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# Impact of cellulose ethers on the cement paste microstructure

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## **ABSTRACT**

Complementary investigation tools (2D and 3D observations by optical microscopy and fast X-ray microtomography and then image analysis) were developed in order to examine the effects of cellulose ethers on the cement paste microstructure. The obtained results show that the presence of cellulose ether may induce an increase of both 50-250  $\mu\text{m}$ -diameter air voids. The chemistry of the cellulose ethers appears as a main controlling factor of this porous media modification. In particular, cellulose ethers seems to play an important role on the air bubbles morphological characteristics, the content of air volume and the stabilisation of the porosity from the fresh cement paste to the hardened cement paste.

## **INTRODUCTION**

The development of organic admixtures, combining rheological and water retention properties, represents significant economic stakes in the mortar industry. Cellulose ethers are organic admixtures usually introduced into mortar formulations to prevent water from draining out too quickly from the mortar to the substrate. Thus, these admixtures lead the fresh mortar to be adjusted at the desired level of workability and water retention capacity. However, cellulose ethers also induce a more or less important slowing down of cement hydration processes, water transport properties and microstructure changes.

Recent insights show that the cellulose ethers chemistry is a key parameter controlling the slowing down of cement hydration kinetics [1-3]. Indeed, although the cellulose ethers molecular mass has no significant impact, the degree of substitution plays an important role on cement hydration. The retarding effect on portlandite precipitation seems not mainly correlated with the increase of the solution viscosity induced by cellulose ethers. Therefore, the pore solution viscosity, reducing the ion mobility, does not appear as the most relevant hydration-controlling factor. On the contrary, a systematic investigation of cellulose ethers adsorption on mineral phases show that hydration kinetics modification may be caused by specific cellulose ethers adsorption on C- S-H, portlandite and calcium-aluminate hydrates [4].

Even if the polymer's key parameters on the cement hydration kinetics are now quite-established, a lack of basic data on the influence of cellulose ethers chemistry on the porous media structuration remains. Macroscopic properties of water transport in mortar mainly depend of local characteristics such as porosity. To improve our knowledge of phenomena and mechanisms governing mortar behaviours, this paper is devoted to a first approach on the impact of cellulose ethers chemistry on cement paste microstructure of both fresh cement material (before the setting) and hardened cement material.

In this frame, to create skills synergy and to improve knowledge and scientific tools to enable manufacturers to develop even more reliable mortars, this study contribute to establish the most appropriate experimental methodologies concerning the impact of cellulose ethers on the cementitious material microstructure. Finally, results generated lead to determine a possible relationship between cellulose ethers chemistry, microstructure and water transport.

## **MATERIALS AND EXPERIMENTAL METHODS**

### **Mineral phase and organic compounds characterisation**

The considered cement was a 52.5 ordinary Portland cement (CE CP2 according to the European standard NF EN 197-1). Its chemical and phase compositions are given in Table 1. To determine the oxide composition as well as the phase composition according to Bogue approximation, X-ray fluorescence spectroscopy (Bruker-AXS, SRS3400, Germany) was conducted. XRD analysis (Siemens, D 5000, Germany) also allowed to quantify the phase composition of the given cement by means of Rietveld method (Siroquant V2.5 software).

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

because of its more simple chemical structure. Three HEC molecules (noted H1, N1 and N7) and two HPMC molecules (named U2 and P1) were selected.

*Table 1: Chemical and phase composition of the investigated cement*

Chemical composition (% wt)		Phase composition (% wt)		
Oxides	XRF analysis	Phases	XRF analysis and Bogue approximation	XRD analysis and Rietveld quantification
CaO	67.11%	C <sub>3</sub> S	67.5%	69.4%
SiO <sub>2</sub>	21.18%	C <sub>2</sub> S	9.8%	9.3%
Al <sub>2</sub> O <sub>3</sub>	4.29%	C <sub>3</sub> A	8.3%	8.3%
SO <sub>3</sub>	4.65%	C <sub>4</sub> AF	5.5%	3.1%
Fe <sub>2</sub> O <sub>3</sub>	1.82%	Gypsum	4.65%	3.6%
MgO	0.5 %	CaCO <sub>3</sub>	-	4.9%
TiO <sub>2</sub>	0.21%	Anhydrite	-	1.2%
P <sub>2</sub> O <sub>5</sub>	0.23%	Quartz	-	0.2%
Na <sub>2</sub> O	0.19%			
K <sub>2</sub> O	0.11%			

Beforehand, a precise characterisation was performed (Table 2) by size exclusion chromatography and near infra-red spectroscopy analyses [4]. 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 hydroxyl propyl substitution groups (% POOH) and the content of methoxyl substitution groups (% OCH<sub>3</sub>).

