# Retarding effectiveness of hexitols on the hydration of the silicate phases of cement: Interaction with the aluminate and sulfate phases

Camille Nalet, André Nonat *

Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), UMR 6303 CNRS Univ. Bourgogne Franche-Comté, France

## ARTICLE INFO

## ABSTRACT

This study focuses on the relationship between the retardation generated by hexitols (D-glucitol, D-galactitol and D-mannitol) on the hydration of the silicate phases of a white cement and on their interactions with the aluminate and sulfate phases. The impact of the aluminate and sulfate content of cement on their retarding effect was identified. The consumption of the stereoisomers as well as their effects on the ionic composition cement in suspension were studied and compared. The results showed that the aluminate and sulfate content of cement reduces the retarding effect of hexitols on the hydration of its silicate phases. Moreover, they adsorb differently on hydrating cement and complex with ions in solution. The impacts of the adsorption of these alditols on ettringite and of their complexation with aluminate ions in solution on their retarding effect on the hydration of the silicate phases of cement are discussed.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Ordinary Portland Cement (OPC) is composed of silicate, aluminate and sulfate phases which interact between each other during its hydration. Alite (impure tricalcium silicate, $C_3S$) and belite ($C_2S$) are the silicate phases mainly composing OPC and are responsible for its setting. The latter can be retarded by using chemical admixtures such as lignosulfonates, carbohydrates and sugar derivatives. Although used since decades, these organic additives are often considered from a performance point of view by focusing on their retarding effectiveness on the setting time of OPC [1–9]. Nevertheless, with the diversity of existing cements and with the increasing levels of Supplementary Cementitious Materials of cement in modern concrete, the knowledge on the interactions between chemical admixtures and mineral surfaces and their influence on the hydration mechanisms of cement seems to be a subject of priority [10,11].

The retarding effect generated by several polysaccharides (dextrin, starch) and saccharides derivatives (D-gluconate, D-glucitol) on the hydration of OPC were reported to be sensitive to its composition and particularly to its aluminate content [1,4,8]. Several setting retarders were also shown to be adsorbed on aluminate hydrates [1,12,13]. Moreover, the presence of D-gluconate was also revealed to enhance the concentration of aluminate ions during the hydration of OPC in suspension [1]. Hence, some setting retarders change the ionic composition of the solution and interact with aluminate hydrates when hydrating OPC.

However, the impacts of the different interactions of the organic molecules with the aluminate phases of OPC on the hydration of its silicate phases are not well identified and understood.

This present study intends to contribute to fill this gap of knowledge by focusing on the interactions of hexitols during the hydration of a white cement and on their effects on the hydration rate of its silicate phases. Table 1 details the structure of the organic molecules studied that are D-glucitol, D-galactitol and D-mannitol which differ from one another in the stereochemistry of their hydroxyl groups. The retarding effects of these organic molecules on the hydration of pure $C_3S$ and of the silicate phases present in cement were first identified by isothermal calorimetry and compared. Secondly, the influence of the aluminate content of cement on the retardation caused by hexitols on the hydration of its silicate phases was assessed. Thirdly, the consumption of these sugar alcohols during the hydration of cement was revealed by Total Organic Carbon measurement. Then, the impacts of these organic compounds on the ionic concentration of cement and $C_3S$ suspensions measured using the Inductively Coupled Plasma – Atomic Emission Spectroscopy are compared. Finally, the relation between the different interactions of hexitols relative to the aluminate phase of cement and their retarding effect on the hydration of its silicate phases are discussed.

## 2. Experimental procedures

### 2.1. Materials

The preparation of all pastes, suspensions and solutions was made with water which was both distilled and deionised. The molecules

* Corresponding author.
  E-mail addresses: camille.nalet@u-bourgogne.fr (C. Nalet),
andre.nonat@u-bourgogne.fr (A. Nonat).

**Table 1**
Chemical structures of the molecules studied.



| D-glucitol | D-galactitol | D-mannitol |
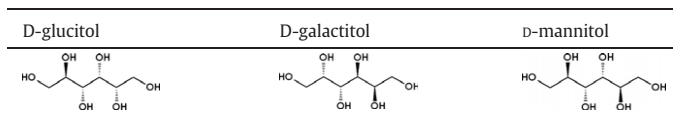
studied were D-glucitol (≥98%), D-galactitol (≥99%) and D-mannitol (≥98%) from Sigma Aldrich in powder form.

A white cement and a $C_3A$–gypsum-hemihydrate mixture both from Lafarge as well as $C_3S$ from Mineral Research Processing were used. Table 2 indicates the physical and chemical characteristics of these minerals. In all the following study, the $C_3A$–gypsum-hemihydrate mixture will be called aluminate-sulfate mixture. White cement with different $C_3A$ contents was made by adding different amounts of the aluminate-sulfate mixture to the initial white cement in order to increase its $C_3A$ content from 2.7 to 15%.

