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HPMC and HEMC influence on cement hydration

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ABSTRACT.

Cellulose ethers such as hydroxyethylmethyl cellulose (HEMC) and hydroxypropylmethyl cellulose (HPMC) are common admixtures in factory made mortars. Nevertheless, their use principally remains empirical, and no cement-admixture interaction mechanism has ever been rigorously demonstrated. The main issue of this publication deals with the control of secondary effects generated by these admixtures such as the retardation of cement hydration. In this frame, a study of the impact of HEMC and HPMC molecule parameters on the modification of cement hydration was carried out. Minor influence of the molecular weight and of the hydroxypropyl or the hydroxyethyl group content was observed. On the contrary, the results emphasize that the methoxyl group content appears as the key parameter of the hydration delay mechanism.

Keywords: cellulose ethers, A. retardation, A. kinetics, conductometry.

1. Introduction

Organic admixtures combining rheological and water retention properties are of significant economic benefit for the mortar industry. Polysaccharides and especially cellulose ethers are usually used to maintain water content in mortars at high levels. These molecules also contribute to good mechanical strength of the final material. Even if some publications deal with monosaccharides [1-3] and polysaccharides [4, 5], the understanding of mineral-organic interaction is still not complete. Indeed, the retardation in the hydration of cement is a secondary and uncontrolled effect which can be induced by some polysaccharide admixtures. Therefore, this study aims at collecting physico-chemical data so as to control the hydration delay.

In order to reach this objective, we tried to identify the molecular parameters, which mainly influence the retarding effect of cellulose ethers. Even though the hydration retardation is generally undesirable, we enhance this phenomenon to identify more precisely the involved parameter. The first parameter was the molecular weight (noted M_w). The corresponding samples have identical chemical structure and only differ by their molecular weight. The second parameter was the substitution degrees. This impact is evaluate with molecules having identical molecular weight and only differ by their hydroxyethyl, hydroxypropyl or methoxyl content.

A characterization of all admixtures was beforehand performed to quantify their structural parameters *i.e.* substitution degrees and molecular weights. Then, the influence of these parameters on hydration delay was assessed by conductometric measurements in water and limewater suspension.

2. Mineral and organic compounds

2.1. Cement analysis

The mineral product used for this study was supplied by Lafarge Company (France). The designation of the investigated cement was a CEM I-52.5R according to the French standard NF P 15-301. Its chemical and phase composition is 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 [6]. 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).

2.2. Admixtures

Cellulose is a polysaccharide in a linear homopolymer form, constituted of anhydroglucose units with β-1.4 linkages (Fig. 1). Since strong intramolecular and intermolecular interactions via hydrogen bonds occur, pure cellulose is insoluble in water. Substitution of the C-2, C-3 or C-6 OH group of an anhydroglycose unit makes the cellulose water soluble. Substitution of cellulose can be realized by etherification. The most frequently introduced substituents are methoxyl groups (noted OCH_3), hydroxypropyl groups (noted POOH) and hydroxyethyl groups (noted EOOH).

Cellulose ethers significantly improve the finishing and internal-strength characteristics of mortar, render or tile adhesive. These admixtures cause a substantial increase in the water retention capacity. They prevent water from draining out too quickly from the mortar into the substrate. In this way, more water is retained in the fresh material which favors cement hydration and thus increases the final mechanical strength. The most widespread cellulose ethers used in building materials are the hydroxyethylmethyl cellulose (HEMC) and the hydroxypropylmethyl cellulose (HPMC). The admixtures chosen for this study were five HPMCs (D1 and D2 ; A1 to A3) and four HEMCs (C1 to C4).

Substituents of cellulose derivatives may have an important influence on cement hydration. Hence, an accurate evaluation of the methoxyl, the hydroxypropyl and the hydroxyethyl group content was essential. This quantification was conducted by near infra-red spectroscopy (NIR) [7]. These data as well as the viscosity range (Brookfield RV, 2%, 20 rpm) of the samples are reported in Table 2. These results emphasize that, for D1 and D2 HPMCs and C1 to C4 HEMCs, viscosity is the only variable parameter within these two groups. Thus, the determination of the molecular weight effect on cement hydration was possible thanks to these molecules. The HPMC samples (A1 to A3) were used to study the influence of chemical structure of the substituents.

3. Methods and experimental procedures

3.1. Determination of molecular weight distribution

Size Exclusion Chromatography (SEC) is a commonly used method to determine the molecular size and weight of polymeric products such as water soluble cellulose derivatives [8]. Separation is based on the hydrodynamic volume of individual molecules. SEC analysis was performed on a Waters apparatus equipped with a Waters 916 pump, a Waters 996 photodiode array detector and a Waters 410 refractometric detector. The specific column used for SEC analysis of polysaccharides was a TOSOHAAS TSK GEL GMPWXL 7.8 mm x 30 cm. During the experiment, this column is maintained at 35°C inside an oven. The eluent was a 0.05 mol/L sodium chloride solution (to prevent molecules agglomeration) obtained with deionised water (Millipore mQ). This solution was previously filtered at 0.22 microns and in-line degassed during the experiments. The eluent flow was set to 0.5 mL/min.

A calibration was performed using standard molecules of well defined molecular weights with a theoretical polydispersity index close to one. Eight polymaltotrioses SHODEX standard P-82 were used with molecular weights ranging from 5 800 daltons to 788 000 daltons. The corresponding retentive times are 17.4 and 12.9 minutes respectively.

3.2. Water retention measurement

Any porous substrate exerts a suction on mortar leading to a weight loss of the mixing water. Water retention is defined as the ability of a mortar to retain water. It can be determined by different flow-after-suction tests [9] which simulate the action of absorptive masonry units on plastic mortar. The used methodology is described in ASTM standards [10]. Water retention was measured with a standardized apparatus composed of a perforated dish attached to a vacuum assembly by a funnel. The perforated dish was filled with the mortar and the excess of mortar was flushed off to obtain a plane surface. The vacuum was adjusted to maintain a depression of 50 mm of mercury during 15 minutes. As the initial mixing water mass in plastic mortar was known, its mass loss was easily determined after the suction period. Hence, on the basis of this data, the retention capacity (called R) was expressed by means of Equation 1 in terms of percentage of initial mixing water mass [11]. The mortar composition for all experiments is described by Table 3.

Equation 1: definition of water retention capacity.

$$R\ (\%) = \frac{E - e}{E} \times 100$$

with “E” the initial mass of mixing water and “e” its loss of mass after suction

3.3. Hydration delay characterization

A systematic study of the effects of lime concentration on C_3S hydration was performed by Nonat [12]. Nonat concludes that the lime concentration is certainly the most important parameter determining the thermodynamic, kinetic, morphologhical and structural features of C-S-H for every ratio water to C_3S (in a suspension as well as in a paste). Moreover, hydration of C_3S in lime solution was carried out by measuring the electrical conductivity of the suspension simultaneously with the heat flow [13]. Thanks to these results the authors demonstrated that:

(1) Similar reactions occur in the C_3S hydration when either pastes or diluted lime suspensions are used in the hydration [12, 13]

(2) The relative magnitude and duration of C-S-H precipitation strongly depend on the lime concentration in solution [13]. Especially it was proved that the lime concentration determines both the number of C-S-H nuclei formed in the first minutes of C_3S hydration (which controls the period of low rate of hydration commonly named “induction period”), and the growth rates of C-S-H parallel and perpendicular to C_3S grain surface [14].

(3) The portlandite precipitation does not cause the acceleratory period which occurs after the “induction period”. Using an isothermal calorimeter adapted to the study of diluted suspensions and conductometric measurement, Damidot showed that the initial portlandite precipitation was represented by an electrical conductivity drop and an endothermic peak [13].

Thus, conductometric measurements in lime solution appear as a powerful tool to monitor the hydration kinetics and lead to reveal the nucleation, growth and precipitation processes of hydrates such as C-S-H or portlandite. Conductometry allows to obtain a global view of the hydration mechanism (Fig. 2). A high concentration of lime suspension allows to obtain hydration kinetics close to cement pastes. In spite of a high liquid to solid (noted L/S) weight ratio (equal to 20), the rate controlling step in lime solution was governed by the hydrates nucleation and growth such as in cement pastes. The determination of the evolution of hydration retardation uses the portlandite (noted CH) precipitation time, represented by an electrical conductivity drop, as a benchmark. Therefore, conductometry enables to classify and to determine the relative retardation capacity of admixtures on cement hydration.

