

Impact of Cellulose Ethers on the C₃S Hydration

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1. Introduction

Cellulose ethers are of universal use in ready-mix mortar formulations. These admixtures allow the fresh mortar to be adjusted at the desired level workability and water retention capacity. However, cellulose ethers also induce a retarding effect on cement hydration processes which is not perfectly understood. Therefore, this research program aims at collecting physico-chemical data so as to improve our knowledge of interactions between cement and cellulose ethers.

In this frame, preliminary researches have demonstrated that the retardation phenomenon mainly depends on the substitution degree of the molecules [1,2]. It has also been shown that cellulose ethers are very stable in alkaline media [3]. Finally, identification and quantification of the hydroxy carboxylic acids generated during alkaline degradation indicated that the influence of cellulose ethers degradation on hydration kinetics is not significant.

However, these results are not sufficient to establish an interaction mechanism. As a result, the main issue of this paper deals with the impact of cellulose ethers on the C₃S hydration. More precisely, our goal is to examine the influence of cellulose ethers specifically on dissolution step of the anhydrous phase C₃S, and on nucleation-growth step of the hydrated phase C-S-H.

2. Materials

2.1. Mineral phase

The C₃S phase used for this study was supplied by Lafarge Company (France). X-ray diffraction analysis (Siemens, D 5000, Germany) allowed to put in evidence a very low content of free lime (approximately 0.5 wt %). The surface area was analyzed by nitrogen adsorption in a Micromeritics ASAP 2000 nitrogen adsorption apparatus. The samples measured were degassed at 100 °C before the measurements. A surface area of $0.92 \pm 0.02 \text{ m}^2 \cdot \text{g}^{-1}$ was determined by the multipoint BET method using the adsorption data.

2.2. Organic compounds

Even if the most widespread cellulose ethers used in building materials are hydroxyethylmethyl cellulose (HEMC) or hydroxypropylmethyl cellulose (HPMC), hydroxyethyl cellulose (HEC) is also chosen in this study because of its more simple chemical structure. One HEC molecule (noted H1) and one HPMC (named U2) were selected. Beforehand, a precise characterization was performed (Table 1) by size exclusion chromatography and near infra red spectroscopy analysis [1]. It allowed to quantify the structure parameters, *i.e.* the weight-average molecular mass (M_w) the content of hydroxy ethyl substitution groups (% EOOH), the content of hydroxy propyl substitution groups (% POOH) and the content of methoxyl substitution groups (% OCH₃).

Table 1: Cellulose ether structure parameters.

Admixtures	M_w (daltons)	% EOOH	% POOH	% OCH ₃
HPMC U2	955 000	-	10.65	27.5
HEC H1	175 000	48.5	-	-

3. Methods and experimental procedures

3.1. Growth-nucleation process of C-S-H

The C-S-H precipitation occurs via a growth-nucleation process. The kinetics of C-S-H formation was perfectly elucidated by Garrault et al. [4-6] The rate of C-S-H formation follows a sigmoid law due to the C-S-H growth which gradually creates a diffusion barrier around the C₃S grain. As a result, two kinetic stage of C₃S hydration can be observed.

The first kinetic stage corresponds to the free growth of C-S-H at the surface of the C₃S grain. The C-S-H growth proceeds by agglomeration of nanometric thin elements. The lime concentration in solution is the key parameter which controls the rate of this agglomeration. The lower the lime concentration, the faster the C-S-H growth rate parallel to the C₃S surface. On the contrary, the higher the lime concentration, the faster the C-S-H growth rate perpendicular to the C₃S surface (Fig 1).

When a continuous C-S-H layer appears, the second kinetic stage begins. A significant slowing down of the hydration rate occurs, since the second kinetic stage of C₃S hydration is limited by the diffusion of ionic species through the C-S-H layer.

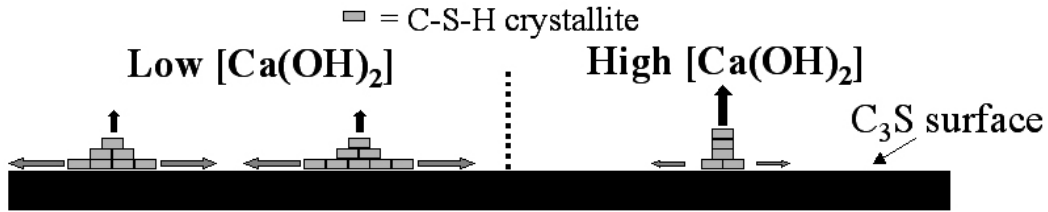


Fig 1: Variation of C-S-H growth, *i.e.* nanometric elements agglomeration, as a function of the lime concentration in solution

Moreover, the lime concentration change also the permeability of the continuous C-S-H layer obtained. The duration of the diffusion period through the C-S-H layer decreases when the lime concentration increases. Therefore, at low lime concentrations, the C_3S grain is covered rapidly with a layer of C-S-H that is thin and few permeable. In contrast, at high lime concentrations, the C_3S grain is covered slowly with finally a thick and high permeable continuous layer of C-S-H that is thick and highly permeable.