Calcium oxide used to make saturated lime solutions was obtained after decarbonation of calcium carbonate (98.5–100%, VWR AnalaR NORMAPUR) at 1000 °C for 24 h. Saturated lime suspensions were first made by equilibrating an excess of freshly decarbonated lime to water kept at 25 °C in a thermoregulated bath during minimum 24 h. Finally, the saturated lime solutions were obtained by filtering the saturated lime suspensions (0.1 μm cellulose ethers, Merck Millipore).

### 2.2. Methods

#### 2.2.1. Study of the effect of hexitols on the hydration rate of $C_3S$ and white cement with different $C_3A$ contents

The heat flow released during the hydration of the different mineral powders in presence of hexitols was monitored by isothermal calorimetry (TAM AIR) at 23 °C. 1 g of powder was mixed with 0.4 mL of aqueous solutions with and without sugar alcohols (Liquid to Solid ratio, L/S = 0.4). All these pastes were stirred for 2 min at 3200 rpm in different plastic ampoules. Then, the latter were immediately capped and inserted in the calorimeter.

The impacts of hexitols on the calorimetric curves monitored during the hydration of $C_3S$ and cement were different than the ones observed

**Table 2**
Physical and chemical parameters of the different mineral phases.

| | Cement | $C_3S$ | $C_3A$–gypsum-hemihydrate |
|---|---|---|---|
| Specific surface area ($m^2$/g) | 0.4[a] | 0.5[b] | 0.3[b,c] |
| Mono. alite (%) | 66.1 | – | – |
| Tric. alite (%) | 0.0 | 100.0 | – |
| Belite (%) | 24.2 | – | – |
| Ferrite (%) | 0.4 | – | – |
| Cub. aluminate (%) | 2.0 | – | 80.5 |
| Ortho. aluminate (%) | 0.7 | – | – |
| Lime (%) | 0.3 | – | – |
| Gypsum (%) | 0.2 | – | 9 |
| Hemihydrate (%) | 0.7 | – | 15.0 |
| Anhydrite (%) | 1.0 | – | – |
| Calcite (%) | 2.4 | – | – |
| Portlandite (%) | 1.8 | – | – |
| Quartz (%) | 0.1 | – | – |

– = not measured items.
[a] Blaine method.
[b] Calculated from particle size distribution assuming that the density of particles is homogeneous with the size, that the particles are spherical and considering these different densities ($C_3S$: 3210 kg/$m^2$ and $C_3A$: 3030 kg/$m^2$). The PSD has been measured by Laser Diffraction (Malvern mastersizer 2000) in ethanol (≥99.5%, Sigma Aldrich). The particle size distributions are given in supplementary material of this paper.
[c] The proportion of $C_3A$/$CaSO_4$ has been chosen to correspond to a properly sulphated cement. The hemihydrate/gypsum proportion has been measured from Rietveld analysis of the XRD pattern. It was initially fixed at 50/50.

during the hydration of cement with different $C_3A$ contents. Hence, they were analyzed differently as described below.

*2.2.1.1. Definition of the retardation generated by hexitols on the hydration of $C_3S$ and cement.* Fig. 1 shows the typical calorimetric curves obtained for $C_3S$ and cement pastes with and without D-glucitol. It represents the evolution of the heat flow resulting from the reactions of dissolution of the anhydrous phases and of the precipitation of hydrates over time. Hence for pure $C_3S$, the calorimetric curve reveals the heat flow released by the hydration of the silicate phase whereas for cement, it reveals the heat flow released by the overall hydration of the silicate, aluminate and sulfate phases. Nevertheless, the peak observed during the hydration of $C_3S$ and cement on the calorimetric curves indicates the acceleration of the hydration of the silicate phases which are the main phases of these two mineral compounds. The shape of the calorimetric curves measured during the hydration of $C_3S$ and cement pastes stays the same in presence of the different hexitols in the range of concentration studied (0–54 mmol/L in cement and 0–11.3 mmol/L in $C_3S$ pastes) compared to their respective reference without additive as can be seen for D-glucitol, Fig. 1. However, the molecules lengthen the induction period during the hydration of $C_3S$ and cement pastes compared to the one of their respective reference. Given that hexitols do not change the shape of the calorimetric curve obtained during the hydration of $C_3S$ and of cement, the retardation was defined as being the difference in time between the maximum heat flow of the samples with alditol and the reference without additive as indicated in Fig. 1. Finally, the retardation induced by different concentrations of hexitols on the hydration of $C_3S$ and on the one of the silicate phases present in cement was measured by using this method.

*2.2.1.2. Definition of the time ending the induction period when hydrating cement with different $C_3A$ contents with and without alditols.* Fig. 2 represents the calorimetric curves obtained during the hydration of cement pastes with 5% of $C_3A$ with and without D-glucitol (20.3 mmol/L). The variation of the percentage of $C_3A$ in cement pastes with hexitols was sometimes changing the shape of the calorimetric curves. In this case, instead of considering the time at the maximum heat flow, the time ending the induction periods was taken into account. This time has been arbitrarily taken being equal to the one found at the intersection between the slope of the calorimetric curve at the inflexion point during the acceleration period (highest acceleration) and the x-axis as shown in Fig. 2, the recorded calorimetric curves are given in suplementary material. Using this method, the concentration of the different hexitols was kept constant (20.3 mmol/L) but the percentage of $C_3A$ of the initial cement was increased from 2.7% to 15%.

