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Effect of polysaccharides on the hydration of cement suspension

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Abstract

This work compares the effects induced by polysaccharides on the hydration of cement. It also brings new insights into the interaction mechanisms between these two components. Several parameters such as structure, concentration, average molecular weight, and the soluble fraction value of the polysaccharides were examined. The hydration of cement was monitored by conductivity measurement, and ionic chromatography. The influence of polysaccharide structure on the kinetics of cement hydration was revealed. The extent of retardation increases when polysaccharide concentration rises. Dextrins with lower average molecular weights compared with starches favor a higher soluble fraction value and further retard hydration. The growth of hydrates seemed to be more affected by the presence of these admixtures than did the dissolution of anhydrous particles or the nucleation of former hydrates.

Keywords: Ionic conductivity; Cement; Composites; Chemical properties

1. Introduction

Among the organic admixtures widely used in the formulation of mortars and concrete, polysaccharides are polymers which can be equally classified in water-reducers, set-retarders, and water retention agents.

Numerous authors have demonstrated that the properties of mortar and concrete can be significantly modified at fresh state as well as at hardened state by the addition of polysaccharides.[1–8]

Several mechanisms were proposed to explain the interactions between cement and set-retarders (i.e. sugars or carboxylic acids).[9–15] Some authors focused their studies on interaction with *anhydrous surfaces*. For Hansen,[16] the adsorption onto anhydrous particles could occur and protect surfaces from initial attack by water. Suzuki and Nishi[17] proposed that the retarding action of admixtures could be linked to the precipitation of insoluble calcium salts at the surface of anhydrous particles even though a clear correlation between solubility and retarding ability of carboxylic acids was not established.

Other studies pointed out that interactions between admixtures and *hydrates* could also exist. According to Thomas and Birchall,[18] the retarding action of sugars is explained in terms of adsorption onto and poisoning of hydrates surfaces. Young[19] suggested that an incorporation of admixtures into crystal lattices could occur. For example, in the case of C_3A hydration, he proposed that organic compounds could enter the interlayer region and stabilize hexagonal hydrates like C_4AH_{13} at the expense of the cubic form C_3AH_6. However, in the case of C_3S hydration, Popova et al.[20] showed that polymer–CSH interaction was restricted to adsorption. Indeed no significant structural modification of CSH were observed by ^{29}Si NMR characterization.

Hence, a mechanism describing the influence of set retarding admixtures on cement hydration is still not well elu-

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cidated. In order to bring new insights, the present study focuses on the hydration of cement in presence of compounds widely used in mortars, i.e. polysaccharides. The few works on this topic were limited to physico-chemical phenomenon occurring in a system that only contains cement and monosaccharides.[11,13,15,21] Most previous studies were carried out in concentrated media (i.e. water-to-cement weight ratio W/C inferior to 1).[12,13,21] The present work was performed on cement suspensions (W/C = 20), by means of conductivity measurement and ionic chromatography, to identify parameters responsible for the set retarding ability of these admixtures. The advantage to work on dilute media is to extend the *x*-axis corresponding to time. The phenomena relevant to hydration, i.e. dissolution, nucleation, and growth of hydrates are easier to observe at W/C = 20 than at ratio inferior to 1.

Table 1
Chemical composition and potential phases 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

2. Experimental

2.1. Raw materials

Two Portland cements from Calcia company were studied: a white cement CPA CEM I 52.5, and a grey cement PMES 42.5 according to the French standard NF P 15-301. They were selected in order to determine the effect of cement composition on set retarding ability of polysaccharides. Chemical composition and mineralogical phases calculated by Bogue approximation[22] are, respectively, listed in Table 1.

The five polysaccharides studied were supplied by several admixtures producers and were of different types, i.e. a cellulose ether (CE), a starch ether (SE), a native starch (NS), a white dextrin (WD) and a yellow dextrin (YD), the last two prepared from NS. Properties of these polysaccharides are given in Table 2.

2.2. Methods of investigation

In each case, cement and polysaccharide powders were mixed together for two periods of 2 min using a shaker-mixer (Wab, Turbula, Germany). Unless otherwise stated, polysaccharide-to-cement weight ratio (P/C) was equal to 0.5% (w/w) and experiments were carried out in triplicate.

