Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 34 (2004) 2153–2158

CEMENT AND CONCRETE RESEARCH

Effect of polysaccharides on the hydration of cement paste at early ages

A. Peschard[1], A. Govin*,[1], P. Grosseau, B. Guilhot, R. Guyonnet

Ecole Nationale Supérieure des Mines de Saint Etienne, LPMG Process in Granular System Laboratory, CNRS UMR 5148, Centre SPIN,
Department of Materials Engineering (PC2M), 158 cours Fauriel, 42023 Saint Etienne cedex, France

Received 18 March 2003; accepted 1 April 2004

Abstract

This work deals with the relative efficiency of polysaccharides and their influence on cement hydration. Several parameters such as the structure, concentration, average molecular weight, and soluble fraction value of polysaccharides were examined. Cement hydration was monitored by isothermal calorimetry, thermogravimetry (TGA), and Fourier transform infrared (FTIR) spectroscopy. Results clearly show that retardation increases with higher polysaccharide-to-cement weight ratio (P/C). Low-molecular-weight starch showed enhanced retarding effect on the hydration of cement. The retardation effect of polysaccharides is also dependent on the composition of cement.

Keywords: Hydration; Polymers; Polysaccharides; Retardation; Cement paste

1. Introduction

Organic admixtures have been widely used in concrete and mortar for several decades, providing advanced specific properties needed during the construction. The European market of coatings is changing to the advantage of the remodelling market. Mortars for this application require a water retention value of at least 95% to prevent water absorption. To obtain this value, polysaccharides, which can be equally classified as water reducers and set-retarding agents, are frequently used. These admixtures can be either native biopolymers (e.g., starch) or substituted polymers [e.g., cellulose ethers (CEs)]. Dewacker and Mcad [1] suggested that a blend of polysaccharides such as cellulose and starch was a good water-retention agent.

These admixtures are also set-retarding agents that improve workability duration and modify cement hydration. Yamamuro [2] showed that a polysaccharide derivative containing an ionic functional and a hydrophobic group increases the viscosity of cement suspensions. In the shotcrete process, Ghio and Monteiro [3] and Ghio et al. [4] showed that concretes formulated with polysaccharides are easier to pump and spray at high shear rates than are unadmixed concrete. Moreover, concrete is more cohesive and viscous at low shear rates. Tanaka et al. [5] patented an additive that contains at least one sulfated polysaccharide to improve fluidity and workability and that supplies higher final compressive strength. Hayakawa and Soshiroda [6,7] reported that CE improves binding between cement matrix and aggregates.

Previous investigations on physicochemical aspects were restricted to the effect of monosaccharides or sugar acids on cement or single-phase hydration [8–11]. The influence of such admixtures on the calcium aluminate phase (C_3A) was studied by Young [8], who showed that the interaction of sugars on C_3A prevents the rapid formation of the cubic phase C_3AH_6 and promotes the formation of the hexagonal phase C_4AH_{13}. Collepardi et al. [9,10] found that the addition of glucose, gluconate, or lignosulfonate stabilizes ettringite in the C_3A–gypsum system. It was also noted that glucose retards gypsum consumption and ettringite formation.

Many studies on the hydration of silicate phase in the presence of admixtures were devoted to the determination of calcium hydroxide content. According to Milestone [11], the retarding effect is as follows: sugar acids>sugars>lignosulfonates. Scanning electron microscopic (SEM) examination showed that in the presence of these admixtures, calcium silicate phase (C_3S) particles are covered by flaky calcium silicate hydrate (CSH) instead of acicular hydrates [11].

Bensted [16] investigated the effect of lignosulfonate on the hydration of cement and found that retardation is linked either to a preferential complexation with calcium and

---

* Tel.: +33-4-77-42-02-74; fax: +33-4-77-49-96-94.
E-mail address: govin@emse.fr (A. Govin).

[1] These authors have contributed equally to this work.

0008-8846/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2004.04.001

silicon or to an introduction of organic admixtures into a precipitated gel. This latter hypothesis postulates that the retarding effect would come from the formation of a less permeable gel coating around the cement grains. However, the mechanism of the cement–admixture interaction is yet to be fully understood.