#### Investigation of the porous media

According to the considered objectives, this study is restrained to basic approaches without any willingness on development of new products nor on evaluation of existing ones. That is why, all the experiments were performed on the simplest model of cementitious material, i.e. a cement paste.

The polymer to cement mass ratio (P/C) used is equal to 0.5% and the water to cement mass ratio (W/C) is always fixed at 0.4, whatever the cellulose ether introduced. Thus, the admixed cement pastes induce different workability level. This point can be astonishing because of in industrial context, the W/C is already changed as a function of polymers employed to produce mortars with the same consistency. However, to evaluate the isolated and actual effect of polymer chemistry, the W/C has to be kept constant.

Different methods were successively examined to establish the microstructural organisation: 2D observations by optical microscopy and 3D observations by synchrotron radiation X-ray microtomography performed at the European Synchrotron Radiation Facility. The specimens were 14 day-stored with controlled storage conditions (100% RH and 20°C). Prior to experiments, the solid was vacuum-dried under P<sub>2</sub>O<sub>5</sub> during 24 hours.

The macropores distribution was investigated from 2D optical observations of 256 cm<sup>2</sup> of cement paste [4]. The protocol developed leads to obtain a spatial resolution of 23.8 μm. 3D porous media was also characterised by synchrotron radiation X-ray microtomography. Fast X-ray imaging experiments (scan time of 1.5 minute) were conducted at the European Synchrotron Radiation Facility (ESRF – ID19 beamline). Results on cylindrical cement paste specimen (1.5 mm-diameter and 1 cm-long) with a spatial resolution of 2.8 μm emphasise precisely the porous structure at the very early age during the first hour of cement hydration, i.e. before the cement setting [4].

To emphasise quantitative data, different steps of 2D/3D image processing and analysis were performed [5]. Firstly, a morphological filtering was applied on images so as to reduce noise and artefacts. Then, smoothed images were thresholded to exhibit air voids. Finally, several size distributions of air bubbles (number, surface or volume) were computed [6].

*Table 2: Chemical structure parameters of cellulose ethers studied.*

Admixtures	Mw (dalton)	EOOH (%)	POOH (%)	OCH <sub>3</sub> (%)
HPMC U2	955 000	-	10.65	27.5
HPMC P1	175 000	-	19	27.5
HEC H1	175 000	48.5	-	-
HEC N1	175 000	56	-	-
HEC N7	1 335 000	56	-	-

## IMPACT OF CELLULOSE ETHERS ON THE CEMENT PASTE MICROSTRUCTURE

### Selective state of the art

Few studies were devoted to the impact of cellulose ethers on the cementitious porous media. Malatrait studied the impact of one cellulose ether molecule on the mortar microstructure [7]. Scanning Electron Microscopy (SEM) observations emphasised that the porous network induced by cellulose ethers may be described such as a network of 100  $\mu\text{m}$ -diameter air voids linked by “small canals” with a size lower than 1  $\mu\text{m}$ -diameter.

Silva investigated the effects of HEC on the structure of cement paste by mercury intrusion porosimetry [8]. Experiments were performed with only one molecule but various curing methods and P/C. For HEC-containing pastes, the pore size distribution curves exhibit four peaks (Figure 1). The first one lies approximately at the 4 nm-diameter while the second and sharpest one corresponds to a diameter around 40-75 nm. The third peak appears in the diameter 100-500 nm and was in accordance with the large capillaries between the air bubbles observed by Malatrait. Finally, a fourth and less sharp peak was observed by Silva on some admixed pastes due to entrained air (pore width larger than 100  $\mu\text{m}$  that may correspond to the air voids network characterised by Malatrait).