3.2. Protocols based on conductometric experiments

Conductometric measurement in various limewater concentrations appears as a powerful tool to monitor the different kinetic stage of the C-S-H growth (Figure 2). As a general rule, the experiments were performed in diluted limewater suspension, thermostated at 25 °C and continuously subjected to stirring. The liquid to solid mass ratio (noted L/S) and the polymer to solid mass ratio (noted P/S) are adapted for each protocol specifically developed to underline the impact of admixtures on dissolution or growth-nucleation process.

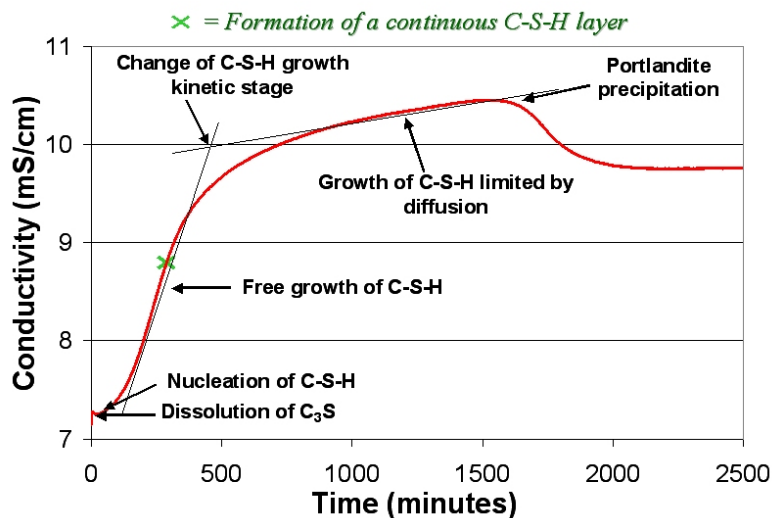


Fig 2: Different steps of the C_3S hydration process (L/S= 160)

The dissolution kinetics of C_3S is monitored by conductometry in dynamic argon environment to prevent carbonation. Actually, the conductivity of the solution is directly proportional to the concentration of calcium and silicate. To avoid reaching the critical supersaturation with respect to C-S-H and consequently its precipitation, a high L/S ratio (5000 or 130 000) was used. These specific hydration conditions allow only one physico-chemical phenomenon to be followed: the C_3S dissolution process.

3.3. Adsorption isotherms

Adsorption isotherms of cellulose ethers on mineral phases were also performed. The protocol developed was based on the quantitative determination of cellulose ethers by a phenol-sulfuric acid method. Given the lack of simple and more specific colorimetric reactions for cellulose ether, the phenol-sulfuric acid method appears as a useful approach. The basic protocol described by Cuesta et al [7] consist in determining the absorbances at 490 nm in a UV/Visible spectrophotometer.

4. Impact of cellulose ethers on C_3S dissolution process

Conductometric experiments with a L/S ratio equal to 5000 and a cellulose ether concentration of 1 g.L^{-1} were performed. The dissolution kinetics in these hydration conditions perfectly emphasize that the cellulose ethers studied have a minor impact on the rate of dissolution of C_3S (Fig 3). A negligible influence of cellulose ethers on the dissolution rate of C_3S is also observed for different experimental conditions with a limewater concentration at 10 mM and a L/S ratio equal to 130 000.