The conductivity equipment consisted of a 25 °C thermostated reactor that contains 1 l of deionised water, a platinum electrode and a conductimeter (Tacussel CD 810, France). Previous to each experiment a calibration was performed with a 0.1 M KCl solution.

Additional data were obtained by the determination of specific ion concentrations (calcium, sulfate and silicate) using ionic chromatography. This was performed on a Dionex apparatus, composed of a GP50 pump, a CS12A column for cation analysis and a AS11HC column for anions, a CD20 conductimetric detector and an AD25 UV–vis detector. From the reactor containing the cement suspension, samples of 10 ml were collected. Two volumes of 1 ml, from previous samples, were diluted 10 times and used to determine calcium and sulfate concentrations. The analysis conditions are given in Table 3.

Dissolution of cement in presence of polysaccharides was also monitored by conductivity measurement. The analysis were performed in very dilute media, i.e. W/C equal to 8000, since Comparet et al.[23] showed that no saturation with respect to hydrates occurred in these conditions. This ratio allows to isolate the dissolution of anhydrous particles during the hydration of cement. Prior to measurement, a calibration was performed with a 10^{-2} M KCl solution.

Table 2
Properties of polysaccharides

Admixture	Solubility at 25 °C	Mw (Da)[a]	Substituent[b]
CE	Yes	$(11.6 \pm 0.1) \times 10^6$	CH_3, $(CH_2)_2$—OH and $(CH_2)_3$—OH
SE	Yes	$(1.48 \pm 0.05) \times 10^6$, $(173 \pm 5) \times 10^3$	$(CH_2)_3$—OH
NS	No	25.2×10^6, $(290 \pm 6) \times 10^3$	–
WD	$5 < S < 35\%$	$(11 \pm 1) \times 10^3$	–
YD	$S > 90\%$	$(8.5 \pm 0.5) \times 10^3$	–

[a] Determined by gel permeation chromatography.
[b] Determined by pyrolysis-gas chromatography–mass spectrometry; *S*: soluble fraction value (producers data).

Table 3
Analysis conditions of ionic chromatography

Chemical species	Elute	Flow (ml/min)	Mode	Post column reactant	Detection
Na^+, K^+, Ca^{2+}	Methanesulfonic acid (HMSA), 20 mM	1	Isocratic	–	Conductimetric
F^-, Cl^-, SO_4^{2-}	NaOH, 25 mM	1	Isocratic	–	Conductimetric
Si	NaOH + HBO_4	1	Isocratic	Sodium molybdate + sodium lauryl sulfate + nitric acid	UV–vis at 410 nm

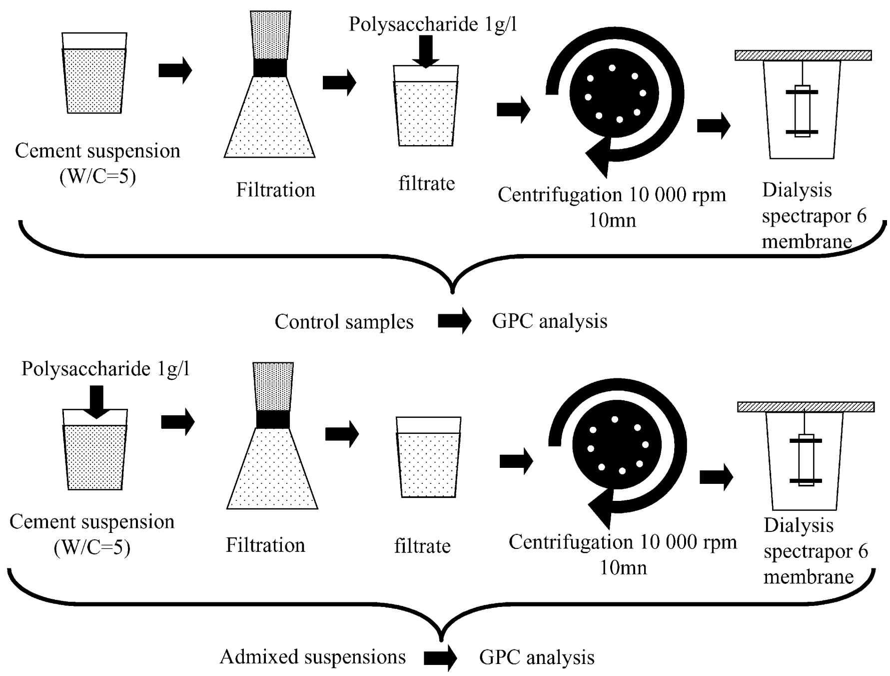

Fig. 1. Sample preparation previous to proportioning polysaccharides in cement suspension.