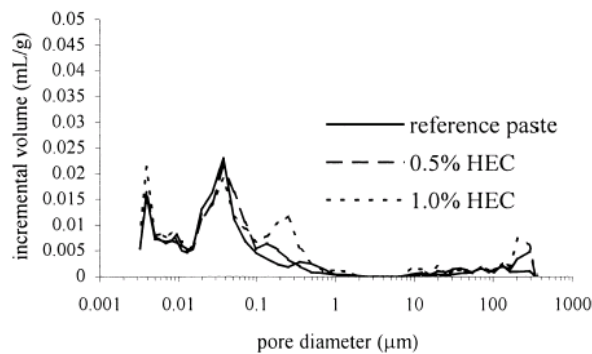


Figure 1: Typical pore size distribution of HEC-containing cement pastes [8].

Jenni investigated the role of one HEMC molecule on changes in mortars microstructures [9-10]. He showed by pycnometry measurements that the air entrained content of mortars containing cellulose ether only is about 20% vol., whereas non-admixed mortars contain only a few volume percent. Jenni proposed that the air bubbles entrained during mechanical mixing are stabilised by cellulose ethers. This assumption seems to be confirmed by the polymer enrichment observed at the interface between air void and cement paste (Figure 2).

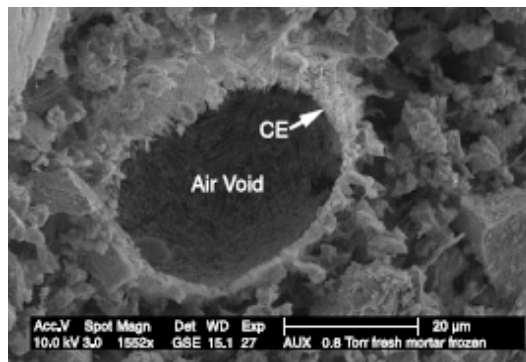


Figure 2: Fracture surface of a previously shock-frozen fresh mortar with an air void surface covered with cellulose ether (ESEM in situ cryo-experiment) [9].

Although reliable and interesting investigations, Malatrait, Silva and Jenni focused their study on the impact of only one cellulose ether molecule. Thus, even if there is an agreement on the specific porous structure generated by cellulose ethers (100  $\mu\text{m}$ -diameter air voids linked by large capillaries inferior to 1  $\mu\text{m}$ ), the effect of the cellulose ethers chemistry on this porous media still remains poorly understood.

### 2D observations of hardened cement pastes by optical microscopy

The 2D observations of cement paste macropores highlight an important influence of cellulose ethers on the air entrained content and on the distribution of pore size (Figure 3). Doubtless, a great influence of the cellulose ethers chemistry on the cement paste porosity is emphasised. Three behaviours are noticed: a high air voids content for the HPMCs (U2 and P1), a medium air voids content for high Mw HEC (N7) and finally a low air voids content for low Mw HECs (N1 and H1) as well as non admixed reference sample.

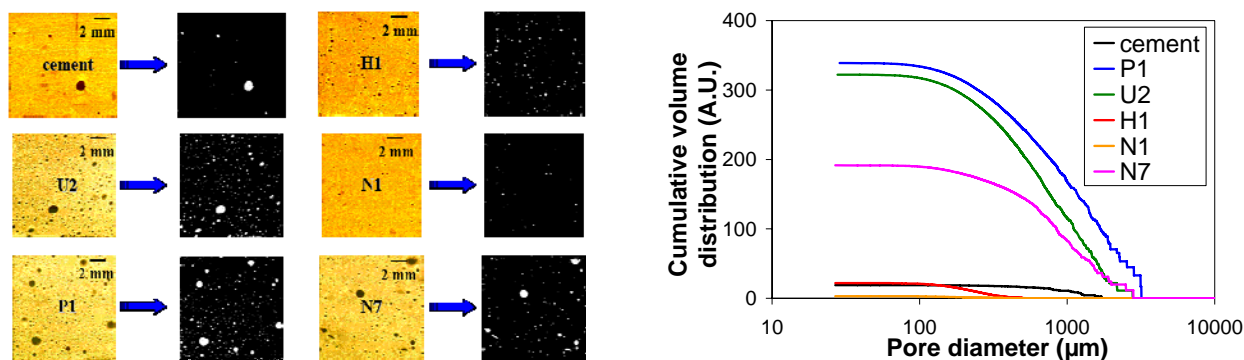


Figure 3: 2D observation by optical microscopy and air bubbles cumulative distribution calculated by image analysis.