### 2.2.2. Adsorption measurements of hexitols during the hydration of cement in suspension

The adsorption of the different organic molecules was measured during the hydration of cement in suspension with L/S = 5 (150 mL of saturated lime solution and 30 g of cement). These suspensions were stirred in thermoregulated cells at 25 °C and under a continuous nitrogen gas atmosphere to prevent the formation of calcium carbonate. Samples of the cement suspensions were collected over time and were centrifuged at 9000 rpm for 5 min in Nalgene tubes. Finally, the supernatants were filtered with a syringe filter (0.2 μm PTFE, VWR). A small known quantity of orthophosphoric acid (85%, Analar Normapur, VWR) was added to the filtrates before their analysis. The adsorption of the organic molecules was determined by using the depletion method. The non adsorbed portion of molecules remaining in the acidified filtrates was measured by analyzing the Total Organic Carbon (TOC) of these solutions (Shimadzu TOC analyser $V_{CPN}$).

The adsorption of polyols on cement in suspension was measured over time and was stable during the induction period. Hence, the value at this plateau of adsorption was used to determine the adsorption of a molecule on cement for a given initial concentration.
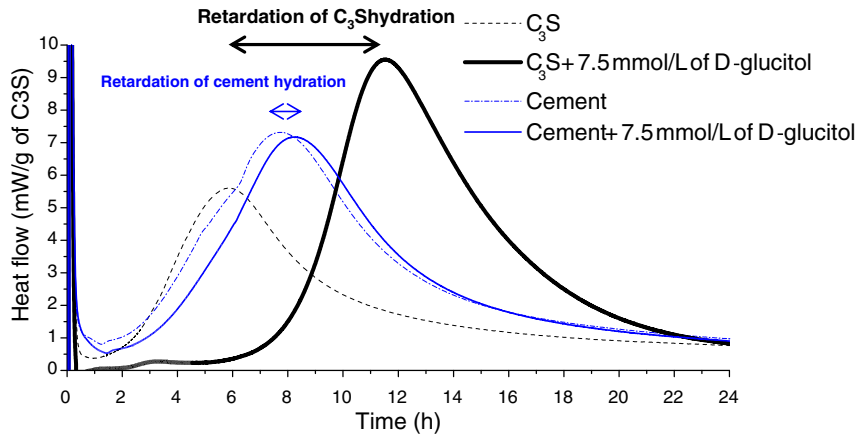
**Fig. 1.** Calorimetric curves monitored during the hydration of $C_3S$ and cement pastes with and without D-glucitol (7.5 mmol/L), L/S = 0.4.

*2.2.3. Analysis of the ionic concentrations during the hydration of cement and $C_3S$ in suspension with and without hexitols*

The concentrations of the species carrying calcium, silicon, aluminium and sulfur which are present in the suspensions of cement and $C_3S$ were continuously measured over time by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, Vista Pro, Varian). 1 g of the mineral powder was added to 100 mL of a saturated lime solution with and without hexitols (20.3 mmol/L) in a stirred reactor, L/S = 100. The latter was connected to the spectrometer after passing through a filter (0.1 μm cellulose ethers, Merck Millipore). The ionic concentrations of the solution were then measured by ICP-AES and the solution was brought back in the reactor where a flow of argon gas was continuously ensured to prevent carbonation of the suspension.

## 3. Results

### 3.1. Retarding effects of hexitols on the hydration of pure $C_3S$ and cement

The retardations generated by the sugar alcohols studied on the hydration of $C_3S$ and on the one of the silicate phases present in cement are compared in Fig. 3. The data represents the average measurement of two replicates and the error bars for the y values represents the standard deviation of the mean. The error bars of the x values indicate 0.2% of uncertainty in the initial concentrations of the organic molecules.

As far as $C_3S$ is concerned, the retardation of its hydration increases with the concentration of hexitols, Fig. 3. In contrast, the retarding effect induced by these organics on the hydration of the silicate phases of cement starts to be strongly enhanced above a threshold dosage of molecules (around 13.5 mmol/L). Indeed, the most retarding molecules on cement hydration that is D-glucitol generates 40 min of retardation at 13.5 mmol/L whereas at 11.3 mmol/L, the less retarding molecule on $C_3S$ hydration that is D-mannitol causes 2h30 of retardation. Hence, the retardation induced by these sugar alcohols on the hydration of the silicate phases present in cement is reduced compared to the one they cause on the hydration of $C_3S$. A similar result was also shown when focusing on the setting time of cement and $C_3S$ pastes in presence of D-sorbitol (D-glucitol) and D-mannitol [4] but also with some water reducers, see [14] and references in.