To highlight the polysaccharide-cement interaction, the quantity of native polymer in a cement filtrate was determined. *Samples* and *control samples* were prepared by introducing polysaccharides at 1 g l^{-1} in cement suspension and cement filtrate respectively. In both cases, several steps were realized, i.e. filtration, centrifugation, dialysis as described in Fig. 1. The samples were analysed by gel permeation chromatography (GPC) equipped with a pump (WATERS 916, USA), a column (TOSOHAAS TSK GEL GMPWXL 7.8 mm × 30 cm, Germany) conditioned in a furnace at 30 °C and a refractometer (WATERS 410, USA). A flow of deionised water (millipore, mQ, USA), previously inline degassed, was maintained at 0.5 ml min^{-1}. Calibration was carried out by the injection of polymaltotrioses samples (Shodex P-82 standards). The quantity of polysaccharide non-adsorbed and not decomposed, determined in cement phases was defined by Eq. (1)

$$\%P = \frac{A_{CF}}{A_{CS}} \times 100 \quad (1)$$

where A_{CF} and A_{CS} represent the peak area of the polysaccharide in the cement filtrate and in the control sample, respectively.

3. Results

3.1. Hydration of C_1

The conductimetric curve of a cement suspension presents different steps (Fig. 2) as described by Comparet et al.[23] and Maximilien et al.[24] The retarding ability of polysaccharide on the hydration of cement was correlated to the slope value

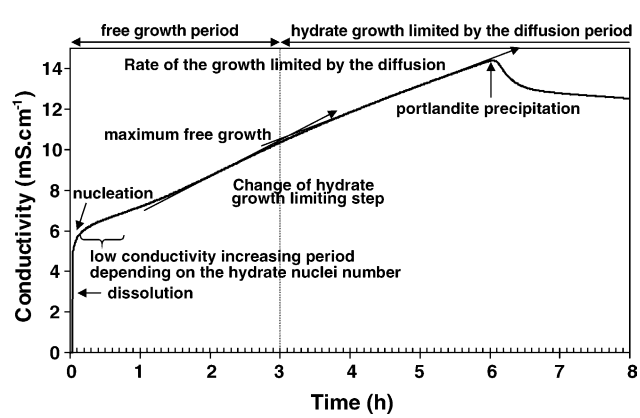

Fig. 2. Different steps of a conductimetric curve.

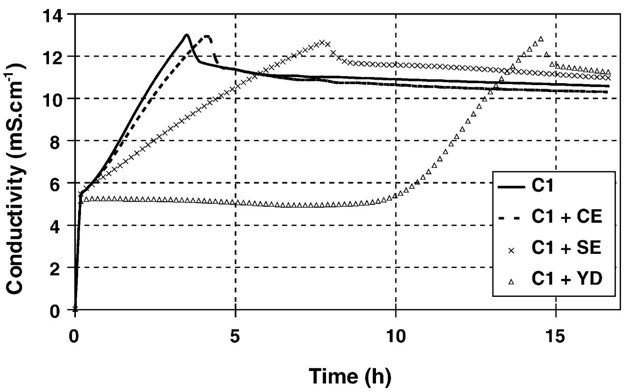

Fig. 3. Effect of the chemical nature of polysaccharides on cement hydration.

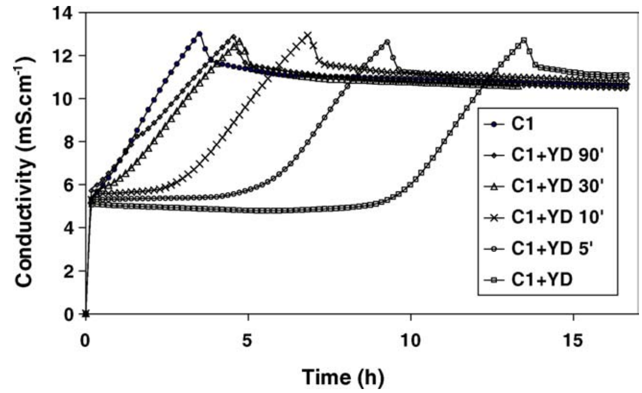

Fig. 4. Effect of a delayed addition of 0.5% YD on cement C_1 hydration.

before the maximum of the conductimetric curve. A low slope value represents a high slowing down of the hydration rate of cement. Fig. 3 shows that admixture CE has little effect on the conductimetric curve contrary to SE which slows hydration significantly and to YD which blocks it for approximately 10 h.

