Alkaline stability of cellulose ethers and impact of their degradation products on cement hydration

J. Pourchez [a,*], A. Govin [a], P. Grosseau [a], R. Guyonnet [a], B. Guilhot [a], B. Ruot [b]

[a] *Ecole Nationale Supérieure des Mines de Saint-Etienne (ENSMSE-SPIN), LPMG: process in granular media laboratory CNRS UMR 5148, 158, cours Fauriel 42023 Saint-Etienne cedex 2, France*
[b] *Scientific and Technical Centre for Building (CSTB), 84, avenue Jean Jaurès Champs-sur-Marne- 77447 Marne-la-Vallée cedex 2, France*

Abstract

Cellulose ethers are polymers frequently introduced into mortar formulations. This study allows to assess the potential role of cellulose ethers degradation on the alteration of the cement hydration kinetics. A retardation mechanism based on the calcium binding capacity of chelates is often proposed to describe the effects of some polysaccharides (e.g. sugars) on cement hydration. The alkaline stability of cellulose ethers has been poorly studied and may represent one way to understand the hydration delay induced by such admixtures. Identification and quantification of the hydroxy carboxylic acids generated during alkaline degradation were performed. The results indicate that cellulose ethers are very stable in alkaline media. We also show that the ability of cellulose ethers to complex calcium ions is negligible. Finally, degradation of cellulose ethers and its impact on the cement hydration kinetics does not seem to be significant.
© 2006 Elsevier Ltd. All rights reserved.

1. Introduction

Cellulose ethers are usually introduced into mortar formulations in order to induce a substantial increase of the water retention capacity. They therefore prevent water from draining out too quickly from the mortar to the substrate. In this way, more water is retained in the fresh material, which favors cement hydration and thereby increases the mechanical strength of the hardened mortar. Hydration delay is an undesired and uncontrolled secondary effect induced by some cellulose ethers. These polysaccharide admixtures retard the hydration of cement through poorly understood mechanisms [1–4]. Nevertheless, it is generally accepted that retardation occurs because of adsorption of admixtures to surfaces of the hydrated and/or anhydrous phases [5]. The adsorption may take place through a process where organic molecules fix metallic ions by complexing or chelating. Concerning the action of sugars on cement hydration, many authors explained that chelation can play an important role on the adsorption ability [6,7]. Moreover, strong evidences proved that complexation of sugars with calcium is responsible for retardation [6,8]. Several studies also indicate that products formed by the alkaline degradation of cellulose (such as α-isosaccharinic acid) have a large effect on the complexation of calcium [9,10].

Pourchez et al. showed evidence of a very disparate delay on portlandite precipitation induced by cellulose ethers (from 10 min up to many hours). This retardation seems to depend mainly on the molecule chemical structure and particularly on the substitution degree [11]. Nowadays, few data are available concerning the capacity of cellulose ethers chelation in alkaline media and its potential influence on the kinetics of cement hydration. As polysaccharides are subject to alkaline degradation with formation of hydroxy carboxylic acids [12,13], which are well-known chelating and retarding agents, the possible impact of this degradation is of greatest importance in order to fully understand the action of cellulose ethers on cement hydration.

---

* Corresponding author. Tel.: +33 4 77 42 66 86; fax: +33 4 77 49 96 94.
 E-mail address: pourchez@emse.fr (J. Pourchez).

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_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			

Thanks to results with sugars [8], we know that there are at least two properties worth considering in this context: the alkaline stability and the calcium binding capacity. This study aims at collecting basic data on these two properties so as to determine the potential role of degradation during cement hydration. More precisely, this paper intends to evaluate the calcium complexing ability of cellulose ethers, to identify and quantify their degradation products in model alkaline environment, and finally to determine the retardation capacity of the different degradation products doubtless identified.

2. Materials

2.1. Cement

The investigated 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 [14]. 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. Cellulose ethers

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 different HEC molecules (noted H1, N1and N7) and two HPMCs (named U2 and P1) were selected. Beforehand, a precise characterization was performed (Table 2) by size exclusion chromatography and near infrared spectroscopy analysis [11]. 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 (% OCH_3).

3. Experimental procedures

3.1. Calcium binding capacity of cellulose ethers

The protocol performed to investigate the calcium binding ability was proposed by Thomas and Birchall [8]. Sugars (50 mM) or cellulose ethers (1 g per liter of deionized water) were stirred with excess calcium hydroxide (6 g per liter of deionized water) for 48 h. The mixture was then filtered through a 0.7 μm membrane. The filtrate was diluted and acidified. Afterwards, the Ca^{2+} concentrations of the filtrate were determined by ionic chromatography. This analysis was performed on a Dionex apparatus composed of a GP 50 pump, a CS 12A column and a CD 20 conductometric detector (the elutent was a solution of metasulfonic acid at 20 mM with isocratic mode).