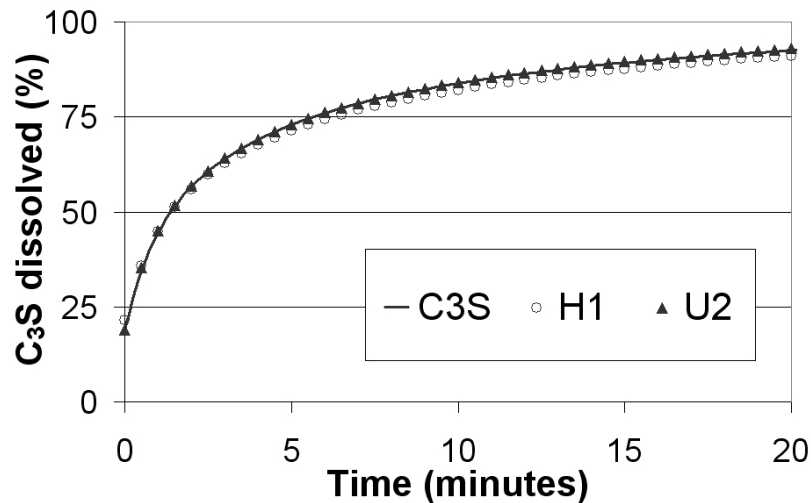


Fig 3: Dissolution kinetics of C_3S in the presence of cellulose ethers at a concentration of 1 g.L^{-1} (water to C_3S mass ratio is equal to 5000)

5. Impact of cellulose ethers on C-S-H nucleation process

During the C_3S hydration, the spontaneous primary nucleation of C-S-H occurs when the composition of the liquid phase reaches the critical supersaturation level with respect to C-S-H. In later time, the initial C-S-H nuclei grow at the C_3S surface thanks to an agglomeration process of nanometric thin elements. The initial amount of C-S-H which precipitates can be calculated with the variation of silicate concentration as a function of time [8]. The impact of cellulose ethers on the gap of silicate concentration and the amount of initial C-S-H nuclei are given in Table 2. In the presence of cellulose ether, a slowing down of initial C-S-H nucleation occurs undoubtedly.

Table 1: Impact of cellulose ethers on primary nucleation of C-S-H (C_3S hydration with L/S equal to 100, P/S equal to 2% and 100 mL of lime solution at 10 mM).

	$\Delta [H_2SiO_4^{2-}] (\mu mol.L^{-1})$	Quantity of initial C-S-H nuclei (μmol)
C_3S	15.50 ± 0.50	3.10 ± 0.10
$C_3S + HPMC U2$	12.50 ± 0.50	2.50 ± 0.10
$C_3S + HEC H1$	8.50 ± 0.75	1.45 ± 0.15

6. Impact of cellulose ethers on C-S-H growth process

The hydration of C_3S was performed in a limewater concentration of 15 mM. In the presence of H1, the conductivity curves show that this cellulose ether significantly retards the formation of the continuous C-S-H layer around the C_3S grain. As a matter of fact, the maximum-curvature point of the conductivity curve, corresponding to the change of C-S-H growth kinetic stage, was observed later in presence of cellulose ether (Fig 4).

As a result, cellulose ethers have a great impact on C-S-H growth. More precisely, additional experiments indicate that the thickness of the C-S-H layer and the permeability through this layer increase for high content of polymer. This observation let to think that cellulose ethers slow down the growth rate of C-S-H parallel to the C_3S grain surface.

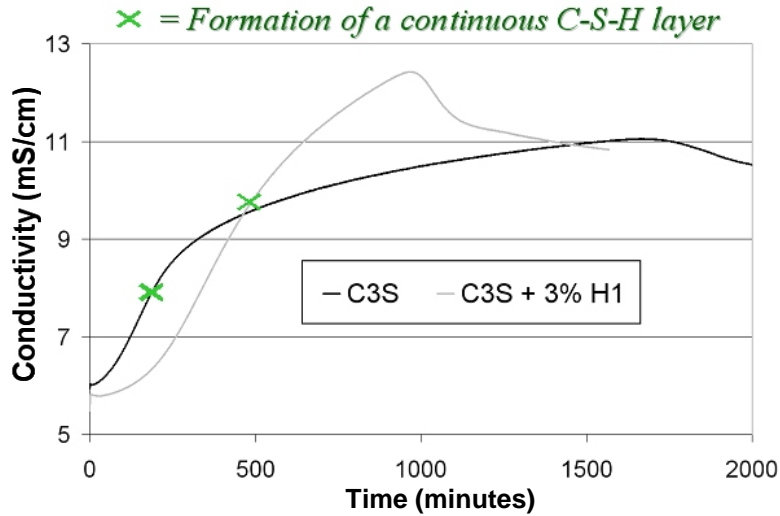


Fig 4: Hydration of C_3S in limewater at 15 mM (L/S is equal to 100)

The impact of cellulose ethers on the growth rate perpendicular or parallel to the C_3S surface were also determined by AFM experiments. The protocol consists in hydrating *in situ* a sintered C_3S pellet in an AFM liquid cell. Without admixture, a continuous layer of C-S-H is rapidly observed (Fig 5). On the contrary, in presence of H1, isolated C-S-H islets were observed at early ages (Fig 5). These observations confirm that the Cellulose ether acts on the growth process of C-S-H by changing the balance between the growth rate perpendicular or parallel at the C_3S surface.