The experiments were performed in diluted suspensions, thermostated at 25°C and continuously subjected to magnetic stirring. Each experiment was carried out in triplicate. The liquid to solid weight ratio used was equal to 20 (100 ml of liquid and 5 g of solid). The solid was a mix of cement and cellulose ether powders which was blended in a shaker (Wab, Turbula, Germany) for 5 minutes. Two different admixture to cement (A/C) weight ratios equal to 0.5% and 2% were studied for each cellulose ether sample. Admixture content in these formulations was important and contributed to enhance the hydration delay phenomenon. The liquid was either deionised water (Millipore mQ) or lime solution.

4. Preliminary chemical and water retention studies

4.1. Determination of molecular weight distribution

The determination of molecular weight distribution was necessary to evaluate its influence on hydration retardation and on water retention. SEC was used to determine the polydispersity index and molecular weight distribution differences. Chromatograms of the nine cellulose ethers illustrate that a main population of polymers is always detected and that a minor oligomer population (just one or two anhydroglucose units) is frequently observable. The intensity of this latter peak was at least ten times smaller than that of the main population one. Due to retentive times of about 19.5 minutes, at the upper limit of the calibration curve, an extrapolation allowed to identify an oligomer population with a calculated molecular weight inferior to 500 daltons. The results of the molecular weight distribution for all cellulose ether samples are listed in Table 4.

4.2. Water retention study and influence of molecular weight

Water retention is the main property induced by cellulose ethers in mortar formulation. According to a French standard [11], a required water retention value higher than 95% has to be verified. The obtained values for the different admixtures used are listed in Table 5. Experimental results show an increase of water retention capacity by comparison with non admixed mortar. A significant influence of the molecular weight is also revealed. As a matter of fact, for a given class of chemical structure, water retention increases with M_w (Fig. 3).

This result seems to be in accordance with the literature data. An admixture of high molecular weight as well as an increase of the A/C ratio contributes to extend significantly the water retention capacity of mortars [15]. However, although fundamental works were devoted to water retention for a C_3S pure phase [16], the water retention mechanism caused by cellulose derivatives is still unclear. The molecular weight is probably not the only parameter which has to be taken into account. The impact of other parameters, such as the porous network could also be examined.

5. Hydration retardation study in water suspension

5.1. Results on portlandite precipitation delay

First of all, it is apparent that the retarding effect of the nine samples is relatively small (Fig. 4). Portlandite precipitation time is only slightly higher for formulations containing 2% of admixture than for those with 0.5%. The most important delay is observed for 2% C3, and reaches hardly 35 minutes compared to a non admixed cement. Furthermore, conductometric results with 2% of C1 to C4 show that whatever the admixture introduced, the same global influence on hydration is observed since the slopes of the conductometric curves are similar (Fig. 5).

5.2. Influence of the molecular weight on portlandite precipitation delay

For this study, admixtures with varying M_w and identical chemical structure (*i.e.* nature and content of substituents) were used. The results show that, in the studied M_w range, M_w has a minor effect on hydration behaviour since the maximum gap is only about 10 minutes (Fig. 6). Hence, M_w is clearly not the key parameter which governs the hydration process.

The influence of A1 and A2 admixtures with different chemical structures (Table 2) and molecular weights (Table 4) was also investigated. The corresponding delays obtained for the 2% formulation show that the lowest M_w admixture (270 000 daltons for A2 versus 650 000 daltons for A1) induces the highest portlandite precipitation time (263 ± 1 minutes for A2 versus 240 ± 3.5 minutes for A1). This result is in contradiction with the tendency established at constant chemical structure *i.e.* higher M_w would favor an increased retardation (Fig. 6). So, the M_w has doubtless a low impact on the hydration kinetics.

5.3. Influence of substituents on portlandite precipitation delay

Even though the substituent effect on hydration is not easy to assess, we applied the same methodology by comparing molecules with only one variable parameter. This study was problematic since the choice of commercially available admixtures is restricted. Indeed, at constant viscosity range, for a given OCH_3 content, it is difficult to find polymers with a EOOH content sufficiently differentiated. Therefore, each substituent impact on cement hydration was only evaluated with pairs of appropriate admixtures.

The influence of hydroxypropyl content was studied using A2 and D2 HPMCs which present similar % OCH_3 and M_w, and different % POOH values. Even though a very short tendency reveals that the portlandite precipitation time decreases slowly with increasing of POOH content, the difference between A2 and D2 formulations is around 5 minutes (Fig. 7a). Furthermore, commercial HPMCs have rarely a POOH content lower than 5% otherwise molecules are not easily water soluble (even if of course the water solubility strongly depends on the other substituent contents and on the temperature). Hence, it seems that no significant increase in retardation is observed with only POOH content variations.

The effect of methoxyl substituents is illustrated in Fig. 7b with D2 and A3. A main tendency was revealed by the rise in hydration retardation with decreasing methoxyl content. Contrary to the molecular weight and the hydroxyethyl content, the increase from 22% to 29% in methoxyl content represents a major parameter since a significant difference of portlandite delay was observed. This variation of 20 minutes between D2 and A3 formulations at 2% is quite important considering the maximum delay of 35 minutes obtained with the C3 admixture (Fig. 4).

5.4. Discussion about cellulose ether influence on cement hydration

Concerning the study in water suspension, the OCH_3 content is doubtless the key parameter for hydration delay in the 22% - 29% range studied. Even if the methoxyl content appears to be the most important parameter which governs the hydration retardation process for HPMC and HEMC admixtures, no important delay in water diluted media (hour scale) can be reached with these molecules. Consequently, highly diluted aqueous systems are not the optimum conditions to investigate the hydration delay mechanism of cellulose ethers.

6. Hydration retardation study in lime solution

6.1. Results on portlandite precipitation delay

The results for the 9 samples show that the hydration in lime suspensions is much more delayed than in aqueous systems, reaching values comparable to those in cement pastes. Even though the hydration delay scale is different, the relative retardation capacity of admixtures is identical (except for D2) in the two hydration media (Fig. 8). For example, although the maximum delay reaches 85 minutes compared to neat cement, this value is again obtained for the C3 admixed suspension (at 2% formulation).

Conductometric curves with 2% of C1 to C4 (Fig. 9) show that the initial period of low rate of hydration is similar for all admixed samples. Indeed, the same shape of conductometric curves is observed at the beginning of the admixed sample hydration. In contrast, different slopes of conductometric curves, during the interval 75-250 minutes, show that the kinetics of the accelerating period of hydration is modified by the action of admixtures.

6.2. Influence of structure parameters on portlandite precipitation delay

The influence of M_w, hydroxypropyl and methoxyl content was successively investigated. Firstly, the impact of M_w in lime solution is coherent with the results in aqueous system. As a matter of fact, the molecular weight seems to have a low impact on hydration delay since the maximum gap is inferior to 30 minutes (Fig. 10) compared to higher relative delays (Fig 8). The hydroxypropyl content leads to a minor impact on hydration delay (Fig. 11a). The difference in portlandite delay between A2 and D2 formulations is around 10 minutes. The effect of methoxyl content is only revealed with D2 and A3 HPMC samples (Fig. 11b). The portlandite precipitation delay seems to increase with decreasing methoxyl values. The substantial difference of delay is about 60 minutes. So in the same way as it was shown in aqueous system, it appears doubtless that the major parameter on hydration delay in lime water suspension is again the OCH_3 content.

6.3. Discussion about cellulose ether influence on cement hydration

Considering these results, the OCH_3 content appears as the key parameter for the portlandite precipitation delay in the 22% - 29% range studied. Two main hypothetical assumptions can be proposed in order to explain the great impact of a low methoxyl content on physico-chemical interaction mechanism between cement phases and HPMCs or HEMCs. Firstly, the impact of cellulose ether degradation products (such as carboxylates) on cement could explain the observed hydration delay on the portlandite precipitation. A second hypothesis postulating a hydration delay mechanism based on cellulose ether adsorption on cement. Nevertheless it seems that the adsorption of ethoxy-containing polymers on cement should be very low according to bibliography data [17].