3.2. Identification and quantification of degradation products

Alkaline degradation of wood polysaccharides in kraft black liquors was commonly studied in order to improve the alkaline pulping processes in the paper industry. Based on this knowledge, Govin et al. developed a procedure in order to show the action of the alkaline degradation products of wood on cement hydration [15]. With specific modifications due to particular properties of cellulose ethers, a similar protocol was elaborated.

All protocol steps of the sample preparation are illustrated in Fig. 1. The first stage of the sample preparation was the degradation of cellulose ethers. This degradation occurred within 12 h in a saturated lime media (0.5 g of cellulose ether for 100 mL of lime water). The saturated lime solution is a model alkaline media which can simulate the alkaline solution in the cement pore. Preliminary results indicated that the concentration of degradation products should be very low. Consequently, a reconcentration was provided. An evaporation with a rotary evaporator followed by a dilution of the dry solids with 2 mL of water, allowed to obtain a 0.5 mL liquor samples. As cellulose ethers are thickener agents, the solution turned into a gel during evaporation. Consequently, some centrifugations were conducted during the reconcentration to separate the non-degraded polymer from the degradation products. The obtained liquor was then passed through a column filled with a weakly acidic cation-exchange resin (Amberlite IRC-50, NH_4^+, 4 mL). The interest of this conversion into ammonium salts is to avoid lactonization reaction and ring-closure of degradation products. The ion-exchange column was then washed with water to obtain an effluent volume of 50 mL. This effluent was evaporated to

Table 2
Cellulose ether structure parameters

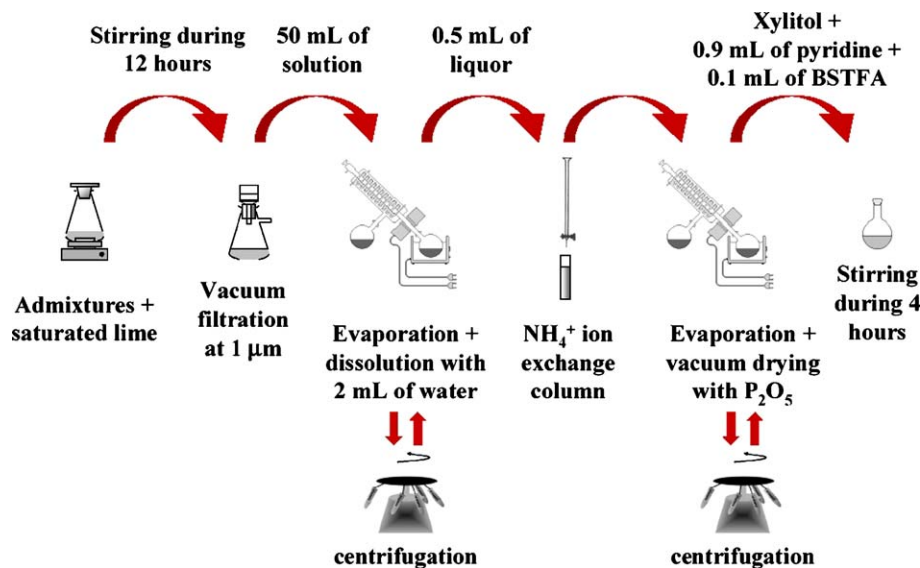| Admixtures	M_w (daltons)	% EOOH	% POOH	% OCH_3
HPMC U2	955 000	–	10.65	27.5
HPMC P1	175 000	–	19	27.5
HEC H1	175 000	48.5	–	–
HEC N1	175 000	56	–	–
HEC N7	1 335 000	56	–	–

Fig. 1. Samples preparation for the analysis of the degradation products.

dryness under reduced pressure. The obtained dry solid was vacuum-dried with P_2O_5 during 12 h. Afterwards, an internal standard (Xylitol) was added to the dry solid. Finally, 0.9 mL of pyridine and 0.1 mL of trifluorobis(trimethylsilyl)acetamide (BSTFA) containing 5% of chlorotrimethylsilane (TMCS) were added to the residue. This reaction was conducted under nitrogen environment and the mixture was stirred during 4 h. This trimethylsilylation allowed the non-volatile degradation products to be more volatile for gas chromatograph analysis. Identification and quantification were performed with a gas chromatograph (Shimadzu GC-17A) equipped with a mass spectrometer (Shimadzu QP 5000). A volume of 1.5 μL was injected. The temperature of the detector and the injector were set at 260 °C. The column was apolar (UptiBond 5 Premium– 30 m × 0.32 mm × 0.25 μm–Interchim).