The porosity induced by the cellulose ethers is directly caused by two phenomena: the quantity of air entrained during the mixing, and then the stabilisation at the hard state of the air voids created during the mixing stage at the fresh state. Results perfectly show that the cellulose ethers can have a great impact on these two phenomena.

The HECs N1 and N7 have the same hydroxyethyl content at 56 % and a great difference of molecular mass (Table 2). Figure 4 highlights that the higher the Mw, the higher the mortar viscosity. Therefore, N1 and N7 are polymers which mainly differ by their capacity to air trap during the mixing stage due to the cement paste consistency. In fact, the 2D macropores quantification emphasises that the high Mw N7 induced a more important air volume in the admixed cement paste compared with low Mw N1. As a result, the impact of cellulose ethers on the cement paste viscosity can play a great role during the mixing stage and represents one way to explain the impact of cellulose ethers on hardened cement microstructure.

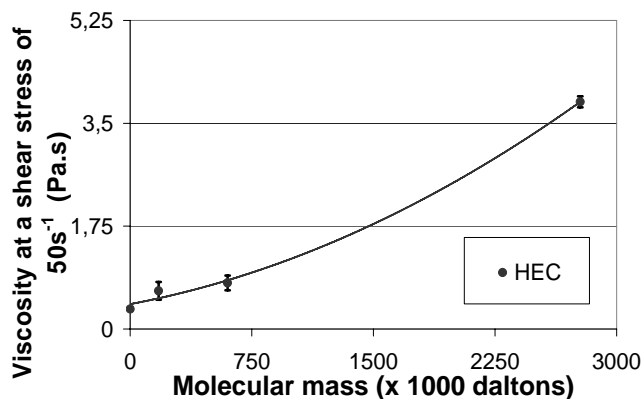


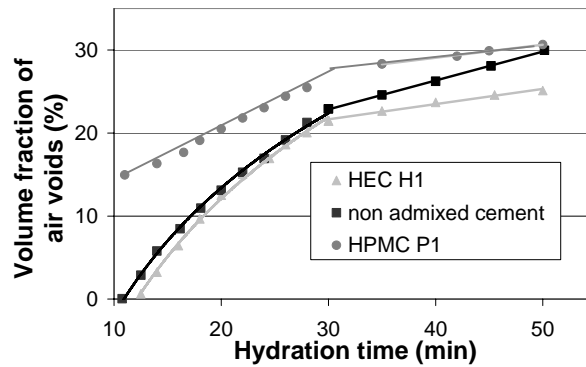
Figure 4: Viscosity of admixed mortars as a function of the molecular mass of HECs at 56% of hydroxyethyl group content (ratio HEC to dry mix equal to 0.27 %).

Furthermore, a great influence of the cellulose ethers chemistry on the cement paste porosity is clearly observed. Indeed, though the pore size distribution of cement paste admixed with low Mw HECs (i.e. H1 and N1) is quite the same of the non admixed cement paste, the total porous volume induced by HPMCs-containing cement paste (i.e. U2 and P1) is significantly increased compared with high Mw HECs-cement paste (i.e. N7). Besides, the mortar consistency caused by HPMCs and high Mw HECs appears equivalent. Thus, the content of air bubbles entrained during the mixing stage due to the mortar viscosity can not explain the difference of microstructure underlined.

As a matter of fact, the capacity of HPMCs to stabilise air voids created during the mixing stage seems to be more important by comparison with HECs. In fact, we proved using FITC-cellulose ethers (FITC is a common fluorescent stain) that HPMCs can stabilise air bubbles thanks to polymer films formation at the air-wet cement interface. This specific behaviour can be assigned to the properties of cellulose ethers as surface-active agent with a strong affinity to the air-water interface.