7. Conclusions

The different studies in water and limewater media are coherent. However, the lime media emphasizes enhanced tendencies. Whatever the hydration kinetics conditions (water or lime solution), the results allow to demonstrate that the methoxyl content is the key parameter concerning the portlandite precipitation delay induced by HPMCs and HEMCs. On the contrary, the molecular weight and the hydroxypropyl content seem to have a lower impact on admixed cement hydration process. Furthermore, these results let us to think that HPMCs and HEMCs with a well known methoxyl content could enable to control hydration delay for applications in the building industry.

8. Acknowledgements

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Table 1

Chemical composition (% wt)		**Phase composition (% wt)**		
Oxides	XRF analysis	Phases	XRF analysis and Bogue approximation	XRD analysis and Rietveld quantification
CaO	67.11%	C_3S	67.5%	69.4%
SiO_2	21.18%	C_2S	9.8%	9.3%
Al_2O_3	4.29%	C_3A	8.3%	8.3%
SO_3	4.65%	C_4AF	5.5%	3.1%
Fe_2O_3	1.82%	Gypsum	4.65%	3.6%
MgO	0.5 %	$CaCO_3$	-	4.9%
TiO_2	0.21%	Anhydrite	-	1.2%
P_2O_5	0.23%	Quartz	-	0.2%
Na_2O	0.19%			
K_2O	0.11%			

Table 1 Chemical and phase composition of the investigated cement.

*J. Pourchez [1 *] — A. Peschard [1] — P. Grosseau [1] — R. Guyonnet [1] — B. Guilhot [1] — F. Vallée [2]*

Fig. 1

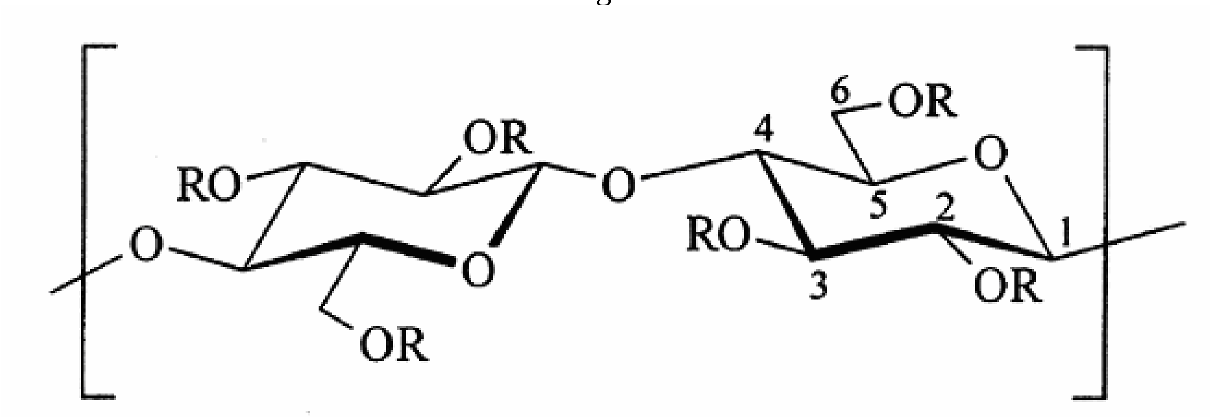


Fig. 1 Structure of water-soluble cellulose derivatives (R=H for cellulose and R=H, CH_3, $(CH_2CH_2O)_nH$ or $(CH_2CH_2CH_2O)_nH$ for HEMC or HPMC respectively).

J. Pourchez [1 *] *— A. Peschard* [1] *— P. Grosseau* [1] *— R. Guyonnet* [1] *— B. Guilhot* [1] *— F. Vallée* [2]

Table 2

	HPMC D1	HPMC D2	HEMC C1	HEMC C2	HEMC C3	HEMC C4	HPMC A1	HPMC A2	HPMC A3
Methoxyl group (% OCH_3)	22	22	25	25	25	25	29	21	29
Hydroxypropyl group (% POOH)	8.1	8.1	-	-	-	-	7	5	7
Hydroxyethyl group (% EOOH)	-	-	3.3	3.3	3.3	3.3	-	-	-
Viscosity* (mPa.s)	100 000	low	400	1 100	14 000	28 000	4 000	80-120	50

* Brookfield RV, 2%, 20 rpm

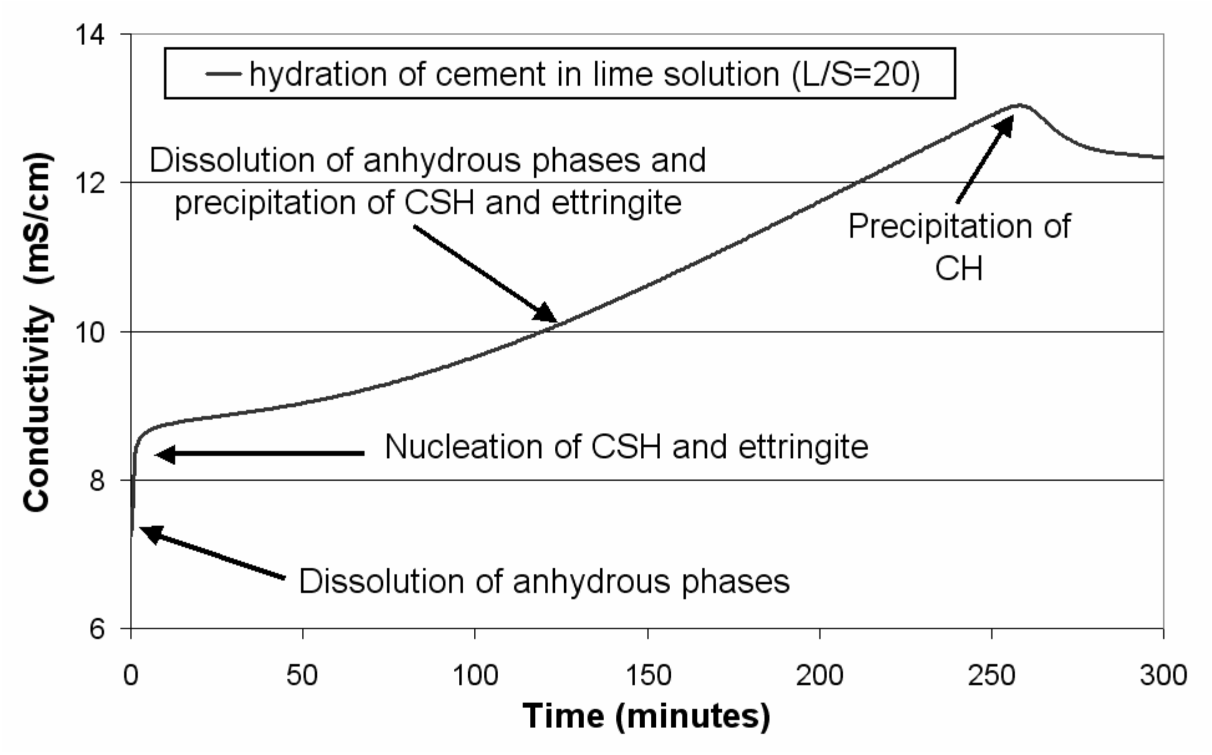
Table 2 Manufacturer data on cellulose ethers substituted groups and viscosities.

Table 3

	Cement	***Normalised sand***	***$CaCO_3$***	***Cellulose ether***	***Water***
Formulation (per *m^3* of the dry mix)	300 kg/m^3	650 kg/m^3	50 kg/m^3	2,7 kg/m^3	300 L/m^3
% wt of the dry mix	30%	65%	5%	0,27%	30%

Table 3 Mortar formulation used for the water retention test

Fig. 2



hydration of cement in lime solution (L/S=20)
Dissolution of anhydrous phases and precipitation of CSH and ettringite
Precipitation of CH
Nucleation of CSH and ettringite
Dissolution of anhydrous phases
Conductivity (mS/cm)
14
12
10
8
6
0
50
100
150
200
250
300
Time (minutes)

Fig. 2 Global view of hydration mechanism on a conductometric curve (ratio liquid to solid equal to 20).

