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ICB

Laboratoire Interdisciplinaire Carnot de Bourgogne



UNIVERSITE DE BOURGOGNE
UFR Sciences et Techniques
Ecole Doctorale Carnot - Pasteur

THESE

Pour obtenir le grade de
Docteur de l'Université de Bourgogne
Discipline : Sciences
Spécialité : Chimie – Physique

Par

Camille Nalet

**Influence de la stéréochimie et de la fonctionnalité de molécules
organiques sur l'hydratation de composés cimentaires**

Le 10 Décembre 2015

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Remerciements

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INTRODUCTION

Ce travail porte sur l'influence de la stéréochimie et de la fonctionnalité de petites molécules organiques sur l'hydratation des différentes phases composant le Ciment Portland Ordinaire (CPO). Il a été réalisé au laboratoire Interdisciplinaire Carnot de Bourgogne (ICB) dans l'équipe Physico-Chimie des Milieux Cimentaires et Colloïdaux (PCMC₂) et a été financé par Nanocem qui est un consortium regroupant des industriels et des universitaires collaborant afin d'améliorer leurs connaissances sur les matériaux de construction. A travers ce projet, le but était de comprendre les effets des adjuvants qui sont des additifs organiques permettant d'améliorer les propriétés du ciment, de manière à développer sur le long terme de nouvelles molécules organiques avec des actions contrôlées.

Malgré une apparence simple du fait de son abondance dans les différents ouvrages qui nous entourent, le ciment fait toujours l'objet de recherches focalisant sur la compréhension de sa chimie lors de son hydratation et sur le développement de nouvelles formulations de manière à augmenter ses performances. En effet, sous des contraintes économiques et environnementales, les constructions se doivent d'être faciles, résistantes et le moins polluantes possible. Des adjuvants organiques ajoutés au ciment permettent ainsi d'améliorer ses propriétés à l'état frais et/ou durci. Ces composés organiques peuvent avoir pour fonction la maîtrise de la porosité finale du matériau (entraîneur d'air) ou du temps de prise du ciment (accélérateur ou retardateur de prise) par exemple. La dernière génération d'adjuvants organiques, celle des superplastifiants, s'est développée dans le but de réduire le temps de mise en place du coulis en augmentant sa fluidité (fluidifiant) ou bien la résistance du matériau durci (réducteur d'eau). Cependant, certains superplastifiants organiques ont pour effet secondaire de retarder la prise du ciment alors que celle-ci se doit d'être rapide de manière à poursuivre la construction.

Par ailleurs, sous des pressions environnementales, des ciments différents du CPO se développent et les effets prévus des molécules organiques sur les propriétés du ciment dont la fluidité du coulis, le retard de la prise ou bien encore la résistance mécanique du matériau durci changent parfois de manière incontrôlée. En effet, afin de réduire les émissions de CO₂ dues à la production du CPO, ce dernier peut être remplacé en partie par des Matériaux Cimentaires Supplémentaires (MCS) qui sont majoritairement des résidus d'autres procédés industriels. Les effets des adjuvants organiques étant différents selon la composition des ciments, des molécules tentent d'être développées de manière à s'adapter à un ciment spécifique ou bien à une majorité d'entre eux. Néanmoins, les mécanismes par lesquels ces molécules organiques entraînent et changent ces effets selon leur nature et la composition des ciments relèvent plus de l'observation expérimentale que d'une compréhension des phénomènes se déroulant. Le développement efficace de nouveaux adjuvants organiques avec des effets contrôlés paraît donc difficile tant que les mécanismes à leur origine n'ont pas été entièrement compris et reliés à la particularité des composés organiques utilisés et à la composition des ciments.

Ainsi, cette présente étude vise à comprendre pourquoi et comment des molécules organiques retardent la prise du CPO en identifiant notamment les caractéristiques du ciment et des composés organiques qui affectent cet effet retardateur. Les petites molécules organiques étudiées diffèrent par des changements progressifs de leurs groupes chimiques (hydroxyle, hydroxy-carboxylate, carboxylate, sulfonate et phosphonate) et de la stéréochimie de leurs groupes hydroxyles. En ce qui concerne les composés minéraux, un CPO blanc composé de phases silicates, sulfates et aluminates ainsi que des phases modèles, du silicate tricalcique pur et un mélange d'aluminate tricalcique-sulfate de calcium, ont été pris en considération. L'hydratation de ces différentes phases minérales se déroule suivant un processus de dissolution de ces composés anhydres et de précipitation d'hydrates. La vitesse d'hydratation du CPO étant liée à la vitesse d'hydratation de son composé principal, le silicate tricalcique, l'étude s'est portée sur l'impact des molécules organiques sur le processus de dissolution-précipitation mais aussi sur leurs interactions en solution et à la surface de l'hydrate (C-S-H) à l'équilibre. Nous nous sommes aussi intéressés à la relation existante entre le retard de l'hydratation du silicate tricalcique pur et les caractéristiques des molécules organiques d'un côté ainsi qu'au lien présent entre le retard de l'hydratation des phases silicates du CPO et la proportion d'aluminate tricalcique de ce dernier.

Pour atteindre ces objectifs, le premier chapitre rappelle tout d'abord des informations de la littérature nécessaires pour la suite de l'étude concernant l'hydratation du CPO et de ses phases minérales avec et sans molécules organiques retardant la prise des phases silicates du CPO. Le second chapitre indique la stratégie suivie en ce qui concerne le choix des matériaux et des méthodes utilisés pour mener à bien ce travail. Ensuite, un troisième chapitre présente les différents résultats obtenus à travers cinq articles consécutifs qui sont discutés au quatrième chapitre. Pour finir, des conclusions et des perspectives à cette thèse sont proposées.

CHAPITRE I : PRESENTATION GENERALE

I.1. Ciment Portland Ordinaire et composés constitutifs

I.1.1. Composés et notation cimentaires

Le Ciment Portland Ordinaire (CPO) est un composé synthétique obtenu à partir de chaux (CaO) et d'argile (SiO_2 , Al_2O_3 , Fe_2O_3) cuites à une température d'environ 1450 °C [1]. Il est constitué de phases minérales pures qui sont nommées suivant le taux d'oxyde qui les compose selon cette notation cimentaire :



Le clinker ainsi produit est composé de phases silicates dont l'alite (Ca_3SiO_5 , C_3S) et la bélite (Ca_2SiO_4 , C_2S) et de phases aluminates dont l'aluminate tricalcique ($\text{Ca}_3\text{Al}_2\text{O}_6$, C_3A) et l'aluminoferrite tétracalcique ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$, C_4AF). Le clinker est alors broyé en présence de sulfate de calcium (CaSO_4 , $x\text{H}_2\text{O}$, $\text{C}\text{\$}$) de manière à former le CPO. Le sulfate de calcium peut être sous forme de gypse (CaSO_4 , $2\text{H}_2\text{O}$), d'hémihydrate ou plâtre (CaSO_4 , $0,5\text{H}_2\text{O}$) et/ou d'anhydrite (CaSO_4).

Le CPO utilisé lors cette étude est un CPO blanc ne comportant pratiquement pas de C_4AF . Il comporte environ 90 % de C_2S et de C_3S , 3 % de C_3A , le reste étant du sulfate de calcium et d'autres composés minéraux.

I.1.2. Hydratation du Ciment Portland Ordinaire

Bien que les phases aluminates soient présentes en plus faible quantité que les composés silicates dans le CPO, l'hydratation des premières phases mentionnées est plus rapide que celle des phases silicates ce qui induit des changements importants au cours des premières minutes suivant le gâchage. En effet, les phases aluminates jouent particulièrement sur l'évolution de la fluidité de la pâte de CPO durant sa période d'ouvrabilité. Néanmoins, la vitesse d'hydratation du CPO est gouvernée par l'hydratation des phases silicates qui sont présentes en plus grande quantité et qui lui confèrent ses propriétés finales.

I.1. Ciment Portland Ordinaire et composés constitutifs

L'hydratation du ciment est un processus de dissolution-précipitation comme indiqué par Le Châtelier [2]. Les anhydres le constituant tels que les composés aluminates, sulfates et silicates se dissolvent et lorsque la solution devient sursaturée par rapport à leur(s) hydrate(s), ces derniers précipitent mais à des vitesses différentes. Immédiatement après le contact avec l'eau de gâchage, il y a donc une dissolution rapide des phases anhydres présentes dans le CPO et une précipitation d'ettringite (trisulfoaluminate de calcium) et de C-S-H (silicate de calcium hydraté). Par la suite, l'hydratation est accélérée entraînant une formation importante de C-S-H et de portlandite (hydroxyde de calcium) : le ciment prend alors. Une fois la vitesse maximale d'hydratation atteinte, il y a un ralentissement de la précipitation des C-S-H et il se forme du monosulfoaluminate de calcium. Le durcissement du ciment progresse alors lentement tant qu'il y a de l'eau libre.

I.1.3. Hydratation des phases aluminates et sulfates

I.1.3.1. Réactivité lors de l'hydratation du C_3A en présence de sulfate de calcium

L'hydratation du C_3A est rapide et entraîne un raidissement rapide de la pâte. Ainsi, du sulfate de calcium est préalablement ajouté et permet de ralentir l'hydratation du C_3A [3].

L'évolution des concentrations en espèces calcium, sulfate, aluminate et hydroxyde et la conductivité de la suspension durant l'hydratation du C_3A en présence de gypse est présentée en Figure 1. La période 1 se rapporte à la présence d'ions sulfate en solution et la période 2 commence lorsqu'ils ont complètement été consommés.

I.1. Ciment Portland Ordinaire et composés constitutifs

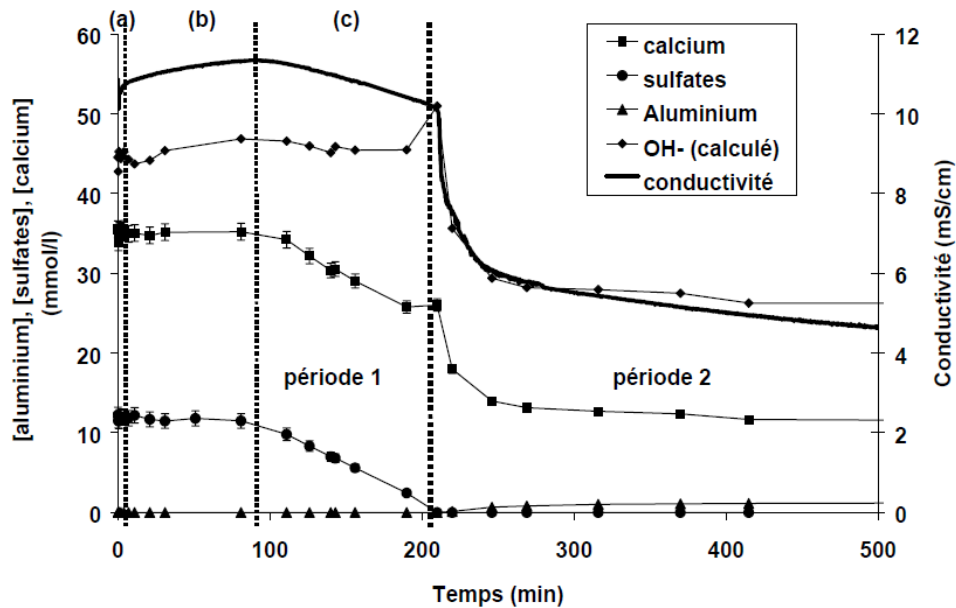
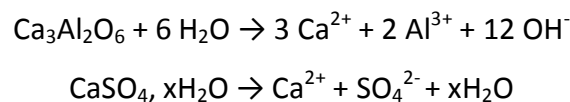
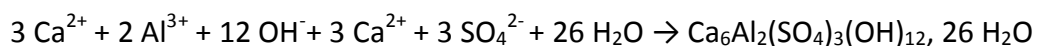


Figure 1 : Evolution des concentrations ioniques (aluminium: ▲, sulfate: ●, calcium: ■ et hydroxide calculée: ◆) et de la conductivité durant l'hydratation de 7.4 mmol de C_3A et de 1.5 mmol de gypse dans 50 mL de solution saturée par rapport à l'hydroxyde de calcium, rapport Liquide sur Solide, L/S, égal à 25, extrait de [3].

Après l'ajout d'eau au C_3A et sulfate de calcium, les anhydres se dissolvent selon les équations suivantes :



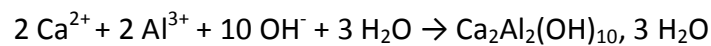
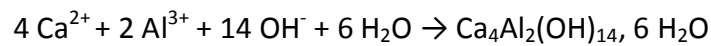
Durant période 1(a) de la Figure 1, la solution poreuse devient sursaturée par rapport au trisulfoaluminate de calcium ou ettringite qui précipite alors [3]. C'est une phase de type Aft (Alumino-Ferrite tri-substituée) qui a pour formule générale $(Ca_3(Al,Fe)(OH)_6 12H_2O)_2 \cdot X_3 \cdot x H_2O$ (avec X qui est un anion divalent ou un double anion monovalent) :



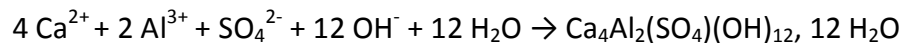
Malgré le fait qu'ils soient plus solubles que l'ettringite, des hydroaluminates de calcium de type AFm (Alumino-Ferrite mono-substituée) de formule générale $Ca_2(Al, Fe)(OH)_6 \cdot X \cdot x H_2O$ (avec X qui est un anion divalent ou un double anion monovalent), peuvent aussi précipiter [3]. Par la suite, la conductivité et les concentrations en ions restent constantes mettant en évidence un état stationnaire où la vitesse des phases dissoutes est

I.1. Ciment Portland Ordinaire et composés constitutifs

égale à celle des composés précipitent, période 1(b). La concentration en sulfate finit par chuter devenant même non mesurable à la fin de la période 1(c) entraînant ainsi une baisse de la conductivité de la suspension : le réservoir de sulfate de calcium solide est épuisé et la précipitation d'ettringite consomme les ions sulfate restant en solution. La fin de la période 1 est caractérisée par l'augmentation des concentrations en ions calcium et hydroxyde due à la dissolution rapide du C₃A en solution dès l'entière consommation des ions sulfate en solution [3]. Il en résulte une chute rapide de la conductivité et des concentrations en ions hydroxyde et calcium ainsi qu'une faible augmentation de la concentration en ions aluminates en période 2 de la Figure 1. Il y a la précipitation de deux hydroaluminates de calcium de type AFm :



La précipitation des hydroaluminates de calcium consomme des ions calcium en solution et l'ettringite n'est alors plus l'hydrate le moins soluble. Devenue métastable, elle se dissout pour former du monosulfoaluminate de calcium de type AFm :



I.1.3.2. Vitesse d'hydratation

Le bilan des réactions durant l'hydratation du C₃A est exothermique : cette dernière peut alors être suivie par calorimétrie. La Figure 2 montre l'évolution du flux de chaleur pendant l'hydratation du C₃A en présence de gypse et fait apparaître un pic exothermique intense dans chacune des périodes 1 et 2. Le pic de flux de chaleur de la période 1 apparaissant dans les quelques premières minutes de l'hydratation du C₃A en présence de gypse révèle la dissolution des composés anhydres qui est fortement exothermique. Une faible activité thermique suit ce premier pic : l'ettringite précipite à une vitesse constante et consomme alors tous les ions sulfate en solution. Durant la période 2, le deuxième pic intense est suivi d'un troisième pic exothermique de faible intensité. Le C₃A se dissout alors

I.1. Ciment Portland Ordinaire et composés constitutifs

rapidement dès l'absence d'ions sulfate en solution entraînant la précipitation des AFm. L'ettringite se dissout alors à leur profit.

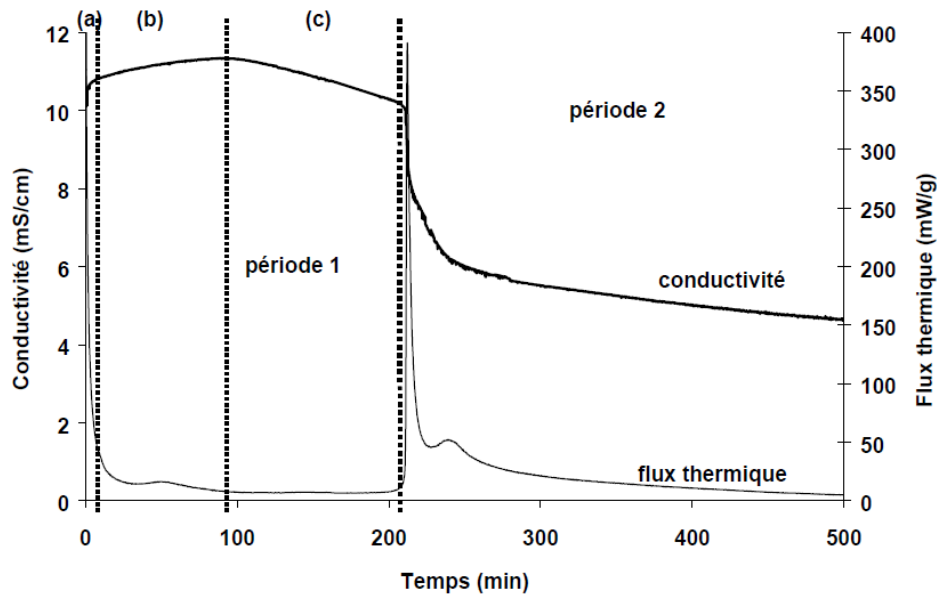


Figure 2 : Evolution du flux de chaleur et de la conductivité durant l'hydratation de 7.4 mmol de C₃A et de 1.5 mmol de gypse dans 50 mL de solution saturée par rapport à l'hydroxyde de calcium, (L/S=25), extrait de [3].

I.1.4. Hydratation des phases silicates

I.1.4.1. Réactivité durant l'hydratation du C₂S et C₃S

L'hydratation du C₂S et C₃S forme du silicate de calcium hydraté, du C-S-H et de l'hydroxyde de calcium, de la portlandite. La Figure 3 montre l'évolution de la concentration des ions calcium et silicates en solution en fonction du temps lors de l'hydratation du C₃S en suspension dans de l'eau et présente trois périodes qui seront décrites par la suite. La Figure 4 présente le diagramme chaux-silice-eau et révèle la courbe de solubilité du C-S-H (courbe S), la courbe de sursaturation maximale par rapport au C-S-H (courbe I) et le chemin cinétique (courbe C) décrit par Barret [4]. Un chemin O₁a₁b₁c₁ est représenté sur la Figure 4 et montre l'évolution des concentrations en espèces calcium et silicates durant l'hydratation du C₃S lorsqu'il est mélangé initialement avec de l'eau. Ces mêmes points O₁, b₁ et c₁ sont reportés sur la Figure 3.

I.1. Ciment Portland Ordinaire et composés constitutifs

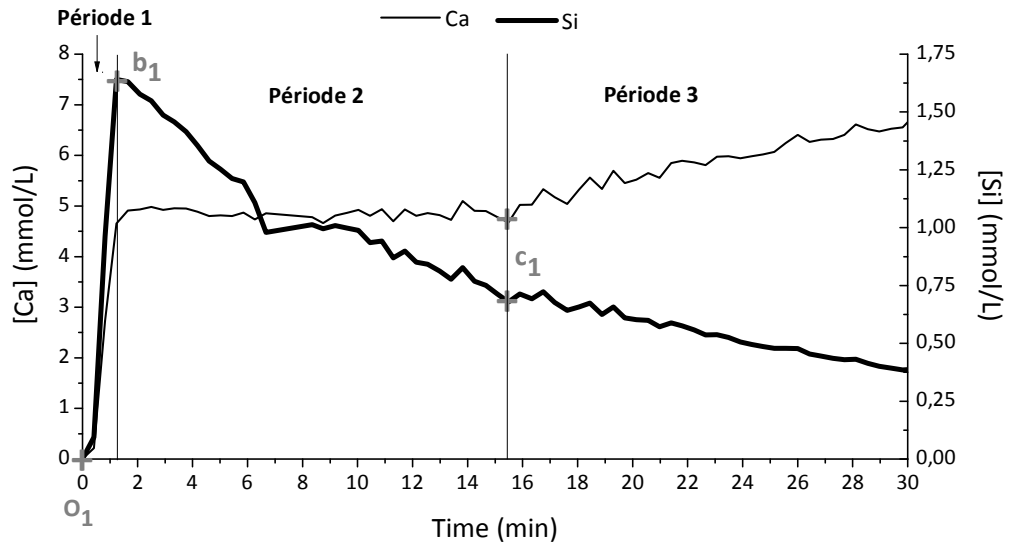


Figure 3 : Evolution des concentrations en ions calcium et silicates en fonction du temps lors de l'hydratation du C_3S dans de l'eau distillée et permutée, $L/S=100$.

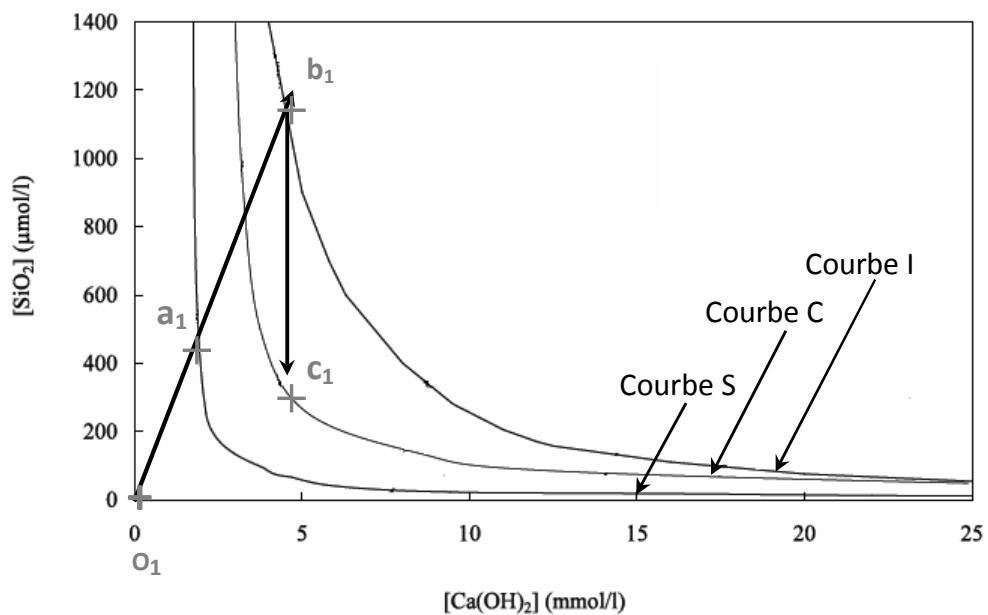


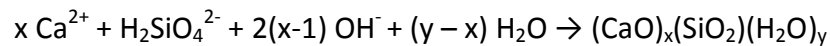
Figure 4: Diagramme chaux-silice-eau montrant l'évolution de la composition ionique de la solution au cours de l'hydratation du C_3S (chemin $O_1a_1b_1c_1$). La courbe S représente la courbe de solubilité du C-S-H, la courbe C est le chemin cinétique décrit par Barret [4], la courbe I est la courbe de sursaturation maximale par rapport au C-S-H.

I.1. Ciment Portland Ordinaire et composés constitutifs

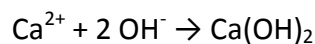
Dès le contact entre l'eau et le C_3S , ce dernier se dissout augmentant ainsi les concentrations en ions calcium et silicates en solution, Figure 3 (période 1) et Figure 4 (segment O_1a_1). Le C_3S se dissout selon la réaction suivante en libérant trois fois plus d'ions calcium que silicates en solution :



Les concentrations en ions calcium et silicates augmentent jusqu'à atteindre la courbe de solubilité de l'hydrate le moins soluble, c'est-à-dire le C-S-H, Figure 4 (point a_1). Avant que le segment O_1a_1 atteigne le point a_1 , c'est-à-dire avant que la composition ionique de la solution atteigne celle caractéristique de la solubilité du C-S-H, la dissolution du C_3S est dite pure car le C-S-H ne peut précipiter. Cependant à partir de ce point a_1 , le C-S-H peut thermodynamiquement précipiter mais ne se forme pas immédiatement car le degré de sursaturation par rapport à l'hydrate n'est pas suffisant pour permettre une précipitation instantanée. De ce fait, les concentrations en ions calcium et silicates en solution continuent d'augmenter jusqu'à atteindre la sursaturation maximale par rapport au C-S-H (point b_1 des Figure 3 et Figure 4) entraînant une précipitation instantanée du C-S-H :



Par la suite, la concentration en ions calcium reste constante alors que celle en ions silicates chute du fait de la germination des premiers germes de C-S-H qui est 3 fois plus rapide que la dissolution du C_3S , Figure 3 (période 2) et Figure 4 (segment b_1c_1). A partir du point c_1 en Figure 4, les concentrations en ions calcium et silicates en solution suivent la courbe C qui est le chemin cinétique décrit par Barret [4]. La concentration en ions calcium augmentent alors que celle des ions silicates continuent de chuter, Figure 3 (période 3). De nouveaux germes se forment sur les particules de C-S-H entraînant la croissance des hydrates à la surface du C_3S . Le rapport stoechiométrique CaO/SiO_2 du C-S-H étant toujours inférieur à 2 et celui du C_3S égal à 3, la solution interstitielle s'enrichit en ions hydroxyde et calcium jusqu'à ce que la solution devienne sursaturée par rapport à l'hydroxyde de calcium ($[Ca(OH)_2]=36 \text{ mmol/L}$ à 25°C) qui précipite sous forme de portlandite :



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Quand la portlandite commence à précipiter, les trois réactions de dissolution du C_3S , de précipitation du C-S-H et de formation de la portlandite sont simultanées et ont la même vitesse. Le mécanisme d'hydratation du C_2S est similaire à celui mentionné pour le C_3S [1].