The time at which portlandite precipitation occurred was defined by $t_{\lambda\max}$. The order of portlandite precipitation is as follows:

$$C_1 < C_1 + CE < C_1 + SE < C_1 + YD.$$

These results clearly showed that the polysaccharide chemical structure is a major parameter and has governed the first hours of the hydration rate of cement. The slope and $t_{\lambda\max}$ values of corresponding cement suspensions are given in Table 4.

3.2. *Influence of polysaccharide SE and YD*

3.2.1. *Influence of concentration*

The increase of P/C ratio and especially for SE, induces an extended reduction of the hydration rate of cement since the slope decreases. It indicates that the balance between dissolution of anhydrous particles and precipitation of hydrates is significantly modified by the addition of SE. The minimum YD/C_1 ratio where a blocking effect was observed was equal to 0.4%. In contrast, the delay observed when $YD/C_1 = 0.5\%$ (10 h) underwent a large increase if $YD/C_1 = 1\%$ (delay 46 h). Corresponding values of slope and blocking effect duration are listed on Table 4.

3.2.2. *Influence of polysaccharides addition timing*

Polysaccharides were added to cement immediately or delayed from 5 to 90 min. For 0.5% YD addition, the duration of the blocking effect gradually decreased and became negligible beyond 30 min (Fig. 4). An increase in YD concentration up to 1% induced a plateau which was still observed for a delayed addition of 30 min but not for a delay of 90 min. Consequently, an increase of the delay to add YD requires a higher concentration to observe a plateau. Two explanations are possible, YD could adsorb either on hydrated or on anhydrous particles. In the first case, the hydrated particles are more numerous and have a larger specific surface area than anhydrous particles. Hence, to inhibit completely the hydration, a higher amount of YD is necessary. In the second case, the adsorption of YD could occur on anhydrous particles. However, they are less accessible due to the formation of hy-

Table 4
Effect of polysaccharides and P/C ratio on the slope, $t_{\lambda\max}$ and duration of the blocking effect

	Slope ($mS\,cm^{-1}\,h^{-1}$)	$t_{\lambda\max}$ (h)	Duration of the blocking effect (h)	Quantity of native polysaccharide in cement filtrate from Eq. (1) (%)
C1	2.6 ± 0.2	3.5 ± 0.1	–	nd
C1 + 0.5% CE	2.23 ± 0.01	4.2 ± 0.2	–	80 ± 3
C1 + 0.5% NS	2.3 ± 0.1	3.9 ± 0.1	–	nd
C1 + 0.5% WD	1.86 ± 0.01	5.6 ± 0.3	–	90 ± 6
C1 + 0.5% SE	1.1 ± 0.1	8.0 ± 0.6	–	10 ± 3
C1 + 1% SE	0.8 ± 0.1	11.1 ± 0.7	–	nd
C1 + 1.2% SE	0.4 ± 0.1	>17	–	nd
C1 + 1.5% SE	0.12 ± 0.06	>17	–	nd
C1 + 2% SE	0.09 ± 0.05	>17	–	nd
C1 + 0.1% YD	2.03 ± 0.12	4.4 ± 0.1	0	nd
C1 + 0.3% YD	1.79 ± 0.08	6.1 ± 0.2	0	nd
C1 + 0.4% YD	1.76 ± 0.09	7.2 ± 0.3	1.7 ± 0.2	nd
C1 + 0.5% YD	2.07 ± 0.13	14 ± 1	10 ± 1	3 ± 1
C1 + 1% YD	nd	nd	46 ± 4	nd

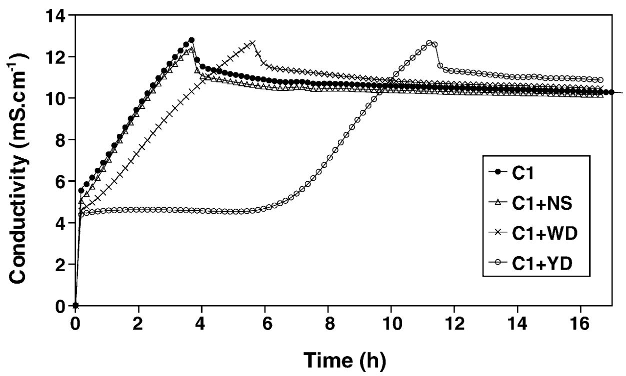

Fig. 5. Effect of dextrinization on the conductimetric curves.