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Table 4

	HPMC D1	**HPMC D2**	**HEMC C1**	**HEMC C2**	**HEMC C3**	**HEMC C4**	**HPMC A1**	**HPMC A2**	**HPMC A3**
M_w main population (daltons)	1 010 000	350 000	270 000	360 000	650 000	985 000	650 000	270 000	210 000
Polydispersity index of the main population	18.5	14	8	9	12	12.75	7.5	6.75	25
Detection of minor oligomer population	yes	no	yes	yes	yes	yes	no	yes	no

Table 4 Determination of weight-average molecular mass determination by SEC.

J. Pourchez [1] [*] — A. Peschard [1] — P. Grosseau [1] — R. Guyonnet [1] — B. Guilhot [1] — F. Vallée [2]

Table 5

	non admixed mortar	HPMC D1	HPMC D2	HEMC C1	HEMC C2	HEMC C3	HEMC C4	HPMC A1	HPMC A2	HPMC A3
Loss of mixing water “e” (g)	54.85	1.9	4.9	1.4	6	3.7	2.6	3.5	8.5	7.1
Water retention capacity “R” (%)	59.4	98.6	96.4	90.8	95.5	97.3	98.1	97.4	93.7	94.7

Table 5 Comparison of water retention obtained for the different cellulose ethers.

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Fig. 3

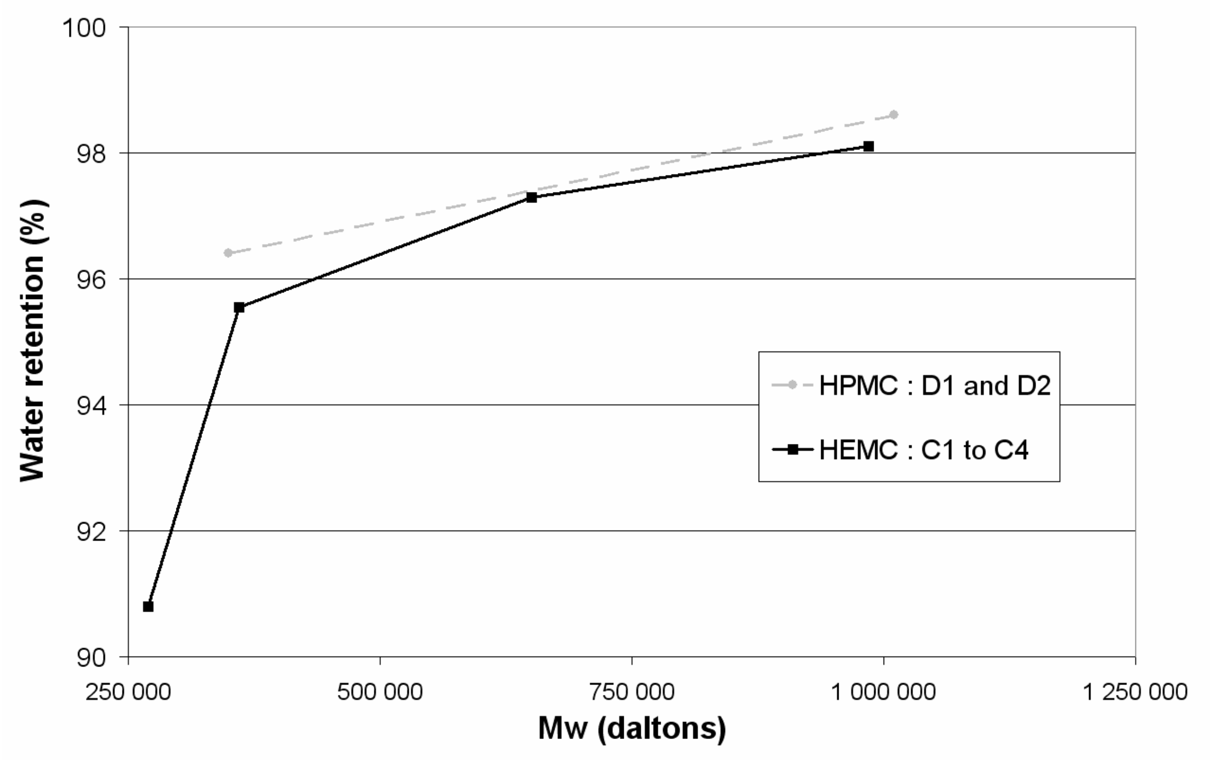
100
98
96
94
92
90
Water retention (%)
250 000
500 000
750 000
1 000 000
1 250 000
Mw (daltons)
HPMC : D1 and D2
HEMC : C1 to C4

Fig. 3 Influence of molecular weight on water retention.

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Fig. 4

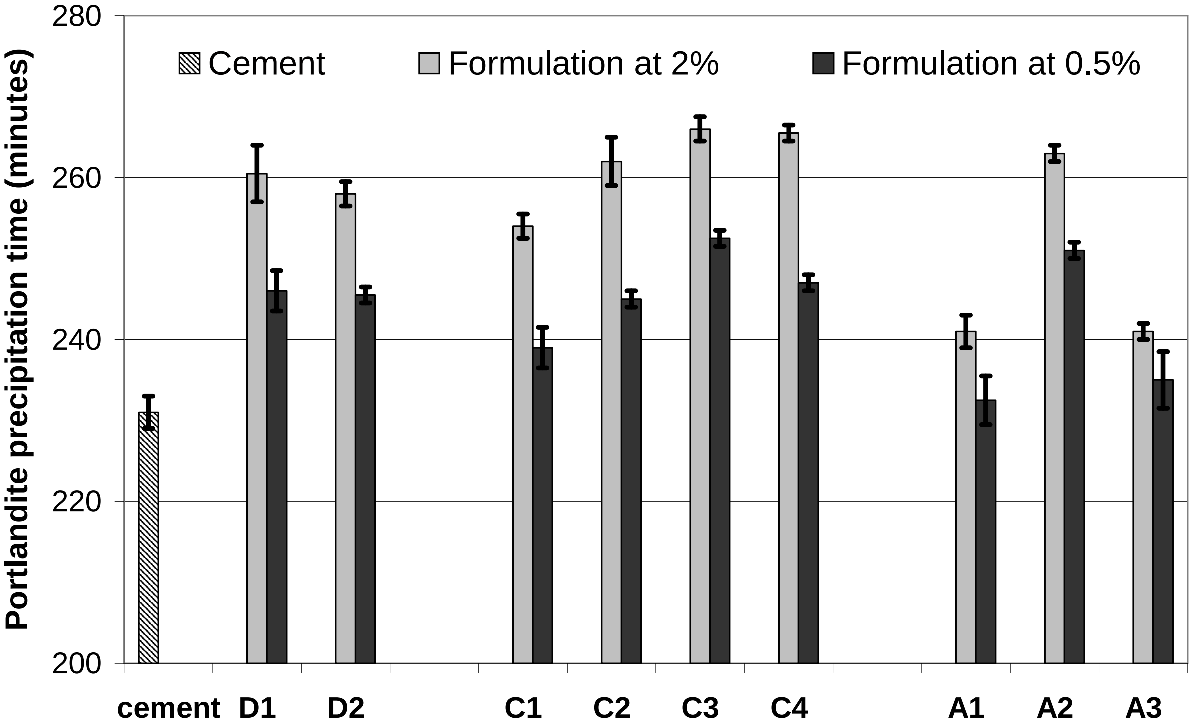
Cement
Formulation at 2%
Formulation at 0.5%
Portlandite precipitation time (minutes)
280
260
240
220
200
cement
D1
D2
C1
C2
C3
C4
A1
A2
A3

Fig. 4 Portlandite precipitation delay in aqueous system (L/S = 20).