The present study was undertaken to determine the relative efficiencies of polysaccharides and to reveal the mechanism of interaction between cement particles and the admixture at the early stages of hydration.

2. Experimental

2.1. Raw materials

White Portland cement (C_1), CPA CEM I 52.5, and grey cement (C_2), PMES 42.5, were used in this study. The designation follows the French standard NF P 15-301. The chemical composition and mineralogical phases of the two cement samples were calculated by the Bogue approximation [12] and are listed in Table 1.

Five powder polysaccharides, CE, a starch ether (SE), a native starch (NS), a white dextrin (WD), and a yellow dextrin (YD), the last two prepared from NS, were tested. The properties of these polysaccharides are given in Table 2.

2.2. Methods of investigation

Isothermal microcalorimetry, thermogravimetry (TGA), and Fourier transform infrared (FTIR) spectrometry were used to monitor the kinetics and mechanism of cement hydration.

Each experiment was conducted in triplicate. In each case, the cement and polysaccharides were mixed for two periods of 2 min using a shaker-mixer (Wab, Turbula, Germany). Unless otherwise stated, the polysaccharide-to-cement weight ratio (P/C) was equal to 0.5 (w/w).

Table 1
Chemical composition of cement and potential phases as determined by Bogue approximation

	C_1	C_2
Chemical composition		
SiO_2	22.2	21.9
TiO_2	0.2	0.4
Al_2O_3	4.4	3.8
Fe_2O_3	0.3	4.3
CaO	67.2	62.8
MnO	0.01	0.04
MgO	0.5	2.2
Na_2O	0.4	0.4
K_2O	0.05	0.39
P_2O_5	0.11	0.26
SO_3	3	2.6
Bogue approximation		
C_3S	66	51
C_2S	14	24
C_3A	11	2.6
C_4AF	1	13.2

Table 2
Properties of polysaccharides

Admixture	Solubility at 25 °C	Molecular weight (Da)[a]	Substituent[b]
CE	Yes	$(11.6 \pm 0.1) \times 10^6$	CH_3, $(CH_2)_3-OH$ and $(CH_2)_2-OH$
SE	Yes	$(1.48 \pm 0.05) \times 10^6$ $(173 \pm 5) \times 10^3$	$(CH_2)_3-OH$
NS	Nd	25.2×10^6 $(290 \pm 6) \times 10^3$	
WD	$5\% < S < 35\%$	$(11 \pm 1) \times 10^3$	
YD	$S > 90\%$	$(4.5 \pm 0.1) \times 10^6$ $(8.5 \pm 0.5) \times 10^3$	

S: soluble fraction value (producers' data).

[a] Determined by gel permeation chromatography.

[b] Determined by pyrolysis–gas chromatography–mass spectrometry.

Deionized water-to-cement ratio (W/C) was approximately 0.3 and was adjusted to have a constant workability. The W/C values of C_1, $C_1 + CE$, $C_1 + SE$, $C_1 + NS$, $C_1 + WD$, $C_1 + YD$, C_2, and $C_2 + YD$ were 0.282, 0.265, 0.342, 0.295, 0.295, 0.267, 0.215, and 0.225, respectively. The cement pastes were obtained using a mixer (Technotest, France) for 1 min at low speed (60 rpm) and 4 min at high speed (120 rpm). Samples were stored in a water-vapour-saturated desiccator and under nitrogen atmosphere. Cement hydration was stopped by breaking and grinding the hydrated samples and washing them with anhydrous ethanol. The samples were ground in an agate mortar until each particle diameter became lower than 100 μm. This step was reproduced at different lengths of time ranging from 1 to 24 h.

Thermal analysis was performed on a TG-DSC 111 thermogravimetric apparatus (Setaram, France). All experiments were conducted from 20 up to 800 °C (heating rate of 10 °C/min) under dynamic argon atmosphere on approximately 25-mg samples.

The amount of portlandite CH(%) was obtained directly from TG curves by Eq. (1):

$$\mathrm{CH}(\%) = \mathrm{WL}_{\mathrm{CH}}(\%)\frac{\mathrm{MW}_{\mathrm{CH}}}{\mathrm{MW}_{\mathrm{H}}} \tag{1}$$

where $WL_{CH}(\%)$ corresponds to the weight loss, in percent, occurring during CH dehydration, and MW_{CH} and MW_H are the molecular weights of portlandite and water, respectively.

