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# *In-situ* reaction of the very early hydration of $C_3A$-gypsum-sucrose system by Micro-Raman spectroscopy

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## ABSTRACT

This paper studied *in situ*, by Micro-Raman spectroscopy, the very early hydration of $C_3A$ in the presence and absence of sulphates and with sucrose as an additive. For $C_3A$ hydration in the absence of gypsum, when carbonation is not avoided, carbonate-AFm phases are formed, but in the presence of gypsum, hydroxi-AFm are the main phases. Ettringite is the AFm stable phase developed initially at 70 min of hydration with gypsum and no monosulphate is formed. In the presence of sucrose, this salt, instead of sulphate, is adsorbed over the surface of the $C_3A$, avoiding its reaction with sulphates until sucrose desorption. Three hours are necessary to lead to ettringite formation. A nucleation poisoning/adsorption surface mechanism is proposed for added sucrose systems.

## 1. Introduction

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 *in situ* experiments can be performed without sample transformation.

Tri-calcium aluminate ($3CaO\cdot Al_2O_3$, $C_3A$) 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 ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) 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

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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 synthetized using stoichiometric proportions of aluminum oxide and calcium oxide. The obtained powder was grounded by hand, pressure-pelletized, and heated in a platinum crucible at temperatures ranging from 1200 to 1400 °C, as explained by Torréns-Martín 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 el 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 50 × 0.75 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 10 s. 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 h maximum (5 s, 10, 20, 30, 40, 50, 60, 70 min and 3 h). 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 $C_3A$ + gypsum + $H_2O$ and $C_3A$ + gypsum + sucrose, were mixed and examined under environmental scanning electronic microscopy with energy dispersive spectrometer (ESEM/EDS, QUANTA-2000) at 28 KV 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.

**Table 1**

Main vibration bands for anhydrous and hydrated phases that can be formed in $C_3A$ hydration and the main bands observed in the Raman spectra of the samples.

| Synthetic samples | | | | | | | Studied phases | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3A$ [12,14] | $C_3AH_6$ [5] | ett [12,13] | $C_4AH_{13}/C_2AH_8$ [12,13] | mCA [12,13] | hCA [12,13] | $CaSO_4$ [14] | $C_3A + H_2O$ | | $C_3A$ + sucrose | | $C_3A$ + gypsum + $H_2O$ | | $C_3A$ + gypsum + sucrose | |
| | | | | | | | 5 min | 30 min | 5 min | 30 min | 5 min | 30 min | 5 min | 30 min |
| | | | | | **3685s** | | 3683sh | **3683s** | 3683sh | | | | | 3683m |
| | | | | **3675s** | | | **3675s** | 3675sh | **3674s** | **3674s** | | | | |
| | | | | | 3659 | | | | | | | | | |
| | **3651s** | | 3650 | 3652 | | | | | | | | | | |
| | | 3642 | | | | | | | | | | | | |
| | | | | 3627 | | | | | | | | | | |
| | | | | | 3592 | | | | | | | | | |
| | | | | | | | | | | | | | | 3566m |
| | | | 3530 | 3540 | | | | | 3540sh | 3540sh | | | | |
| | | 3458 | | | | | | | | | | | | |
| | | | | **1067s** | **1067s** | | 1067w | 1067w | 1067w | 1067m | | | | |
| | | | | | | **1015vs** | | | | | | | **1015s** | 1015m |
| | | **989vs** | | | | | | | | | 989w | 989w | 986w | 986w |
| | | | | | | | | | | | | | 770 | |
| **754vs** | | | | | | | **754s** | **754s** | **754s** | **754s** | **754s** | 754w | 755m | 754m |
| | | | | | | 676 | | | | | | | | |
| | | | | | | 627 | | | | | | | | |
| | | | | | | 609 | | | | | | | | |
| | | 605 | | | | | | | | | | | | |
| | 540 | 550 | | 530 | | | 529m | 529m | 529w | 530m | | 510-520b | | 522b |
| 508s | | | | | | | 508s | 508s | 508m | 508w | 508m | | 508m | 508w |
| | | | | | | 499 | | | | | | | | |
| | | | | | | 417 | | | | | | | | |
| | 327 | | | | | | | | | | | | | |

vw, very weak; s, strong; m, medium; b, broad; w, weak; sh, shoulder; vs, very strong.
Bold numbers are for the main bands used for compounds identification.