L'état d'équilibre entre un solide et une solution est décrit par sa solubilité. La force motrice de la dissolution et de la précipitation est l'écart à l'équilibre [5], la sous-saturation pour la dissolution du C_3S , β_{C_3S} et la sursaturation pour la précipitation du C-S-H, β_{C-S-H} , décrites comme suivant :

$$\beta_X = PAI/K_{sp\ X}$$

Où PAI est le Produit d'Activité Ionique de la solution et K_{sp} le produit de solubilité de la phase X.

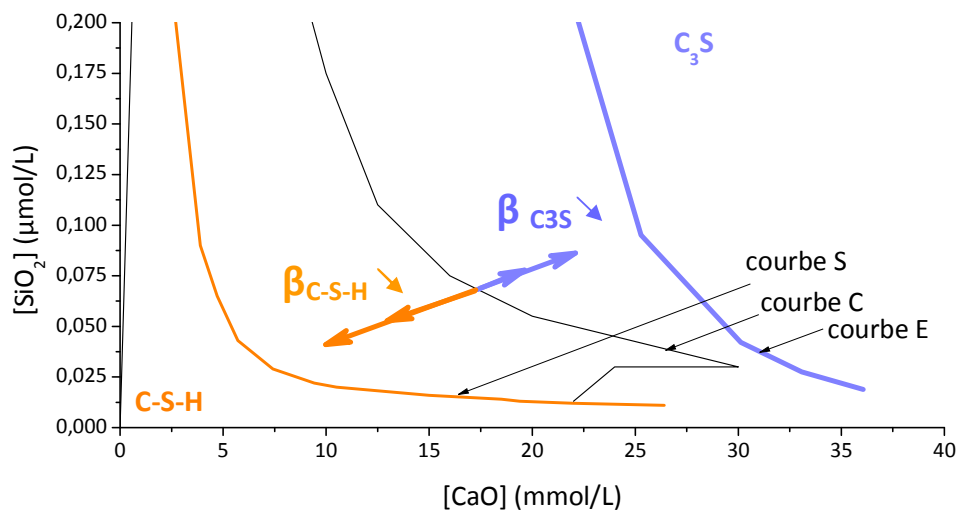


Figure 5 : Diagramme chaux-silice-eau montrant le déplacement de la composition ionique en fonction de l'évolution des coefficients de sursaturation par rapport au C-S-H, β_{C-S-H} et de sous-saturation par rapport au C_3S , β_{C_3S} . La courbe C représente le chemin cinétique décrit par Barret [4], la courbe S celle de la solubilité du C-S-H et la courbe E celle de la solubilité du C_3S .

La vitesse de dissolution du C_3S et de précipitation du C-S-H dépend de l'écart à l'équilibre et donc de la sous-saturation par rapport à l'anhydre et de la sursaturation par rapport à l'hydrate. Plus l'écart à l'équilibre est grand, plus la vitesse de ces réactions augmente et inversement. La Figure 5 montre le déplacement de la composition ionique de la solution en fonction de la sous-saturation par rapport au C_3S et de la sursaturation par rapport au C-S-H sur le diagramme chaux-silice-eau.

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Lorsque la composition ionique de la solution se rapproche de la courbe de solubilité du C_3S (Figure 5, courbe E), la sous-saturation par rapport à l'anhydre diminue et entraîne une augmentation de la sursaturation par rapport au C-S-H. Ainsi, la vitesse de précipitation de l'hydrate augmente et celle de la dissolution de l'anhydre diminue de manière à ce que la composition ionique de la solution rejoigne le chemin cinétique (courbe C, Figure 5)) où ces deux vitesses sont alors égales. A l'inverse, lorsque les concentrations en ions calcium et silicates sont telles que la composition ionique de la solution est proche de la courbe de solubilité du C-S-H (Figure 5, courbe S), la sursaturation par rapport à cet hydrate diminue et la sous-saturation par rapport au C_3S augmente. La vitesse de dissolution de l'anhydre augmente alors et celle de la précipitation du C-S-H diminue jusqu'à ce qu'elles deviennent égales.

I.1.4.2. Vitesse d'hydratation

L'hydratation d'une pâte de C_3S ou d'une suspension de C_3S dans une solution saturée par rapport à l'hydroxyde de calcium étant exothermique, le flux de chaleur est mesuré au cours du temps. La courbe calorimétrique montrée sur la Figure 6 est découpée en trois périodes caractéristiques. Le flux de chaleur mesuré est proportionnel à la vitesse d'hydratation de la phases anhydre durant les périodes 2 et 3.

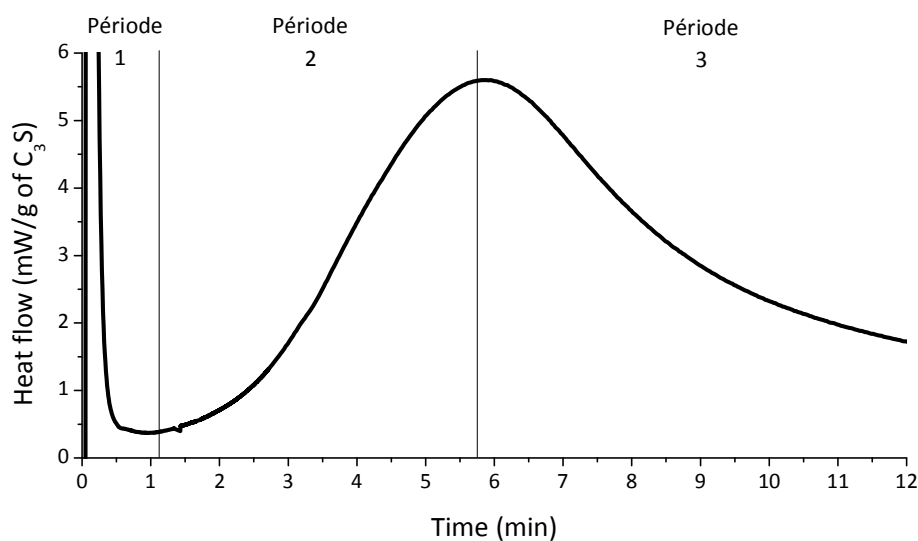


Figure 6 : Flux de chaleur mesuré par calorimétrie isotherme durant l'hydratation du C_3S dans de l'eau, $L/S=0.4$.

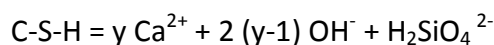
I.1. Ciment Portland Ordinaire et composés constitutifs

Dès le contact entre l'eau et le C_3S , l'anhydre se dissout produisant un pic de flux de chaleur intense sur la courbe calorimétrique et les premiers germes de C-S-H précipitent sur le C_3S . Par la suite une période de faible activité thermique est observée et est appelée période d'induction ou période dormante (Figure 6, période 1). Durant la période d'accélération (Figure 6, période 2), la vitesse d'hydratation du C_3S augmente : les germes de C-S-H croissent librement à la surface du C_3S . La vitesse d'hydratation de l'anhydre et donc le flux de chaleur atteint un maximum à la fin de la période 2. La période 3, nommée période de décélération, est caractérisée par une diminution de la vitesse d'hydratation du C_3S , Figure 6. Il a été récemment proposé que le ralentissement de la dissolution du C_3S et par conséquent la diminution de la vitesse de précipitation du C-S-H provient de la coalescence des cavités d'attaque à la surface de l'anhydre[6]. Cette interprétation va à l'encontre de la théorie de la croissance des C-S-H expliquant le ralentissement de l'hydratation du C_3S par une coalescence des particules de C-S-H à la surface de l'anhydre qui limiterait ainsi la diffusion de l'eau et des réactifs à travers la couche continue d'hydrates [7].

I.1.4.3. Le C-S-H

I.1.4.3.a. Composition et solubilité

L'hydratation des phases silicates forment des particules de C-S-H. Leur composition est définie par le rapport molaire CaO/SiO_2 noté Ca/Si qui est régie par la concentration en hydroxyde de calcium présent de la solution dans laquelle les hydrates sont à l'équilibre. L'équilibre de solubilité du C-S-H peut s'écrire comme suivant :



$$K_{sp\ C-S-H} = (Ca^{2+})^y (OH^-)^{2(y-1)} (H_2SiO_4^{2-}) \text{ avec } (X) = [X] \cdot \gamma_X$$

Où $K_{sp\ C-S-H}$ est le produit de solubilité du C-S-H à l'équilibre, (X) l'activité, $[X]$ la concentration et γ_X le coefficient d'activité des espèces X présentes en solution. y correspond au rapport Ca/Si du C-S-H qui est une variable.

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Différents travaux montrent que plus la concentration en hydroxyde de calcium est élevée en solution, plus le rapport Ca/Si du C-S-H augmente, Figure 7 [8-10]. La constante de solubilité du C-S-H ($K_{sp \text{ C-S-H}}$) étant elle-même fonction du rapport Ca/Si, cela suggère la présence de plusieurs phases de C-S-H ayant chacune sa propre K_{sp} . Différentes phases de C-S-H nommées α , β et γ sont en effet distinguées en fonction de la concentration en hydroxyde de calcium à travers les travaux de Lecoq [9] :

C-S-H(α) : $0.66 < \text{Ca/Si} < 1$ avec $1 \text{ mmol/L} < [\text{CaO}] < 2 \text{ mmol/L}$

C-S-H(β) : $1 < \text{Ca/Si} < 1.5$ avec $2 \text{ mmol/L} < [\text{CaO}] < 20 \text{ mmol/L}$

C-S-H(γ) : $\text{Ca/Si} > 1.5$ avec $20 \text{ mmol/L} < [\text{CaO}] < 30 \text{ mmol/L}$

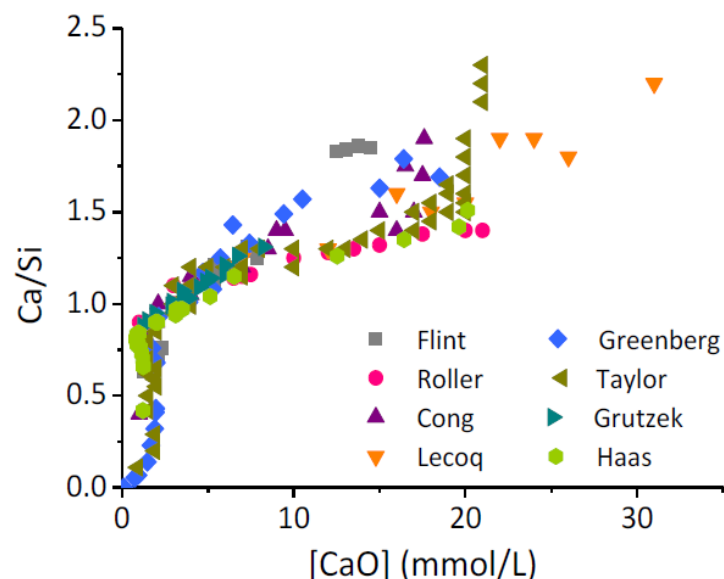


Figure 7 : Evolution de la stoechiométrie du C-S-H en fonction de la concentration en hydroxyde de calcium en solution selon différents auteurs, extrait de [11].

Grâce à des calculs réalisés à partir de données expérimentales telles que le rapport Ca/Si, la charge de surface du C-S-H ainsi que le pH et la concentration en ions calcium et silicates de la solution d'équilibre, Haas a récemment déterminé le produit de solubilité de ces trois phases de C-S-H alors caractérisées par un unique rapport Ca/Si chacune [8].

I.1. Ciment Portland Ordinaire et composés constitutifs

I.1.4.3.b. Structure et charge de surface

Les particules de C-S-H sont des matériaux faiblement cristallins [12,13] et de taille nanométrique : 60x50x5 nm mesuré par microscope à force atomique [7] et 4,2 nm mesuré par diffusion de neutrons aux petites angles [14]. La tobermorite est un hydrate possédant une stoechiométrie et une densité proche de celle du C-S-H de bas rapport Ca/Si. Les diffractogrammes expérimentaux de C-S-H de différents rapports Ca/Si ont d'ailleurs pu être simulés à partir du modèle de la tobermorite monoclinique de Hamid [15] grâce à la méthode de Rietveld en ajustant les paramètres d'un cristal modèle [16]. C'est un minéral naturel avec une structure en feuillet dont trois types existent selon la taille de leur empilement, leur structure en feuillets et leur degré d'hydratation : la tobermorite-14 Å, la tobermorite-11 Å, et la tobermorite-9 Å, [17]. La tobermorite-11 Å de formule moyenne $\text{Ca}_{2,25}[\text{Si}_3\text{O}_{7,5}(\text{OH})_{1,5}] \cdot \text{H}_2\text{O}$ et de densité égale à 2.43 g/cm^3 sert généralement de modèle pour décrire la structure du C-S-H [15], Figure 8.

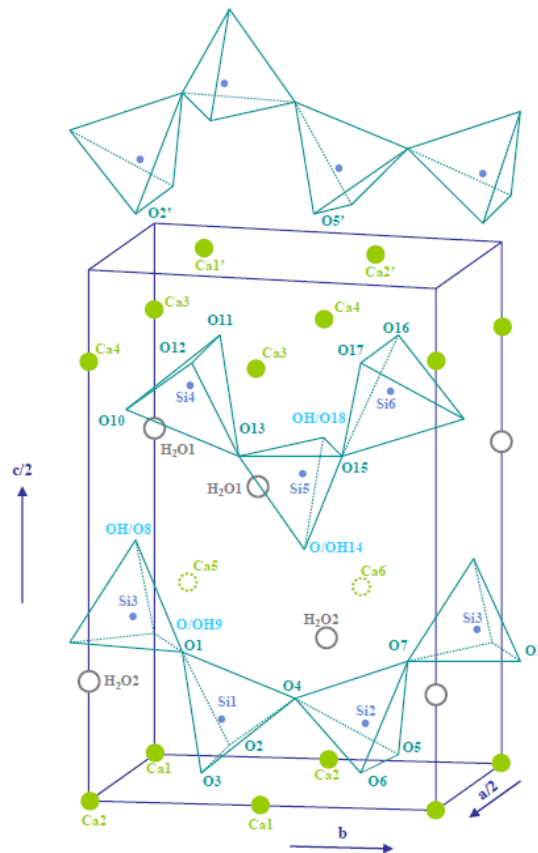
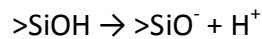


Figure 8 : Modèle cristalllographique du C-S-H : structure de la tobermorite-11 Å, Hamid [15], extrait de [11].

I.1. Ciment Portland Ordinaire et composés constitutifs

Le C-S-H a une structure en feuillets avec une couche d'ions calcium comprise entre deux couches de silicates [30]. La couche de calcium est composée en moyenne de deux plans décalés l'un par rapport à l'autre. Les couches de silicates sont formées de chaînes linéaires de tétraèdres de silicates ayant un motif appelé « dreierketten » comprenant trois tétraèdres qui se répètent [18]. Deux tétraèdres de ce motif coordonnent deux de leurs atomes d'oxygène avec le plan de calcium et le troisième appelé tétraèdre pontant, relie deux dimères de silicates consécutifs. L'interfeuille est composé par des molécules d'eau et des ions calcium lorsque le rapport Ca/Si est supérieur à 0.66.

Les nanoparticules de C-S-H sont composées de quatre feuillets séparés par trois interfeuillets donnant lieu à deux surfaces externes pour six surfaces internes, [7,19]. Les tétraèdres de silicates pontants et les tétraèdres aux extrémités des chaînes possèdent des atomes d'oxygène non liés ce qui forme des groupes SiOH aussi appelés silanols. L'augmentation de la concentration en hydroxyde de calcium et donc du pH de la solution d'équilibre des C-S-H induit une ionisation de ces groupes silanols, donnant ainsi une charge de plus en plus négative à la surface du C-S-H [20,21] :



Pour une concentration en hydroxyde de calcium supérieure à 2 mmol/L, il y a une compensation de la charge négative des C-S-H par la présence d'ions calcium qui entraîne même une surface de charge apparente positive [20]. Une modélisation du potentiel électrocinétique de surface des C-S-H par la méthode de Monte Carlo a permis de montrer que l'inversion de charge est uniquement due aux interactions électrostatiques et non pas à une adsorption spécifique [22,23].

A travers cette partie concentrée sur le C-S-H, il a pu être noté que l'augmentation de la concentration en hydroxyde de calcium de la solution à l'équilibre avec les hydrates augmente leur rapport Ca/Si, entraîne un changement de leur structure mais aussi de leur charge de surface comme résumé à travers la Figure 9. Lorsque le rapport Ca/Si du C-S-H augmente, les tétraèdres pontants disparaissent aléatoirement et la longueur moyenne des chaînes silicates diminue jusqu'à devenir essentiellement des dimères ayant une charge de surface de plus en plus négative surcompensée par la présence d'ions calcium [24,25].

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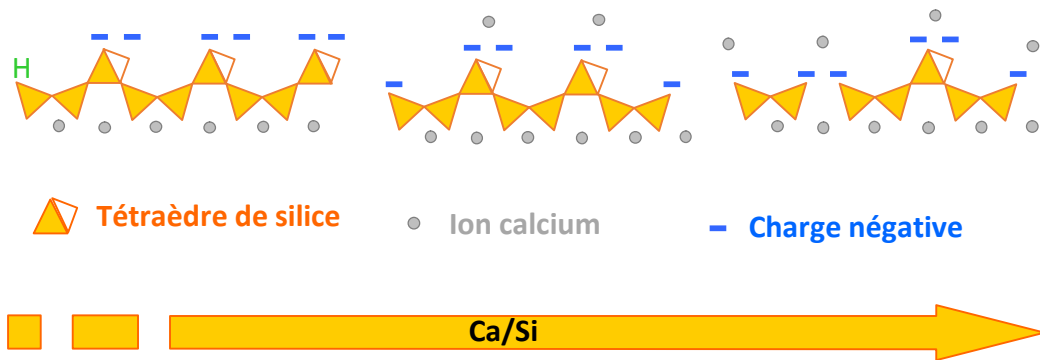


Figure 9 : Structure simplifiée du C-S-H en fonction de son rapport Ca/Si, [8].

I.2. Adjuvants organiques

I.2.1. Intérêts et inconvénients de certains additifs organiques

Les retardateurs sont des composés majoritairement organiques qui sont ajoutés au béton dans le but d'allonger la période d'ouvrabilité afin d'éviter le raidissement du coulis lorsque celui-ci commence à prendre. Ils sont utilisés pour contrebalancer l'accélération de la prise du ciment quand la température extérieure est élevée, lors de longs transports mais aussi lorsque le temps de mise en place du coulis qui est important. D'autres molécules organiques sont aussi additionnées au béton telles que des plastifiants ou superplastifiants de manière à abaisser la quantité d'eau pour une même fluidité de la pâte (réducteur d'eau) ou à augmenter la fluidité du coulis pour une même quantité d'eau (fluidifiant). Néanmoins, la plupart de ces additifs organiques retardent aussi la prise du ciment [26,27]. Ainsi, il paraît important de comprendre pourquoi et comment certaines molécules organiques entraînent un retard de la prise du ciment afin d'éviter ce phénomène s'il ne correspond pas à la fonction initiale de l'additif ou bien de mieux le contrôler s'il est volontaire.

I.2.2. Nature des adjuvants organiques retardant la prise du ciment

Les molécules organiques qui retardent la prise du ciment peuvent être des polymères ou bien encore des composés simples comme décrit ci-dessous :

Lignosulfonates : découverts dans les années 30, ce sont les premiers polymères utilisés en tant réducteur d'eau mais ils génèrent parfois un retard de la prise du ciment important [28-30]. Ces composés organiques sont des sous-produits de l'industrie du papier (dérivés de la lignine) qui peuvent contenir jusqu'à 30 % de sucres et de dérivés de sucres en fonction du traitement qu'ils ont suivis. Le polymère ramifié est principalement constitué de groupes phényle, hydroxyle (OH) et sulfonate (SOO⁻). Les lignosulfonates diffèrent en fonction de leur composition, de leur structure fondamentale et de leur longueur.

Ethers de polycarboxylate et phosphonates polyéthylène glycol : certains de ces superplastifiants induisent un retard sur l'hydratation du ciment [31-34]. Les éthers de polycarboxylate sont constitués de copolymères branchés comportant des groupes

I.2. Adjuvants organiques

carboxylates (COO^-) dans leur chaîne principale sur laquelle sont greffées des chaînes latérales neutres de polyéthylène glycol. Ces polymères varient en fonction de leur chaîne principale (longueur, nature des groupements fonctionnels, densité de charges anioniques) et de leurs chaînes latérales (longueur, densité de greffage, distribution). Contrairement aux éthers de polycarboxylate qui sont des composés anioniques avec des chaînes latérales neutres de polyéthylène glycol, les phosphonates polyéthylène glycol sont constitués de chaîne d'oxyde de polyéthylène de différentes longueurs avec un ou deux groupes phosphonates ($\text{PO}(\text{O})_2$) à l'une des extrémités.

Sucres et dérivés : des saccharides (sucrose, glucose...) ainsi que des polysaccharides (amidon, cellulose...) sont utilisés en tant que retardateur de prise du ciment [28,35-38]. Des dérivés de sucres comme les sucres alcools (D-glucitol, D-mannitol...) et les anions de sucres acides (D-gluconate, D-galactarate...) sont des composés organiques de courtes chaînes carbonées aussi connus comme retardateurs [29,39-42]. Toutes ces molécules organiques possèdent de multiples groupes hydroxyles. Les glucides possèdent aussi des groupes aldéhydes (R-CH=O) ou cétone (R-CO-R) alors que les anions de sucres acides ont un ou deux groupes carboxylates supplémentaires.

Amino-carboxylates et amino-phosphonates : la présence de ces petites molécules organiques telles que l'EDTA entraînent un retard sur l'hydratation du ciment [43-45]. Elles diffèrent les unes des autres par la taille de leur chaîne principale ainsi que par le nombre de groupe carboxylate ou phosphonate qu'elles portent.

I.2.3. Paramètres jouant sur le retard de l'hydratation des phases silicates du ciment

La prise du ciment est due à l'hydratation de ses phases silicates formant majoritairement du C-S-H mais aussi de la portlandite. Les retardateurs de prise changent la vitesse d'hydratation du ciment en modifiant celle de ses phases silicates dont l'alite, du C_3S impur, est le composé principal. Ainsi, l'effet retard de différentes molécules organiques sur l'hydratation des phases silicates du ciment et du C_3S pur a été particulièrement étudié et comparé [28-33,35,42-44,46-48]. Cependant, ce retard a souvent été relié à leur dosage c'est-à-dire à une concentration massique et non à une concentration molaire [49-51]. Les

I.2. Adjuvants organiques

composés organiques étant souvent très différents du point de vue de la nature et du nombre de leurs éléments chimiques, le retard qu'ils engendrent sur l'hydratation des phases silicates ne peut être simplement corrélé à la fonction chimique portée par une molécule organique. La structure de ces composés organiques varie aussi et joue un rôle important sur le retard qu'ils induisent sur l'hydratation des phases silicates du ciment comme le montrent différentes études concernant les molécules de type polycarboxylate [50-52]. De plus, la stéréochimie des groupes hydroxyles de différents sucres alcools, c'est-à-dire l'arrangement relatif de ces groupes dans l'espace, change leur effet retardateur sur la prise du ciment et du C_3S malgré une formule chimique identique [42].

Néanmoins, malgré le fait que la vitesse d'hydratation du ciment soit contrôlée par l'hydratation des phases silicates, il a aussi été montré que le retard induit par certaines molécules organiques sur l'hydratation des phases silicates est sensible à la composition du ciment et plus particulièrement à la présence des phases aluminates et sulfates. En effet, le retard généré par des polysaccharides et des dérivés de sucres sur l'hydratation des phases silicates est révélé être réduit par la présence de phases aluminates et/ou de leurs hydrates [38,40,42]. De plus, l'hydratation du C_3A pur qui forme alors des AFm est aussi retardé par diverses molécules organiques comme le D-gluconate, glucose, lignosulfonates, éthers de cellulose [53-56]. En présence de sulfate de calcium, l'hydratation du C_3A formant de l'ettringite est elle aussi modifiée par le glucose, des lignosulfonates, polysaccharides, éthers de cellulose [55,57,58].

Il apparaît alors que les caractéristiques structurelle et chimique des molécules organiques jouent un rôle sur le retard qu'elles entraînent sur l'hydratation des phases silicates mais aussi que leurs interactions avec les autres phases du ciment, autrement dit avec les phases aluminates et sulfates changent ce pouvoir retardateur.

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I.2.4. Origine du retard et interactions des molécules organiques avec les composés cimentaires

L'hydratation du ciment suivant un processus de dissolution-précipitation, le retard de la prise du ciment est lié à un impact des molécules organiques sur la dissolution des composés silicates anhydres et/ou de la précipitation de leur produit hydraté, c'est-à-dire le C-S-H. De nombreuses études portant sur l'origine du retard proposent une perturbation de la précipitation des C-S-H engendrée par les composés organiques [28,57,59-61]. Cependant, il a été montré que certains retardateurs affectent la dissolution du C_3S pur ou des phases silicates dans le ciment [40,62,63]. Des éthers de cellulose retardant l'hydratation du C_3S montrent toutefois un faible effet sur la dissolution de cet anhydre pur [60]. Ainsi, l'origine du retard de l'hydratation des phases silicates n'est pas encore bien identifiée sachant que certaines molécules organiques pourraient à la fois avoir des effets sur la dissolution du C_3S et la précipitation des C-S-H.