3.3. Hydration delay characterization

Conductometric measurement in lime solution appears as a powerful tool to monitor the hydration kinetics [2,11,15,16]. The determination of hydration delay is based on the portlandite precipitation time, represented by an electrical conductivity drop as a benchmark. The experiments were performed in diluted water lime suspension, thermostated at 25 °C and continuously subjected to magnetic stirring. The liquid to solid (L/S) weight ratio used was equal to 20 (100 mL of liquid and 5 g of solid).

To evaluate the impact of degradation products on the kinetics of cement hydration, conductometric measurements of a cement suspension with synthetic solutions of degradation products were performed. A synthetic solution of degradation products corresponded to a solution without the cellulose ether molecule, but containing all the identified degradation products (with a concentration corresponding to the degradation of a cellulose ethers to cement weight ratio of 2%).

4. Results and discussion

4.1. Calcium binding capacity of cellulose ethers

The calcium complexing ability of cellulose ethers (H1, N1, N7, U2 and P1) and sugars (glucose, sucrose, maltose, cellobiose, raffinose and lactose) were conducted. The results are featured in Fig. 2. Two points are immediately obvious on this figure. All the cellulose ethers investigated had a calcium concentration closed to the reference sample (calcium hydroxide and deionized water). As a result, the value of Ca^{2+} ion concentration reached for the cellulose ether samples (approximately 22 mM) is only due to the calcium hydroxide solubility. On the contrary, all the sugars made calcium hydroxide soluble to some extent. The excess of Ca^{2+} ion concentration observed, by comparison with the reference sample, showed a great calcium binding capacity of sugars. These results were coherent according to the data of Thomas and Birchall on the solubilization of calcium hydroxide by sugars [8]. Therefore, this protocol was perfectly adapted to
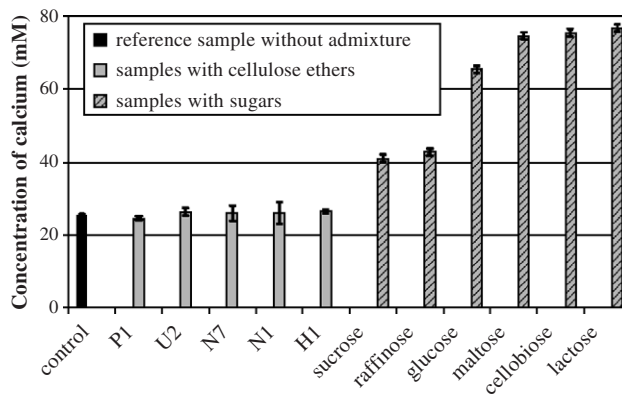

Fig. 2. Calcium binding capacity of cellulose ethers and sugars.

Table 3
Major degradation products detected

Products	Formula
Lactic acid	
Glycolic acid	
Oxalic acid	
Diethylene glycol	
Glycerol	

Fig. 4. Quantification of HECs degradation products.

4.2. Results concerning HPMCs and HECs degradation

Five major degradation products were identified: three hydroxy carboxylic acids (lactic acid, glycolic acid and oxalic acid) and two alcohols (diethylene glycol and glycerol). The chemical structure of these compounds is featured in Table 3. The detection of hydroxy acids is not amazing. Several authors showed that such hydroxy acids were commonly identified for the alkaline degradation of cellulose, hemicelluloses and monosaccharides [10,12,13,15]. The detection of the alcohols is more surprising. According to manufacturers' data, the alcohols are certainly synthesis by-products rather than alkaline degradation products. The concentrations of all degradation products are very low, lower than 1 mg per gram of HPMC introduced (Fig. 3). The concentrations of the hydroxy acids were ten times higher than that of the alcohols. Thus, we demonstrated that HPMCs are very stable in alkaline media.

In agreement with the HPMCs degradation, the same degradation products were detected for HECs degradation except oxalic acid. The same order of magnitude of concentration was obvious. The concentrations of hydroxy acids and alcohols were respectively lower than 2 mg g^{-1} and 0.2 mg g^{-1} of HEC introduced (Fig. 4). We could conclude that all cellulose ethers investigated were stable in alkaline media. Moreover, these results let us think that the substitution degrees were the key parameter which protected molecules from alkaline degradation. Indeed, the less the hydroxyethyl content, the more important the degradation. These observations were coherent with the end-wise and peeling reactions which

investigate the calcium binding ability of molecules. To sum up, cellulose ethers induced a negligible complex formation with calcium ions, unlike sugars.