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Fig. 5

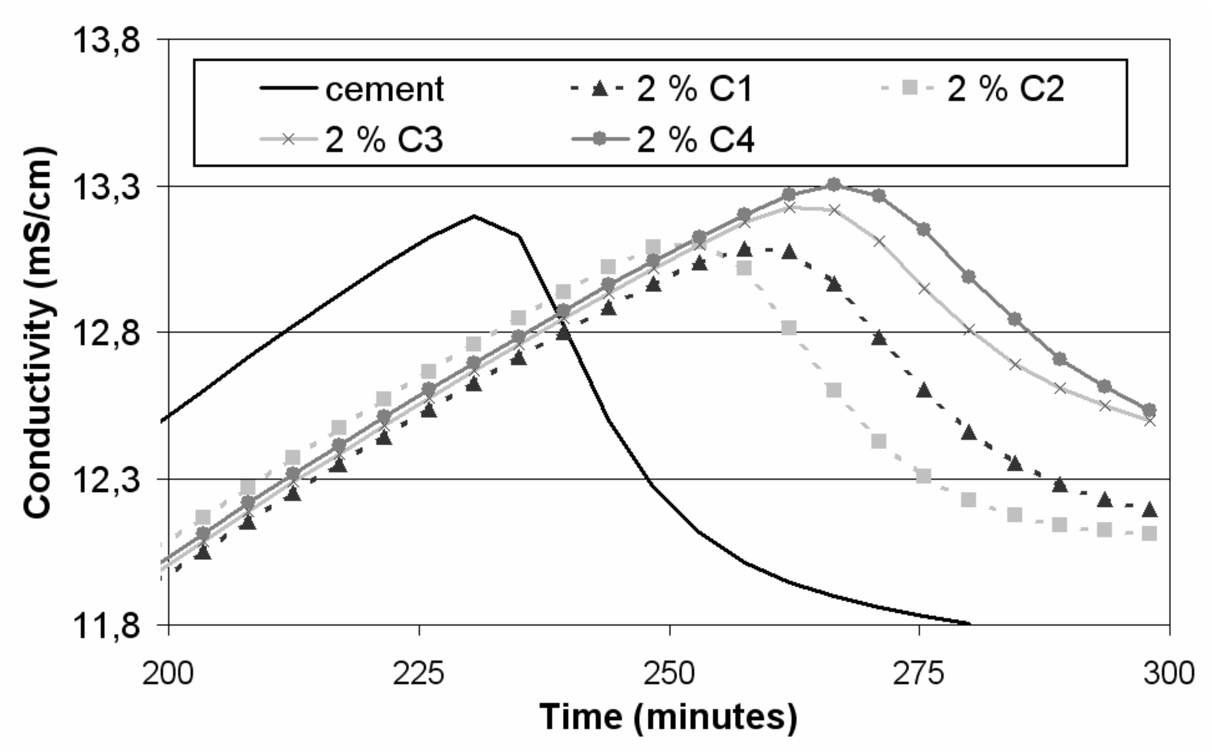

13,8
13,3
12,8
12,3
11,8
Conductivity (mS/cm)
200
225
250
275
300
Time (minutes)
cement
2 % C1
2 % C2
2 % C3
2 % C4

Fig. 5 Conductometric curves of cement admixed with 2% of C1 to C4 in aqueous system.

*J. Pourchez [1] * — A. Peschard [1] — P. Grosseau [1] — R. Guyonnet [1] — B. Guilhot [1] — F. Vallée [2]*

Fig. 6

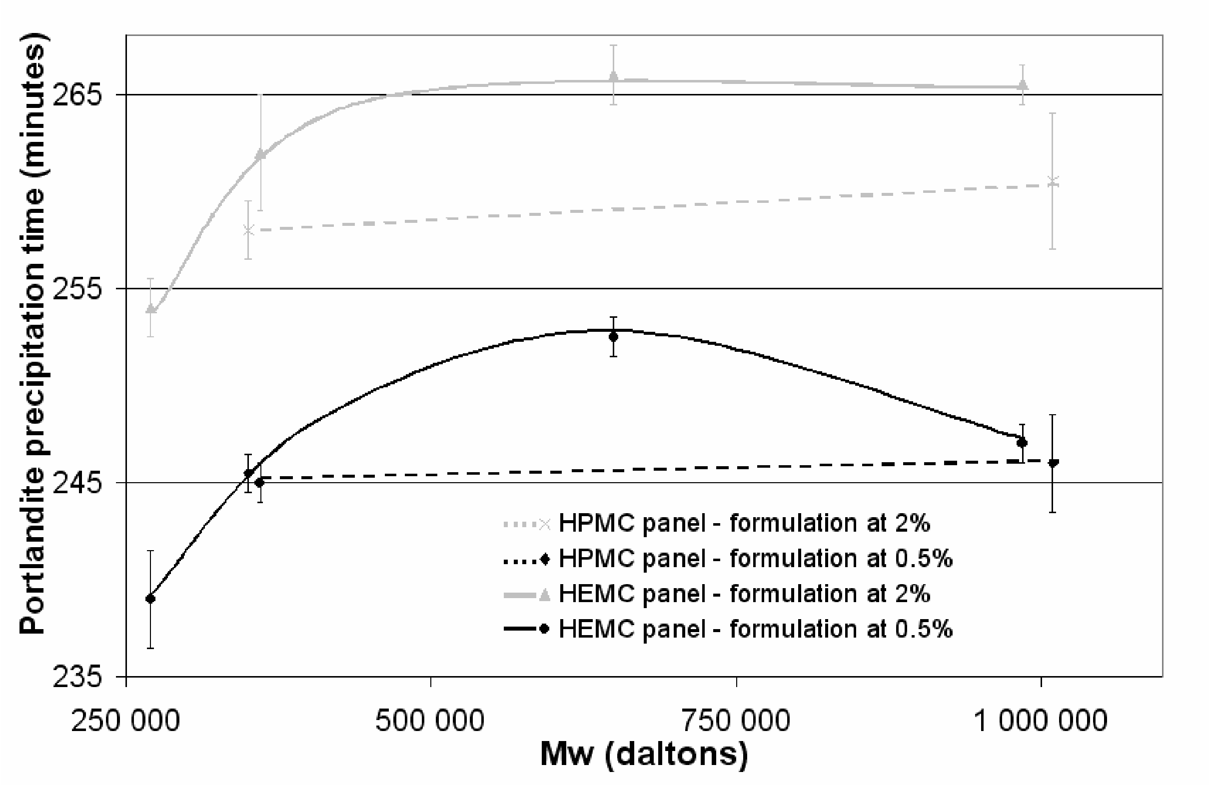

Portlandite precipitation time (minutes)
265
255
245
235
250 000
500 000
750 000
1 000 000
Mw (daltons)
HPMC panel - formulation at 2%
HPMC panel - formulation at 0.5%
HEMC panel - formulation at 2%
HEMC panel - formulation at 0.5%

Fig. 6 Influence of M_w on portlandite precipitation delay in aqueous system.