Infrared spectra were collected with a spectrometer (Biorad FTS 185, Digilab, USA) equipped with a Harrick scattering reflexion accessory. Analysis was conducted on hydrated samples diluted at 5% in KBr. The spectra were converted by the Kubelka–Munk algorithm.

Admixtures can be classified in the retarders or accelerators category using isothermal microcalorimetry [13]. It enables the hydration process to be monitored continuously and was conducted on a C80 calorimeter (Setaram). The temperature of the calorimetric block was maintained at 25 °C, and the experiments were conducted on a 250-mg sample at a W/C ratio of 0.4. Cement and water mixing was done outside the calorimeter, according to the procedure described by Sauvat et al. [14] and Ramachandran and Lowery [15]. Consequently, only the exothermic hydration peak was encountered.

3. Results and discussion

3.1. Hydration of C_1

Investigations were first focused on C_1 because this type of cement is frequently used in coating formulas. The calorimetric curve of neat cement exhibits two separate exothermic peaks. According to Sauvat et al. [14], they correspond to the C_3A and C_3S hydration peaks, respectively, whereas Bensted [16] suggested the reverse order. The retarding ability of polysaccharides on cement hydration is obtained from the curves of the heat evolution rate. Three different times were defined, as proposed by Sauvat et al. [14], t_1, t_2, and t_3, which correspond to the minimum flux, second peak, and third peak times, respectively. Heat released in 24 h of hydration was calculated by curve integration from t_1 to t_{24h} (Table 3). The intensity and shape of the exothermic peaks are not significantly modified by CE and NS addition. The intensity of heat flow for the cement formulated with SE is lower. The cement admixed with YD presents a larger wetting peak, which induces a shift of the minimum heat flow to 10 h. Moreover, the heat released during the first 24 h of hydration is smaller. These results confirm previous studies regarding the effects of set-retarding agents on cement hydration [14,15]. Ramachandran and Lowery [15] found that sucrose is an efficient retarder, which extends the induction period for several hours. Similar result was obtained with YD in the present study.

Previte [17] suggested that alkali-stable and high-molecular-weight sugars are more efficient to retard hydration. It should be noted that the oligomers used by this author had a maximum chain length of three units. To extend this previous study, the present results focus on polysaccharides with a much higher degree of polymerization. Polysaccharides with a strong set-retarding ability, i.e., SE and YD, have a lower average molecular weight than CE and NS. A weak average molecular weight favors the alkali degradation of polysaccharides [18,19]. Several authors have shown that products from the decomposition of sugar are more effective than native sugars [15,20].

Table 3
Times and heat released in 24 h as a function of polysaccharide added

Formula	t_1 (h)	t_2 (h)	t_3 (h)	Q_{24h} (J/g)
C_1	2.4 ± 0.3	7.2 ± 0.3	11.2 ± 0.6	99 ± 5
C_1 + CE	3.5 ± 0.5	9.5 ± 0.7	13.5 ± 0.7	97 ± 5
C_1 + SE	2.2 ± 1.5	8.2 ± 2.1	14.5 ± 4.1	60 ± 8
C_1 + NS	2.9 ± 0.2	7.7 ± 0.1	11.4 ± 0.1	94 ± 7
C_1 + YD	7.9 ± 0.4	18.2 ± 1.1	–	9 ± 1