Moreover, we noticed that the filtrate obtained with the reducing sugar (glucose, lactose, maltose and cellobiose) was always yellow, contrary to the non-reducing sugars (sucrose and raffinose) and cellulose ethers. This coloration was an additional evidence of the great alkaline degradation of reducing sugars, whereas cellulose ethers seemed to be inert to degradation in saturated lime solution. In order to investigate the presence of different compounds generated during the alkaline degradation, all filtrates were examined by ultra-violet spectroscopy. It was found that spectra of cellulose ethers didn't show any peak in the UV region. On the contrary, the sugars spectra showed a large peak between 250 and 300 nm. This peak was principally detected for the reducing sugars. The presence of such a peak could be the sign of either the formation of saccharinic acids, or the enolization of the reducing sugars [8–10].
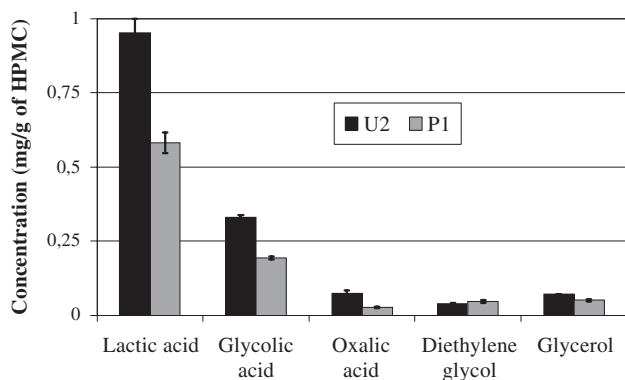

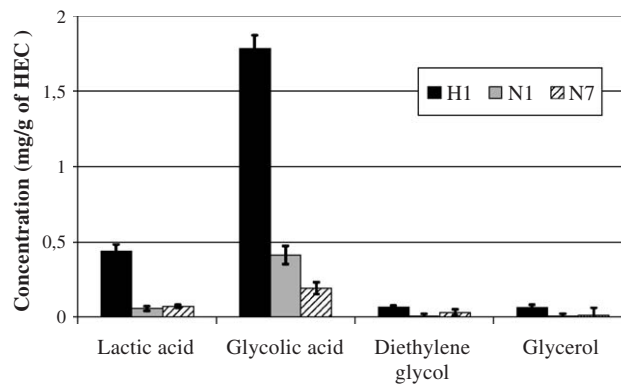Fig. 3. Quantification of HPMCs degradation products.

Table 4
Composition of the synthetic solutions of HECs degraded

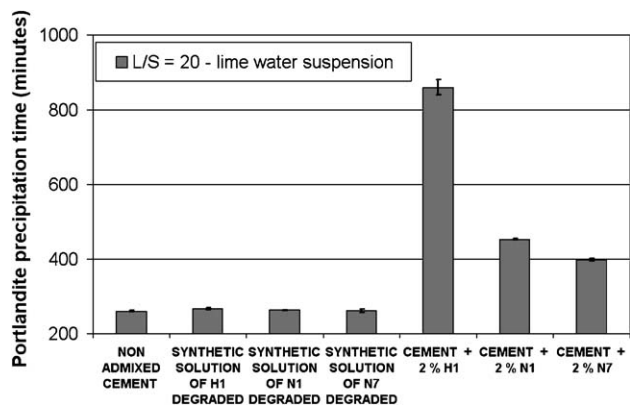| Degradation products	Synthetic solution of H1 degraded	Synthetic solution of N1 degraded	Synthetic solution of N7 degraded
Lactic acid (mg L^{-1})	1.76	0.22	0.29
Glycolic acid (mg L^{-1})	7.12	1.65	0.76
Diethylen Glycol (mg L^{-1})	0.27	0.03	0.12
Glycerol (mg L^{-1})	0.24	0.04	0.056

Fig. 5. Hydration delay on CH precipitation induced by HEC and synthetic solution of HEC degraded.

involved the effects of specific linkages on alkaline degradation of polysaccharides [13].

4.3. Influence of degradation products on cement hydration

Even if the concentrations of degradation products were very low, these molecules may have a great impact on cement hydration. Conductometric measurements of a cement suspension with synthetic solutions of degradation products were performed. For example, the compositions of the synthetic solutions for HECs are described in Table 4. The low retardation induced by synthetic solutions of degraded HECs proved that the degradation products had a minor impact on the kinetics of cement hydration. The results are presented in Fig. 5. The retardation on the portlandite precipitation due to the degradation products was always lower than 15 min. This is really negligible in comparison with the delay induced by the cellulose ether H1 (approximately 10 h). The retardation caused by synthetic solutions of HPMCs (not described in this paper) had the same order of magnitude with that of the synthetic solutions of HECs. These experiments allowed to determine the real influence of degradation products on the hydration delay induced by cellulose ethers: there was no significant degradation of the cellulose ethers, and therefore its impact on cement hydration was negligible.