### 3D observations of fresh cement pastes by fast X-ray microtomography

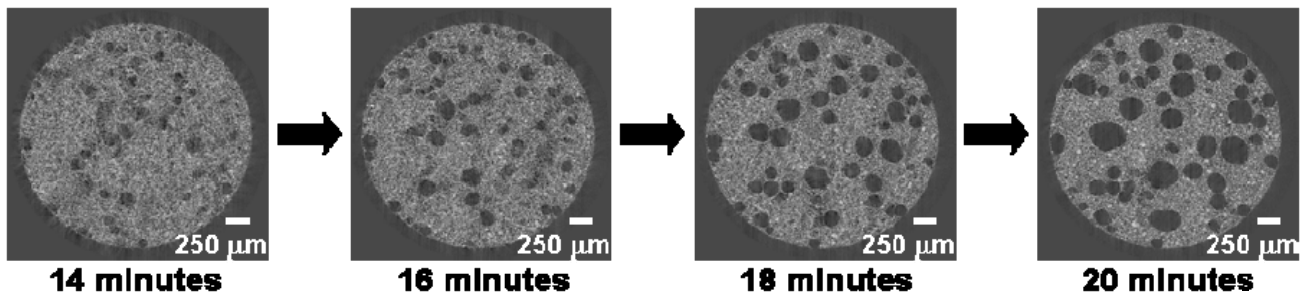
The main interest of fast X-ray microtomography is to elucidate the structuration of the porous media during the first hour of cement hydration as a function of the cellulose ether introduced. The quantification by image analysis of the volume fraction of air voids clearly shows a progressive increase of the global porous volume until around 30% vol. at 50 minutes of hydration (Figure 5).



*Figure 5: Impact of the cellulose ethers chemistry on the structuration of the porous media detected by fast X-ray microtomography and image analysis.*

However, it appears that this evolution of the total porous volume do not reflect the real evolution of the global air entrained volume. Indeed, the content of air bubbles in the fresh cement paste is mainly caused by the mixing stage. That is why it is not credible to observe an increase of the global air content of the fresh cement paste during the first hour of hydration. Therefore, variations of porous media volume measured by image analysis were mainly due to changes of morphological and mobility porosity characteristics according to both the spatial and temporal resolution of the fast X-ray microtomography.

Nevertheless, even if the volume fraction measured do not correspond to the “real” porous media characterisation, the results allow to obtain interesting quantitative data on the air voids structuration. At first, fast X-ray microtomography leads to doubtless establish the impact of cellulose ethers on the number, size and mobility of air bubbles created during the mixing stage. Indeed, at the very beginning of the cement paste hydration (between 10 and 20 minutes), a low content of air voids was observed and then detected by image analysis for the reference cement paste and H1-containing cement paste (Figure 5). Thus, in presence of H1 as well as for the non admixed cement paste, it seems that the moving rate of air voids is high and the air bubbles size is small regarding to respectively the temporal and spatial resolution needed to perform a fast X-ray microtomography scan. Consequently, at 14 or 16 minutes of hydration, we observe a few content of blurred air voids (examples of 2D images extracted from 3D volume are shown in Figure 6).



*Figure 6: Evolution of the porosity observed between 10 and 20 minutes of hydration.*

On the contrary, Figure 5 emphasises that the volume of global air entrained detected for the HPMC P1-containing cement paste is significantly higher by comparison of non admixed and H1-containing cement pastes. So, these results underlined that the porous network caused by HPMCs is more and more easily observed during the hydration processes because of the air bubbles created during the mixing stage seem to have a bigger size and a lower mobility.

Moreover, the evolution of the cement paste porosity exhibits a phenomenon of air voids coalescence (Figure 7). This coalescence phenomenon provokes a decrease of the volume fraction of small air voids and an increase of the volume fraction of big air entrained (Figure 8). This observation clearly confirms that the cement paste microstructure at the hardened state is caused by both the content and the morphological characteristics of air entrained during the mixing stage and also the coalescence phenomenon which occurs during the first hour of hydration.