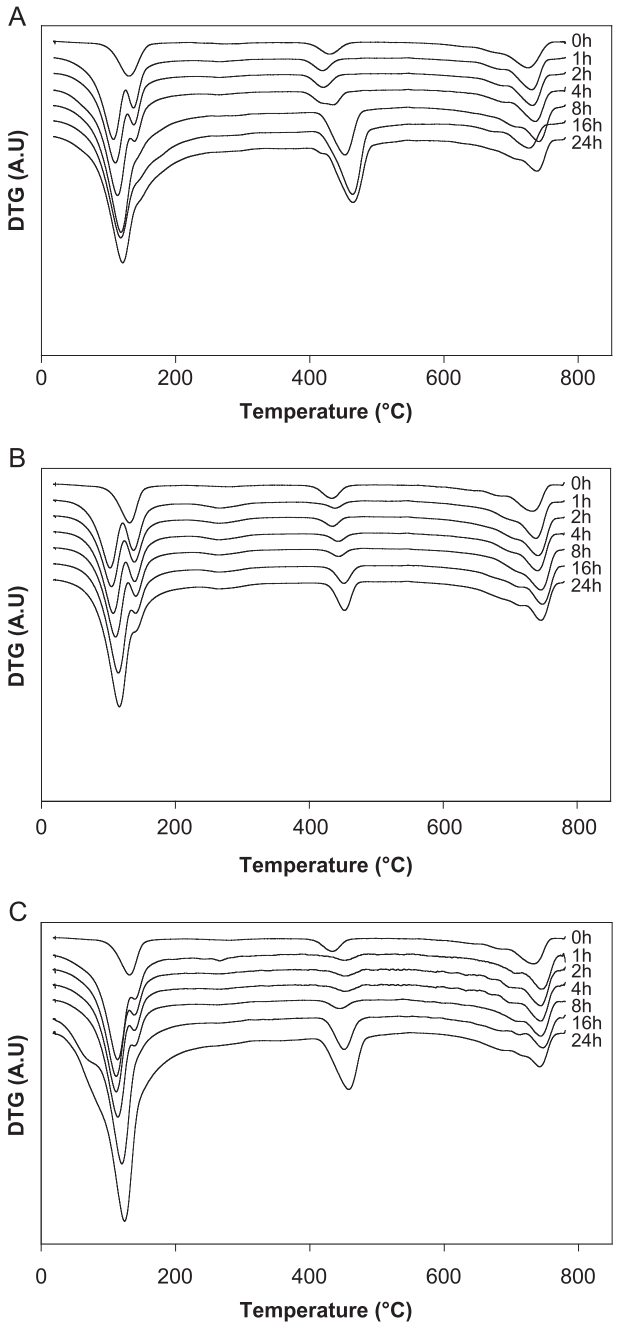

Fig. 1. DTG curves of (A) C_1, (B) C_1 + SE, and (C) C_1 + YD.

Differential thermal analysis (DTA) and TGA were used to study the effects of sugars and hydroxycarboxylic acids on the hydration of different cement phases. As Bensted and Varma [21] and Odler and Abdul-Maula [22] suggested, it is possible to assign the first two peaks at 120 and 145 °C to ettringite and gypsum decomposition, respectively (Fig. 1A). Beyond 4 h of hydration, the decomposition peaks of CSH and ettringite overlap. It is also possible to monitor gypsum consumption until it completely disappears because no other phase interferes with it. The decomposition peak of CH occurs between 420 and 460 °C.

The $C_1 + SE$ formula revealed a smaller amount of ettringite and a smaller gypsum consumption than C_1 (Fig. 1B). However, the admixture YD accelerated gypsum consumption and ettringite formation (Fig. 1C) as compared with C_1. It can be at the origin of the wetting peak broadening on the calorimetric curve. Between 4 and 8 h of hydration, the ettringite phase seems to be stabilized, and gypsum is no longer consumed for both formulas. Moreover, the decomposition peak of portlandite is less intense for $C_1 + SE$ and $C_1 + YD$. Further information is obtained by the calculation of portlandite content, as specified by Eq. (1). Portlandite formation depends strongly on the type of polysaccharide introduced in the cement (Fig. 2). YD stops portlandite formation during 8 h. Beyond this period, the formation rate increases, and, finally, portlandite content is very close to those of pure cement. Conversely, CE and NS have had no significant effect on gypsum consumption, on ettringite as well as on portlandite formation (Fig. 2).

A smaller amount of portlandite could be associated with greater carbonation, as proposed by Silva et al. [23], for cement admixed with ethylene/vinyl acetate copolymer. Weight losses occurring during decarbonation were compared. Carbonation does not significantly increase upon polysaccharide incorporation. Thus, at a given time, the presence of admixtures YD and SE induces a smaller content of portlandite.