5. Conclusions

Through this study, the stability of cellulose ethers in alkaline media was demonstrated. Negligible calcium binding capacity of cellulose ethers was observed. Afterwards, the alkaline degradation of the selected cellulose ethers showed that the major hydroxy acids detected were lactic acid and glycolic acid. The degradation products had always a concentration lower than 2 mg g^{-1} of cellulose ether introduced. The very low influence of these degradation products on the kinetics of cement hydration was also proved.

It is well-known that the retarding action of sugars on cement hydration was due to the remarkable ability of the

degradation products to be more effective retarders than the sugars themselves. We verified that the hydrolysis of sugars in strong alkali media gives rise to compounds with a high calcium binding capacity. However, the mechanism of the hydration delay induced by HECs and HPMCs cannot be explained thanks to the impact of hydroxy carboxylic acids generated during their alkaline degradation. Therefore, new assumptions shall be proposed and examined to understand what happens when various cellulose ethers are added to Portland cement.

Acknowledgements

References

[1] A. Peschard, A. Govin, P. Grosseau, B. Guilhot, R. Guyonnet, Effect of polysaccharides on the hydration of cement paste at early ages, Cem. Concr. Res. 34 (2004) 2153–2158.

[2] A. Peschard, A. Govin, J. Pourchez, E. Fredon, L. Bertrand, S. Maximillien, B. Guilhot, Effect of polysaccharides on the hydration of cement suspension, J. Eur. Ceram. Soc. 26 (2006) 1439–1445.

[3] G. Bruere, Set-retarding effects of sugars in Portland cement pastes, Nature 212 (1966) 502–503.

[4] K. Luke, G. Luke, Effect of sucrose on retardation of Portland cement, Adv. Cem. Res 12 (2000) 9–18.

[5] C. Jolicoeur, M.A. Simard, Chemical admixture–cement interactions: phenomenology and physico-chemical concepts, Cem. Concr. Compos. 20 (1998) 87–101.

[6] J.H. Taplin, Discussion of the paper by H.E. VIVIAN "Some chemical additions and admixtures in cement paste and concrete", Proceeding of the 4th international symposium on the chemistry of cement, Washington, vol. VII-1, 1962, pp. 909–926.

[7] M.E. Tadros, J. Skalny, R.S. Kalyoncu, Early hydration of tricalcium silicate, J. Am. Ceram. Soc. 59 (1976) 344–347.

[8] N.L. Thomas, J.D. Birchall, The retarding action of sugars on cement hydration, Cem. Concr. Res. 13 (1983) 830–842.

[9] K. Vercammen, M.A. Glaus, L.R. Van Loon, Complexation of calcium by α-isosaccharinic acid under alkaline conditions, Acta Chem. Scand. 53 (1999) 241–246.

[10] M.A. Glaus, L.R. Van Loon, S. Achatz, A. Chodura, K. Fischer, Degradation of cellulosic materials under alkaline conditions of a cementitious repository for low and intermediate level radioactive waste: Part I. Identification of degradation products, Anal. Chem. Acta 398 (1999) 111–122.

[11] J. Pourchez, A. Peschard, P. Grosseau, B. Guilhot, R. Guyonnet, F. Vallee, HPMC and HEMC influence on cement hydration, Cem. Concr. Res. 36 (2006) 288–294.

[12] R.L. Whistler, J.N. Bemiller, Alkaline degradation of polysaccharides, Adv. Carbohydr. Chem. Biochem. 13 (1958) 289–329.

[13] C.J. Knill, J.F. Kennedy, Degradation of cellulose under alkaline conditions, Carbohydr. Polym. 51 (3) (2003) 281–300.

[14] H.F.W. Taylor, Cement chemistry, Telford, New York, 1997, pp. 60–63.

[15] A. Govin, A. Peschard, E. Fredon, R. Guyonnet, New insights into wood and cement interaction, Holzforschung 59 (2005) 330–335.

[16] A. Nonat, J.C. Mutin, X. Lecocq, S.P. Jiang, Physico-chemical parameters determining hydration and particle interactions during the setting of silicate cements, Solid State Ionics 101–103 (1997) 923–930.