Certains auteurs expliquent ce retard par une adsorption des molécules organiques sur les C-S-H et/ou sur la portlandite qui gênerait ainsi le cours de l'hydratation des phases silicates [35,42,44,64]. Il a aussi été montré que des retardateurs de prise solubilisent la portlandite suggérant ainsi une complexation entre les molécules organiques et les ions calcium et/ou hydroxyde en solution [35]. Une complexation des composés organiques avec les ions silicates présents dans la solution poreuse lors de l'hydratation du ciment a de même été proposée [28,44,65]. Cependant, le sucre qui retarde pourtant l'hydratation des phases silicates ne complexe pas les ions silicates [35]. De plus, certaines molécules organiques retardant l'hydratation des phases silicates comme le D-gluconate et les éthers de cellulose s'adsorbent sur les aluminates hydratés [40,55]. Une étude indique aussi que le D-gluconate augmente fortement la concentration en ions aluminate en solution lors de l'hydratation du ciment, laissant supposé l'existence de complexe(s) entre les molécules organiques et ces ions [40]. Ainsi, les molécules organiques qui retardent l'hydratation des phases silicates du ciment sont présumées interagir avec les phases silicates et/ou aluminates hydratées ou non ainsi qu'avec des ions en solution.

I.2. Adjuvants organiques

Etant donné que la vitesse d'hydratation des phases silicates résulte du couplage existant entre la dissolution de ces phases et la précipitation des C-S-H, l'origine du ralentissement de leur l'hydratation en présence de molécules organiques et donc de la formation d'hydrates n'est pas évidente. De plus, les interactions existantes entre les composés organiques et les différentes phases cimentaires, anhydres et hydratés, ne sont pas encore bien identifiées. L'étude du lien entre ces différentes interactions et l'effet retard induit par les composés organiques sur la vitesse d'hydratation des phases silicates du ciment reste ainsi difficile avec les connaissances actuelles. Le chapitre suivant expose alors les molécules organiques, les composés cimentaires et les méthodes utilisés dans cette présente étude afin d'identifier les interactions des composés organiques en solution et à l'interface solide-liquide ainsi que les effets engendrés sur l'hydratation des différentes phases minérales.

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CHAPITRE II : STRATEGIE DE L'ETUDE

II.1. Choix des molécules organiques

Nous avons donc pu voir qu'il y a de nombreux composés organiques entraînant un retard sur l'hydratation des phases silicates présentes dans le ciment. Néanmoins, ces molécules organiques sont des composées simples ou des polymères de tailles et de structures diverses. De plus, elles contiennent des groupes fonctionnels différents : des groupes hydroxyle, hydroxy-carboxylate, carboxylate, sulfonate et/ou phosphonate. Le nombre de ces groupes varie aussi d'une molécule organique à l'autre entraînant un changement de la charge portée par les composés dont les groupes sont anioniques. Pour une formule chimique identique, des molécules organiques de différente stéréochimie peuvent aussi exister. Ainsi de nombreux paramètres changent et il est difficile de relier le retard induit par les molécules organiques à leur propre stéréochimie, fonctionnalité et charge respectivement.

Ainsi, l'étude rapportée dans ce manuscrit porte sur des molécules organiques de petite taille avec des chaînes linéaires ou ramifiées. Le nombre et la nature de leur(s) fonction(s) chimique(s) ou bien encore leur stéréochimie sont bien définis de manière à pouvoir relier leurs effets et interactions à leur(s) paramètre(s) caractéristique(s). Des sucres alcools, des anions de sucres acides, des amino-sulfonates, carboxylates, phosphonates ont été étudiés et sont représentés dans le Tableau 1. Pour les sucres alcools, l'étude s'est focalisée plus particulièrement sur des hexitols qui diffèrent uniquement selon la stéréochimie de leurs groupes alcools (composés (A), (B) et (C)). Concernant, les anions des sucres acides, il y a la molécule (D) qui est le mono-carboxylate correspondant au composé (A) et la molécule (E) qui est le di-carboxylate correspondant au composé (B). La molécule (F) est un di-carboxylate correspondant à l'anion de sucre acide (E). Les amino-carboxylates ((G) et (J)), sulfonates ((H) et (K)), et phosphonates ((I) et (L)) sont linéaires et varient en fonction de la longueur de leur chaîne carbonée qui passe de deux à trois carbones. Les amino-carboxylates ((M) et (O)) et phosphonates ((N) et (P)) qui eux sont ramifiés, sont composés de trois ou quatre groupes identiques.

II.1. Choix des molécules organiques

Tableau 1 : Représentation de Cram des molécules organiques étudiées.

D-glucitol (A)	D-galactitol (B)	D-mannitol (C)
D-gluconate (D)	D-galactarate (E)	Adipate (F)
3-aminopropanoate (G)	2-aminoethanesulfonate (H)	2-aminoethylphosphonate (I)
4-aminobutanoate (J)	3-amino-1-propanesulfonate (K)	3-aminopropylphosphonate (L)
EDA¹ (M)		HEDTMP³ (N)
EDTA² (O)		EDTMP⁴ (P)

¹EDA: 2-aminoéthyl 2-hydroxy éthylaminoacétate ; ²EDTA : éthylènediamine tétraacétate ; ³HEDTMP : 2-hydroxyéthyl éthylènediamine tri(méthylènéphosphonate) ; ⁴EDTMP : éthylènediamine tétra(méthylène phosphonate).

II.2. Choix des composés minéraux

L'étude bibliographique a permis de mettre en évidence que des molécules organiques retardent l'hydratation des phases silicates du CPO dont l'alite (C_3S impur) est la phase majoritaire. De plus, certains composés organiques interagissent aussi avec les phases aluminates présentes dans le CPO lors de son hydratation changeant ainsi leur effet sur l'hydratation des phases silicates.

De plus, face à l'importante émission de gaz carbonique lors de la fabrication du CPO, une proportion de ce dernier se voit remplacer par d'autres composés minéraux tels que des Matériaux Cimentaires Supplémentaires (MCS). Ce sont des résidus d'autres procédés industriels comme des laitiers de haut-fourneau, cendres volantes, fumées de silice, fines calcaires... Ainsi avec la diversité des ciments actuels et donc avec la variabilité qu'il y a dans leur composition, il est primordial d'identifier les interactions entre des molécules organiques et différents composés cimentaires ainsi que leur effet sur l'hydratation de ces phases minérales de manière à pouvoir être prédictif sur le long terme.

Par conséquent, cette étude s'est focalisée sur les interactions et impacts de molécules organiques sur l'hydratation des phases aluminates, sulfates et silicates du CPO. Des systèmes modèles dont du C_3S pur d'un côté et un mélange de C_3A -gypse-hémihydrate de l'autre ont été utilisés. Les interactions possibles entre les molécules organiques et les produits d'hydratation du C_3S , c'est-à-dire avec du C-S-H et de la portlandite ont aussi été étudiées. De manière à s'affranchir de la cinétique lors de l'hydratation du C_3S , des particules de C-S-H ont été synthétisées et de la portlandite commerciale a été utilisée. Des études sur un système réel, c'est-à-dire sur un CPO blanc comportant uniquement du C_3A comme phase aluminate ont aussi été faites. La proportion du mélange de C_3A -gypse-hémihydrate dans le CPO a été augmentée de manière à enrichir ce ciment en phase aluminate à taux de sulfate constant.

II.3. Méthodes et techniques utilisées

La présentation des méthodes choisies pour mener à bien cette étude est ici succincte. Elles seront décrites plus en détails et adaptées aux problématiques traitées dans les divers articles du Chapitre III. Dans ce paragraphe sont présentés les outils expérimentaux et les moyens de calculs utilisés.

II.3.1. Procédures expérimentales

II.3.1.1. Suivi de l'hydratation des pâtes et des suspensions diluées

Le flux de chaleur émis durant l'hydratation des systèmes modèles et du ciment en pâte a été suivi par calorimétrie isotherme. Le rapport Liquide sur Solide (L/S) des pâtes était de 0.4 pour le ciment ainsi que le C_3S et de 1 pour le mélange C_3A -gypse-hémihydrate. En revanche, lorsque l'analyse de la composition ionique et/ou organique de la solution était nécessaire durant l'hydratation des composés cimentaires, des suspensions diluées ont été réalisées (L/S=100). L'hydratation de ces suspensions a été suivie par en mesurant la conductivité de la solution qui est elle-même fonction de la concentration et de la conductivité molaire ionique des différents ions présents.

II.3.1.2. Analyse des solutions

La composition ionique et/ou organique des solutions prélevées durant l'hydratation des composés cimentaires ou bien encore les solutions à l'équilibre avec les particules de C-S-H et/ou de portlandite avec et sans molécule organique a été analysée après filtration de ces suspensions.

La concentration en molécules organiques a été identifiée en mesurant le Carbone Organique Total (COT) des solutions après filtration. L'adsorption des composés organiques sur les anhydres et/ou hydrates a été calculée en utilisant la méthode du reste : la concentration initiale en molécules organiques étant connue, la mesure de la concentration mesurée par COT nous permet de déterminer la quantité de molécules considérées comme adsorbées.

Le pH de ces solutions a été mesuré grâce à un pHmètre immédiatement avoir été filtrées. Les concentrations ioniques des filtrats ont quant à elles été déterminées par

II.3. Méthodes et techniques utilisées

spectrométrie d'émission optique avec plasma à couplage inductif (Inductively Coupled Plasma-Atomic Emission Spectroscopy, ICP-AES). La mesure de la concentrations en ions calcium, silicates, aluminates et/ou sulfates en fonction du temps (en continu ou par prélèvement) nous a permis de suivre la dissolution pure ($L/S=10\,000$) ou l'hydratation ($L/S=100$) des composés cimentaires avec et sans molécule organique dans les suspensions diluées.

II.3.1.3. Analyse des solides

La Diffraction des Rayons X (DRX) nous a permis d'identifier la nature des phases cristallines et la Microscopie Electronique à Balayage (MEB) nous a révélé la morphologie des minéraux présents au cours de l'hydratation des composés cimentaires après séchage.

II.3.2. Calculs de spéciation chimique

La complexation des molécules organiques avec les ions calcium, silicates et/ou hydroxyde a été révélée en mesurant la concentration en composés organiques, en ions calcium et le pH des solutions à l'équilibre avec un réservoir de portlandite et en mesurant la concentration en ions calcium, silicates et le pH des solutions à l'équilibre avec des particules de C-S-H. Des simulations ont été réalisées de manière à déterminer l'équilibre et la constante de complexation entre les ions calcium et/ou hydroxyde et différentes molécules organiques. Des calculs ont aussi permis de mettre en évidence une complexation possible entre des molécules organiques et les ions silicates.

Les simulations ont été faites en utilisant le programme PHREEQC qui est un logiciel de calculs géochimiques nous ayant permis d'identifier la composition solide-liquide des nos différents systèmes. Les calculs reposent sur des équilibres de solubilité, sur l'équilibre entre des espèces en solution et à la surface d'un solide et donc sur le bilan des charges et des masses à 25 °C. Ces calculs-ci nécessitent la connaissance de l'activité des espèces présentes en solution et donc plus particulièrement de leur coefficient d'activité étant donné le caractère non idéal des solutions aqueuses étudiées. Ces calculs ont alors été réalisés à partir de l'expression de Debye-Hückel considérant les espèces comme des charges

II.3. Méthodes et techniques utilisées

ponctuelles pour de faibles forces ioniques. Cependant, même à de faibles forces ioniques, des interactions entre espèces peuvent exister mais ne sont pas prises en compte par cette expression. Ainsi, notre étude s'est aussi basée sur le modèle de Pitzer qui prend en compte des interactions de courtes distances entre les espèces.

De manière à identifier la composition ionique des solutions à l'équilibre avec les particules de C-S-H avec et sans molécules organiques présentes, le modèle développé par Haas qui prend en compte la variation de la solubilité et de la stoechiométrie des différentes phases de C-S-H a été utilisé [8].

II.4. Développement de l'étude

Les résultats obtenus durant cette thèse sont présentés à travers cinq articles qui traitent de thématiques complémentaires et qui ont été soumis au journal Cement and Concrete Research.

L'Article 1 présente l'influence de la charge, de la fonctionnalité et de la stéréochimie de petites molécules organiques sur la vitesse d'hydratation du C_3S . Leur adsorption sur le C-S-H et leur complexation ionique en solution ont aussi été étudiées et reliées à leur effet retard généré sur l'hydratation du C_3S dans l'Article 2. Par la suite, l'Article 3 traite de l'impact de trois hexitols qui diffèrent selon la stéréochimie de leurs groupes alcools sur le processus de dissolution-précipitation de l'hydratation du C_3S . L'Article 4 concerne l'identification des effets et des interactions de ces sucres alcools durant l'hydratation du C_3A -gypse-hémihydrate. Pour finir, l'Article 5 se focalise sur le retard induit par les hexitols sur l'hydratation des phases silicates présentes dans le ciment. Les résultats exposés à travers ces cinq articles sont discutés au Chapitre IV.

CHAPITRE III : RESULTATS

III.1. Effets de la charge, de la fonctionnalité et de la stéréochimie de petites molécules organiques sur le retard et la vitesse maximale de l'hydratation du silicate tricalcique

Effects of the charge, functionality and stereochemistry of small organic molecules on the retardation and on the maximum rate of tricalcium silicate hydration

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Abstract

The retardation and the maximum rate of tricalcium silicate (C_3S) hydration induced by organic molecules were rarely measured as a function their molar concentration and prevent us to identify the effect of specific functional groups carried by the molecules. In this study, the maximum rate of C_3S hydration which is proportional to the maximum heat flow and the retardation led by different concentrations of organic molecules were determined using the monitored calorimetric curves of the C_3S pastes. The effect of the charge, functionality and stereochemistry was studied by using a set of sugar alcohols (D-glucitol, D-galactitol...), sugar acid anions (D-gluconate, D-galactarate...), carboxylate (adipate) and amines with functionalized sulfonate, carboxylate and phosphonate groups (EDTA, EDTMP...).

This study revealed that the maximum rate of C_3S hydration is enhanced by the presence of the organic molecules and that the retardation is increased with their concentration. The nature of the ending functional group of the molecules (hydroxyl, hydroxy-carboxylate, carboxylate, sulfonate or phosphonate), their main chain group (hydrocarbon or polyol chain) and the stereochemistry of their hydroxyl groups are shown to play a role.

Keywords: charge, functionality, hydration, retardation, stereochemistry, tricalcium silicate

III.1. Effets de la charge, de la fonctionnalité et de la stéréochimie de petites molécules organiques sur le retard et la vitesse maximale de l'hydratation du silicate tricalcique

1. Introduction

Retarding admixtures are used to delay the setting time of concrete by preventing early stiffening. They are added to keep workable concrete when counteracting the accelerating effect of hot weather, for long distance transport or extended placement time. Several dispersing agents and/or water reducers also retard cement hydration depending on their dosage which can lead to uncomfortable situations when it is unexpected or not regulated [1,2]. Retarding additives are composed of different carbohydrates and sugar derivatives (glucose, D-gluconate,...) and of several polymeric dispersing admixtures (lignosulfonates, polynaphthalene sulfonates, polyethylene oxide phosphonates and some polycarboxylate ethers). They are composed of small organic molecules or polymers with different functional groups such as hydroxyl ($-OH$), hydroxy-carboxylate ($HO-C-COO^-$), carboxylate ($-COO^-$), sulfonate ($-S(O)_2O^-$) or phosphonate ($-PO(O^-)_2$).

The retarding effect of organic admixtures on the hydration of cement is well documented and compared [3-10]. However, the former is often studied as a function of the dosage of the organic molecules but rarely depending on their molar concentration which prevents us to relate the retardation to their charge and functional group [11,12]. Moreover, indirect comparisons are often made when studying the retarding effectiveness of carboxylate, sulfonate or phosphonate based admixtures because not only their main anionic function changes but their structure as well. Now, it is well known that the retardation generated by polymers also depends on their main chain and side-chains length [13,14]. As far as hydroxyl groups are concerned, their number and stereochemistry are reported as an important parameter controlling the retardation generated by sugar alcohols and phenols on cement hydration [15-18]. Moreover, the number of hydroxy-carboxylate groups present in organic molecules is also shown to play an important role on their retarding effectiveness [17,19]. The effects of the polyol chains and of the hydroxy-carboxylate groups were often studied separately but their coupled effects on the retardation when using sugar acid anions has never been evaluated.

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Hence, this study used isothermal calorimetry to investigate the retardation and maximum rate of pure tricalcium silicate (C_3S) hydration caused by small organic molecules (short carbon chains) having different main chain and ending functional groups but also various orientations in space of their main chain groups (stereochemistry). The hydration of C_3S was studied to simplify the investigation of the hydration kinetics of Ordinary Portland Cement (OPC), as alite (impure C_3S) is its major compound and to avoid possible interactions of the organic molecules with the aluminate and sulfate phases present in OPC. The charge and functionality of the organic molecules were varied by using compounds differing from one another with small progressive modifications of their ending functional group (hydroxyl, hydroxy-carboxylate, sulfonate, carboxylate or phosphonate group) and of their main chain group (hydrocarbon chain, $-CH_2-$ or polyol chain, $-CH(OH)-$) as shown in Table 1. The effect of the stereochemistry was studied by using sugar derivatives that have different 3-D arrangements of their hydroxyl groups. Figure 1 presents the Fischer projections of the sugar alcohols and of some of their corresponding sugar acid anions studied and details the threo and erythro sequences of their hydroxyl groups.

To proceed, the retarding effect generated by the organic molecules on the hydration of C_3S was identified and related to their ending functional group and to their main chain properties. Then, their impacts on the maximum rate of C_3S hydration were compared. Finally, the effect induced by the organic molecules on the maximum rate of C_3S hydration was correlated to their retarding effectiveness. The retardation and the maximum rate of C_3S hydration were measured for different molar or equivalent concentrations of molecules. The equivalent concentration of anion is defined as being the molar concentration of the molecules normalized to their charge and allows us to reveal the properties of the main chain and ending groups of the charged molecules for a given amount of charge.

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Table 1: Chemical structures of the molecules studied at pH found in cement paste (≈ 12.5).

Changes in the stereochemistry of the hydroxyl groups	D-glucitol	D-galactitol	D-mannitol
Presence or not of hydroxyl groups in the main chain and changes in their stereochemistry	D-gluconate	D-galactarate	Adipate
Various anionic groups and hydrocarbon chain lengths	3-aminopropanoate	2-aminoethanesulfonate	2-aminoethylphosphonate
	4-aminobutanoate	3-amino-1-propanesulfonate	3-aminopropylphosphonate
Different nature and number of the anionic groups	EDA		EDTA
	HEDTMP		EDTMP

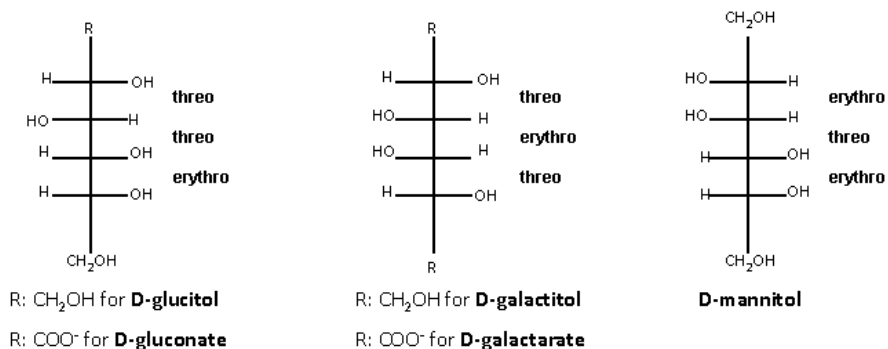


Figure 1: Fischer projections of hexitols and some of their corresponding sugar acid anions. “threo” stands for two hydroxyl groups on opposite sides and “erythro” for two hydroxyl groups on the same side of the carbon chain.

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2. Materials and methods

2.1. Materials

Pure triclinic C_3S was obtained from Mineral Research Processing. The particle size distribution was determined in ethanol by light scattering (Mastersizer 2000 from Malvern Instruments). The grain size distribution of C_3S is reported in Table 2.

Table 2: Grain size distribution of C_3S .

Sample	D[4,3] ^a (μm)	D[3,2] ^b (μm)	S _{sa} ^c (m ² /g)
C_3S	7.68	3.80	0.49

^a D[4,3]: the volume mean diameter of particles

^b D[3,2]: the surface mean diameter of particles

^c $S_{sa}=6/(\rho_{C_3S} \cdot D[3,2])$: the specific surface area when considering that the density of particles is homogeneous with the size, that the particles are spherical and where $\rho_{C_3S}=3.21 \text{ g/cm}^3$ is the density of C_3S .

The water used for the preparation of the pastes and solutions was both distilled and deionised. The molecules studied were sodium gluconate ($\geq 98 \%$) from Merck, D-glucitol ($\geq 98 \%$), D-mannitol ($\geq 98 \%$), D-galactitol ($\geq 99 \%$), adipic acid ($\geq 99,5 \%$), 2-aminoethanesulfonic acid ($\geq 99 \%$), 3-amino-1-propanesulfonic acid ($> 97 \%$), 3-aminopropanoic acid ($> 99 \%$), 4-aminobutyric acid ($\geq 99 \%$), 2-aminoethylphosphonic acid ($> 99 \%$), 3-aminopropylphosphonic acid ($> 98 \%$) and D-galactaric acid ($\geq 97 \%$) from Sigma Aldrich, all as a powder form. D-galactarate is water-soluble while D-galactaric acid is only sparingly so. Hence, di-sodium galactarate solutions were made by dissolving D-galactarate in aqueous sodium hydroxide ($> 97 \%$, Merck). Sodium salts of 2-aminoethyl 2-hydroxy ethylaminoacetate (EDA, 36.3 weight percent, wt%), ethylenediamine tetraacetate (EDTA, 32.9 wt%), 2-hydroxyethyl ethylenediamine tri(methylenephosphonate) (HEDTMP, 25.9 wt%) and ethylenediamine tetra(methylene phosphonate) (EDTMP, 26.1 wt%) from Bozzetto were as aqueous solution form.

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2.2. Methods

2.2.1. Isothermal calorimetry measurements

The mixing protocol was as follow: 1 g of C_3S was put in a plastic ampoule and mixed with 0.4 mL of aqueous solutions with and without organic molecules (Liquid to Solid ratio, $L/S=0.4$) at 3200 rpm for 2 minutes with a stirrer. After mixing, the ampoules were capped and inserted in the calorimeter. Then, the hydration of C_3S pastes was followed by monitoring the heat flow over time by isothermal calorimetry (TAM AIR) at 23 °C. The weight loss of the paste left on the stirrer was taken into account by recording the weigh of the samples before and after mixing.

2.2.2. Analysis of the calorimetric curves

Figure 2 represents the heat flow followed during the hydration of C_3S pastes with and without organic compounds. Their presence increases the time and the maximum heat flow compare to the ones of the reference. Given that the hydration rate is proportional to the heat flow, the effect of the molecules on the maximum heat flow was followed by measuring the maximum rate of C_3S hydration on the calorimetric curves. For the retardation generated by the molecules, it could be measured by comparing the time ending the induction period on the calorimetric curves with and without molecules in the pastes. Nevertheless, in the range of concentration studied (0 to 75 mmol/L depending on the additive studied), the shape of the calorimetric curve is not changed with and without molecules in the hydrating pastes. Hence, it was easier to calculate the retardation as being the difference in time between the maximum heat flow of the samples with and without additives. The retardation of C_3S hydration and the maximum heat flow were identified on the calorimetric curves obtained in presence of different concentrations of organic molecules in the pastes as define in Figure 3. The data present in the following study results from the average measurements of two replicates except in Figure 7 where a single measurement was performed. The error bars for the y values represent the standard

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deviation of the mean. The error bars of the x values indicate 0.2 % of uncertainty in the initial concentrations of the organic molecules.

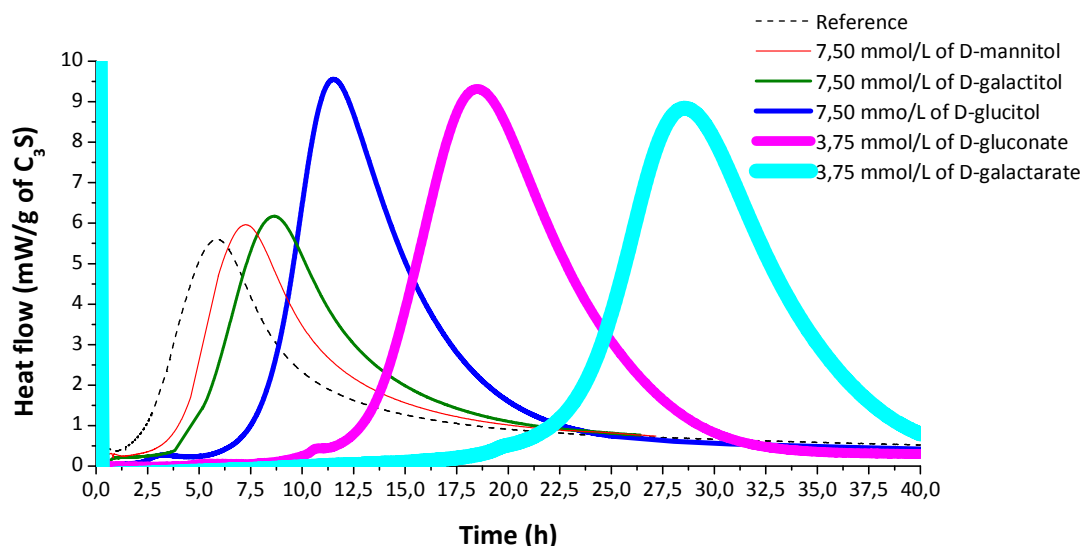


Figure 2: Calorimetric curves followed during the hydration of C_3S with and without the presence of different sugar alcohols and sugar acid anions, L/S=0.4.