CSH formation was monitored by infrared spectroscopy because monitoring by thermal analysis at early ages is not possible. CSH is usually observed by a gradual shift of band centered from 925 to 970 cm^{-1}, which is assigned to the asymmetrical SiO_4 stretching frequency [21]. It indicates the polymerization of silicate units SiO_4^{4-} with the formation of the CSH phase [24]. CSH has already been formed for C_1 and $C_1 + CE$ at 8 h of hydration (Fig. 3). On the contrary, $C_1 + SE$ and $C_1 + YD$ revealed no shift attributed to CSH formation.

Results obtained from these studies are consistent. CE has no significant effect on hydrate formation. YD extends the induction period, favors ettringite formation at very early ages, and retards CSH and CH formation. SE slows ettringite formation and gypsum consumption and delays considerably CSH and CH formation.

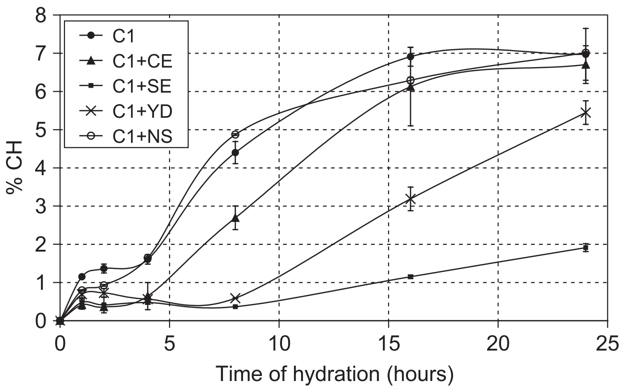

Fig. 2. Evolution of portlandite content in admixed cement pastes.

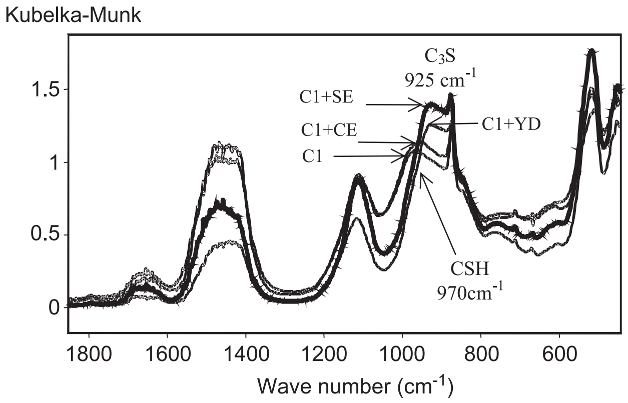

Fig. 3. FTIR spectra of hydrated admixed cements.

3.2. Influence of SE and YD concentration on cement hydration

Results obtained by isothermal microcalorimetry for an increasing amount of polysaccharides are listed in Table 4. It shows that t_1 and t_2 are not significantly modified by an increase of SE concentration and that t_3 is not defined for SE concentration over 0.5%. As YD concentration rises, t_1 and t_2 are shifted to later times. In both formulas, the evolution of heat released is inversely proportional to concentration. The results of $C_1 + YD$ are consistent with those of Ramachandran and Lowery [15], who proposed a linear relation between the concentration of retarders and the duration of the induction period.

3.3. Study on the admixture YD

3.3.1. Influence of cement composition on the retarding ability of YD

To determine the effect of cement composition and especially the C_3A content on the set-retarding ability of polysaccharides, cement C_2 was studied. For this experiment, admixture YD was used, as it has a strong retarding effect on cement hydration. As illustrated in Fig. 4A,

Table 4
Times and heat released in 24 h for increasing concentrations of SE and YD

Formula	t_1 (h)	t_2 (h)	t_3 (h)	Q_{24h} (J/g)
C_1	2.4 ± 0.3	7.2 ± 0.3	11.2 ± 0.6	99 ± 5
C_1 + 0.5% SE	2.2 ± 1.5	8.2 ± 2.1	14.5 ± 4.1	60 ± 8
C_1 + 1.2% SE	3 ± 0.2	7.8 ± 0.4	–	45 ± 5
C_1 + 1.5% SE	3 ± 0.2	7.9 ± 0.3	–	28 ± 5
C_1 + 2% SE	3.8 ± 0.3	7.9 ± 0.4	–	8 ± 1
C_1 + 0.1% YD	2.2 ± 0.2	8.0 ± 0.3	12.2 ± 0.5	78 ± 5
C_1 + 0.3% YD	4.6 ± 0.3	15.0 ± 0.5	–	48 ± 5
C_1 + 0.4% YD	7.2 ± 0.3	16.4 ± 0.8	–	37 ± 4
C_1 + 0.5% YD	7.9 ± 0.4	18.2 ± 1.1	–	9 ± 1