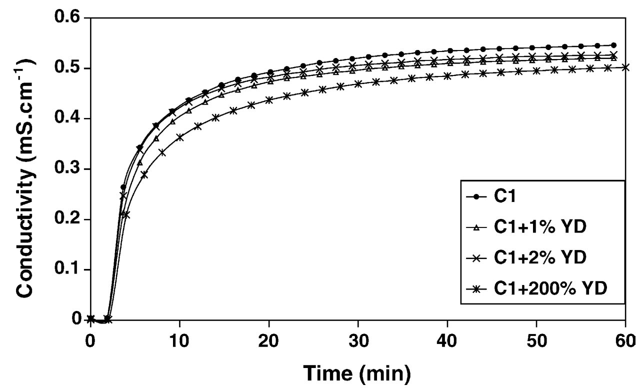

Fig. 6. Effect of YD addition on cement dissolution.

drates when the addition is delayed. In the case of the delayed addition of SE, the slope increases but does not recover to the value for the neat cement. This shows that YD and SE do not act in the same way on the hydration of cement.

3.2.3. *Effect of starch dextrinization on cement hydration*

To explain the singular effect of YD, the hydration of cement in the presence of native starch (NS) and dextrins (WD, YD) was more specifically studied. Dextrins were prepared by a thermal treatment (140–180 °C) in hydrochloric acid of NS (Evans and Wurzburg[25] and Satterwaite and Iwinski[26]) by the Roquette Company (France). The admixture WD presents a weak conversion from starch to dextrins in contrast to YD. A lower average molecular weight favours a higher soluble fraction value which is, according to the supplier, greater than 90%, between 5 and 35%, and less than 5% for YD, WD and NS, respectively. Conductivity measurement shows that NS has no effect, WD slows down and YD blocks for 10 h, the hydration of cement (Fig. 5). Interaction between WD and cement was limited since more than 80% of WD (determined by GPC Eq. (1)) was still present in cement suspension. Furthermore, the cement composition does not seem to have any effect on the set retarding ability of dextrin YD. Similar to the case for cement C_1, a blocking effect on C_2 hydration occurs for 10 h when 0.5% of YD was added.

The increase of WD/C ratio from 0.5 to 2.5% leads to a blocking effect and suggests that the difference in the set retarding ability of WD and YD is more attributed to the gap in the soluble fraction value than to the difference in the average molecular weights.

3.3. *Hypothesis concerning interaction mechanisms*

3.3.1. *Highlight of cement polysaccharide interaction*

In order to investigate the cement polysaccharide interaction, the proportion of admixture in the filtrate was determined by GPC according to Eq. (1). This protocol is a way to measure the quantity of polysaccharide adsorbed and/or decomposed by mineral phases. Results reveal that more than 80% of CE quantity was still present in the filtrate. In contrast, C_1 + SE and C_1 + YD exhibit residual concentrations of admixture in the filtrate of less than 10%. Consequently, it indicates that CE was not "trapped" contrary to the most efficient set retarding admixtures, i.e. SE and YD which are probably adsorbed and/or decomposed by cement.

3.3.2. *Effect of polysaccharides on the dissolution of cement*

The dissolution of cement was studied on very diluted suspensions (W/C = 8000). Even though these under-saturated conditions are very far from the hydration at W/C equal to 20, they make it possible to isolate the dissolution phenomena. Any differences, observable between the formula C1 and C1 + 200% YD, is hidden by the repeatability variation. Consequently, the addition of polysaccharides at P/C ratio from 0.5% to 200% does not affect significantly the dissolution rate (Fig. 6). Hence, a mechanism which postulates that the retardation is linked to an adsorption of organic molecules on anhydrous particles as proposed by Seligmann and Grenning[27] does not seem to be valid in the case of cement admixed with polysaccharides.