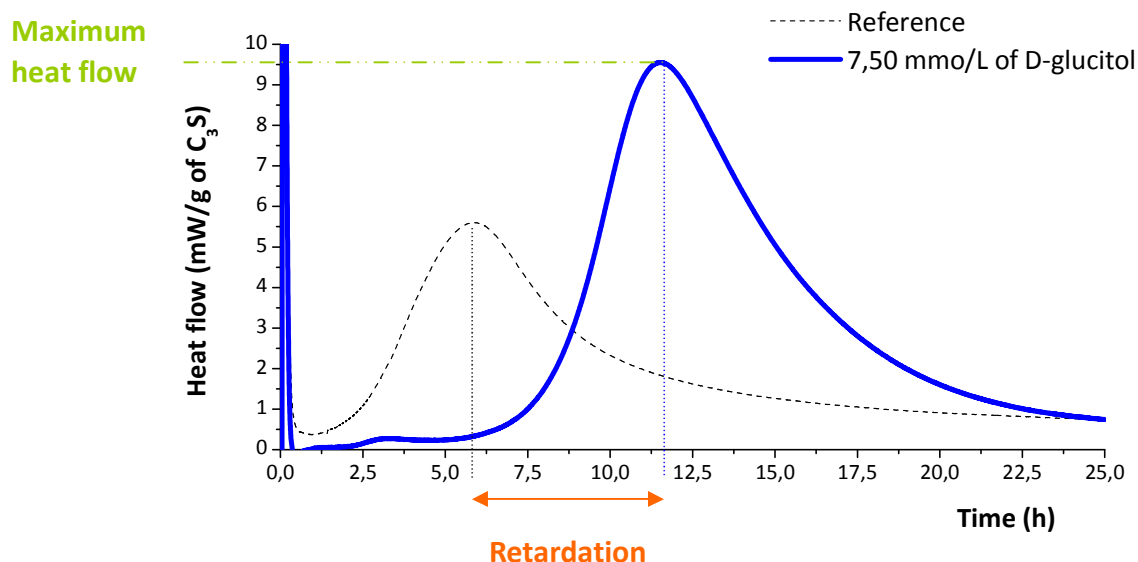


Figure 3: Definition of the retardation (difference in time between the maximum heat flow with and without molecules) and of the maximum heat flow.

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3. Results and discussion

3.1. Influence of the organic molecules on the retardation of C_3S hydration

3.1.1. Variations concerning the ending functional groups carried by the molecules

3.1.1.a. Presence or not of charged ending groups: alcohol versus hydroxy-carboxylate groups

The retarding effects led by sugar alcohols (D-glucitol and D-galactitol) and some of their corresponding sugar acid anions (D-gluconate and D-galactarate) on the hydration of C_3S are presented in Figure 4. D-galactitol has a lower retarding effect than its corresponding di-carboxylate, D-galactarate and D-glucitol generates a lower delay than its corresponding mono-carboxylate, D-gluconate. Moreover, D-galactarate carrying two charges leads to a higher retarding effect than D-gluconate only possessing one charge. These results indicate that the retardation of C_3S hydration is enhanced by the presence of charged groups.

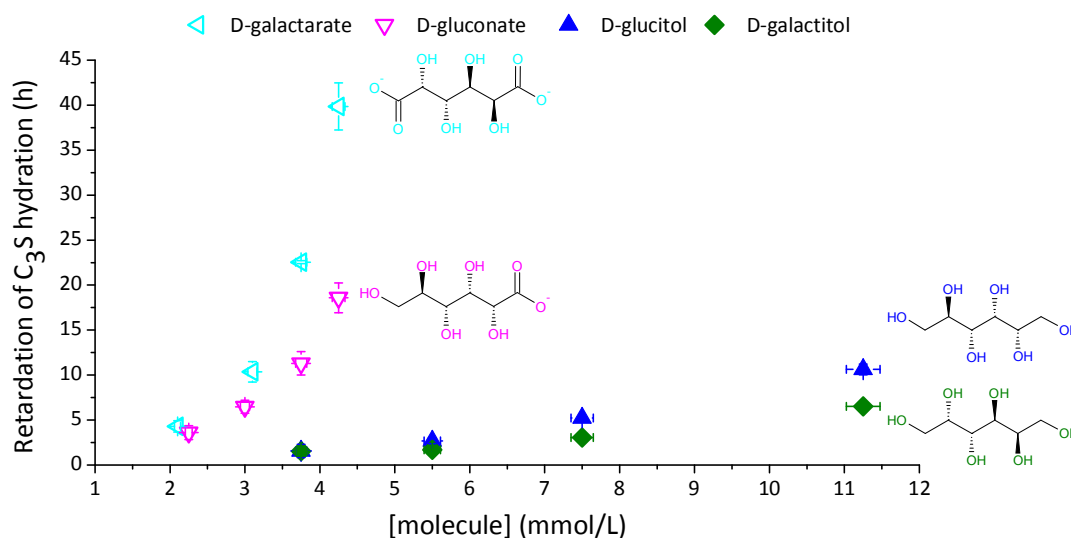


Figure 4: Retardation of C_3S hydration as a function of the concentration of sugar alcohols and of some of their corresponding sugar acid anions, $L/S=0.4$.

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3.1.1.b. Modification of the number of ending groups: 1 to 4 carboxylate groups

The retardation caused by hydroxy-carboxylate, carboxylate and amino carboxylate containing from 1 to 4 carboxylates groups were studied, Figure 5. EDTA which possesses 4 charges induces a higher retardation than adipate which has 2 charges. However, D-gluconate which only carries 1 charge delays more the hydration of C_3S than EDTA and adipate. It can be concluded that the retarding effect of these small molecules on C_3S hydration is not only controlled by their charge.

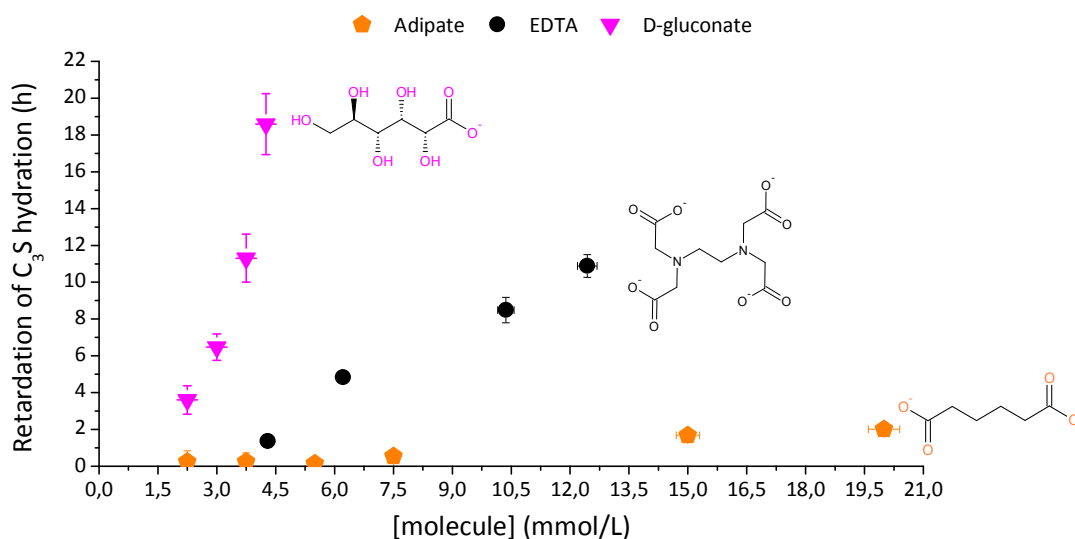


Figure 5: Retarding effect generated by molecules carrying different numbers of carboxylate groups depending on their concentration, L/S=0.4.

3.1.1.c. Change in the ending functional groups: carboxylate versus phosphonate groups

The importance of the anionic group on the delay generated by organic molecules on C_3S hydration was identified by comparing the effects of amines with functionalized mono, tri, tetra-carboxylates and phosphonates. The mono substituted molecules are primary amines (RNH_2 , R standing for an alkyl group) whereas the tri and tetra substituted molecules are tertiary amines (NR_3). The retarding effect induced by these molecules is represented in Figure 6 as the function of their equivalent concentration of anion.

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For a given equivalent concentration of anion, tri-phosphonate induces a higher retarding effect than tetra-phosphonate. For amino-carboxylates, the tri and tetra-substituted molecules cause similar delays on the hydration of C_3S . It can be observed that the mono-substituted phosphonate and carboxylate have a lower retarding effectiveness than the tetra and tri-substituted ones. Whatever the number of functional group, amino-phosphonates demonstrate an enhanced retarding effectiveness on the hydration of C_3S than amino-carboxylates for a given equivalent concentration of anion. Hence, the class of the amines and the anionic functional groups play a role on the retardation generated by the molecules on C_3S hydration.

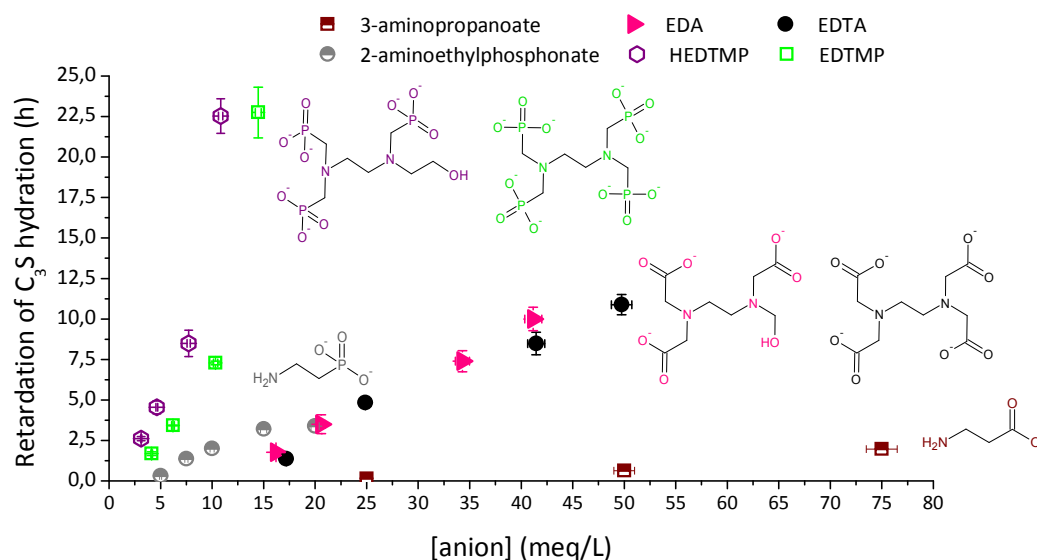


Figure 6: Retardation of C_3S hydration as a function of the equivalent concentration of mono, tri, tetra amino-carboxylates and phosphonates, L/S=0.4.

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3.1.2. Modification of the main chain properties of the molecules

3.1.2.a. Different lengths of the hydrocarbon chain: 2 to 3 methylene bridges

The retarding effects induced by amines with functionalized mono-carboxylate, sulfonate and phosphonate group are compared in Figure 7. For each amino functionalized molecule, there are different hydrocarbon chain lengths. First, it can be noted that the small variation in the hydrocarbon chain length does not strongly change the retarding effect generated by these small linear molecules in the range of equivalent concentration studied. Secondly, it reveals that for a given equivalent concentration of anion, amines bearing mono-carboxylate or sulfonate group induce similar delays on the hydration of C_3S .

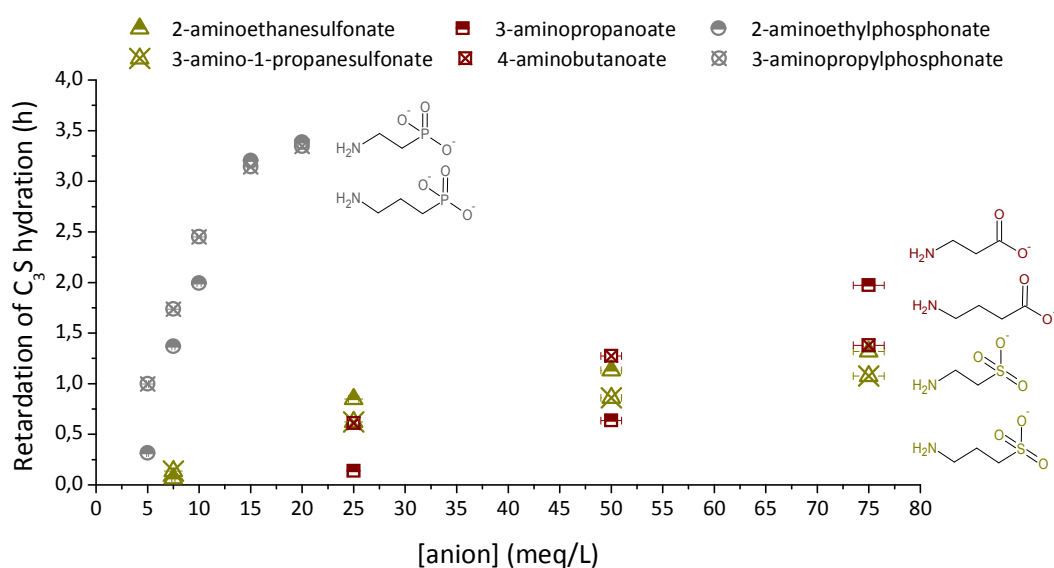


Figure 7: Retardation caused by amines functionalized with mono-sulfonate, carboxylate and phosphonate groups (different carbon chain lengths) on C_3S hydration depending on their equivalent concentration, $L/S=0.4$.

3.1.2.b. Change in the functional groups: hydrocarbon chain versus polyol chain

The delays induced by hydroxy-carboxylates (D-gluconate and D-galactarate) and by a carboxylate (adipate) on C_3S hydration are exposed in Figure 10 as a function of their equivalent concentration of anion.

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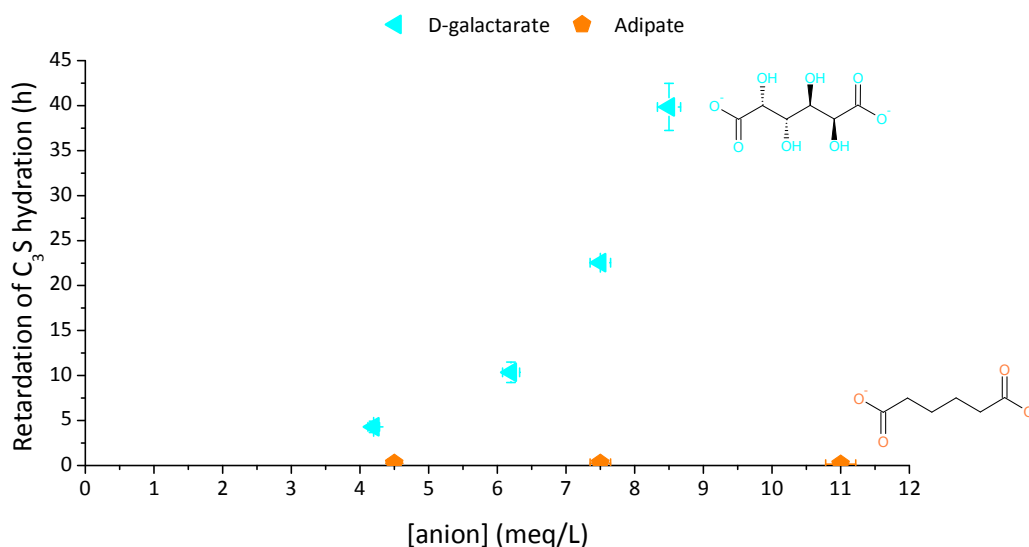


Figure 8: Retarding effects of hydroxy-carboxylates and of a carboxylate on C₃S hydration as a function of their equivalent concentration, L/S=0.4.

For a given equivalent concentration of anion, D-gluconate and D-galactarate which possess hydroxy-carboxylate groups have a higher retarding effectiveness than adipate which carries simple carboxylate groups. Hence, the presence of hydroxyl groups in the main chain of charged organic molecules play a role on their retarding effect.

3.1.2.c. Variation of the stereochemistry of hydroxyl groups: sugar alcohols and sugar acid anions

The retarding effects generated by sugar alcohols (D-glucitol, D-galactitol and D-mannitol) and the one led by sugar acid anions (D-gluconate and D-galactarate) on the hydration of C₃S are presented in Figure 9 and Figure 10 respectively. Even though hexitols have the same chemical formula C₆H₁₄O₆, these stereoisomers generate different retardations on the hydration of C₃S pastes as a function of their concentration, Figure 9. D-glucitol which is the most retarding hexitol is followed by D-galactitol and then by D-mannitol. A similar effect was also shown by Zhang who studied the setting times of C₃S and OPC pastes in presence of D-sorbitol (D-glucitol) and D-mannitol [16]. Moreover, for a given equivalent concentration of anion, D-gluconate which is the corresponding sugar acid

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anion of D-glucitol causes a higher delay on the hydration of C_3S than D-galactarate which is the corresponding sugar acid anion of D-galactitol, Figure 10.

The Fischer projections of these sugar derivatives in Figure 1 indicate that D-glucitol (**threo-threo**-erythro) and D-galactitol (**threo**-erythro-**threo**) both have two threo hydroxyl groups and that D-mannitol (erythro-**threo**-erythro) only carries one. Moreover, it was shown that the two first mentioned molecules retard more C_3S hydration than D-mannitol. Hence, the ability of hexitols to retard C_3S hydration increases with the number of threo hydroxyl groups. This result confirms what was already observed when studying different polyols [16]. D-glucitol and D-gluconate which carry adjacent hydroxyl pairs in threo configuration were revealed to generate higher retarding effects than D-galactitol and D-galactarate which have separated ones. Consequently, the retarding effectiveness of hexitols is enhanced when they have adjacent hydroxyl pairs in threo configuration: **threo-threo-erythro** > **threo**-erythro-**threo**.

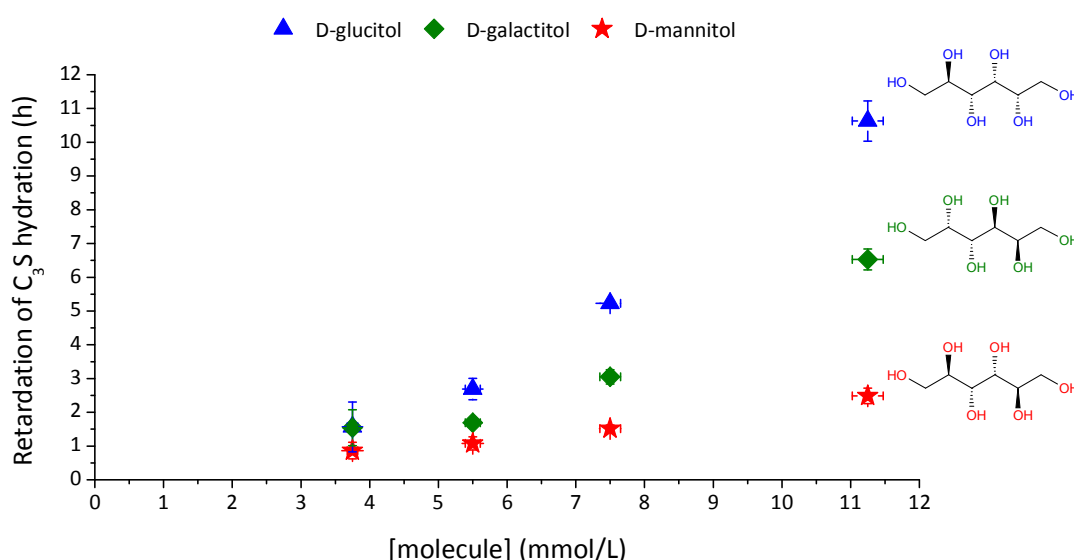


Figure 9: Retardation of C_3S hydration as a function of the concentration of hexitols, L/S=0.4.

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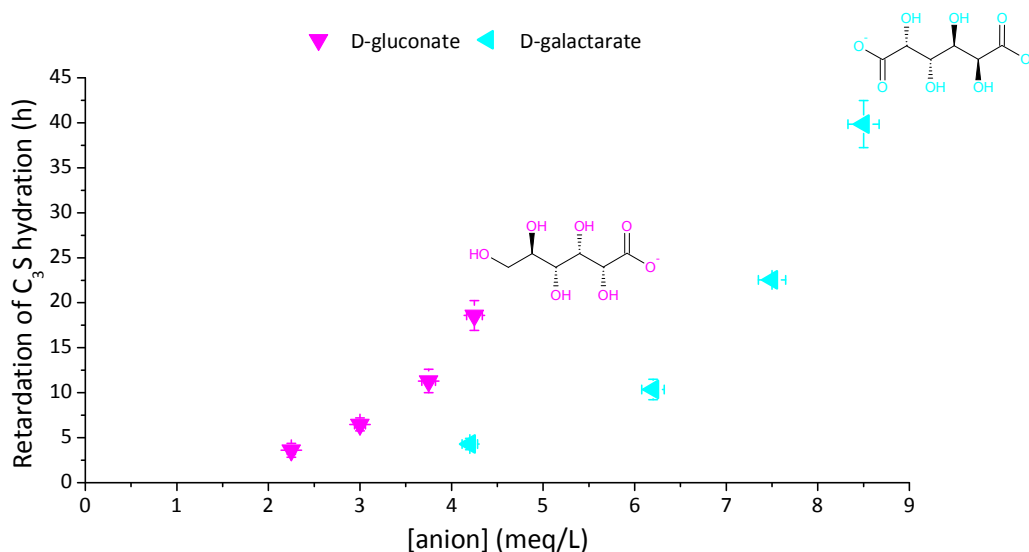


Figure 10: Retarding effects of sugar acid anions on the hydration of C₃S depending on their equivalent concentration, L/S=0.4.

3.2. Influence of the organic molecules on the maximum heat flow

The value of the maximum heat flow was identified on the calorimetric curve in presence of different concentrations of molecule. For the charged organic compounds, the evolution of the maximum heat flow is presented as a function of their equivalent concentration in Figure 11-a and for the uncharged ones depending on their concentration in Figure 11-b. The presence of the organic additives studied increases the maximum heat flow with their equivalent concentration of anion or their concentration of molecule compare to the one of the reference which equals to 5.5 ± 0.2 mW/g.

Figure 11-a indicates that amino-phosphonates (HEDTMP and EDTMP) lead to similar maximum heat flows for an equivalent concentration of anion. However, they generate higher maximum heat flows than amino-carboxylates (EDA and EDTA). At high and given equivalent concentration of anion, EDTA generates a higher maximum heat flow than EDA. Hydroxy-carboxylates (D-galactarate and D-gluconate) particularly enhance the maximum heat flow compare to amino-carboxylates and carboxylate (adipate) for a given equivalent concentration of anion. Moreover, molecules containing carboxylate groups generate maximum heat flows which seem to reach a short plateau before decreasing at different

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equivalent concentrations of anion. It means that different phenomena occur on the hydration of C_3S depending on the respective concentration of molecules bearing carboxylate groups.

As far as hexitols are concerned, Figure 11-b reveals that for a given concentration, D-glucitol leads to higher maximum heat flow than D-galactitol and D-mannitol. The latter seems to generate the lower maximum heat flow at the highest concentration studied (12 mmol/L). Consequently, the maximum heat flow is enhanced by the number hydroxyl groups in the threo configuration and more particularly with adjacent hydroxyl pairs in threo configuration: D-glucitol (**threo-threo**-erythro) > D-galactitol (**threo**-erythro-**threo**) > D-mannitol (erythro-**threo**-erythro).