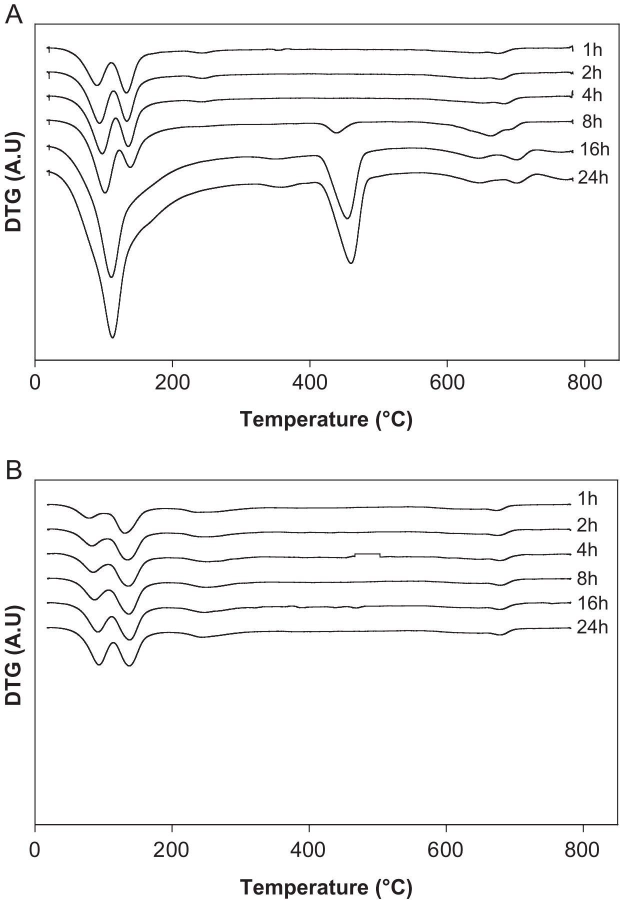

Fig. 4. DTG curves of (A) C_2 and (B) $C_2 + YD$.

gypsum was totally consumed for pure C_2 after 16 h of hydration. The introduction of YD revealed a decomposition peak at 145 °C, attributed to gypsum up to 24 h (Fig. 4B).

Portlandite formation rate is higher for C_1 than for C_2 (Fig. 5). It can be associated with a higher C_3S content for C_1. C_3A amount seems to be an important parameter because 0.5% of YD totally inhibits portlandite formation up to 48 h. The present results are similar with those of Singh [25]. Monosi et al. [26] found that lignosulfonate totally stops C_3S hydration up to 2 weeks without C_3A. The inhibiting effect lasts only 1 day with C_3A. This reveals the importance of C_3A content in cement, which acts as a sink for retarders [15].

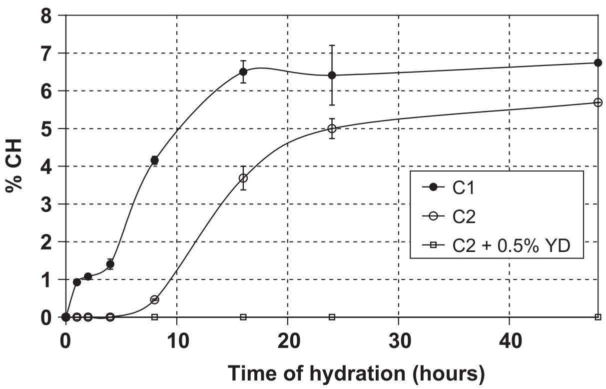

Fig. 5. Effect of cement composition on the retarding ability of YD.