It can also be observed in Fig. 3 that D-glucitol is the most retarding organic molecule in both $C_3S$ and cement pastes compared to D-galactitol and D-mannitol. However, the retarding effectiveness of D-galactitol is higher than the one of D-mannitol when hydrating $C_3S$ whereas in cement these two molecules induce approximately the same delay on the hydration of its silicate phases. Consequently, there is a reduction of the retardation induced by hexitols on the hydration of the silicate phases of cement but also a change in their relative retarding effect when hydrating $C_3S$ or cement. These variations of the retardation caused by hexitols on the hydration of the silicate phases of cement suggest different interactions of the molecules with the anhydrous and/or hydrated aluminate and sulfate phases present in cement.
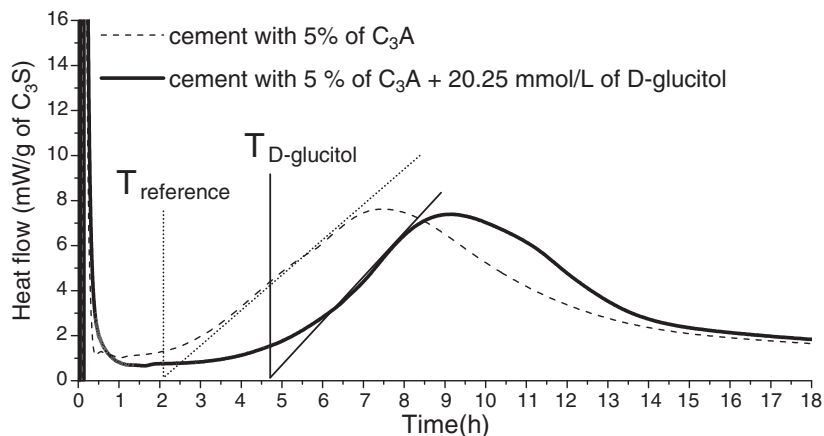


**Fig. 2.** Calorimetric curves obtained during the hydration of cement with 5% of $C_3A$, with and without the presence of D-glucitol (20.3 mmol/L), L/S = 0.4.
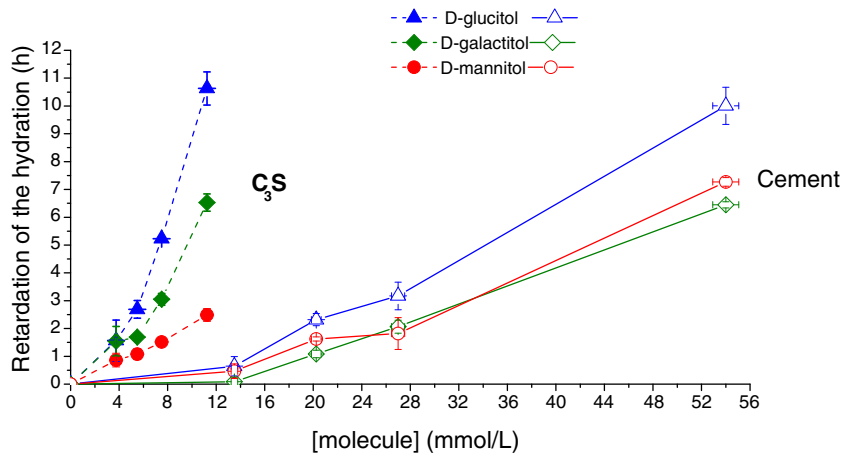
**Fig. 3.** Retarding effects caused by hexitols on the hydration of the silicate phases of cement and of $C_3S$ depending on the concentrations of the organic molecules, L/S = 0.4.

### 3.2. Impacts of the $C_3A$ content of cement on the retarding effect of alditols

The effect of the variation of the $C_3A$ percentage of cement on the time ending induction period obtained from the calorimetric curves of the pastes with and without hexitols (20.3 mmol/L) is exposed in Fig. 4. An average measurement of two replicates was done and the error bars for the y values reveal the standard deviation of the mean.

In presence of the three polyols, the time ending the induction period is decreasing and gets closer to the one of the reference when increasing the amount of $C_3A$ in cement, Fig. 4. By extrapolation, it can be argued that increasing the $C_3A$ content of cement would inhibit the retarding effect of hexitols on the hydration of its silicate phases. Thus, these sugar alcohols reduce their retardation on the hydration of the silicate phases of cement by interacting with its anhydrous and/or hydrated $C_3A$ phases.

### 3.3. Adsorption of hexitols on hydrating cement

Fig. 5 shows the pseudo adsorption isotherm of hexitols present in saturated lime solution on hydrating cement. The term pseudo adsorption isotherm is used to highlight the fact that equilibrium is probably not reached and also because in some case a solubility limit can be reached [15]. The value of the adsorption corresponds to the amount of molecules adsorbed or consumed during the induction period by the amount of dry cement. Indeed, the phase(s) on which the organic

molecules are adsorbed and its/their specific surface is unknown. The data present on the graph reveals the average measurement of two replicates. The error bars for the x and y values represent the standard deviation of the mean.