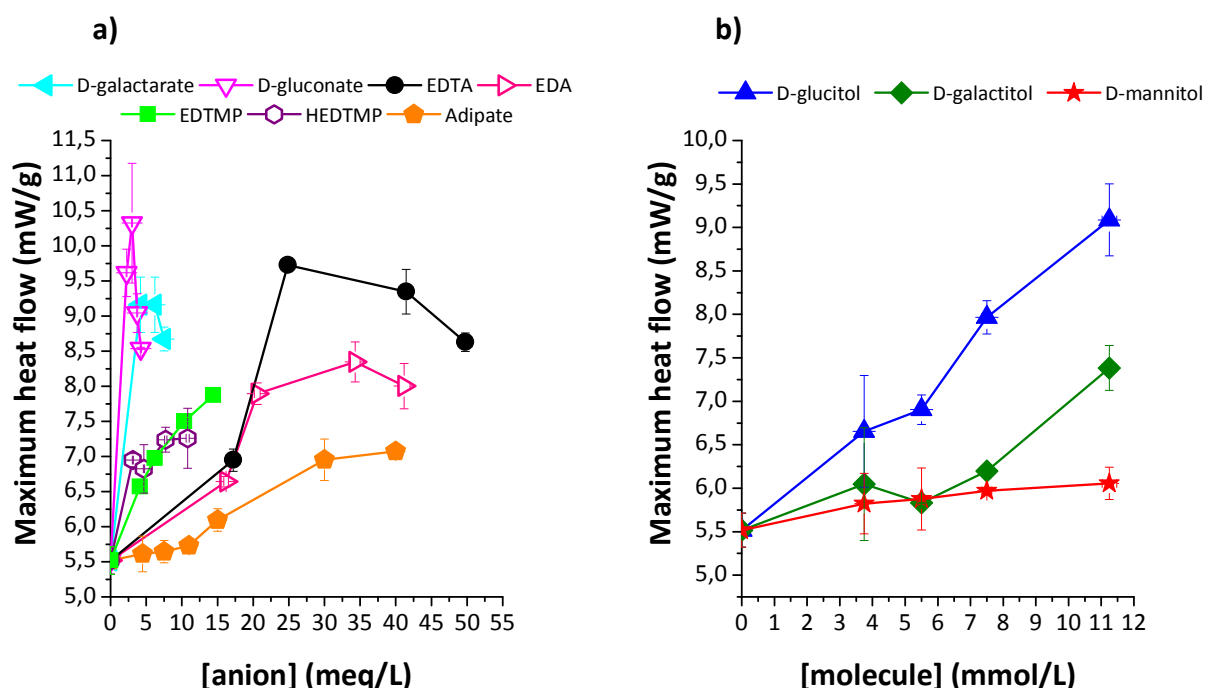


Figure 11: Evolution of the maximum heat flow as a function of a) the equivalent concentration of anions and b) the concentration of uncharged molecules.

From these results, one can observe that the maximum rate of C_3S hydration which is proportional to the maximum heat flow induced by the presence of organic molecules does not only depend on their charge and that there is a role played by the main chain and by the ending functional groups as well as by the stereochemistry of the hydroxyl groups.

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3.3. Relation between the maximum heat flow and the retardation induced by organic molecules on C_3S hydration

The maximum heat flow is related with the retardation caused by the different molecules on the hydration of C_3S in Figure 12. Figure 12-a) concerns the charged molecules and Figure 12-b) the uncharged ones.

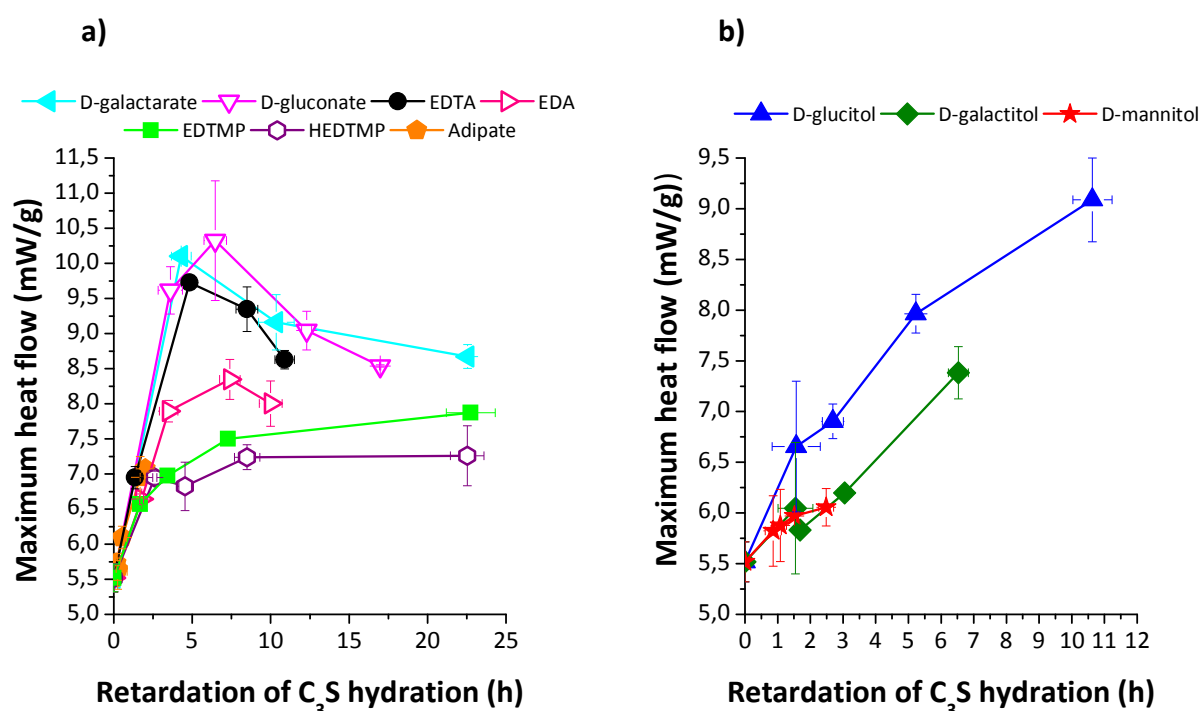


Figure 12: Evolution of the maximum heat flow with the retardation induced on the hydration of C_3S by a) charged molecules and b) uncharged ones.

In Figure 12-a, similar trends are observed for the evolution of the maximum heat flow with the retardation in presence of molecules containing carboxylate and phosphonate groups respectively. For the former, the maximum heat flow increases up to 4 h of retardation, seems to reach a short plateau and then starts to decrease. For molecules carrying phosphonate groups, the maximum heat flow increases up to 2 h of retardation and reaches a plateau in the range of retardation studied. For a given retardation, molecules bearing carboxylate groups generate higher maximum heat flows than the ones containing

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phosphonate groups. Among carboxylates, EDTA, D-galactarate and D-gluconate induce similar maximum heat flow whereas EDA causes a lower one. Amino-phosphonates generate comparable maximum heat flows for a given retardation.

For hexitols, D-glucitol generates the highest maximum heat flows, Figure 12-b. In the range of retardation studied, D-galactitol and D-mannitol induce similar effects on the maximum heat flow. Hence, D-glucitol which has adjacent hydroxyl pairs in threo configuration (**threo-threo**-erythro) has a strong impact on the maximum heat flow compare to D-galactitol (**threo**-erythro-**threo**) and D-mannitol (erythro-**threo**-erythro) which do not have.

Finally, for a given retardation, the maximum heat flow and so the maximum rate of C₃S hydration is affected by the adjacent hydroxyl pairs in threo configuration and by the nature of the ending functional groups. The presence of molecules carrying carboxylate groups particularly enhances the maximum rate of C₃S hydration compare to the ones with phosphonate groups. Moreover, it can be noted that for a given retardation, a reduction of the maximal rate of C₃S indicates a particularly long induction period. Hence, in presence of molecules containing phosphonate groups, the induction period is particularly lengthened and the hydration of C₃S starts decelerating whereas the mineral phase is less hydrated than in presence of molecules with carboxylate groups.

4. Conclusions

This study has compared the effects induced by different organic molecules on the hydration of C₃S in order to identify the main parameters playing a role on their retarding effect and on the maximum rate of C₃S hydration.

The retarding effectiveness of hexitols can be correlated with the number of hydroxyl pairs in threo configuration and is particularly enhanced with adjacent ones. The retardation of C₃S hydration generated by charged molecules is not only controlled by their charge but also depends on their ending group (sulfonate $\approx$ carboxylate < phosphonate and hydroxyl < hydroxy-carboxylate) and on their main chain group (hydrocarbon chain < polyol chain).

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The maximum rate of C_3S hydration is shown to be increased by the presence of retarding organic additives. It mainly differs depending on the stereochemistry of the hydroxyl groups and on the ending and chain functional groups carried by the molecules. Hence, organic compounds retard the hydration of C_3S but also increase the maximum rate of C_3S hydration in the range of concentrations studied. The acceleration of C_3S hydration is delayed due to a lengthening of the induction period but the presence of the organic molecules also enhances the quantity of hydrates from which C_3S hydration starts decelerating.

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III.1. Effets de la charge, de la fonctionnalité et de la stéréochimie de petites molécules organiques sur le retard et la vitesse maximale de l'hydratation du silicate tricalcique

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III.2. Complexation ionique et adsorption de petites molécules organiques sur le silicate de calcium hydraté : relation avec leur effet retard sur l'hydratation du silicate tricalcique

Ionic complexation and adsorption of small organic molecules on calcium silicate hydrate: relation with their retarding effect on the hydration of tricalcium silicate

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Abstract

The ion complexing power and the adsorption of set-retarders such as sugar derivatives (D-glucitol, D-gluconate...), amino-carboxylates and phosphonates (EDTA, EDTMP,...) on C-S-H were identified and compared. The complexation equilibria of the predominant calcium and/or hydroxide complex and its relative constant were determined after measuring the solubilizing effect of the molecules in suspensions buffered by portlandite. The adsorption of the molecules on C-S-H with an initial Ca/Si below and above 1 as well as their possible complexation with silicate ions in solution were also investigated.

All the organic molecules studied are shown to complex calcium and/or hydroxide ions but only amino-phosphonates, D-gluconate and D-glucitol complex silicate ions. They all adsorb on portlandite and C-S-H but to different extent. These organic compounds are also revealed to be sensitive to the presence of calcium counter-ions at the surface of C-S-H at Ca/Si upper than 1. Finally, the relation between their ionic complexing powers, adsorption properties and retarding effects on the hydration of C_3S are discussed.

Keywords: admixtures, adsorption, complexation, calcium silicate hydrate, retardation

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1. Introduction

The addition of organic admixtures to Ordinary Portland Cement (OPC) sometimes retards the hydration of its silicate phases that are mainly alite and belite as when using setting retarders or as a side effect when using some plasticizers and superplasticizers. The hydration of alite, an impure tricalcium silicate (C_3S) is a dissolution-precipitation process forming calcium silicate hydrate (C-S-H) and portlandite. C-S-H are characterized by a molar CaO/SiO_2 ratio noted Ca/Si which increases with the calcium hydroxide concentration [1]. Cellulose ethers which retard C_3S hydration were revealed to slow down the precipitation of C-S-H [2]. Moreover, a study only focused on the precipitation of calcium hydroxide correlates the fact that organic molecules having an important retarding effect on the hydration of the silicate phases of OPC particularly delay the formation of calcium hydroxide [3].

Retarding molecules were also found to solubilize solid calcium hydroxide suggesting a complexation of the molecules with calcium and/or hydroxide ions in solution [4]. The interaction of the organics with silicates in solution was also proposed to be at the origin of their retarding effect [5-7] but a strong retarder such as sucrose was not shown to complex silicates in alkaline solution [4]. Moreover, a possible adsorption of the retarders on calcium hydroxide and/or on C-S-H was often suggested but was rarely investigated [3,4,7-9]. In fact, above the threshold Ca/Si of C-S-H equals to one, its surface charge is apparently positive due to the overcompensation of the highly deprotonated silanol groups in the high pH solution by the adsorption calcium ions and may favour the adsorption of negatively charged molecules [10-12]. As a consequence, one can see that the possible complexation of retarders with calcium, silicate and/or hydroxide ions as well as their adsorption on C-S-H and on calcium hydroxide are not well identified and so can not be easily compared.

III.2. Complexation ionique et adsorption de petites molécules organiques sur le silicate de calcium hydraté : relation avec leur effet retard sur l'hydratation du silicate tricalcique

Hence, this paper proposes to study the ionic complexation and the adsorption on portlandite and C-S-H of different small organic molecules known to retard the hydration of C_3S [13]. The molecules differ depending on the stereochemistry of their hydroxyl groups, on the nature and number of their functional groups that are hydroxyl, hydroxy-carboxylate, carboxylate and phosphonate groups. To do so, their complexing power with calcium and/or hydroxide ions were identified by studying their solubilizing effect and their adsorption in suspensions buffered portlandite. Their adsorption properties on portlandite and/or on C-S-H with an initial Ca/Si equals to 0.80 (negatively charged surface) and to 1.58 (surface charge apparently positive) were determined and compared. The possible complexation of the molecules with silicate ions was also investigated. At the end of the study, a discussion concerning the interactions of the molecules and their impacts on the retarding effect induced on the hydration of C_3S is given.

2. Materials and methods

2.1. Materials

The water used for the preparation of the suspensions and solutions was both distilled and deionised. The molecules studied were D-glucitol ($\geq 98\%$), D-mannitol ($\geq 98\%$) from Sigma Aldrich, sodium gluconate ($\geq 98\%$) from Merck, all as a powder form, sodium salts of 2-aminoethyl 2-hydroxy ethylaminoacetate (EDA, 36.3 weight percent, wt%), ethylenediamine tetraacetate (EDTA, 32.9 wt%), 2-hydroxyethyl ethylenediamine tri(methylenephosphonate) (HEDTMP, 25.9 wt%) and ethylenediamine tetra(methylene phosphonate) (EDTMP, 26.1 wt%) from Bozzetto as aqueous solution form. The chemical structure of these organic molecules is shown in Table 1.

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Table 1: Chemical structure of the molecules studied.

D-mannitol	D-glucitol	D-gluconate
EDA	EDTA	
HEDTMP	EDTMP	

Portlandite came from Merck and has a specific surface area of $7 \text{ m}^2/\text{g}$ obtained by the BET method. Calcium oxide was obtained after decarbonation of calcium carbonate (98.5-100 %, VWR AnalR NORMAPUR) at 1000°C for 24 h.

Stock suspensions of C-S-H were synthesized by mixing calcium oxide freshly decarbonated, aerosil silica (Evonik) and water. The proportions of calcium oxide, aerosil silica were chosen (see Table 2) in order to obtain C-S-H in suspension with different initial Ca/Si equal to 0.80 and to 1.58 which will be called low Ca/Si and high Ca/Si respectively in the following study. The liquid to solid ratio (L/S) of the C-S-H was 20 (L=250 mL and S=12.5 g). These stock suspensions of C-S-H were stirred at 23°C for a month in order to reach equilibrium [1] without any organic molecule present.

Table 2: Quantity of lime and silica added in 250 mL of water in order to synthesized C-S-H in suspension with a L/S=20.

Sample	Ca/Si	CaO (g)	SiO ₂ (g)
C-S-H	0.80	5.37	7.13
	1.58	7.29	4.96

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2.2. Experimental

All the experiments described below were performed at 23 °C.

2.2.1. Methods of preparation

2.2.1.a. Addition of the molecules to the suspensions of portlandite and/or C-S-H

Organic molecules at equilibrium with portlandite in suspension:

150 mg of portlandite was added to 3 mL of aqueous solutions containing different concentrations of molecules in 10 mL Nalgene tubes. The amount of portlandite was purposely put in excess to buffer the solution.

Organic molecules at equilibrium with C-S-H and/or portlandite in suspension:

After the stock suspensions of C-S-H with initial high and low Ca/Si reached their equilibrium (a month), they were split into 10 mL Nalgene tubes. Some samples of the suspensions with C-S-H at high initial Ca/Si were buffered by adding 200, 300 or 400 mg of portlandite to 6 mL suspensions. The organic compounds were added to obtain the initial targeted concentration of molecule in the samples of C-S-H suspensions with and without portlandite.

After the addition of the molecules, the samples of C-S-H at initial low and high Ca/Si without portlandite in suspension were shaken during a day at 120 rpm. The ones containing portlandite and C-S-H at high Ca/Si in suspension buffered by portlandite were agitated at the same speed but during a week in presence of the molecules.

2.2.1.b. Preparation of the samples

The different samples of C-S-H and/or portlandite in suspension were centrifuged at 9000 rpm for 5 min. Finally, the supernatants were filtered with a 0.20 µm syringe filter (PTFE, VWR).

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2.2.2. Methods of characterization

2.2.2.a. Adsorption of the organic compounds on portlandite and/or C-S-H

The possible adsorption of the organic compounds on C-S-H and/or portlandite in suspension was identified by using the depletion method. The non adsorbed portion of molecules remaining in the solution at equilibrium with C-S-H and/or portlandite was measured by analyzing the Total Organic Carbon (TOC, Shimadzu TOC analyser V_{CPN}) of the filtrates. The latter were acidified with a small and known quantity of orthophosphoric acid (85 %, Analar Normapur, VWR) before their analysis with the TOC device.

Due to the non-Langmuir type of the adsorption isotherms found for the different molecules on portlandite and/or on C-S-H, the affinity of the organic compounds with the surface of these hydrates is defined as being the slope of the linear part at the beginning of the isotherm curve.

2.2.2.b. Ionic concentrations of the equilibrium solutions

The pH of the filtrates was immediately measured with a pH meter (Consort C931, Schott Instruments electrode) after filtration. The total concentrations of the ions (calcium and/or silicates) present in the filtrates were measured by using the Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES, Vista Pro, Varian). The filtrates were acidified with a small known amount of hydrochloric acid (37 %, Analar Normapur, VWR) before being analyzed by ICP-AES.

2.2.2.c. Size of the particles

In order to identify the presence and size of particles in the solutions at equilibrium with portlandite in presence of EDTMP, Dynamic Light Scattering was used (DLS, Zetasizer Nano, Malvern Instruments). Immediately after filtration of the suspensions, the equilibrium solutions were left 5 min in an ultrasonic device and analysed by DLS.

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2.3. Calculations of chemical speciation

Some simulations were carried out in order to identify the complexation equilibria between the molecules and calcium and/or hydroxide ions in the solution at equilibrium with portlandite as well as its formation constant. They were also used to reveal their possible complexation with silicate ions in the solution at equilibrium with C-S-H at high Ca/Si in suspensions buffered by portlandite.

These different simulations were carried out with the PHREEQC program performing aqueous geochemical calculations in order to identify the composition of solid-solution assemblages. They are based on the solubility equilibria, on the equilibrium between solution and surface species, mass and charge balance. PHREEQC uses the extended Debye-Hückel expression which accounts for the non-ideality of aqueous solutions in calculating the activity coefficient of the species in solution and considers the ions as punctual charges. The Pitzer expression which is an extension of the Debye-Hückel expression takes into account short distance interactions of the ions in the system. The calculations made to identify the ionic composition of the solution at equilibrium with C-S-H in suspensions buffered by portlandite with and without molecules used the model of Haas taking into account the variation of the solubility and stoichiometry of C-S-H phases [1].

3. Results

3.1. Interaction of the organic molecules with portlandite in suspension

3.1.1. Complexation of the organic compounds with calcium and/or hydroxide ions in solution

3.1.1.a. Effects of the molecules on the ionic composition of the solution at equilibrium with portlandite

The complexation of the organic compounds with calcium and/or hydroxide ions was studied by measuring the total concentration of calcium ions and of the pH in presence of the molecules in the solution at equilibrium with portlandite. The evolution of the total concentration of calcium ions and of the pH as a function of the concentration of the molecules present in portlandite in suspension at equilibrium is shown in Figure 1-a and b

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respectively. The data presents the average of two replicate measurements and the error bars reveals the standard deviation of the mean.

The total concentration of calcium ions increases as a function of the concentration of all the molecules at equilibrium with portlandite in suspension, Figure 1-a. The former takes into account the concentration of free calcium ions and of the ones which are complexed by the organic molecules in the equilibrium solution with portlandite, see Eq(1).

$$\text{Eq(1)} \quad [X_{\text{total}}] = [X_{\text{free}}] + [X_{\text{complexed}}] \text{ where } [X] \text{ is the concentration of the X species.}$$

In a similar fashion, the pH of the equilibrium solutions is noted to be enhanced by increased concentration of the organic molecules in solution except for hexitols where it decreases at the first point measured and then keeps pretty much stable as indicated in Figure 1-b. The change in the pH of the equilibrium solutions results from both the complexation of the molecules with calcium ions and possibly with hydroxide ions.

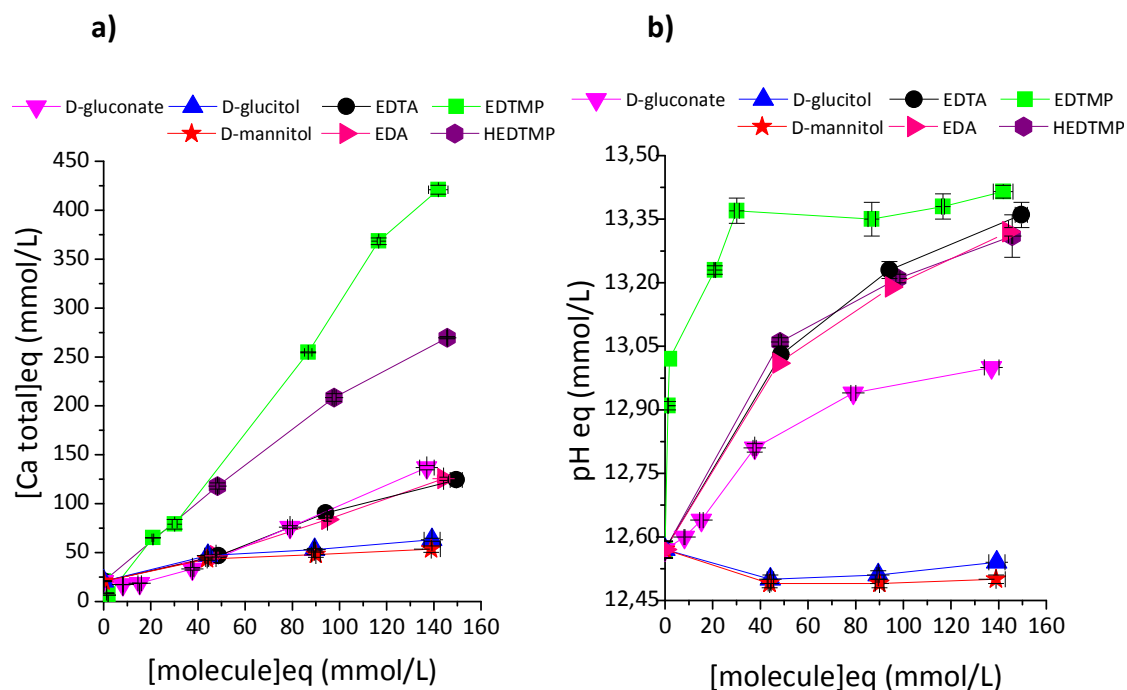


Figure 1 : Evolution of a) the total concentration of calcium ions and b) the pH as a function of the concentration of the different molecules at equilibrium with portlandite in suspension.

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3.1.1.b. Identification of the stoichiometry and of the stability constants of calcium and/or hydroxide complexes: comparison of the ionic complexing powers of the molecules.

The measurement of the pH, of the total concentration of calcium ions and of the concentration of the organic molecules present in the solution at equilibrium with portlandite allowed us to determine the complex formation equilibria between the molecules and calcium and/or hydroxide ions as well as their associated constant. The Debye-Hückel expression was used to calculate the activity coefficient of the species present in the solution at equilibrium with an excess of portlandite in suspension. Although there are several complex forms in equilibrium, only one preponderant species was considered. The stoichiometry of the calcium and/or hydroxide complex and its associated formation constant were adjusted until the experimental data and the calculated values showed a good agreement. The predominant complex of the molecules with calcium and/or hydroxide ions and their stability constant are listed in Table 3 except for hexitols because it has not been possible to find a dominating complex. It can be observed that amines with functionalized phosphonate groups and the sugar acid anion studied form hydroxy calcium complexes whereas the amines with functionalized carboxylate groups do not.

Table 2: Description of the dominating calcium and/or hydroxide complexes of the organic molecules and of their stability constant ((X) is the activity of the X species, M is the molecule).

Molecules	Complexes	Stability constants	Definitions	Log K
EDA	CaM^-	K_1	$(\text{CaM}^-)/((\text{Ca}^{2+})(\text{M}^{3-}))$	5.3
EDTA	CaM^{2-}	K_2	$(\text{CaM}^{2-})/((\text{Ca}^{2+})(\text{M}^{4-}))$	5.4
D-gluconate	$\text{Ca}_3\text{M}_2(\text{OH})_4$	K_3	$(\text{Ca}_3\text{M}_2(\text{OH})_4)/((\text{Ca}^{2+})^3(\text{M}^-)^2(\text{OH}^-)^4)$	14.8
HEDTMP	$\text{Ca}_2\text{M}(\text{OH})^{3-}$	K_4	$(\text{Ca}_2\text{M}(\text{OH})^{3-})/((\text{Ca}^{2+})^2(\text{M}^{6-})(\text{OH}^-))$	12.5
EDTMP	$\text{Ca}_3\text{M}(\text{OH})_2^{4-}$	K_5	$(\text{Ca}_3\text{M}(\text{OH})_2^{4-})/((\text{Ca}^{2+})^3(\text{M}^{8-})(\text{OH}^-)^2)$	19.5

Thanks to the identification of the complexation constants, the concentration of calcium and hydroxide ions which are complexed in solution were computed and are

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presented as a function of the concentration of the molecules present in the solution at equilibrium with portlandite in Figure 5-a and b respectively. Molecules bearing carboxylate groups such as amino-carboxylates (EDTA and EDA) and the sugar acid anion (D-gluconate) have comparable calcium complexing properties. Amines with functionalized phosphonates groups have the highest calcium complexing powers but EDTMP (tetra-phosphonate) is more complexing than HEDTMP (tri-phosphonate). EDTMP is also the strongest molecule complexing hydroxide ions in solution and is followed by D-gluconate and by HEDTMP.

