural analysis of the sample over the first 30 minutes (ESEM, Figure 7b) shows that no ettringite was formed and only small particles with high calcium and aluminium and low sulphur content are present (Table 2). This can confirm the previous results [10] of sucrose adsorption over the calcium aluminate.

Table 3 summarizes the phases identified at the very early hydration of C₃A in the presence of gypsum and sucrose. It can be observed that in the presence of sucrose and gypsum, no sulphates have been adsorbed at the C₃A active points in the very early hydration stage and gypsum is present during the first 70 minutes of hydration.

4 CONCLUSIONS

In this manuscript, the effect of sucrose on the very early hydration of C₃A with and without gypsum and in conditions allowing the exposure of samples to ambient CO₂ was followed *in situ* by Micro-Raman spectroscopy. No manipulation of the samples was necessary resulting in no modification of the hydration compounds. In the case of samples without gypsum and hydrated with sucrose solution, monocarboaluminate to hemicarboaluminate evolution was low when compared to the samples hydrated with water.

When gypsum is present in the C₃A hydration, adsorption of sulphate over the C₃A produces an intermediate phase previous to ettringite formation. In the presence of sucrose, this salt instead of sulphate is adsorbed, poisoning over the surface of the C₃A, and no sulphate hydration products are formed until 3 hours.

ESEM/EDS show that needles have been formed in the sample hydrated with water, with a low amount of Al and a high amount of sulphur. For the samples hydrated with sucrose, no needles were formed and the sulphur present in the particles was very low.

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264 Figure 1.-Raman spectra of anhydrous C_3A (laser $\lambda = 532$ nm).

265 Figure 2.-DTA/TG of the initial C_3A .

266 Figure 3.- Micro-Raman spectra of early hydration of C_3A in water (laser $\lambda = 532$ nm). CH =
267 $Ca(OH)_2$.

268 Figure 4.- Micro-Raman spectra of early hydration of C_3A in 0.05% sucrose solution (w/w) (laser
269 $\lambda = 532$ nm). CH = $Ca(OH)_2$; mCA = monocarboaluminate.

270 Figure 5.- Micro-Raman spectra of early hydration of C_3A + 10% gypsum (laser $\lambda = 532$ nm).Et =
271 ettringite; G = gypsum.

272 Figure 6.- Micro-Raman spectra of early hydration of C_3A + 10% gypsum in 0.05% sucrose
273 solution (w/w) (laser $\lambda = 532$ nm) a) from 5 to 70 minutes; b) 3 hours.Et = ettringite; G =
274 gypsum.

275 Figure 7.- ESEM image of the C_3A + gypsum a) hydrated with water and b) hydrated with
276 sucrose solution.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6a (left) and 6b (right)

Figure 7a (left) and 7b (right)

Table 2.- Ca/Al, Al/S and Ca/S (%wt) ratio calculated by Energy Dispersed Spectrometer (EDS)
in samples hydrated 30 minutes

sample	Ca/Al (%wt)	Al/S (%wt)	Ca/S (%wt)
C ₃ A + gypsum + H ₂ O	4.3	1.1	4.5
C ₃ A + gypsum + sucrose	3.2	4.5	14.3
Ettringite (Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O)	4.4	0.6	2.5
C ₃ A	2.2	--	
CaSO ₄ ·2H ₂ O			1.2

Table 3.- Main phases detected by in situ Micro-Raman spectroscopy at different times

	Time (minutes)			
	5	20	30	70
C ₃ A + H ₂ O	hCA mCA	hCA↑↑ mCA↓↓	hCA↑↑ mCA↓↓	hCA↑↑ mCA↓↓
C ₃ A + sucrose + H ₂ O	mCA	mCA	mCA	mCA
C ₃ A + gyp + H ₂ O	Gyp↓	ett↓	Ca, SO ₄ adsorbed C ₃ A	Ca, SO ₄ adsorbed C ₃ A
C ₃ A + gyp + sucrose + H ₂ O	Gyp ett↓	Gyp ettr↓	Gyp ett↓	Gyp ett↓

mCA = monocarboaluminate; hCA= hemicarboaluminate; Gyp = gypsum; Ett = ettringite

301 Table 1.- Main vibration bands for anhydrous and hydrated phases that can be formed in C₃A hydration and the main bands observed in the Raman spectra
 302 of the samples.

Synthetic samples							Studied phases							
C ₃ A [12, 14]	C ₃ AH ₆ [5]	ett [12, 13]	C ₄ AH ₁₃ / C ₂ AH ₈ [12, 13]	mCA [12,13]	hCA [12, 13]	CaSO ₄ [14]	C ₃ A+H ₂ O		C ₃ A+ sucrose		C ₃ A+gypsum+H ₂ O		C ₃ A+gypsum+sucrose	
							5 minutes	30 minutes	5 minutes	30 minutes	5 minutes	30 minutes	5 minutes	30 minutes
	3651s	3642	3650	3675s 3652 3627	3685s 3659 3592		3683sh 3675s	3683s 3675sh	3683sh 3674s	3674s				3683m
		3458	3530	3540					3540sh	3540sh				3566m
				1067s	1067s	1015vs	1067w	1067w	1067w	1067m			1015s	1015m
754vs		989vs					754s	754s	754s	754s	989w 754s	989w 754w	986w 770 755m	986w 754m
508s	540	605 550		530		676 627 609 499 417	529m 508s	529m 508s	529w 508m	530m 508w	508m	510-520b	508m	522b 508w

303 vw, very weak; s, strong; m, medium; b, broad; w, weak; sh, shoulder; vs,very strong.

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