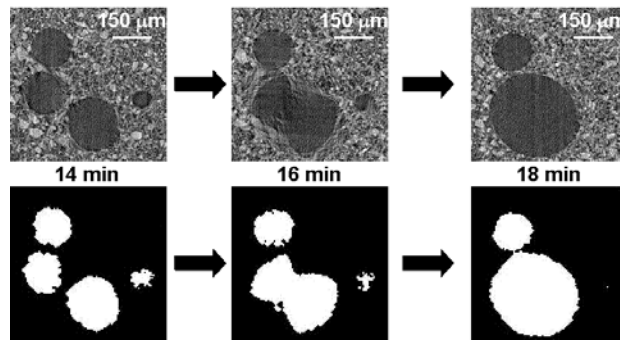


Figure 7: air voids coalescence phenomenon observed on the non admixed cement paste.

The chemistry of the cellulose ether introduced seems to have a great impact on the coalescence rate of air bubbles. Indeed, in presence of cellulose ethers, we observe a slowing down of the coalescence phenomenon from 30 to 50 minutes illustrated by a decrease of the considered curve slope.

All signs point to show that the volume of global air voids may be constant during the first hour of cement hydration. In fact, the evolution of the total porosity observed in Figure 5 notices a size and mobility variation of air bubbles between HPMCs and HECs cement pastes. As a matter of fact, during the cement hydration, the size of the air voids increases (coalescence phenomenon) and their mobility decreases (cumulative effect of the cement setting and the increasing of air bubbles). As a result, the porosity becomes more and more easily observed during the cement hydration (Figure 6) regarding to both temporal (1.5 minutes per scan) and spatial (2.8  $\mu\text{m}$  per pixel) resolution of fast X-ray microtomography.

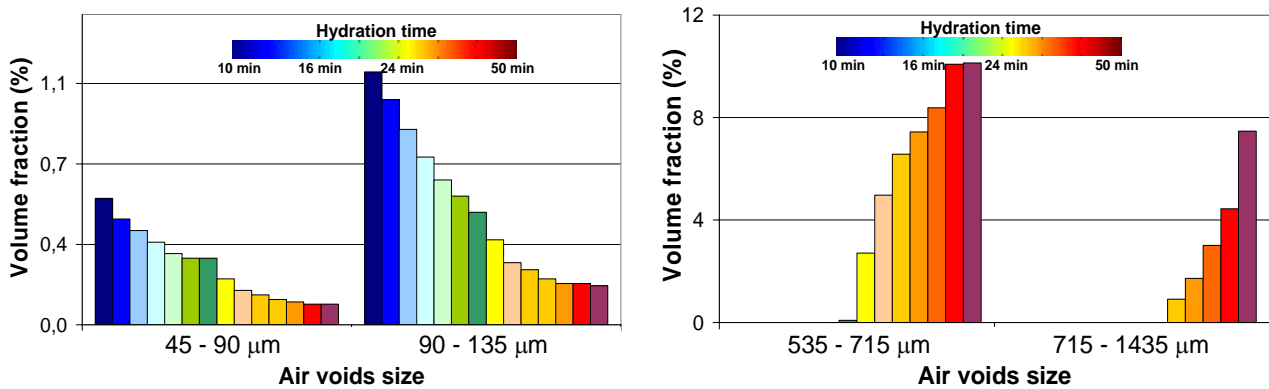


Figure 8: Evolution of the size distribution of air bubbles as a function of the hydration time (example for the non admixed cement paste, small air voids size at the top and big air voids at the bottom).

## CONCLUSIONS AND NEW INSIGHTS

Finally, the 3D observations of the microstructure of cellulose ethers-containing cement paste, exhibit a similar behaviour of the 2D observations by optical microscopy. It appears that HPMCs favour the formation of a high content of spherical air voids in the diameter range 50-250  $\mu\text{m}$ . Furthermore, X-ray microtomography appears as a remarkable investigation tool to elucidate microstructure characteristics of fresh polymer modified cement paste.

Image analysis highlights a strong impact of the chemical structure of admixtures on the porous network.

A substantial increase of the porosity was observed in presence of few cellulose ethers. We also clearly establish that cellulose ethers can act strongly on:

- ❖ the number, size and mobility of air bubbles generated during the mixing stage,
- ❖ the progressive increase of the air voids during the first hour of hydration by means of a coalescence phenomenon,
- ❖ the stabilisation of the air entrained thanks to a polymer film formation at the interface air-wet cement paste.

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