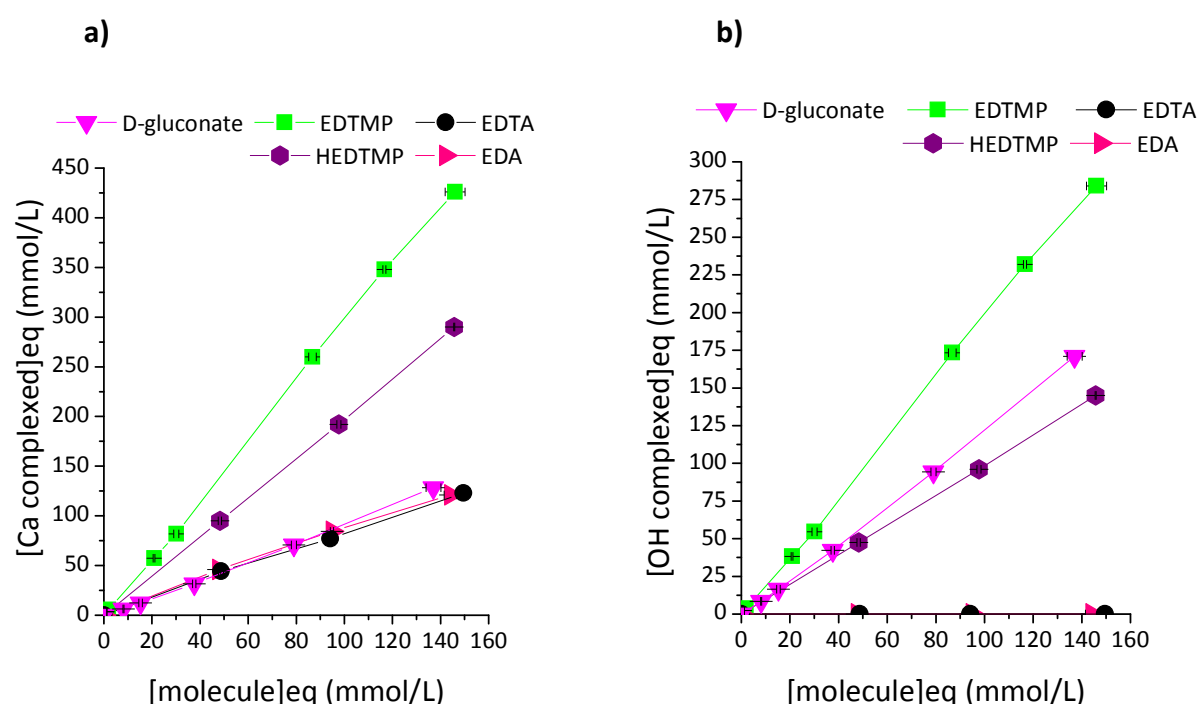


Figure 2: Concentration of the calculated a) complexed calcium ions and b) complexed hydroxide ions as a function of the concentration of the molecules at equilibrium in portlandite suspensions.

As far sugar alcohols are concerned, the Debye-Hückel equation which does not take into account interactions between different species when calculating the activities did not allowed us to find a dominating complex between hexitols and calcium and/or hydroxide ions. This way some simulations using the Pitzer expression considering short distance interactions between the ions and neutral molecules in the system were carried out (not shown). No good correlation between the experimental and simulated total calcium concentration and pH were obtained but it was shown that to get a decrease and then a plateau of the pH as observed in Figure 1-b in presence of polyols, hexitol-hexitol-hydroxide

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interactions were necessary present. Moreover, the increase of the total calcium concentration in solution in presence of polyols (Figure 1-a) can not be described without a complexation of the molecules with calcium ions.

3.1.1.c. Relation between the ionic complexing power of anions and their charge

The graphs representing the amount of calcium and hydroxide ions complexed by charged molecules as a function of their equivalent concentration are presented in Figure 3-a and Figure 3-b respectively. This equivalent concentration of anion equals to the molar concentration of the molecules normalized to their charge.

No master curve can be identified when studying the complexation of calcium ions on one hand (Figure 3-a) and of hydroxide ions on the other hand (Figure 3-b) depending on the equivalent concentration of anion. For a given equivalent concentration of anion, D-gluconate has a higher complexing power with both calcium and hydroxide ions than amino-carboxylates and phosphonates. Consequently, the complexation of the molecules with calcium and hydroxide ions does not only depend on the charge carried by the anions. These molecules are then supposed to have specific interactions with calcium and hydroxide ions.

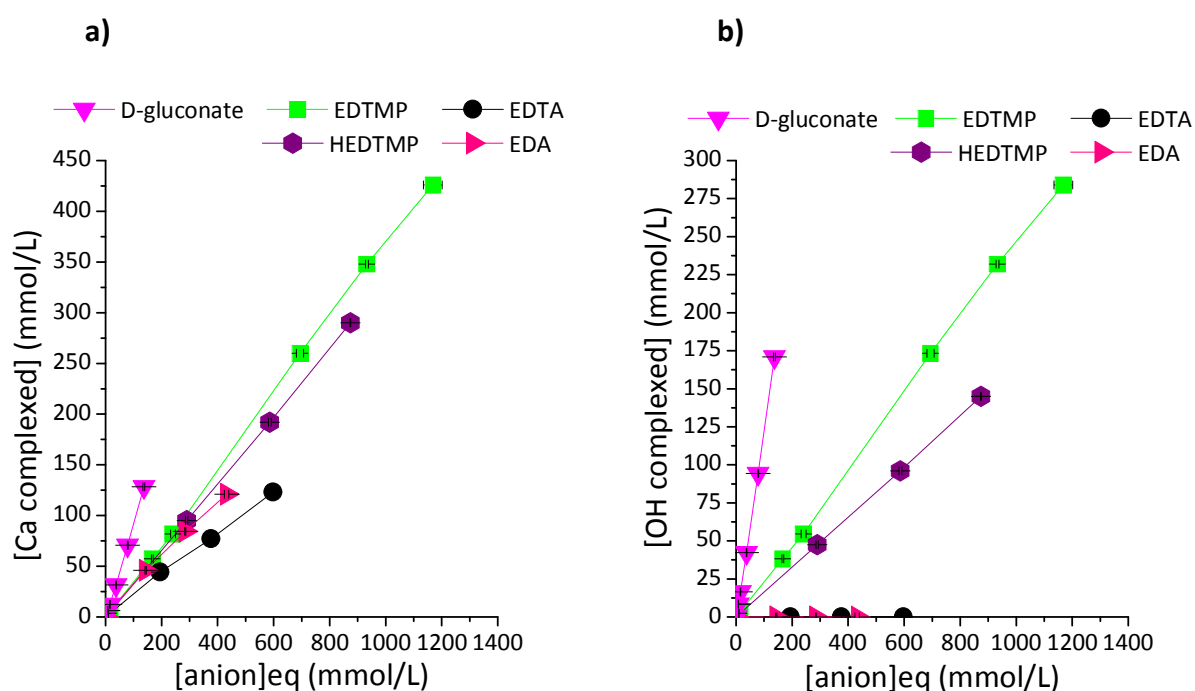


Figure 3: Evolution of the amount of a) complexed calcium ions and b) complexed hydroxide ions depending on the equivalent concentration of anion in the solution at equilibrium with portlandite.

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3.1.2. Adsorption of the organic molecules on portlandite in suspension

The adsorption of the molecules on portlandite is described as the ratio of the amount of molecules adsorbed to the left amount of solid portlandite. The latter was calculated by taking into account the amount of solid portlandite dissolved by the complexation of the molecules with calcium and/or hydroxide ions in solution. The adsorption isotherms of the different molecules on portlandite in suspension are shown in Figure 4. The data shown on this figure are the average of two replicate measurements whereas the error bars represent the standard deviation of the mean. It can be seen that the stereoisomers that are D-glucitol and D-mannitol have a comparable adsorption on portlandite. For EDA and EDTA, similar adsorptions on portlandite are found but their affinity with this phase is lower than the one of the studied hexitols. As far as D-gluconate is concerned, it has a higher affinity with portlandite and a higher value at the plateau of adsorption compare to the ones of its corresponding sugar alcohol, D-glucitol. Consequently, the presence of the ending hydroxy-carboxylate group of D-gluconate particularly enhances the adsorbing property of this sugar acid anion on portlandite. Concerning EDTMP and HEDTMP, the latter has a really low adsorption on portlandite and is at least the lowest adsorbing molecules studied whereas the former has the strongest affinity with this compound. However, from 30 to 87 mmol/L of EDTMP at equilibrium, the amount of molecules adsorbed passes from 80 to 30 mmol of molecule/mmol of portlandite and keeps constant up to 146 mmol/L of tetra-phosphonate at equilibrium. Finally, EDTMP strongly adsorbs on portlandite up to a threshold equilibrium concentration equals to 30 mmol/L and then there is a reduction of its adsorbed amount up to 87 mmol/L from which a plateau of adsorption occurs.

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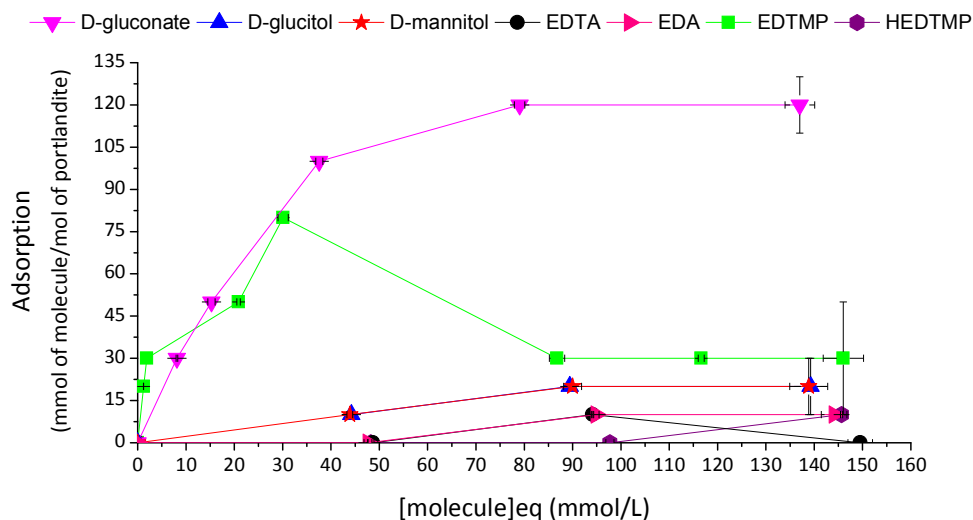


Figure 4: Adsorption isotherms of the organic molecules on portlandite in suspension.

3.2. Interaction between the molecules and C-S-H with high Ca/Si in suspensions buffered by portlandite

3.2.1. Complexation of the organic molecules with silicate ions in the equilibrium solution

3.2.1.a. Charged molecules

The total concentrations of calcium and silicate ions as well as the pH of the solution at equilibrium with C-S-H at high Ca/Si and portlandite were measured in presence of different concentrations of amino-carboxylates, phosphonates and of a sugar acid anion after a week. Then, the composition of the solution at equilibrium with C-S-H at high Ca/Si in suspension buffered by portlandite was simulated by only using the equilibria and the complex formation constant between organic molecules and the calcium and/or hydroxide ions in solution described in Table 2. The total concentrations of silicate and calcium ions and the pH which were experimentally measured and the ones obtained after simulation of the composition of the solution are respectively compared in Figure 5, Figure 6-a and b.

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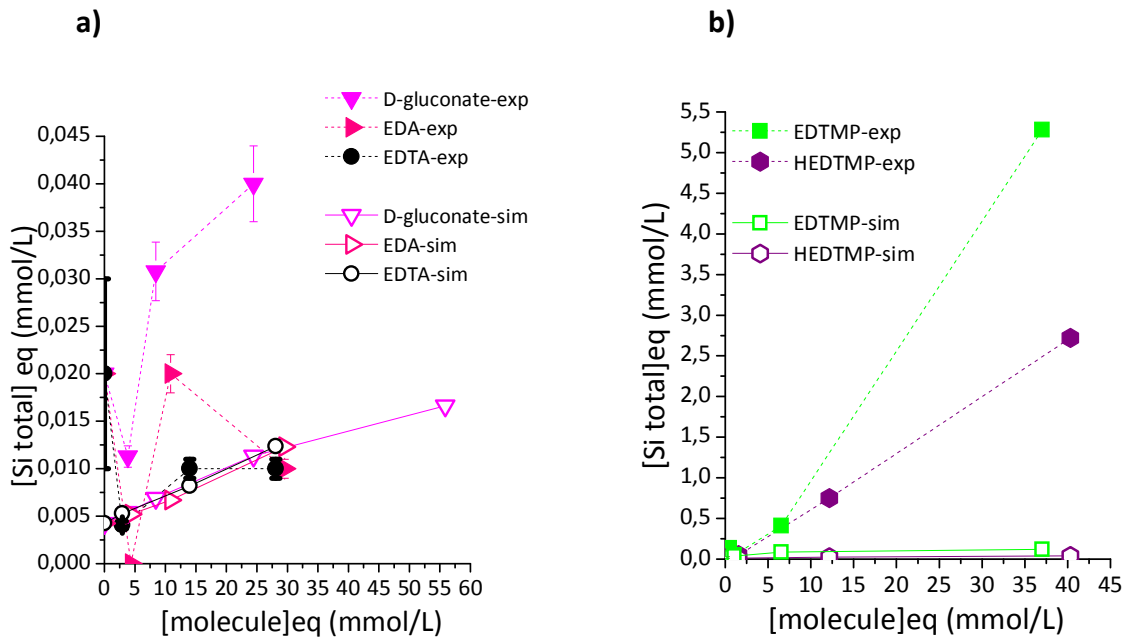


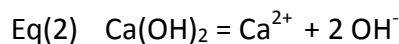
Figure 5 : Comparison between the experimental and simulated total concentrations of silicates in the solution at equilibrium with C-S-H at high Ca/Si in suspensions buffered by portlandite when only taking into account a calcium and/or hydroxide complexation of a) a sugar acid anion and amino-carboxylates and b) amino-phosphonates (200 mg of portlandite in 6 mL of C-S-H suspension).

The simulated total concentrations of silicate ions are similar to the experimental one for EDTA and EDA but is slightly lower for D-gluconate, Figure 5-a. For EDTMP and HEDTMP, the measured total concentrations of silicate ions are much more important than the calculated ones, Figure 5-b. The high total concentrations of silicate ions which were measured compare to the simulated ones may be explained by a complexation of the molecules with silicates in solution and/or by the presence of nano-clusters or dispersed particles of C-S-H in the filtered solution as observed by Sowoidnich when hydrating C_3S in presence of polymeric admixtures [14]. Nevertheless, in our case, the molecules were added to already made and equilibrated suspensions of C-S-H and not during the formation of C-S-H. According to Turesson [15], the energy needed to separate C-S-H particles after the addition of anionic copolyers in suspensions is really high. In no case, such an energy was provided to our system. On top of that, there is a good reproducibility of the total silicate concentrations of the samples of C-S-H with different amount of portlandite in the suspensions in presence of the molecules (not shown) which would probably not be the case in presence of nano-clusters or dispersed particles of C-S-H. Finally, the important total

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silicates concentrations measured in presence of some molecules might come from their complexation with silicate ions in solution as already revealed for some sugar derivatives [16-18].

The experimental total concentrations of calcium ions are higher than the simulated ones for D-gluconate, EDTMP and HEDTMP but are comparable for amino-carboxylates, Figure 6-a. Moreover, the simulated and experimental pH's are similar in presence of the different molecules except in presence of amino-phosphonates and D-gluconate where the measured pH is slightly lower than the calculated one. The complexation of the molecules with silicates in solution dissolves C-S-H and increases the activity of calcium or hydroxide ions. Given that the total concentration of calcium ions which was measured is higher in presence of the molecules complexing silicates than the simulated one, it suggests that the formation of these complexes enhances the concentration of free calcium ions and so their activity (Eq(1)). Hence, to keep the solubility product of portlandite constant when the activity of calcium ions increases, the one of hydroxide ions should decrease (Eq(2)). In fact, the pH of the suspensions which was experimentally measured is lower than the simulated one where the silicate complexes in solution were not taken into account. This result reinforces the fact that the important total silicates concentrations are connected to a complexation of the molecules with these ions.



$$K_{\text{sp portlandite}} = (\text{Ca}^{2+}) (\text{OH}^-)^2 \text{ with } (X) = [X] \cdot \gamma_X$$

Where $K_{\text{sp portlandite}}$ is the solubility product of portlandite, (X) the activity, $[X]$ the concentration and γ_X the activity coefficient of the X species in solution.

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The difference between the experimentally measured and simulated total concentrations of silicates, calcium and pH changes depending on the molecules as follow: EDTMP > HEDTMP > D-gluconate. Hence, it can be assumed that EDTMP is the strongest silicates complexing molecule followed by HEDTMP and then D-gluconate. Unfortunately, it was difficult to simulate the total concentration of silicates by using only one complex between the molecules and silicate ions in solution either because the stoichiometry of the complex was not well identified or because not only one dominating complex exists but different ones are present.

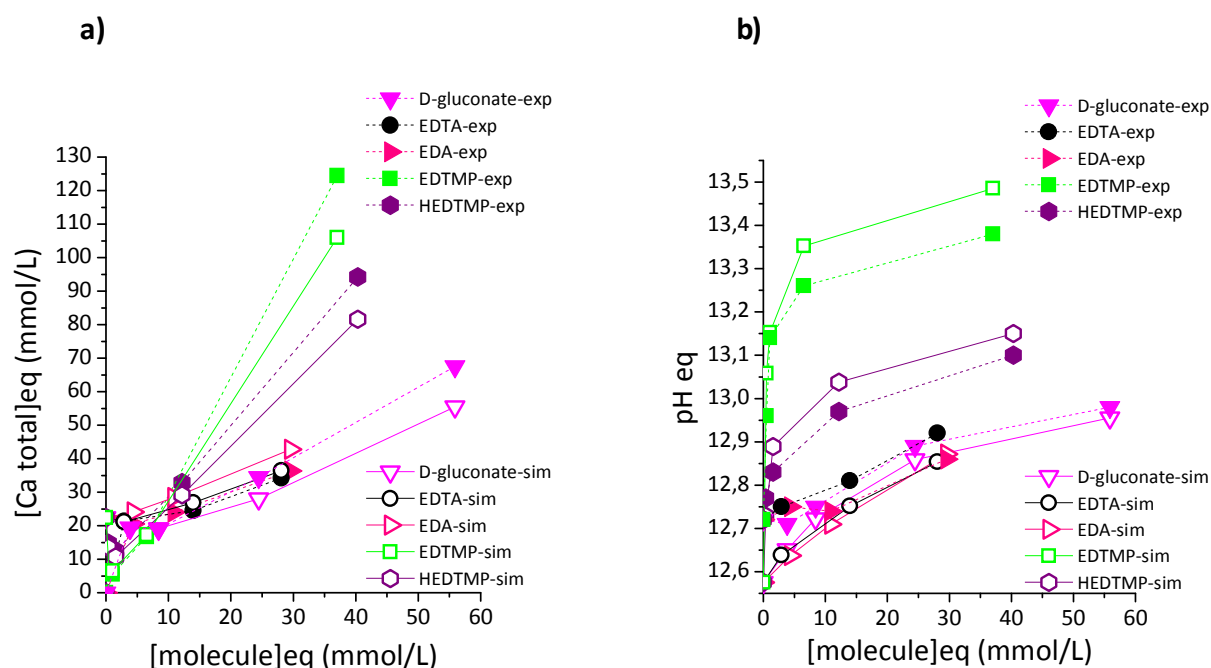


Figure 6 : Comparison between the experimental and simulated a) total calcium concentrations and b) pH of the solution at equilibrium with C-S-H at high Ca/Si in suspensions buffered by portlandite when only taking into account a calcium and/or hydroxide complexation with amino-carboxylates, phosphonates and a sugar acid anion (200 mg of portlandite in 6 mL of C-S-H suspension).

3.2.1.b. Uncharged molecules

For hexitols that are D-glucitol and D-mannitol, the total concentrations of calcium and silicate ions which were measured in the solution at equilibrium with C-S-H at high Ca/Si in suspensions buffered by portlandite are presented in Figure 7-a whereas the pH of the solution is in Figure 7-b. It can be observed that the total calcium concentration increases as a function of the concentration of hexitols at equilibrium and particularly in presence of D-

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glucitol. On top of that, with this molecule the total concentration of silicates is also enhanced whereas the one in presence of D-mannitol keeps constant in the range of concentrations studied.

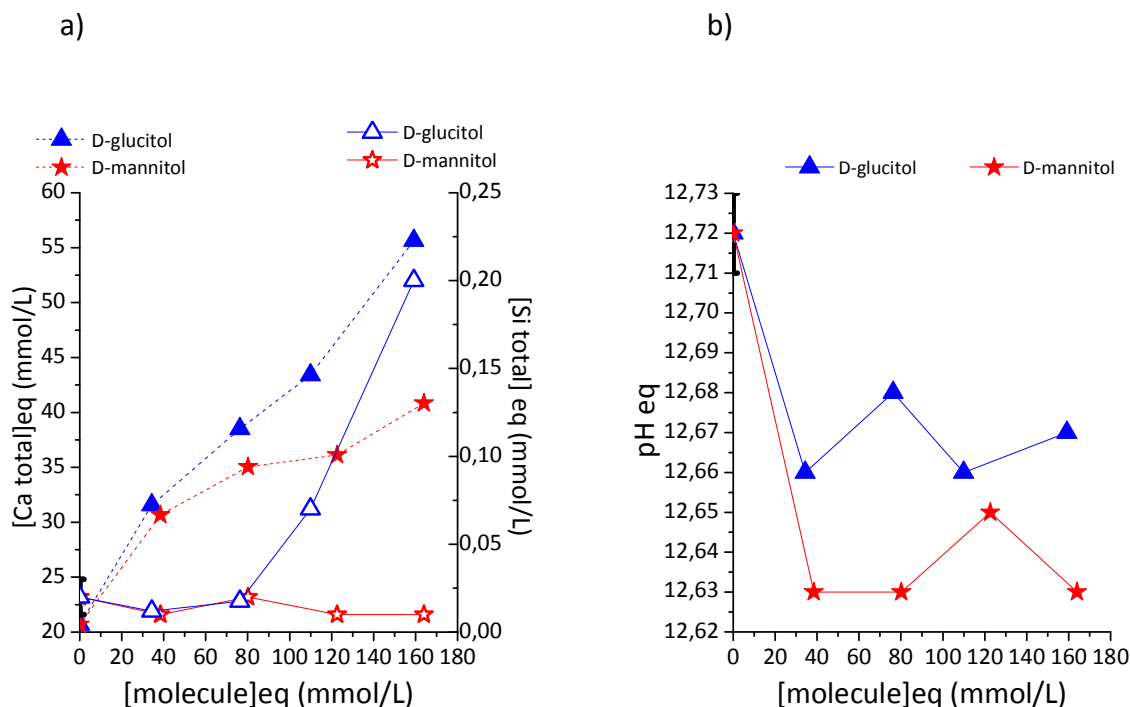
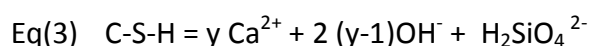


Figure 7: Evolution of a) the total concentration of calcium and silicate ions, b) the pH of the solution at equilibrium with C-S-H at high Ca/Si in suspensions buffered by portlandite in presence of hexitols (200 mg of portlandite in 6 mL of C-S-H suspension).

Given that the interactions of these sugar alcohols with calcium and/or hydroxide ions are not completely known, the simulation of the composition of the solution at equilibrium with C-S-H at high Ca/Si in suspensions buffered by portlandite was not possible. However, one can see on Figure 7-b that from around 36 to 162 mmol/L of hexitols at equilibrium, the pH and so the activity of hydroxide keeps pretty much constant. From the solubility product of portlandite Eq(2), it can be deduced that the activity of calcium ions is also constant. Hence, the increase of the total calcium concentration observed in Figure 7-a, which passes from 31 mmol/L to 55 mmol/L for D-glucitol and to 41 mmol/L for D-mannitol in this range of concentrations of molecule confirms the presence of complexes between calcium ions and hexitols. It also suggests that D-glucitol has a stronger complexing power with this ion than D-mannitol.

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$$K_{\text{sp C-S-H}} = (\text{Ca}^{2+})^\gamma (\text{OH}^-)^{2(\gamma-1)} (\text{H}_2\text{SiO}_4^{2-}) \text{ with } (X) = [X] \cdot \gamma_X$$

Where $K_{\text{sp C-S-H}}$ is the solubility product of C-S-H at equilibrium, (X) is the activity, $[X]$ the concentration and γ_X the activity coefficient of the X species in solution. γ is the Ca/Si of C-S-H.

From the solubility product of C-S-H (Eq(3)), given that the activity of calcium and hydroxide ions keeps constant from around 36 to 162 mmol/L of hexitol, the activity of silicates must be constant as well. Nevertheless, the total concentration of silicates increases in presence of D-glucitol at equilibrium with C-S-H and reveals a complexation of this polyol with silicate ions in solution.