The pseudo adsorption isotherm on Fig. 5 indicates that there are different behaviors depending on the stereochemistry of the hydroxyl groups carried by hexitols. The consumption of D-galactitol and D-mannitol reaches a saturation plateau whereas the one of D-glucitol does not reach any plateau in the range of concentrations studied (0–54 mmol/L). In fact, the consumption of D-glucitol even diverges suggesting a massive precipitation of the organic molecules at some point. In the initial linear part of the adsorption isotherm, for a given concentration in solution, D-glucitol has the highest adsorption followed by D-galactitol and then by D-mannitol, Fig. 5. Hence, D-glucitol has the most important affinity with the anhydrous and/or hydrated component(s) of white cement compared to the two other polyols.

### 3.4. Influence of hexitols on the ionic concentrations of cement and $C_3S$ suspensions

#### 3.4.1. Ionic concentrations of cement suspensions with and without of polyols over time

The evolution of the concentrations of aluminate, sulfate, silicate and calcium ions of cement suspensions with and without alditols (20.3
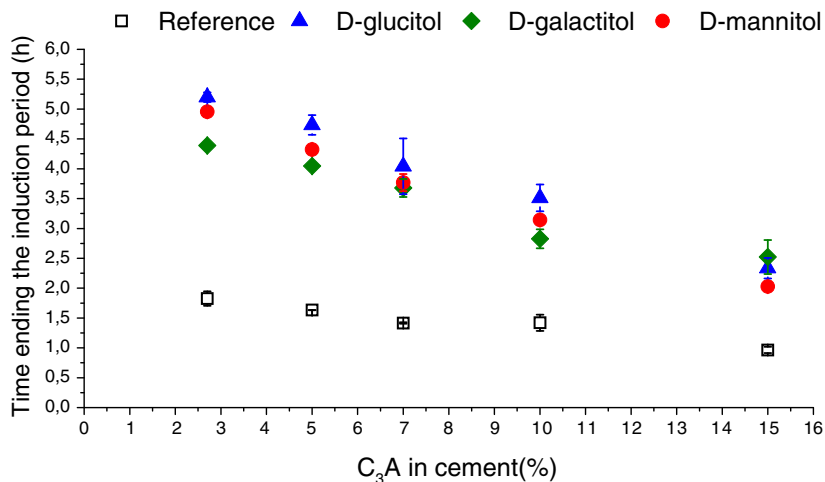


**Fig. 4.** Evolution of the time ending the induction period from the calorimetric curves as a function of the percentage of $C_3A$ in white cement pastes with and without hexitols (20.3 mmol/L), L/S = 0.4.
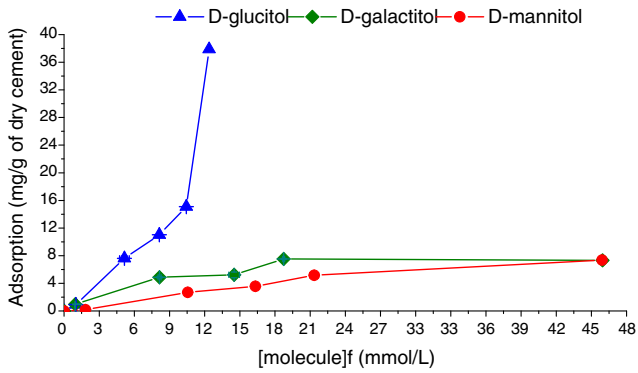
**Fig. 5.** Pseudo adsorption isotherm of sugar alcohols on hydrating white cement during the induction period, $[Ca(OH)_2] = 22$ mmol/L and L/S = 5.

mmol/L) in saturated lime solutions is presented in Fig. 6 as a function of time.

For the reference sample without additive, the concentrations of aluminate and sulfate ions reach their maximum at 30 s of hydration revealing the precipitation of ettringite when the ionic composition of the solution reaches the critical super-saturation with respect to this hydrate, as shown in Fig. 6. Then, the concentration of aluminate ions decreases until becoming lower than the limit of detection of the ICP-AES measurement while the one of sulfate ions remains pretty much constant up to 10 min of hydration: a stationary state is established. The presence of the sugar alcohols studied increases similarly the concentrations of aluminate ions over time which reaches 1 mmol/L after 10 min of hydration. On the other hand, the evolution of the calcium and sulfate concentrations over time is comparable with and without organic molecules respectively. Indeed, the slight differences between the concentration of these ions with and without polyols were not significant when repeating the experiments.

Therefore, this study points out that hexitols strongly enhance the concentration of aluminate ions during the hydration of cement in suspension compared to the one observed in the reference sample. However, there is a precipitation of ettringite in presence of alditols as indicated by the drop of the sulfate concentration when they are present on the cement suspensions, Fig. 6. Hence, these high concentrations of aluminate ions do not result from an impact of the organic molecules on the precipitation of ettringite but might come from their complexation with aluminate, silicate, calcium, and/or hydroxide ions in solution [13,16].