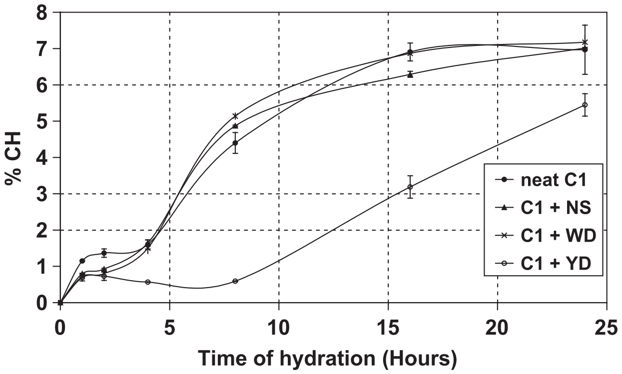

Fig. 6. Effect of starch dextrinization on the evolution of CH formation in C_1.

C_2 hydrated with 0.5% YD suggests an excess of admixture with respect to cement. P/C_3A ratio for this formula is 0.2 instead of 0.045 for $C_1 + 0.5\%$ YD. To verify the fact that an excess of YD with respect to C_2 was introduced, an experiment on $C_1 + 3\%$ YD was performed (P/C_3A ratio equal to 0.25). The results obtained with this formula are similar with that of $C_2 + 0.5\%$ YD; that is, portlandite formation was completely inhibited.

3.3.2. Influence of dextrinization on the set-retarding ability of starch compounds

WD and YD were obtained from NS by dextrinization, which is a combination of an acid and a thermal treatment. It allows starch solubilization by a decrease of average molecular weight. The soluble fraction value increases with the degree of conversion of starch to dextrin (Table 2). Thermal analysis is performed on C_1 with 0.5% of admixture. YD delays portlandite formation, whereas NS and WD have no effect (Fig. 6).

The average molecular weights and soluble fraction of starch derivatives are given in Table 2. At a given P/C ratio, YD concentration in the liquid phase is higher than the WD and NS concentrations. Portlandite rate formation is more dependent on the soluble fraction than on the molecular weight of compounds. The dextrinization of NS is a predominant parameter on the retarding ability of starch derivatives.

4. Conclusions

The results obtained by thermal analysis show that the introduction of a small amount of polysaccharide (0.5% by weight of cement) induces a strong modification of cement hydration. Retarding ability is dependent on polysaccharide variety and is as follows: NS < WD < CE < YD < SE.

A mechanism that describes the cement–polysaccharide interaction is difficult to establish. The first step of C_3A hydration leading to ettringite is accelerated by YD and retarded by SE. These polysaccharides then stabilize ettringite and gypsum content. This observation will induce a delay in the conversion of ettringite to monosulfoaluminate phase. From these results, the action of polysaccharides on C_3A hydration seems more restricted to the growth of hydrates than to nucleation. Consequently, the origin of retardation could be linked to an adsorption of admixtures on the first hydrates forming a less permeable coating. As far as silicate hydration is concerned, SE and YD (the most effective polysaccharides) slow and delay the formation of both CSH and portlandite, respectively.

Polysaccharide retarding effect depends on cement composition. C_3A content might be considered as a key parameter. The extent of retardation is higher for cement with low C_3A content, which is in accordance with other authors [15,25,26]. The retarding effect depends also on the chemical structure of the admixtures. With respect to starch compounds, YD, with a higher soluble fraction than NS and WD, is more effective to retard cement hydration. A study with polysaccharides that have only one variable parameter, like degree of polymerization or of substitution, would produce valuable results in terms of admixture selection and properties prediction. Experiments on pure cement phase would provide useful information. It could be a first step to model pure phase hydration in the presence of polysaccharide.

Acknowledgements

The authors acknowledge the financial support of Weber & Broutin (Servas, France) and Rhône-Alpes Region. The authors are grateful to J.F. Halet for his assistance.

References

[1] D.R. Dewacker, B. Mcad, Cement mortar systems using blends of polysaccharides and cold-water-soluble unmodified starches, US Patent 5,575,840, 1996.

[2] H. Yamamuro, Property of new polysaccharide derivative as a viscosity agent for self compacting concrete, First International Rilem Symposium on Self Compacting Concrete, Stockholm, Sweden, RILEM publications, Bagneux, France, 1999, pp. 449–459.

[3] V.A. Ghio, P.J.M. Monteiro, The effects of polysaccharide gum additives on the shotcrete process, ACI Mater. J. 95 (2).