*J. Pourchez [1] * — A. Peschard [1] — P. Grosseau [1] — R. Guyonnet [1] — B. Guilhot [1] — F. Vallée [2]*

Fig. 7a

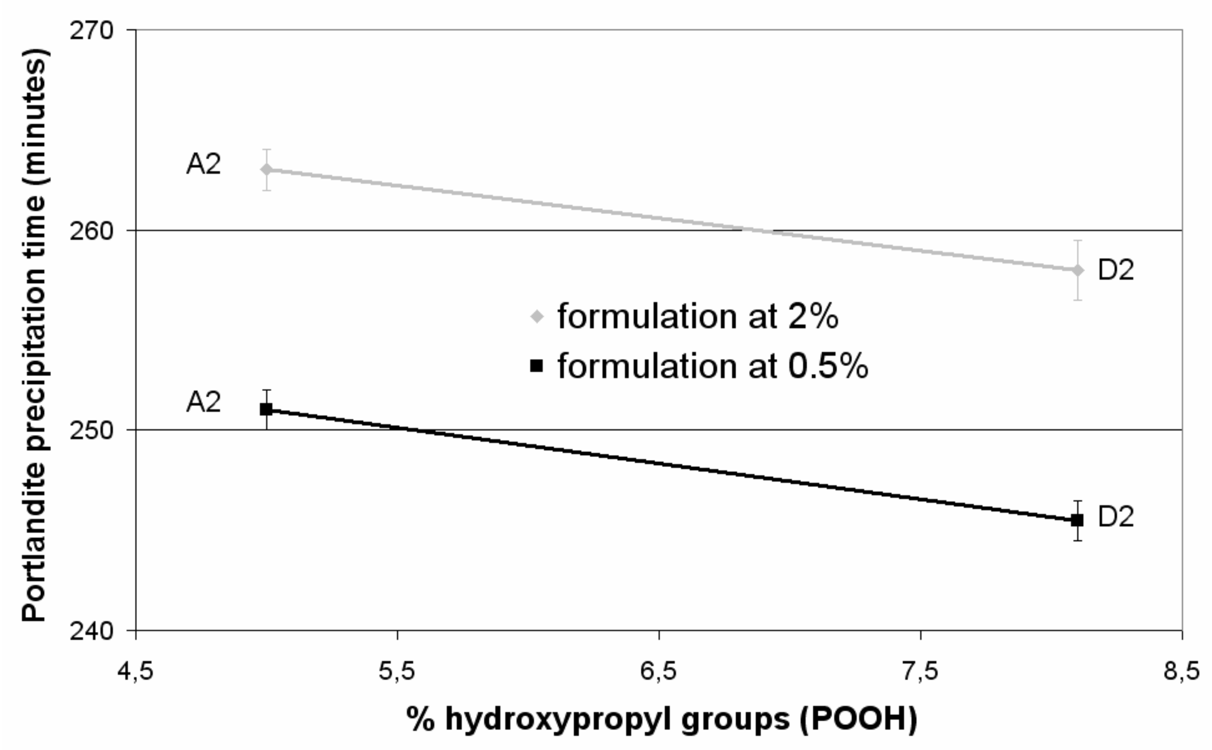

270
260
250
240
4,5
5,5
6,5
7,5
8,5
Portlandite precipitation time (minutes)
% hydroxypropyl groups (POOH)
A2
D2
A2
D2
◆ formulation at 2%
■ formulation at 0.5%

Fig. 7a Influence of % POOH on portlandite precipitation delay in aqueous system.

*J. Pourchez [1] * — A. Peschard [1] — P. Grosseau [1] — R. Guyonnet [1] — B. Guilhot [1] — F. Vallée [2]*

Fig. 7b

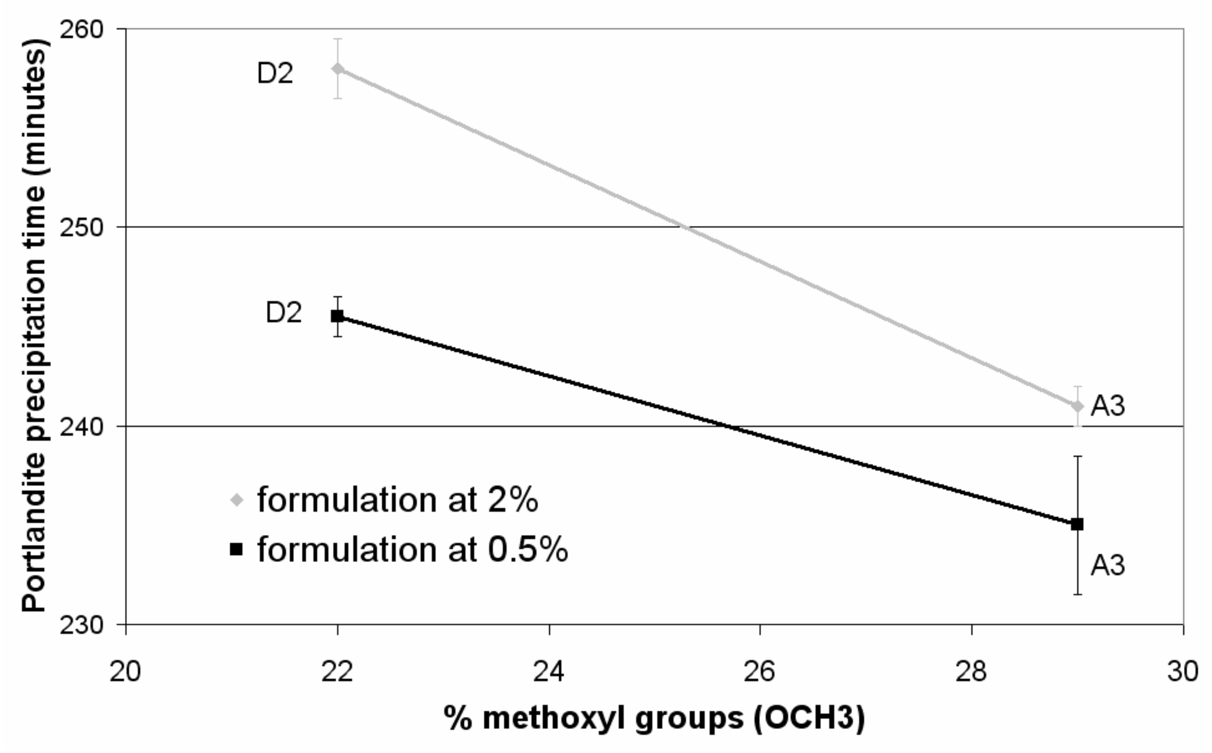
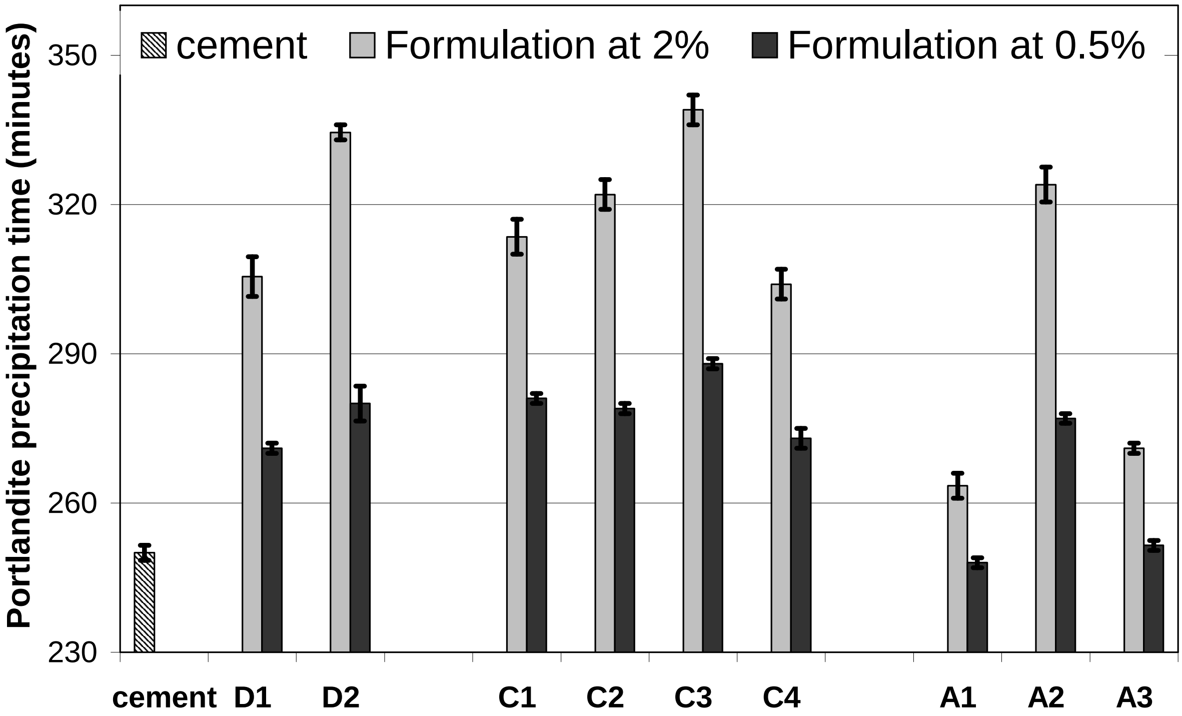

Portlandite precipitation time (minutes)
260
250
240
230
D2
D2
A3
A3
◆ formulation at 2%
■ formulation at 0.5%
20
22
24
26
28
30
% methoxyl groups (OCH3)

Fig. 7b Influence of % OCH_3 on portlandite precipitation delay in aqueous system.