As far as the concentration of silicates is concerned, it reaches a maximum value equals to 0.04 mmol/L after 1.5 min of hydration in the
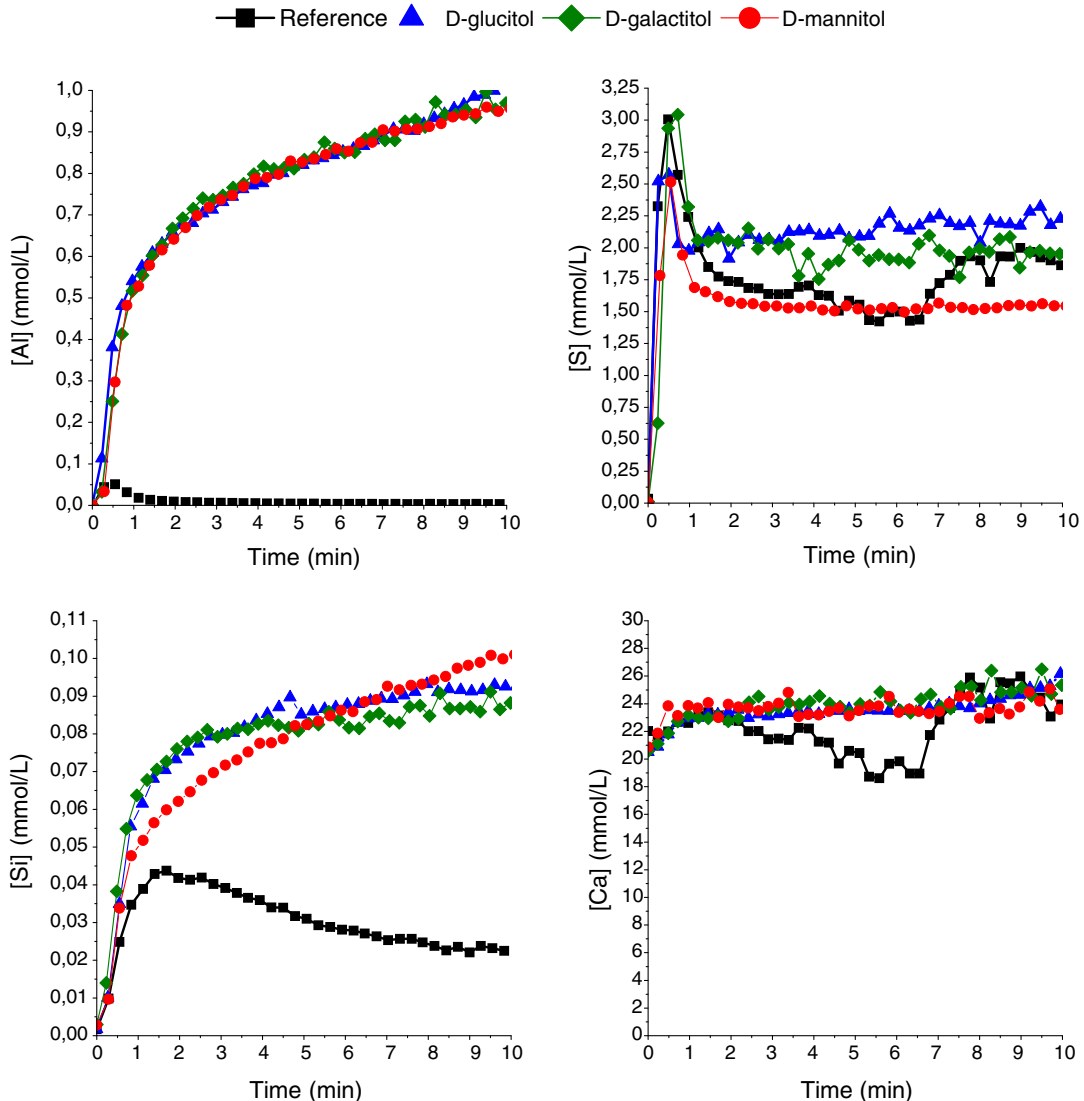


**Fig. 6.** Evolution of the ionic concentrations during the hydration of white cement suspensions with and without hexitols (20.3 mmol/L), $[Ca(OH)_2] = 22$ mmol/L and L/S = 100.
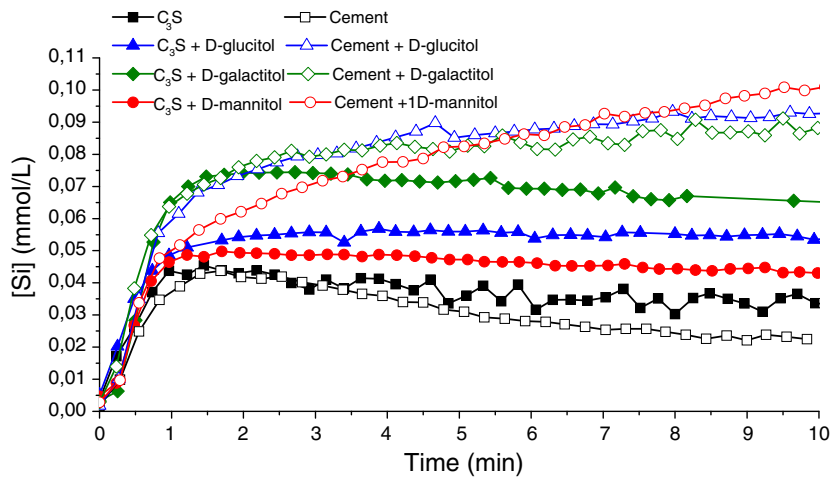
**Fig. 7.** Comparison of the evolution of the silicate concentration over time during the hydration of C₃S and cement suspensions with and without hexitols (20.3 mmol/L), [Ca(OH)₂] = 22 mmol/L and L/S = 100.