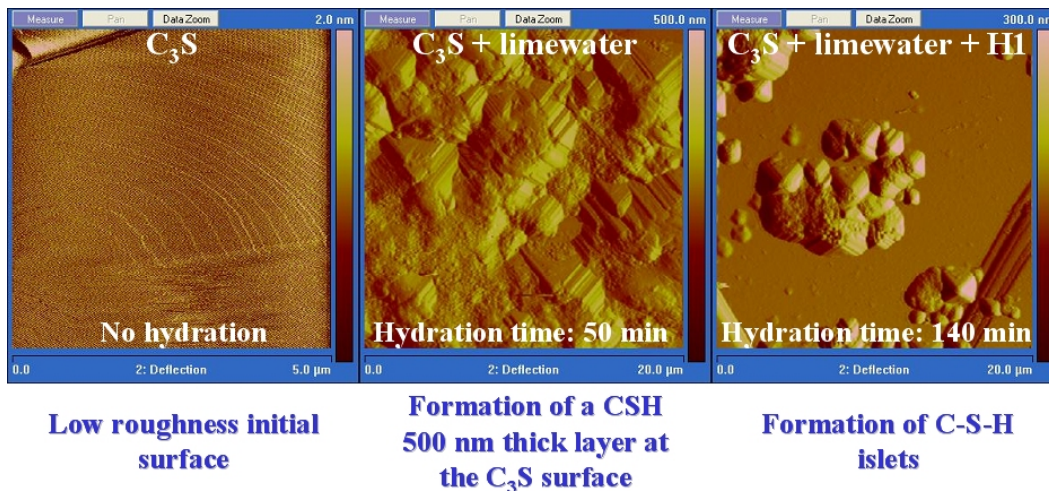


Fig 5: AFM observation of *in situ* C_3S Hydration at various time of hydration

To improve our knowledge of the actions of H1 on the C-S-H growth, adsorption isotherms on C-S-H synthesized by pozzolanic reaction were performed. Results emphasize that H1 has a high affinity for the C-S-H phase (Fig 6). Doubtless, an adsorption of H1 on C-S-H is demonstrated. This adsorption could induce structural changes of C-S-H nanometric elements and could strongly modify the growth rate parallel or perpendicular at the C_3S surface.

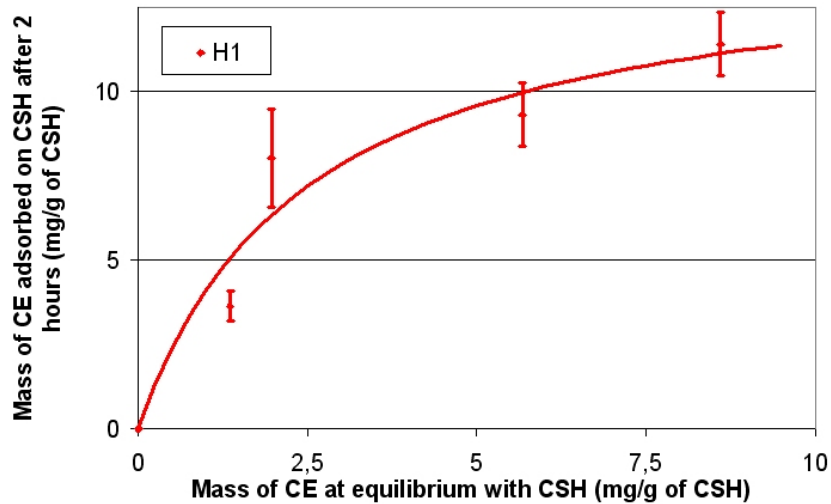


Fig 6: Adsorption isotherm of H1 on C-S-H

7. Conclusions

Basic and reliable data on cellulose ether – C_3S interactions are collected. The results allow demonstrating that the polymers studied have a negligible influence on the dissolution of C_3S . On the contrary, cellulose ethers act mainly on the C-S-H nucleation-growth process. As a matter of fact, a slowing down of the initial quantity of C-S-H nuclei is noticed. Admixtures have also a strong impact on C-S-H growth. All things considered, in the presence of cellulose ether the C-S-H layer is clearly thicker and more permeable. The significant adsorption of cellulose ether on C-S-H could enable to induce structural changes of C-S-H nanometric elements. As a result, the agglomeration of the C-S-H nanometric elements could be modified in order to favor the perpendicular growth rate rather than the parallel growth rate.

8. Bibliography

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