J. Pourchez[1 *] *— A. Peschard*[1] *— P. Grosseau*[1] *— R. Guyonnet*[1] *— B. Guilhot*[1] *— F. Vallée*[2]

Fig. 8

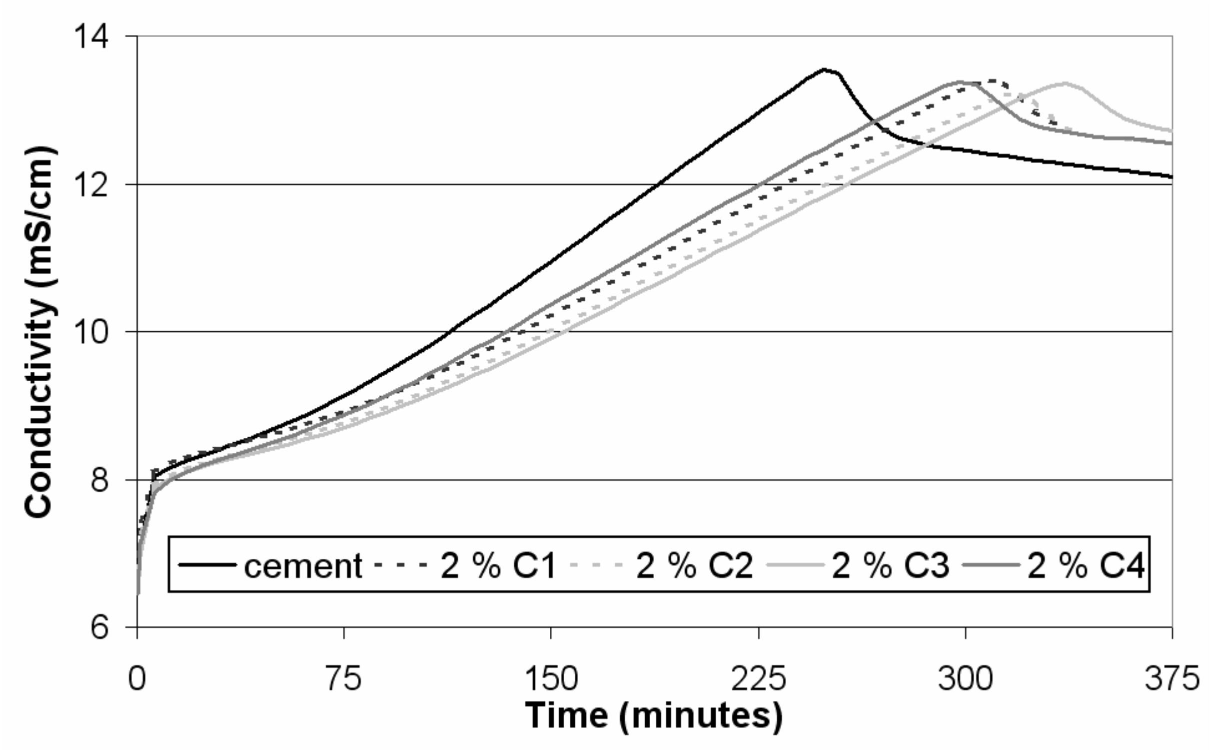


cement
Formulation at 2%
Formulation at 0.5%
Portlandite precipitation time (minutes)
350
320
290
260
230
cement
D1
D2
C1
C2
C3
C4
A1
A2
A3

Fig. 8 Portlandite precipitation delay in lime solution (L/S = 20).

J. Pourchez [1] [*] — A. Peschard [1] — P. Grosseau [1] — R. Guyonnet [1] — B. Guilhot [1] — F. Vallée [2]

Fig. 9



14
12
10
8
6
Conductivity (mS/cm)
cement
2 % C1
2 % C2
2 % C3
2 % C4
0
75
150
225
300
375
Time (minutes)

Fig. 9 Conductometric curves of cement admixed with 2% of C1 to C4 in lime solution.

Fig. 10

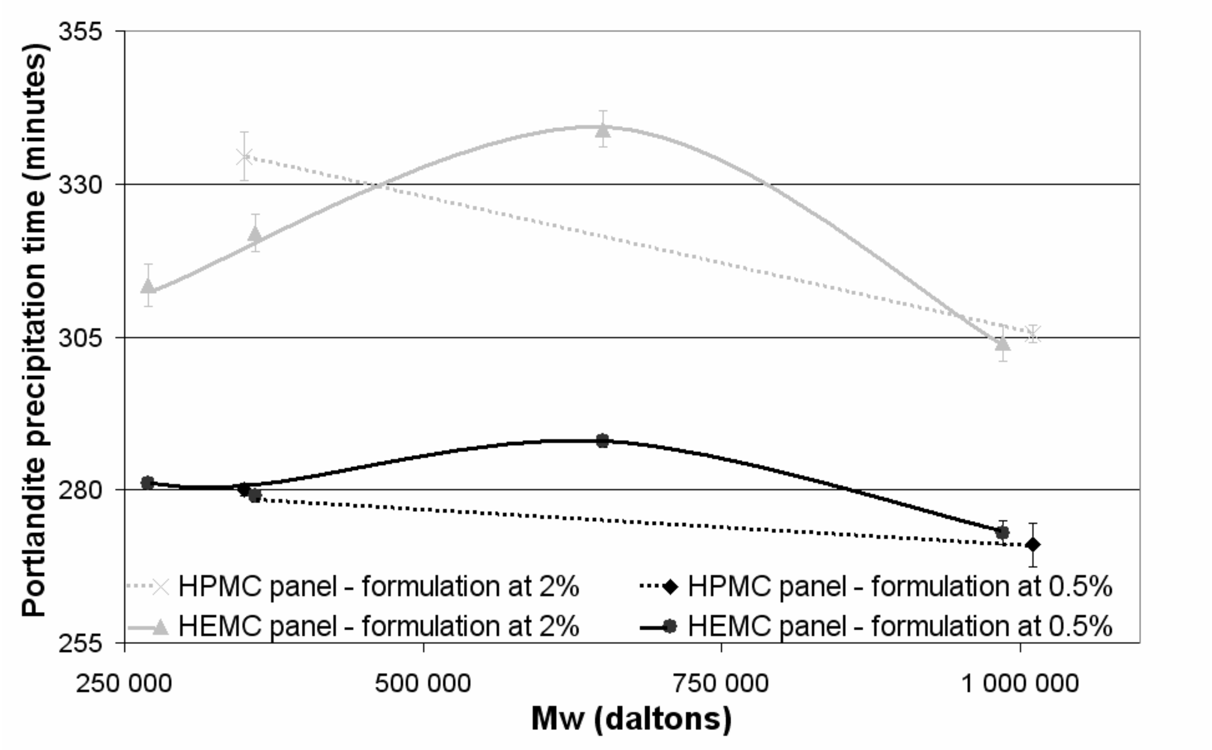

Portlandite precipitation time (minutes)
355
330
305
280
255
250 000
500 000
750 000
1 000 000
Mw (daltons)
HPMC panel - formulation at 2%
HEMC panel - formulation at 2%
HPMC panel - formulation at 0.5%
HEMC panel - formulation at 0.5%

Fig. 10 Influence of M_w on portlandite precipitation delay in lime solution.