cement suspension without additive and then decreases due to the nucleation and growth of C-S-H, Fig. 6. At 1.5 min, the concentrations of silicates are around 0.9 mmol/L in presence of D-glucitol and D-galactitol and then slowly increases. For the cement suspension with ᴅ-mannitol, the concentration of silicates increases over time and reaches a higher value than the ones measured with the two other hexitols after 10 min of hydration. Given that the concentrations of silicate ions keep increasing in presence of the polyols studied and do not decrease as the one of the reference sample, it can be suggested that the precipitation of C-S-H does not occur and/or that it is the consequence of their ionic complexation in solution.

*3.4.2. Comparison of the concentrations of silicates present in cement and C₃S suspensions in presence of hexitols*

The evolution of the concentration of silicate ions during the hydration of pure C₃S and cement in suspension with and without sugar alcohols are compared in Fig. 7. For C₃S suspensions, the concentrations of silicates increase up to 1 min of hydration with and without molecule and are similar to the one of the reference in presence of ᴅ-mannitol and D-glucitol (0.45 mmol/L) whereas in presence of D-galactitol, it reaches a higher value (0.70 mmol/L). Comparable calcium concentrations were measured in the C₃S suspensions with and without hexitols (not shown). The important concentration of silicate ions observed with D-galactitol in the C₃S suspension might be related to its impact on the precipitation of C-S-H and/or to its ionic complexation in solution which would be particularly different than the one of ᴅ-mannitol and D-glucitol.

After the maximum concentrations of silicates are reached in the C₃S suspensions, the one of the reference sample starts decreasing whereas it keeps constant in presence of D-glucitol, Fig. 7. In presence of ᴅ-mannitol and D-galactitol, it barely decreases. Given that the concentrations of silicates doe not decrease in presence of hexitols as the one of the reference sample does, it reveals that the precipitation of C-S-H is particularly slowed down by the molecules and/or that they complex with calcium, silicate and/or hydroxide ions. Moreover, one can see that in presence of hexitols, the concentrations of silicates are lower during the hydration of pure C₃S than during the hydration of the silicate phases of cement, Fig. 7. Consequently, this increase of the concentration of silicate ions in cement suspensions is assumed to be the consequence of the complexation of the organic molecules with aluminate ions.

## 4. Discussion

Through this study, the retarding effects caused by hexitols on the hydration of the silicate phases of cement were found to be reduced by the C₃A content of the powder. These organic molecules were

shown to be consumed during the hydration of cement and to complex with ions in solution. The relation between the adsorption of hexitols on hydrating cement and their retarding effectiveness on the hydration of its silicate phases is shown in Fig. 8. The retardation values induced by sugar alcohols correspond to the ones determined using the calorimetric curves during the hydration of cement pastes as shown in Fig. 3. The values of the adsorption of hexitols on hydrating cement correspond to the ones revealed in the pseudo adsorption isotherm in Fig. 5.

For all the polyols studied, the retardation of the hydration of cement increases as a function of their adsorption on hydrating cement but the trends are different, Fig. 8. For a given amount of hexitols adsorbed, there is a lower retardation of the hydration of the silicate phases present in cement with D-glucitol than with D-galactitol and ᴅ-mannitol. This result shows that adsorption of the organic molecules expressed in terms of moles per gram is not sufficient to account for retardation.

In two previous studies, we have shown that hexitols adsorb on ettringite and AFm [13] but also on C-S-H as indicated for ᴅ-mannitol and D-glucitol [17]. However, D-glucitol was found to have a favored adsorption on both C-S-H and ettringite compare to ᴅ-mannitol. This way, the high amount of D-glucitol adsorbed on ettringite would particularly reduce the amount of organic molecules able to affect the next hydration of the silicate phases of cement and so would decrease its retarding effect. The complexation between hexitols and aluminate ions which enhances the concentration of silicates in solution and so the dissolution of the silicate phases of cement might also play a role on the reduction of their retarding effect. Nevertheless, the effects as
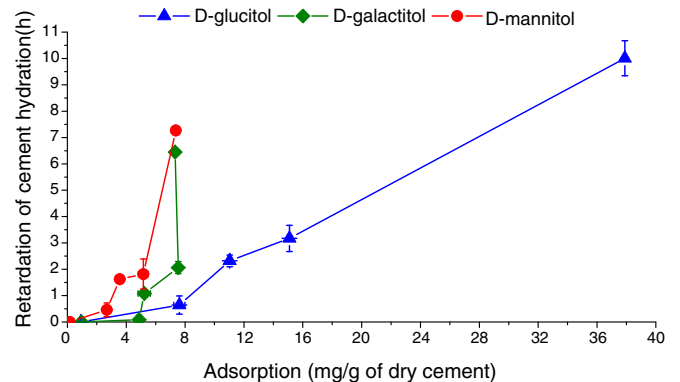