3.3.3. *Effect of polysaccharides on the interstitial phase*

The studying phase supplies supplementary information compared with conductivity measurement which only gives a global evolution. Fig. 7 shows that calcium concentration evolution is similar to conductimetric curves. The increase

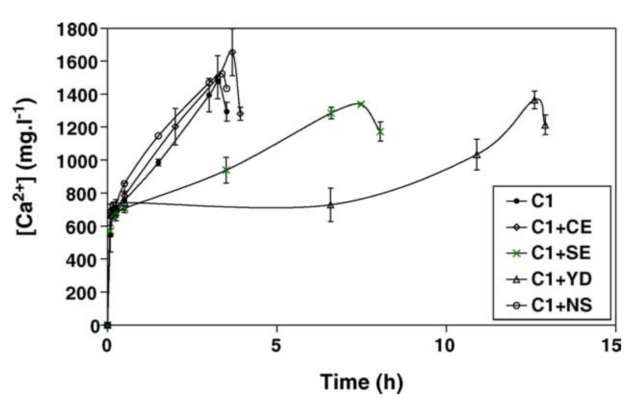

Fig. 7. Evolution of calcium concentration in admixed suspensions.

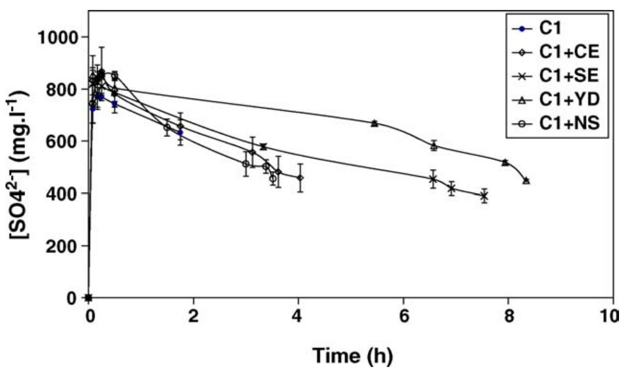

Fig. 8. Evolution of sulfate concentration of admixed cement suspensions.

of calcium concentration for suspensions that contain CE or SE respectively is equivalent to and much lower than that for pure cement. The addition of YD creates a blocking effect in the rise of calcium concentration equivalent to the plateau observed on the conductimetric curves. Consequently, it seems that calcium diffusion through the solution is inhibited.

The sulfate concentration decreases since this species is consumed to react with C_3A to form ettringite (Fig. 8). For all formulae, in the first 30 min, the sulfate concentration decreases indicating that ettringite is forming. Beyond this period, the concentration decrease is similar to that of neat cement for the suspensions $C_1 + NS$ and $C_1 + CE$ but is lower for suspensions that contain SE and YD. These observations for the latter formula could indicate either a decrease in the precipitation rate and an unchanged dissolution rate or a reduction in the dissolution and the precipitation rates due to the self-regulation process. From these results, it could be assumed that the beginning of C_3A hydration, leading to ettringite formation, is not modified and that the ettringite amount is then stabilized for $C_1 + SE$ and $C_1 + YD$ samples. This observation will induce a delay in the conversion of ettringite to monosulfoaluminate phase. These results are in good accordance with those obtained in concentrated media which revealed, a stabilisation of ettringite and a lower gypsum consumption, for cements formulated with SE or YD.[28]

The concentration of silicate ions rises rapidly as a consequence of C_3S dissolution and then subsequently decreases due to the nucleation of CSH. In all the tested formula within the first hour of hydration, silicate concentration decreases. This suggests that polysaccharides do not affect significantly CSH nucleation rate. Nevertheless for $C_1 + YD$, a plateau of silicate concentration is observed (results not shown). This phenomena could be linked to an adsorption of YD on CSH nuclei, forming protective barriers which inhibit further hydration.

4. Conclusion

This study revealed that it was difficult to establish a global mechanism of interaction between cement and polysaccharides since it seems to depend on the mineralogical phase studied and the admixture chemical structure. Nevertheless, interesting results were obtained. First, this work reveals the importance of the chemical nature of the polysaccharides. The set retarding ability decreases in the order YD > SE > WD > CE. Second, a higher P/C ratio leads to an extended delay in hydration. Third, starch dextrinization leads to a higher soluble fraction value, and hence, to a higher set retarding effect than native starch.

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