3.2.2. Adsorption of the organic molecules on C-S-H with a high Ca/Si in suspension buffered by portlandite

The adsorption of organic molecules on C-S-H at a high Ca/Si in suspension buffered by portlandite is described as the ratio of the amount of molecules adsorbed to the amount of silicon composing C-S-H particles in suspension. The amount of silicon gives a measure of the amount of solid C-S-H in the suspension. From the initial amount of silica and water which are known and from the measurement of the total concentration of silicates in the solution at equilibrium with C-S-H, the amount of silicon composing C-S-H at high Ca/Si in presence of the organic molecules is determined by using the Eq(4).

$$\text{Eq(4)} \quad n_{\text{Si C-S-H eq}} = n_{\text{Si total initial}} - n_{\text{Si total eq}} \text{ where } n_X \text{ is the number of mole of } X.$$

The complexation of the molecules with calcium, silicates and/or hydroxide in solution dissolves C-S-H and so reduces the amount of the particles. Nevertheless, the high Ca/Si of the C-S-H present in the suspension was maintained by the presence of a buffer of portlandite.

The amount of portlandite in the solid buffer was varied from 200 to 400 mg in 6 mL of C-S-H suspension. It was found that the adsorption isotherms of the molecules on C-S-H in presence of the varied amounts of portlandite were not significantly different (not shown).

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This result may be explained by the low specific surface area of portlandite ($7 \text{ m}^2/\text{g}$) compare to the one of C-S-H ($200 \text{ m}^2/\text{g}$) and/or by a specific adsorption on C-S-H.

Finally, the adsorption isotherms of the organic molecules on C-S-H at high Ca/Si in suspension are only shown with a buffer of 200 mg of portlandite present in 6 mL of C-S-H suspension, Figure 8. Figure 8-a compares the adsorbing properties of sugar derivatives and Figure 8-b the ones of the charged molecules studied.

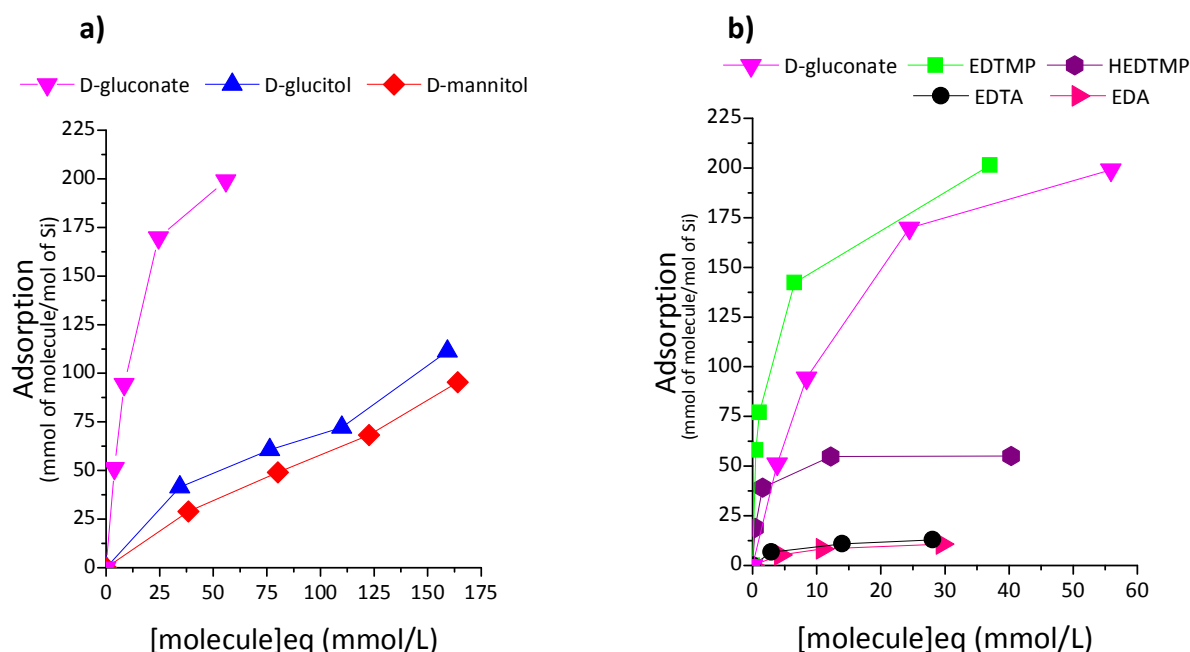


Figure 8: Adsorption isotherms of a) sugar derivatives b) charged molecules on C-S-H with a high Ca/Si in suspensions buffered with portlandite (200 mg of portlandite in 6 mL of C-S-H suspension).

D-glucitol has a slightly higher affinity with C-S-H than D-mannitol. D-gluconate has an enhanced affinity with C-S-H compare to its corresponding sugar alcohol that is D-glucitol. Hence, the ending hydroxy-carboxylate function facilitates the interaction of D-gluconate with C-S-H. Concerning amines with functionalized carboxylate groups, EDTA and EDA have similar behaviours: they have the lowest affinity with C-S-H and the lowest amount at the plateau of adsorption among all the charged molecules studied. Amino-phosphonates have different adsorption properties on C-S-H: EDTMP has a higher affinity with C-S-H and a higher amount at the plateau of adsorption which is 3 times more important than the one of HEDTMP. On top of that, these molecules have a stronger affinity with C-S-H than D-

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gluconate but the latter has an enhanced amount at the plateau of adsorption compare to HEDTMP.

3.3. Interaction between the molecules and C-S-H with low and high initial Ca/Si without any buffer of portlandite

3.3.1. Impact of the ionic complexation on the quantity and structure of C-S-H

Figure 9 shows the evolution of the total concentration of silicate ions present at equilibrium with C-S-H at high initial Ca/Si (Figure 9-a) and at low initial Ca/Si (Figure 9-b).

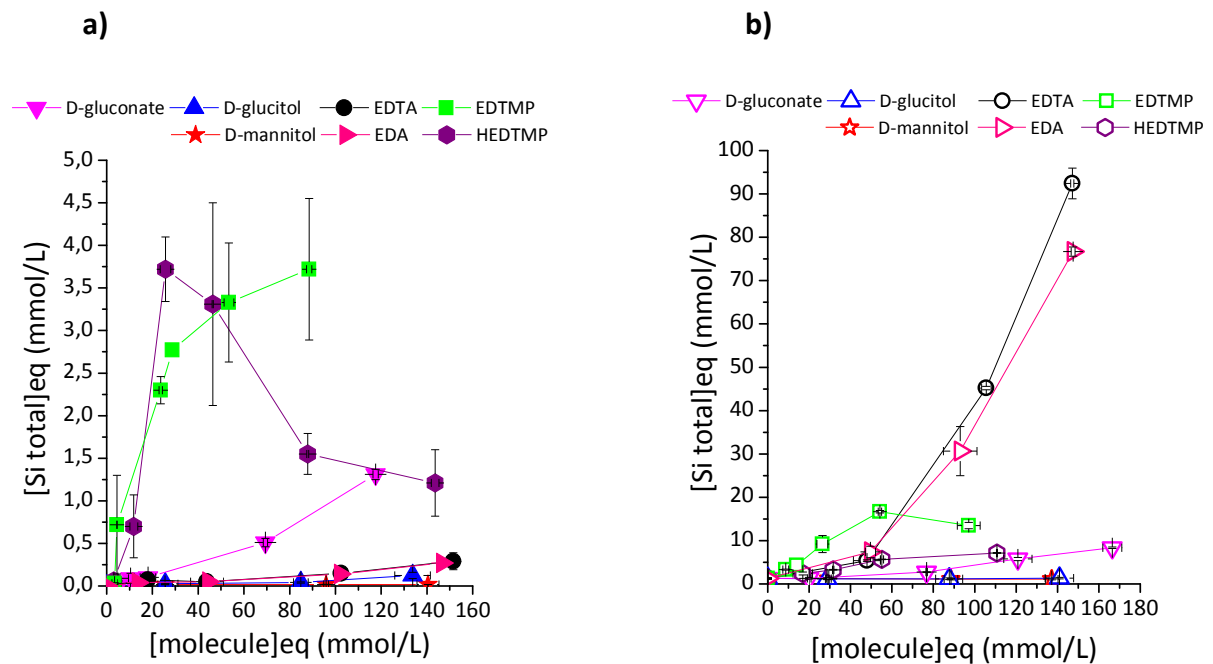


Figure 9: Evolution of the total concentrations of silicate ions in the solution at equilibrium with a) C-S-H at initial Ca/Si=1.58 and b) C-S-H at initial Ca/Si=0.80 depending on the concentration of the different organic compounds.

It can be observed that the total concentrations of silicates present in the solution at equilibrium with both C-S-H's are increased by the presence of the molecules, Figure 9. They also enhance the total calcium concentrations of the equilibrium solutions (not shown). Due to the complexation of the molecules with silicates, calcium and/or hydroxide in solution, the amount of calcium and silicon composing C-S-H is lowered down. Hence, the quantity of C-

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S-H present in the suspensions is reduced and their structure is modified. The Ca/Si of C-S-H in suspension was then recalculated thanks to the Eq(5). The evolution of the Ca/Si of C-S-H depending on the concentration of the molecules at equilibrium is shown in Figure 10-a for C-S-H at high initial Ca/Si and in Figure 10-b for C-S-H at low initial Ca/Si.

$$\text{Eq(5)} \quad \text{Ca/Si} = ([\text{Ca total}]_{\text{initial}} - [\text{Ca total}]_{\text{eq}}) / ([\text{Si total}]_{\text{initial}} - [\text{Si total}]_{\text{eq}})$$

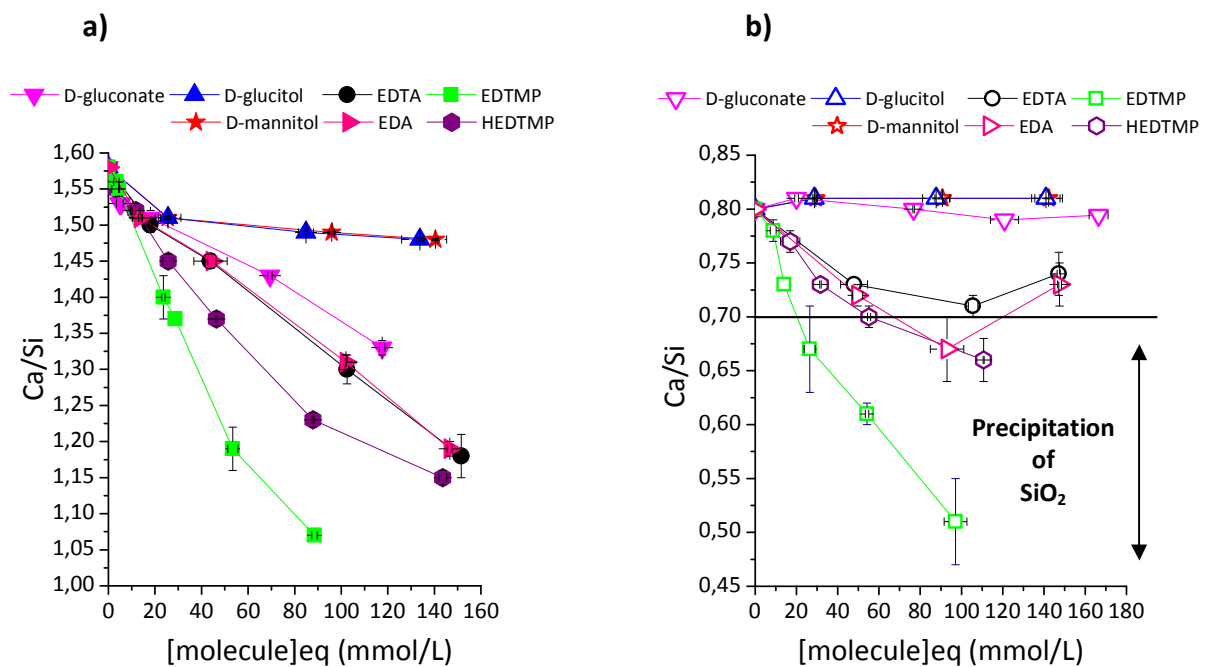


Figure 10: Evolution of the Ca/Si of C-S-H as a function of the concentration of the molecules at equilibrium with a) C-S-H at initial high Ca/Si=1.58 and b) C-S-H at initial low Ca/Si=0.80.

One can observe that the initial Ca/Si of the C-S-H particles is lowered down with increasing concentrations of the organic compounds at equilibrium and particularly in presence of EDTMP, Figure 10. In fact, this molecule was shown to particularly complex with calcium, hydroxide and silicate ions in solution. Concerning C-S-H at high initial Ca/Si=1.58, the presence of the molecules reduces the Ca/Si of C-S-H up to 1.07 in presence of 89 mmol/L of EDTMP. For C-S-H at low initial Ca/Si=0.80, the presence of the organics decreases the Ca/Si of C-S-H which reaches values below 0.70 above threshold concentrations of amino-carboxylates and phosphonates. This result indicates that no more C-S-H exists in the suspensions above these concentrations of molecules but that silica is precipitating [19].

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Finally, the presence of the organic molecules in the suspensions of C-S-H with a high initial Ca/Si generates C-S-H with a surface charge which becomes less and less positive and which is more and more negative when starting with C-S-H at low Ca/Si [12].

3.3.2. Adsorption of the organic molecules on C-S-H with low and high initial Ca/Si

Figure 11 and Figure 12 show the average measurements of two replicates of the adsorption measurements on C-S-H of sugar derivatives and substituted amines respectively. The error bars represent the standard deviation of the mean. The adsorption isotherms of the molecules on C-S-H with high initial Ca/Si are presented in Figure 11-a and Figure 12-a, and on C-S-H with initial low Ca/Si in Figure 11-b and Figure 12-b. The decrease of the amount of silicon composing C-S-H due to the ionic complexation of the molecules in solution (Figure 9) was taken into account when evaluating the adsorption of the molecules on C-S-H and was calculated using Eq(4).

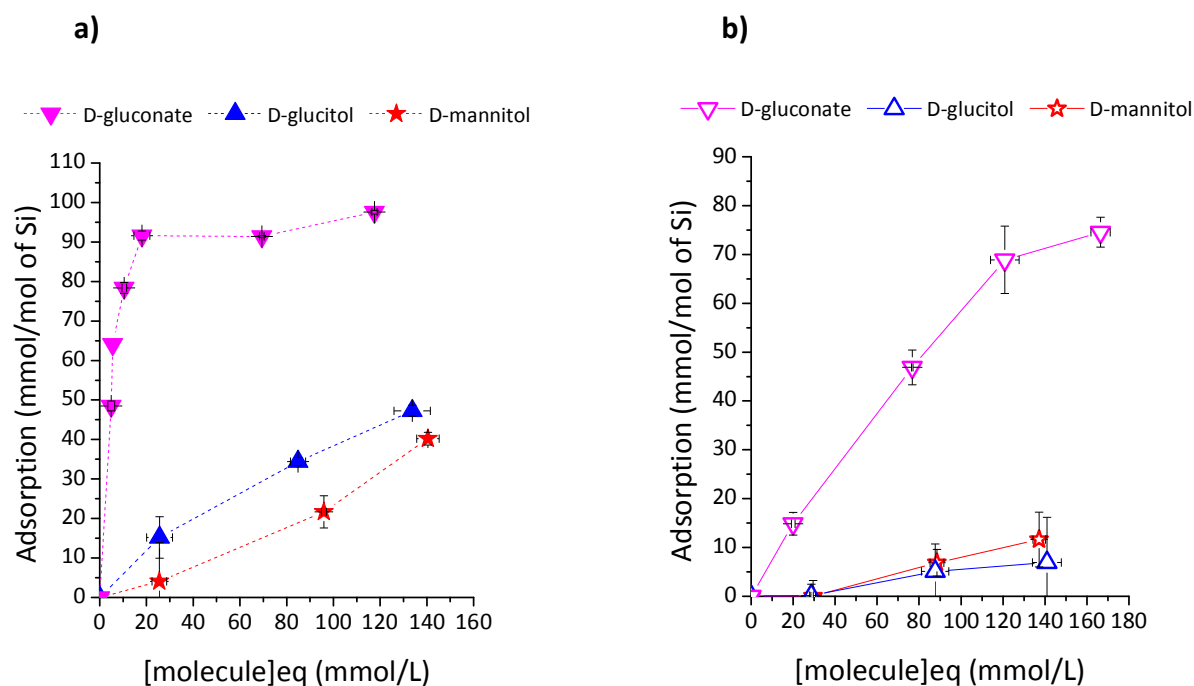


Figure 11: Adsorption isotherms of sugar derivatives on C-S-H with initial a) Ca/Si=1.58 and b) Ca/Si=0.80.

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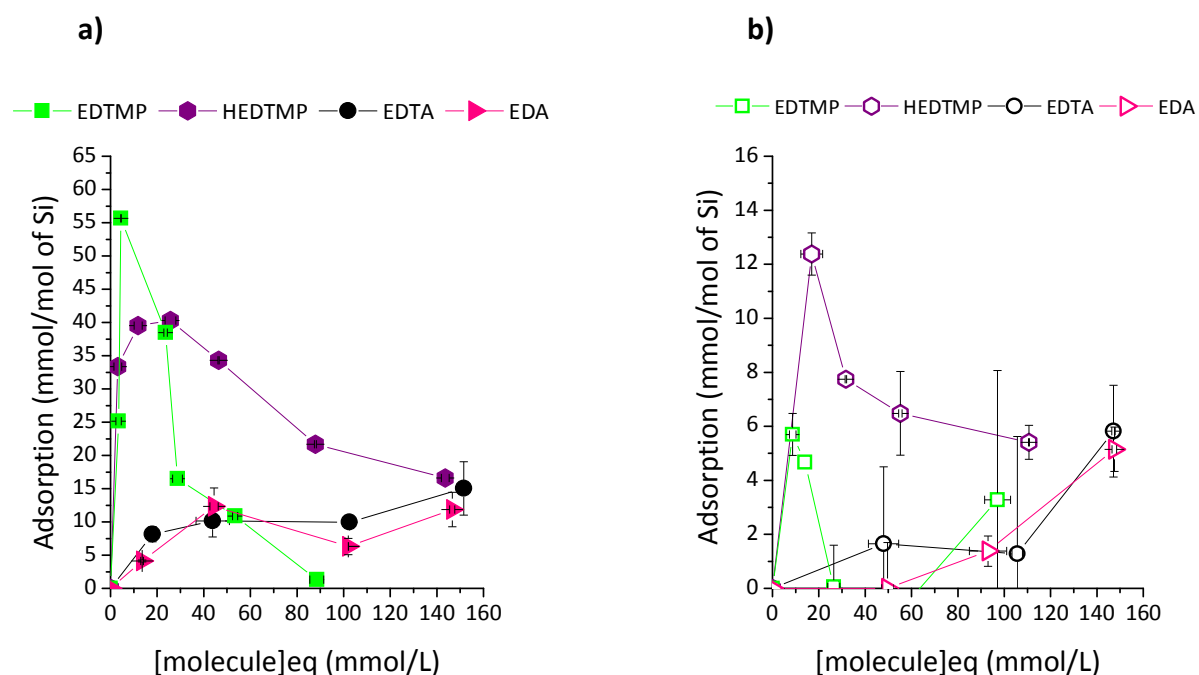


Figure 12: Adsorption isotherms of amines with functionalized carboxylate and phosphonate groups on C-S-H with initial a) high Ca/Si=1.58 and b) low Ca/Si.

The results observed in Figure 11-a correlates well with the results of Figure 8-a concerning the adsorption of sugar derivatives on C-S-H at high Ca/Si in suspensions buffered by portlandite: D-glucitol has a slightly higher affinity with C-S-H than D-mannitol but a lower one than its corresponding sugar acid anion that is D-gluconate. For C-S-H with a low initial Ca/Si, hexitols have a similar affinity with these hydrated particles but the one of D-gluconate is still higher than the one of sugar alcohols, Figure 11-b. It can also be added that the affinity of these sugar derivatives is higher with C-S-H at high than at low initial Ca/Si.

Concerning amines with functionalized carboxylate and phosphonate groups, Figure 12 shows that the former has a lower affinity with C-S-H at high and low initial Ca/Si than the latter. As for sugar derivatives, the affinity of amino-carboxylates and phosphonates with C-S-H at high initial Ca/Si is higher than with C-S-H at low initial Ca/Si.

Amino-carboxylates have similar adsorption properties on C-S-H's with high and low initial Ca/Si respectively. The adsorption of amino-phosphonates on both C-S-H's reaches a maximum and then decreases. The desorption of the molecules from C-S-H at high initial

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Ca/Si starts from a concentration of 5 mmol/L for EDTMP and of 26 mmol/L for HEDTMP. For C-S-H at low initial Ca/Si, EDTMP desorbs from a concentration equals to 9 mmol/l and HEDTMP from 17 mmol/L. This way, EDTMP starts desorbing from C-S-H at high and low initial Ca/Si in suspensions from a lower concentration of molecules than HEDTMP.

4. Discussion

It was observed that the adsorption of EDTMP and HEDTMP on C-S-H at high and low initial Ca/Si without any buffer of portlandite in the suspensions go through a maximum, Figure 12. EDTMP desorbs from C-S-H at high Ca/Si from a concentration of molecules equals to 5 mmol/L when there is no buffer of portlandite whereas no desorption is observed up to 31 mmol/L of molecules when the C-S-H suspension is buffered (Figure 13). Finally, the desorption of this amino-phosphonate from C-S-H at high initial Ca/Si occurs at a lower concentration of molecules when the suspensions are not buffered by portlandite.

A similar trend was partially predicted by Turesson who studied the calcium-mediated adsorption of a comb polyelectrolyte onto like-charged surfaces thanks to Monte Carlo simulations with and without a buffer of lime in suspension [20], see Figure 14. The adsorption of the molecules on these surfaces reaches a maximum value in suspensions without any buffer of lime whereas a plateau of adsorption is reached in the suspensions buffered by lime. No desorption of the molecules was identified in the suspensions buffered by lime in the conditions of this study. The desorption of the polyions from the surface of the particles when the solution is not buffered by lime, is explained to be the consequence of an apparent surface charge which is reduced by an accumulation of charged molecules at the surface.

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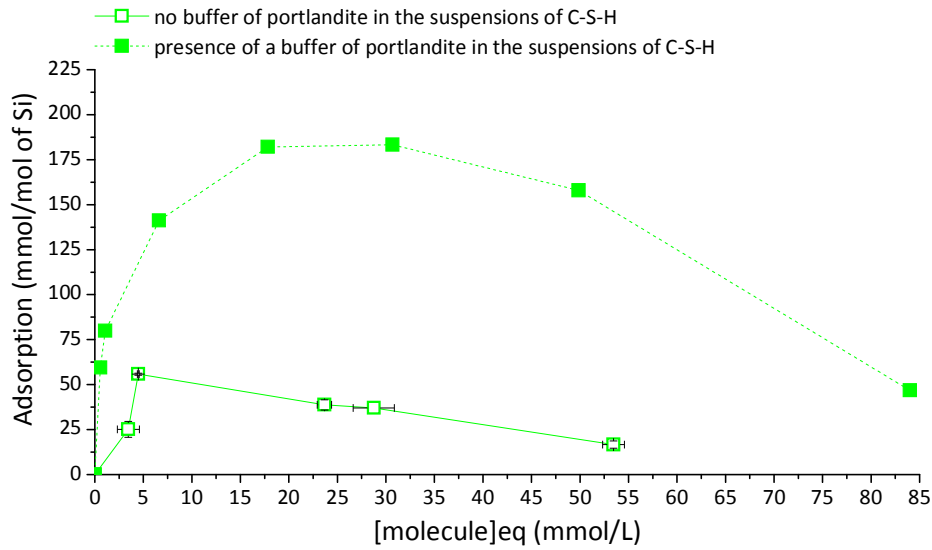


Figure 13: Adsorption isotherm of EDTMP on C-S-H with a high initial Ca/Si in suspensions without (a) and with (b) a buffer of portlandite (400 mg of portlandite in 6 mL of C-S-H suspension).

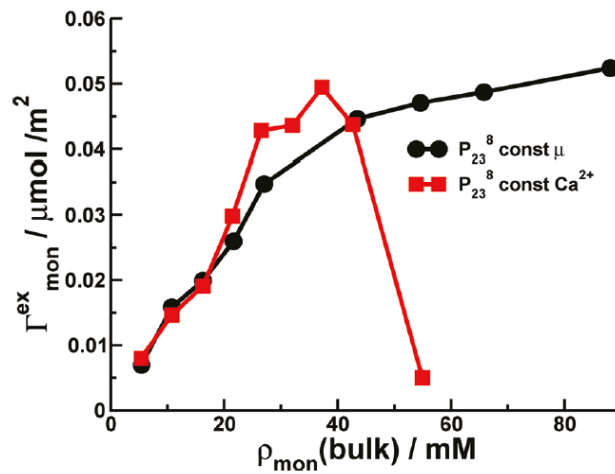


Figure 14: Adsorption isotherm of a comb polymer (polyion) as a function of its bulk concentration with (const μ) and without (const Ca^{2+}) a buffer of lime, from [20].

In our study, the desorption of amino-phosphonates from C-S-H might be related with the reduction of the high and low initial Ca/Si of C-S-H particles without a buffer of portlandite in the suspensions observed in Figure 10 which lows down the apparent charge or the charge of their surfaces respectively and so might affect the interaction of the molecule with these hydrates. Nevertheless, a desorption of EDTMP was also identified on portlandite (Figure 4) and on C-S-H at high Ca/Si in suspensions with a reservoir of

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portlandite (Figure 13). For the last system mentioned, the Ca/Si of C-S-H and so the apparent surface charge was kept constant thanks to the buffer of portlandite. Hence, the desorption of EDTMP and HEDTMP from C-S-H at high and low initial Ca/Si is not only related to the decrease of their Ca/Si.