*J. Pourchez [1] * — A. Peschard [1] — P. Grosseau [1] — R. Guyonnet [1] — B. Guilhot [1] — F. Vallée [2]*

Fig. 11a

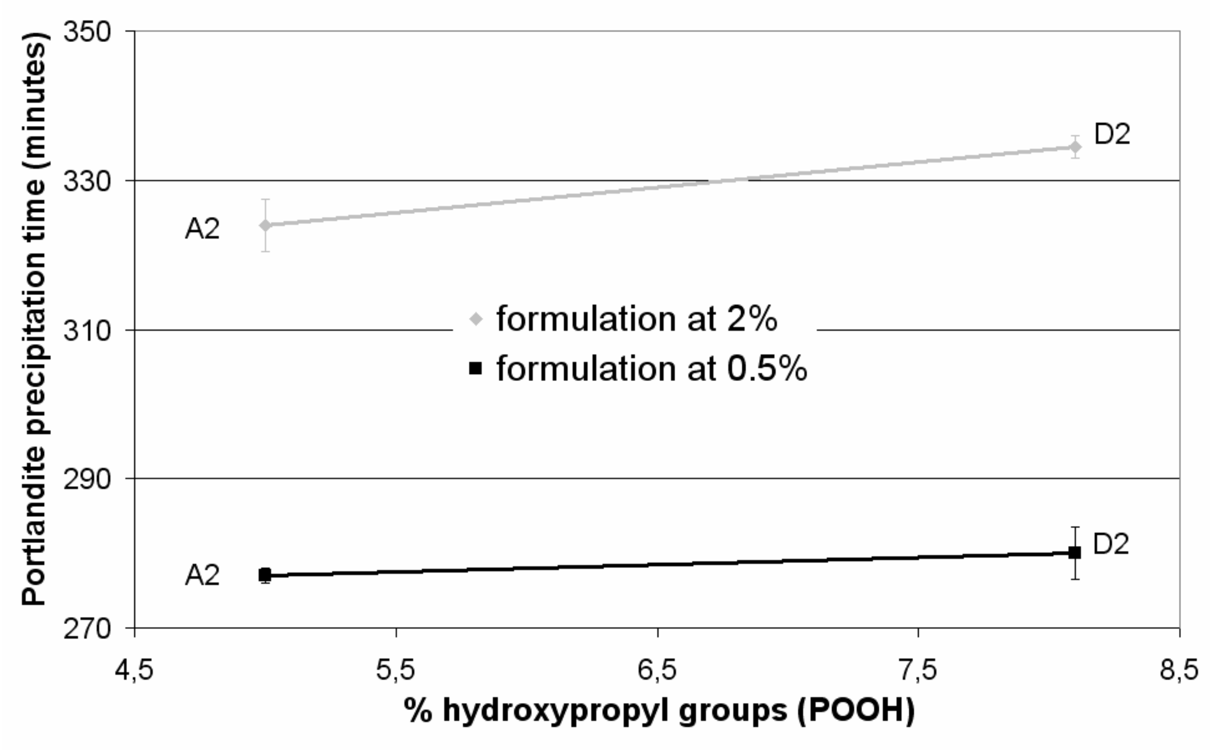
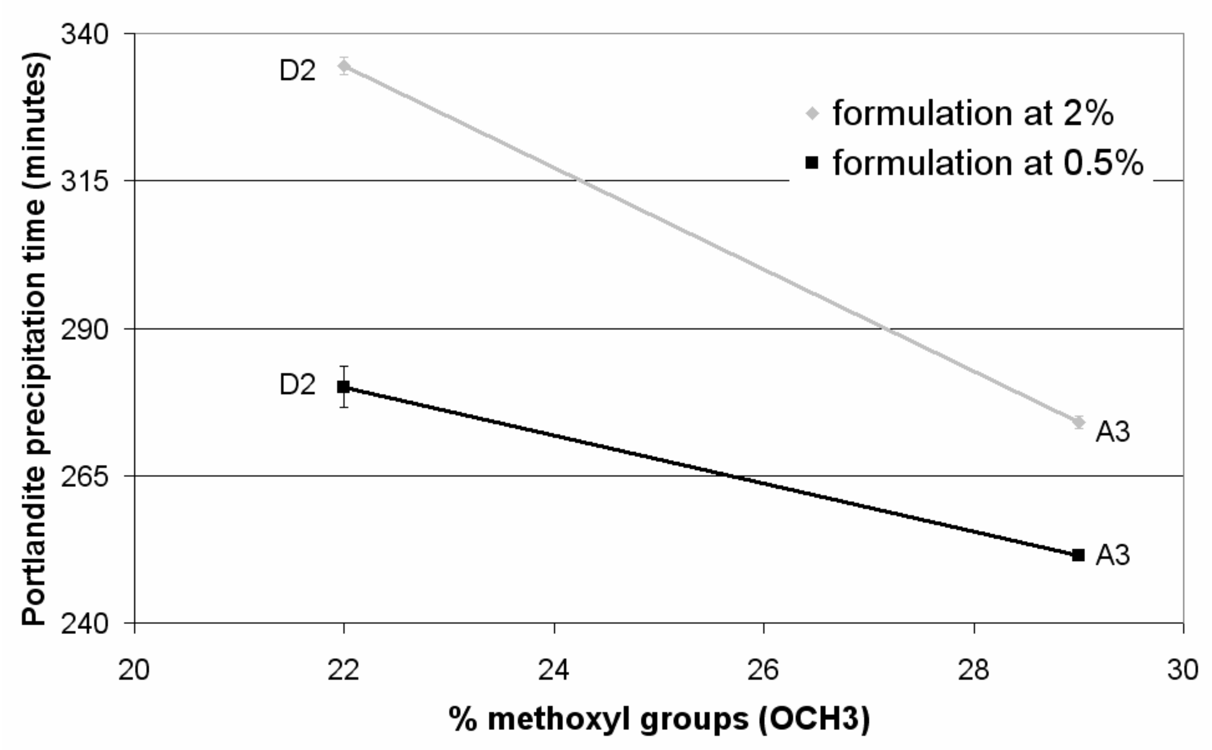

Portlandite precipitation time (minutes)
350
330
310
290
270
4,5
5,5
6,5
7,5
8,5
% hydroxypropyl groups (POOH)
A2
D2
A2
D2
◆ formulation at 2%
■ formulation at 0.5%

Fig. 11a Influence of % POOH on portlandite precipitation delay in lime solution.

*J. Pourchez [1 *] — A. Peschard [1] — P. Grosseau [1] — R. Guyonnet [1] — B. Guilhot [1] — F. Vallée [2]*

Fig. 11b



340
315
290
265
240
Portlandite precipitation time (minutes)
20
22
24
26
28
30
% methoxyl groups (OCH3)
formulation at 2%
formulation at 0.5%
D2
D2
A3
A3

Fig. 11b Influence of % OCH_3 on portlandite precipitation delay in lime solution.

*J. Pourchez [1] * — A. Peschard [1] — P. Grosseau [1] — R. Guyonnet [1] — B. Guilhot [1] — F. Vallée [2]*

Captions

Table 1 Chemical and phase composition of the investigated cement.

Table 2 Manufacturer data on cellulose ethers substituted groups and viscosities.

Table 3 Mortar formulation used for the water retention test.

Fig. 1 Structure of water-soluble cellulose derivatives (R=H for cellulose and R=H, $CH_{3,}$ $(CH_2CH_2O)_nH$ or $(CH_2CH_2CH_2O)_nH$ for HEMC or HPMC respectively).

Fig. 2 Global view of hydration mechanism on a conductometric curve (ratio liquid to solid equal to 20).

Table 4 Determination of weight-average molecular mass determination by SEC.

Table 5 Comparison of water retention obtained for the different cellulose ethers.

Fig. 3 Influence of molecular weight on water retention.

Fig. 4 Portlandite precipitation delay in aqueous system (L/S = 20).

Fig. 5 Conductometric curves of cement admixed with 2% of C1 to C4 in aqueous system.

Fig. 6 Influence of M_w on portlandite precipitation delay in aqueous system.

Fig. 7 Influence of % POOH (a) and % OCH_3 (b) on portlandite precipitation delay in aqueous system.

Fig. 8 Portlandite precipitation delay in lime solution (L/S = 20).

Fig. 9 Conductometric curves of cement admixed with 2% of C1 to C4 in lime solution.

Fig. 10 Influence of M_w on portlandite precipitation delay in lime solution.

Fig. 11 Influence of % POOH (a) and % OCH_3 (b) on portlandite precipitation delay in lime solution.