**Fig. 8.** Retardation of the hydration of the silicate phases of cement in paste induced by hexitols depending on their adsorption on hydrating cement during the induction period.

well as the kinetics of the interactions of these organic molecules in solution and at the surface of the solids on the precipitation rate of C-S-H during cement hydration should be more deeply studied.

## 5. Conclusions

The retarding effect of hexitols on the hydration of the silicate phases present in cement was related to its $C_3A$ content. Their consumption during cement hydration and their impact on the ionic composition of cement suspensions were identified and compared.

It was found that the $C_3A$ content of cement reduces the retardation generated by hexitols on the hydration of its silicate phases. These sugar alcohols are consumed during cement hydration and complexes form in solution. A relation was made between the adsorption of the polyols on ettringite and the reduction of their retarding effect on the hydration of the silicate phases of cement. Thus, the organic compounds adsorbed on ettringite would not be free any more to disturb the hydration of the silicate phases of cement and would induce a lower retardation. On top of that, a complexation of hexitols with aluminate ions in solution could contribute to the reduction of the retarding effect induced by these organics on the hydration of the silicate phases of cement.

## Acknowledgments

## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.cemconres.2016.09.018.

## References

[1] Y. Sallier, Influence du gluconate de sodium et du D75 sur l'hydratation du ciment de classe G, Université de Bourgogne, Dijon, 2008 https://www.theses.fr/2008DIJOS076.

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

[3] D.D. Double, New developments in understanding the chemistry of cement hydration, Phil. Trans. R. Soc. A 310 (1983) 53–66.

[4] L. Zhang, L.J.J. Catalan, R.J. Balec, A.C. Larsen, H.H. Esmaeili, S.D. Kinrade, Effect of saccharide set retarders on the hydration of ordinary portland cement and pure tricalcium silicate, J. Am. Ceram. Soc. 93 (1) (2010) 279–287.

[5] N.B. Singh, Effect of gluconates on the hydration of cement, Cem. Concr. Res. 6 (4) (1976) 455–460.

[6] K. Luke, G. Luke, Effect of sucrose on retardation of Portland cement, Adv. Cem. Res. 12 (1) (2000) 9–18.

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

[8] 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.

[9] C. Nalet, A. Nonat, Effects of functionality and stereochemistry of small organic molecules on the hydration of tricalcium silicate, Cem. Concr. Res. 87 (2016) 97–104.

[10] D. Marchon, R.J. Flatt, 12 - Impact of chemical admixtures on cement hydration, in: A. P.-C., R.J. Flatt (Eds.), Science and Technology of Concrete Admixtures, Woodhead Publishing 2016, pp. 279–304.

[11] D. Marchon, R.J. Flatt, A. P.-C., R.J. Flatt, 8 - Mechanisms of cement hydration, Science and Technology of Concrete Admixtures, Woodhead Publishing 2016, pp. 129–145.

[12] J. Pourchez, P. Grosseau, B. Ruot, Current understanding of cellulose ethers impact on the hydration of $C_3A$ and $C_3A$-sulphate systems, Cem. Concr. Res. 39 (2009) 664–669.

[13] C. Nalet, A. Nonat, Impacts of hexitols on the hydration of a tricalcium aluminate-calcium sulfate mixture, Cement and Concrete Research, 2016 accepted.

[14] M.M. Collepardi, 6 - Water reducers/retarders, in: V.S. Ramachandran (Ed.), Concrete Admixtures Handbook, William Andrew Publishing 1996, pp. 286–409.

[15] D. Marchon, S. Mantellato, A.B. Eberhardt, R.J. Flatt, 10 - Adsorption of chemical admixtures, in: A. P.-C., R.J. Flatt (Eds.), Science and Technology of Concrete Admixtures, Woodhead Publishing 2016, pp. 219–256.

[16] P. Smith, H. Watling, P. Crew, The effects of model organic compounds on gibbsite crystallization from alkaline aluminate solutions: polyols, Colloids Surf. A Physicochem. Eng. Asp. 111 (1–2) (1996) 119–130.

[17] C. Nalet, A. Nonat, Ionic complexation and adsorption of small organic molecules on calcium silicate hydrate: relation with their retarding effect on the hydration of C3S, Cem. Concr. Res. 89 (2016) 97–108.