[4] V.A. Ghio, P.J.M. Monteiro, L.A. Demsetz, The rheology of fresh cement paste containing polysaccharide gums, Cem. Concr. Res. 24 (2) (1994) 243–249.

[5] Y. Tanaka, T. Uryu, M. Yaguchi, Cement compositions containing a sulfated polysaccharide and method, US Patent 5,573,589, 1996.

[6] K. Hayakawa, T. Soshiroda, An experimental study on the concrete containing cellulose ether, Trans. Jpn. Concr. Inst. 7, (1985) 17–24 (Japan Concrete Institute, Tokyo).

[7] K. Hayakawa, T. Soshiroda, Effects of cellulose ether on bond between matrix and aggregate in concrete, Adhesion Between Polymers and Concrete Proceedings, Chapman & Hall, London, 1986, pp. 22–31.

[8] J.F. Young, The influence of sugars on the hydration of tricalcium aluminate, Proceedings of the Fifth International Symposium on the Chemistry of Cement, Cement Association of Japan, Tokyo, 1968, pp. 256–267.

[9] M. Collepardi, S. Monosi, G. Moriconi, M. Pauri, Influence of gluconate, lignosulfonate or glucose on the C_3A hydration in the presence of gypsum with or without lime, Cem. Concr. Res. 14 (1984) 105–112.

[10] M. Collepardi, S. Monosi, G. Moriconi, M. Pauri, Influence of gluconate, lignosulfonate, and glucose admixtures on the hydration of tetracalcium aluminoferrite in the presence of gypsum with or without calcium hydroxide, J. Am. Ceram. Soc. 68 (5) (1985) c126–c128.

[11] N.B. Milestone, Hydration of tricalcium silicate in the presence of lignosulfonates, glucose and sodium gluconate, J. Am. Ceram. Soc. 62 (7–8) (1979) 321–324.

[12] H.F.W. Taylor, Cement Chemistry, Academic Press, New York, 1990, pp. 62–63.

[13] C.R. Wilding, A. Walter, D.D. Double, A classification of inorganic and organic admixtures by conduction calorimetry, Cem. Concr. Res. 14 (1984) 185–194.

[14] N. Sauvat, R. Sell, E. Mougel, A. Zoulalian, A study of ordinary Portland cement hydration with wood by isothermal calorimetry, Holzforschung 53 (1) (1999) 104–108.

[15] V.S. Ramachandran, M.S. Lowery, Conduction calorimetric investigation of the effects of retarders on the hydration of Portland cement, Thermochim Acta 195 (1992) 373–387.

[16] J. Bensted, Some applications of conduction calorimetry to cement hydration, Adv. Cem. Res. 1 (1) (1987) 35–44.

[17] R.W. Previte, Some insights on the mechanism of saccharide set retardation of Portland cement, Cem. Concr. Res. 1 (1971) 301–316.

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

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

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

[21] J. Bensted, S.P. Varma, Some applications of infrared and Raman spectroscopy in cement chemistry: Part 3. Hydration of portland cement and its constituents, Cem. Technol. (1974 September/October) 440–450.

[22] I. Odler, S. Abdul-Maula, Possibilities of quantitative determination of the Aft-(ettringite) and Afm-(monosulphate) phases in hydrated cement pastes, Cem. Concr. Res. 14 (1984) 133–141.

[23] D.A. Silva, H.R. Roman, P.J.P. Gleize, Evidences of chemical interaction between EVA and hydrating Portland cement, Cem. Concr. Res. 32 (2002) 1383–1390.

[24] M.Y.A. Mollah, W. Yu, R. Schennach, D.L. Cocke, A Fourier transform infrared spectroscopic investigation of the early hydration of Portland cement and the influence of sodium lignosulfonate, Cem. Concr. Res. 30 (2000) 267–273.

[25] N.B. Singh, Effect of gluconates on the hydration of cement, Cem. Concr. Res. 6 (1976) 455–460.

[26] S. Monosi, G. Moriconi, M. Collepardi, Combined effect of lignosulfonate and carbonate on pure Portland clinker compounds hydration: III. Hydration of tricalcium silicate alone and in the presence of tricalcium aluminate, Cem. Concr. Res. 12 (1982) 425–435.