It is important to note that some particules smaller than the size of the filter (0.20 μm) were found in the solution at equilibrium with portlandite after filtration for concentrations of EDTMP above 31 mmol/L whereas these particles were not found below (DLS measurements, not shown). Hence, the desorption of the molecules from the surface of portlandite is assumed to be the consequence of the formation of aggregates of complexed EDTMP expected to be thermodynamically more stable than their adsorbed form on portlandite. The adsorption of EDTMP on C-S-H at high Ca/Si in suspensions buffered by portlandite may suffer from a similar fact.

Finally, the present study showed that sugar derivatives, amino-carboxylates and phosphonates both complex calcium ions in solution and adsorb on C-S-H. Figure 15 represents the affinity of different molecules with C-S-H at high Ca/Si in suspensions buffered by portlandite as a function of their calcium complexing power. The latter is described as being the amount of calcium ions complexed per molecule present in solution and equals to the slope of the linear regression of the curves presented in Figure 2-a.

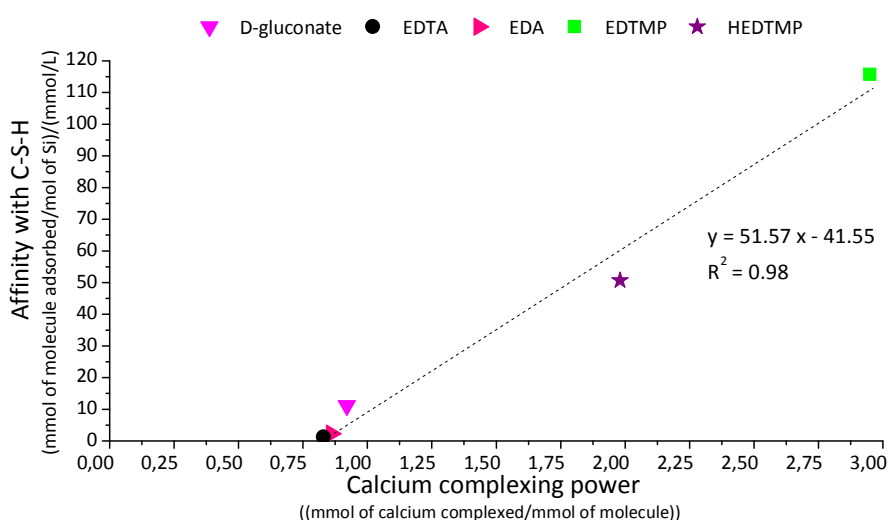


Figure 15: Evolution of the affinity of the molecules with C-S-H at high Ca/Si in suspensions buffered by portlandite as a function of their complexing power with calcium ions in solution.

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It can be seen from Figure 15 that there is a linear relation between the affinity of the molecules with C-S-H at high Ca/Si and their calcium complexing power. Consequently, molecules having an important calcium complexation in solution also have an enhanced affinity with C-S-H at Ca/Si above 1. Moreover, it was shown that the affinity of the organic compounds with C-S-H at Ca/Si higher than 1 was always more important than with C-S-H at lower Ca/Si. C-S-H particles with a Ca/Si above 1 get an apparent surface charge which is positive due to the overcompensation of the highly negative surface charge by the adsorption of calcium ions. The adsorption of the additives on C-S-H at Ca/Si above 1 is then supposed to occur through an interaction with calcium ions at its surface. Nevertheless, the complexation of the organic compounds with calcium ions in solution was not related to pure electrostatic interactions. Consequently, the molecules may interact specifically with calcium ions at the surface of C-S-H and possibly by a surface complexation.

The molecules studied are known to retard the hydration of C_3S [13]. In attempts to identify the interaction(s) which is (are) at the origin of this retardation, the retarding effectiveness of the molecules is represented as a function of their affinity with the surface of C-S-H or of their complexation with calcium ion in solution in Figure 16. The retardation caused by the organics on the hydration of C_3S increases according to their affinity with calcium ions on C-S-H or in solution but is not only function of this parameter. In fact, amino-phosphonates (EDTMP and HEDTMP) have similar retarding effects on C_3S hydration but different affinities with calcium ions. It is also important to note that strong retarders such as D-gluconate and amino-phosphonates also complex hydroxide and silicate ions compare to amino-carboxylates. Consequently, the complexation of the molecules with hydroxide and/or silicates is not only at the origin of their retarding effect but seems to reinforce it.

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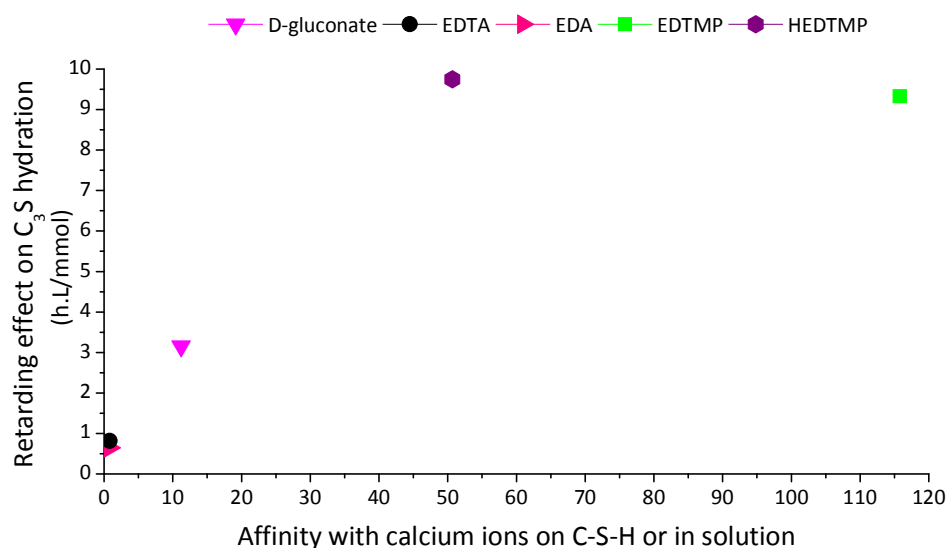


Figure 16: Relation between the retardation generated by different organic molecules on the hydration of C_3S hydration [13] depending on their affinity with the surface of C-S-H at high Ca/Si.

5. Conclusions

This study compares the ion complexing power and the adsorption of retarders such as sugar derivatives, amino-carboxylates and phosphonates on portlandite and/or C-S-H. The results showed that these molecules form calcium and/or hydroxide complexes in solution, adsorb on C-S-H and portlandite but to different extents. An important complexation of silicate ions in solution was also observed in presence of amino-phosphonates and to a lower extent with D-gluconate and its corresponding sugar alcohol that is D-glucitol.

All the molecules studied are also sensitive to the calcium counter-ions present at the surface of C-S-H at Ca/Si above 1. Moreover, a linear relation between the affinity of the molecules with these C-S-H particles and their calcium complexing power was found whereas the latter is not function of their charge. The adsorption of the additives on C-S-H particles is then supposed to occur by a specific interaction with calcium ions at their surfaces.

The retardation caused by the organic molecules on the hydration of C_3S is not only controlled by their calcium complexing power: their complexation with silicate and/or hydroxide ions seems to play a role. A competition between the adsorption of the molecules

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on C-S-H and/or portlandite and their interaction in solution (ionic complexation and possibly aggregation) may also affect their retarding effectiveness on C₃S hydration.

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Effects of hexitols on the hydration of tricalcium silicate

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Abstract

The hydration of tricalcium silicate (C_3S) in presence of hexitols (D-glucitol, D-galactitol and D-mannitol) which only differ depending on the stereochemistry of their hydroxyl groups was followed by using calorimetric and conductimetric measurements of the pastes and of the diluted suspensions respectively. To correlate the results obtained in paste and in diluted suspension, the hydration of C_3S in suspension started in initial solutions with different pH and calcium concentrations in presence of the molecules was investigated. It was completed by studying the effects of alditols on the pure dissolution of C_3S and on the precipitation of calcium silicate hydrate (C-S-H) by continuously measuring the concentration of silicates present in C_3S suspensions by Inductively Coupled Plasma-Atomic Emission Spectroscopy.

Hexitols delay the acceleration of the growth of C-S-H and enhance the quantity of C-S-H when the maximum rate of C_3S hydration is reached in relation to the stereochemistry of their hydroxyl groups: D-glucitol > D-galactitol > D-mannitol. Their relative retarding effect is shown to change depending on their sensitivity to calcium ions at pH found in cement paste. Alditols are shown to retard C_3S hydration whereas its dissolution is not limited suggesting an impact of the molecules on the precipitation of C-S-H.

Keywords: sugar, dissolution, precipitation, hydration, tricalcium silicate

1. Introduction

Cement set retardation generated by organic admixtures is a practical concern for industrial applications and needs to be controlled if desired or counteracted if undesired. Cement setting results from the nucleation and growth of calcium silicate hydrates (C-S-H) due to the hydration of the major phase of cement which is tricalcium silicate (C_3S) [1]. Many authors investigated the retardation caused by carbohydrates, sugar alcohols and phenols on cement hydration and tried to understand the mechanism responsible of this delay [2-16]. It is mainly reported that the time at which the acceleration of the growth of C-S-H starts is enhanced with increasing concentrations of retarders but their action mechanism is still not well understood [3,8-12].

The hydration of C_3S is a dissolution-precipitation process so the retardation induced by the organic molecules may come from an effect of the molecules on the dissolution of the anhydrous and/or on the nucleation-growth of C-S-H. The retardation generated by organic admixtures was often mentioned to result from a disruption of the nucleation-growth process of C-S-H [4,13,17-19] but a polycarboxylate functionalized latex and D-gluconate which also retard C_3S hydration were shown to strongly decrease the dissolution rate of the mineral phase [20-22]. Given that the hydration kinetics of C_3S results from a chemical coupling between C_3S dissolution and C-S-H precipitation, the origin of the effects of the organic molecules on the formation of hydrates is not obvious. Consequently, one can realize that the mechanism(s) by which organic chemicals act(s) on the dissolution-precipitation process of C_3S hydration is not clearly identified and prevents us from understanding why and how do these molecules really retard cement hydration.

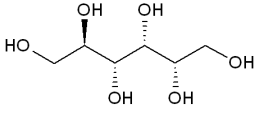
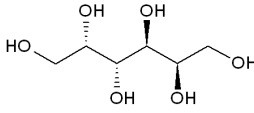
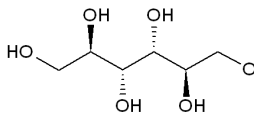
This study proposes to investigate the action mechanism(s) of three sugar alcohols which were recently reported to delay the hydration of C_3S pastes [3,23]. These polyols that are D-glucitol, D-galactitol and D-mannitol have the same chemical formulae $C_6H_{14}O_6$ and only differ depending on the stereochemistry of their hydroxyl groups as shown in Table 1. Here, the investigation focuses on the effects of alditols on the advancement of C_3S hydration in paste and on their impacts on the dissolution-precipitation process with C_3S in diluted suspension. In fact, C_3S suspensions are more diluted systems than C_3S pastes and allow us to identify the influence of the molecules on the dissolution-precipitation process of

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C₃S hydration from the study of the composition of solutions. During the hydration of C₃S in paste, due to the low amount of water in contact with C₃S, the dissolution of the powder rapidly increases the calcium hydroxide concentration and saturates the solution with respect to calcium hydroxide. This way, the effects of the calcium concentration and of the pH of the initial solutions on the hydration of C₃S in suspension were also considered in presence of hexitols.

To proceed, the effects induced by the stereoisomers on the advancement of C₃S hydration in paste were first studied by using isothermal calorimetry. Secondly, the hydration of C₃S in suspension started in solutions with different concentrations of calcium and pH with hexitols was followed by conductimetric experiments. Then, the influence of alditols on the dissolution-precipitation process of C₃S hydration were investigated by following evolution of the composition of the solution with conductimetric and ionic measurements of the suspensions. Finally, a discussion focused on the interactions of the molecules in C₃S pastes and on the origin of their retarding effect is given.

Table 1: Chemical structures of the hexitols studied.

D-glucitol	D-galactitol	D-mannitol
		

2. Materials and methods

2.1. Materials

The water used for the preparation of the pastes, suspensions and solutions was distilled and deionised. The hexitols studied were D-glucitol ($\geq 98\%$), D-mannitol ($\geq 98\%$) and D-galactitol ($\geq 99\%$) from Sigma Aldrich, all as a powder form.

C₃S was supplied by Mineral Research Processing with a granulometric distribution centred around 7 μm . Calcium oxide used in the different experiments was obtained after decarbonation of calcium carbonate (98.5-100 %, VWR AnalaR NORMAPUR) at 1000 °C for

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24 h. Sodium chloride (> 99.5 %, AnalaR NORMAPUR, VWR), calcium chloride (> 96 %, Acros Organics), sodium hydroxide (> 97 %, Merck) used to make salt solutions were dried minimum a day in an oven at 180 °C. Saturated lime solutions were obtained by filtering (0.1 µm cellulose ether, Merck Millipore) saturated lime suspensions made by adding an excess of freshly decarbonated lime to water left to equilibrate minimum a day in a thermoregulated bath at 25 °C.

In order to study the effect of seeding during the hydration of C_3S with hexitols, C-S-H suspensions were synthesized by mixing calcium oxide, aerosil silica (Evonik) and water. The proportions of calcium oxide, aerosil silica were chosen in order to obtain an initial Ca/Si equals to 1.58 and a Liquid to Solid ratio (L/S) equals to 20. These stock suspensions were stirred for a month at 23 °C, which is long enough to reach equilibrium [24].

2.2. Methods

2.2.1. Calorimetric measurements during the hydration of C_3S pastes with hexitols

The pastes were made by adding 0.4 mL of aqueous solutions at different concentrations of sugar alcohols (0-11.3 mmol/L) to 1 g of C_3S (L/S=0.4). The pastes were mixed at 3200 rpm for 2 min with a stirrer. Then, they were immediately put in a TAM AIR isothermal calorimeter at 23 °C where the heat flow was measured during their hydration.

The cumulated heat flow was calculated by integrating the measured curve of heat flow. Finally, the advancement of C_3S hydration was obtained by the product of the cumulated heat flow and the enthalpy of hydration at 23 °C ($\Delta H=460.16$ J/g). This enthalpy was calculated like Grant [26] for the following reaction: $5 C_3S + 12 H_2O \rightarrow C_8S_5H_{10} + 7CH_2$.

2.2.2. Conductimetric studies during the hydration of C_3S suspensions in presence of alditols

During the hydration of C_3S , the concentrations of calcium, silicate and hydroxide ions present in the suspension evolves over time. Hydroxide ions are particularly conductive and allow us to follow the hydration of C_3S with and without organics by measuring the conductivity of the suspensions with an electrode related to a CDM210 conductivity meter

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(both from Radiometer Analytical). The suspensions with L/S=100 (1 g of C_3S added to 100 mL of different initial solutions) were stirred in thermoregulated cells at 25 °C. A flow of nitrogen gas was ensured in all the cells to prevent the formation of calcium carbonate.

2.2.2.a. Hydration of C_3S in suspension started in solutions with different initial pH and calcium concentrations with hexitols

In order to reproduce the calcium concentration and/or the pH of the pore solution of C_3S pastes at a given time when hydrating C_3S in suspension, C_3S was added to different initial solutions composed of NaCl, NaOH at 44 mmol/L; $CaCl_2$, $Ca(OH)_2$ at 22 mmol/L; $Ca(OH)_2$ at 11 mmol/L and water. The amount of alditols was added to the different initial solutions to fix the initial concentration of molecule at 7.50 mmol/L in order to distinguish the impact of the molecules on C_3S hydration within a reasonable time. After 30 min to equilibrate the initial solutions, the C_3S powder was added.

2.2.2.b. Delayed addition of C-S-H in C_3S suspensions with D-glucitol in saturated lime solutions

Different amounts of the C-S-H suspension were added 30 min after the hydration of C_3S has started in saturated lime solutions with a constant concentration of D-glucitol (7.5 mmol/L). The amount of the C-S-H suspension was weighed in order to fix the amount of initial C-S-H added. Due to the low volume of water put in the C_3S suspension when adding the small amount of the C-S-H suspension (maximum 19 μ L of solution), the total volume of the C_3S suspensions was considered as unchanged.

2.2.3. Ionic concentration measurements during the pure dissolution and hydration of C_3S in suspension with alditols

The pure dissolution and hydration of C_3S was followed by continuously measuring the silicon composing silicate ions present in the C_3S suspensions by Inductively Coupled Plasma – Atomic Emission Spectroscopy. The hydration of C_3S was followed in suspensions with L/S=100 (L=100 mL of water) whereas the pure dissolution of C_3S was followed in highly diluted C_3S suspensions with L/S=10 000 (L=100 mL of a solution at 11 mmol/L of $Ca(OH)_2$) in

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order to obtain solutions under-saturated with respect to C-S-H (no precipitation of hydrates).

The C_3S powder was added to the initial solution put in a stirred reactor which was connected to the spectrometer in a room maintained at 23 °C. The suspension was continuously passing through a filtering device (0.1 μm cellulose ether, Merck Millipore) before measuring the silicates concentration of the solution as described in [27] where a similar experimental set-up was used. After this measurement, the left solution which was not analyzed was brought back in the reactor which was under an argon gas atmosphere.

3. Results

3.1. Effects of hexitols on the advancement of C_3S hydration

The advancement of C_3S hydration calculated from the heat flow obtained by isothermal calorimetry in presence of different initial concentrations of hexitols is shown in Figure 1. The presence of these sugar alcohols in C_3S pastes extends the induction period depending on the stereochemistry of their hydroxyl groups compare to the one of the reference without additive: D-glucitol > D-galactitol > D-mannitol. At the end of the induction period, the strong increase of the advancement of C_3S hydration is not affected by the organic molecules given that the slope of the curve do not strongly change compare to the one of the reference. However, after the maximum rate of C_3S hydration is reached (inflection point), the advancement of C_3S hydration is higher in presence of the molecules than without. Similar results were revealed when hydrating C_3S with sucrose [12] or a cellulose ether [19] in solution by measuring the Bound Water of the paste or the conductivity of the suspension respectively.

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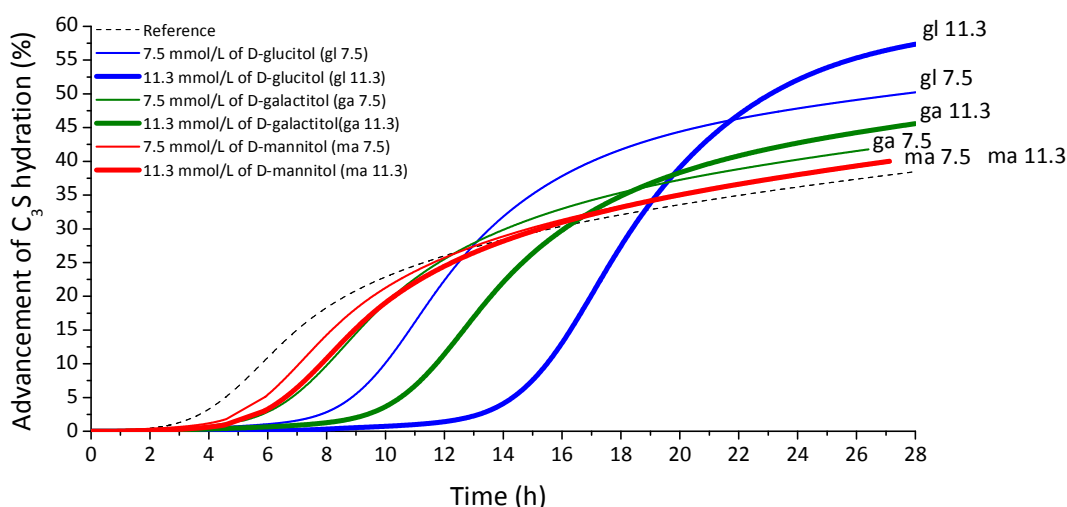


Figure 1: Advancement of C_3S hydration in presence of different concentrations of hexitols, $L/S=0.4$.

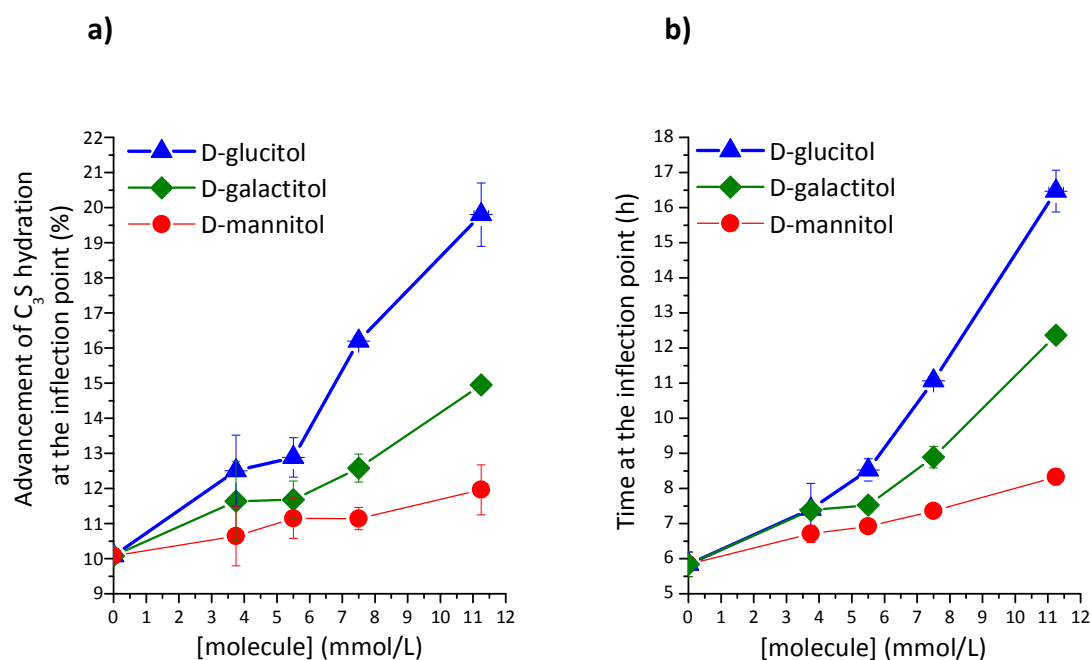


Figure 2: Evolution of a) the advancement of C_3S hydration and b) the time at the inflection point depending on the concentration of alditols.

The evolution of advancement of C_3S hydration and of the time at the inflection point are represented as function of the concentration of hexitols in Figure 2-a and b respectively. The data results from the average measurements of two replicates and the y error bars indicate the standard deviation of the mean. It can be observed that both the advancement of C_3S hydration and the time at the inflection point increase with the concentration of

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alditols. Nevertheless, their impact is different depending on their stereochemistry. For a given concentration of polyols, D-glucitol particularly enhances the advancement of C_3S hydration and the time at the inflection point and is followed by D-galactitol and then by D-mannitol. Figure 3 indicates that the advancement of C_3S hydration increases with the time at the inflection point but that the effect is different depending on the hexitols present. For a given time at the inflection point, the advancement of C_3S hydration is higher with D-glucitol than with D-galactitol and D-mannitol. This result reveals that the presence of D-glucitol particularly enhances the amount of hydrates compare to two other sugar alcohols when the maximum hydration rate of C_3S is reached.

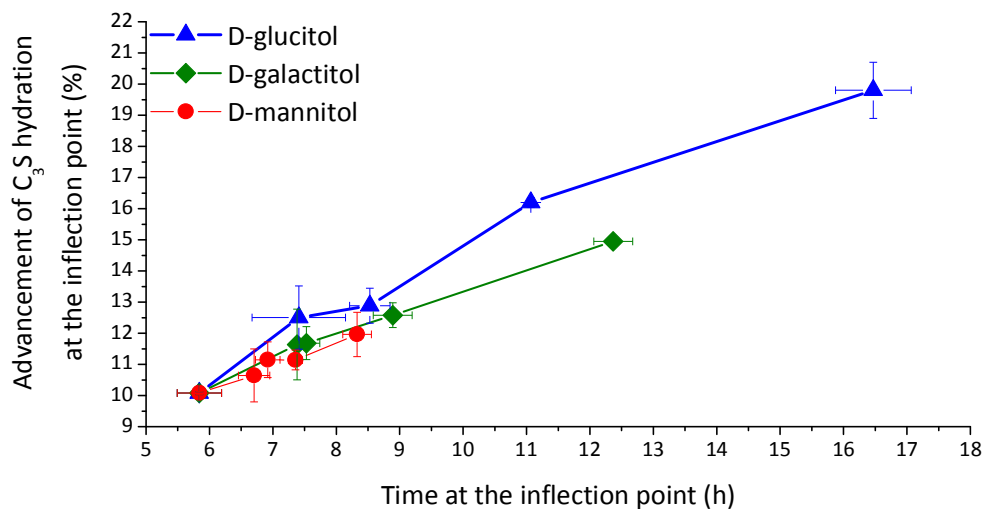


Figure 3: Representation of the advancement of C_3S hydration as a function of the time at the inflection point in presence of the different hexitols.

3.2. Influence of the calcium concentration and of the pH of the solutions on the hydration of C_3S suspensions in presence of alditols

Conductivity measurements of C_3S in suspension were made over time to follow its hydration with and without hexitols (7.5 mmol/L) in different initial solutions and are shown in Figure 4. The pH and the calcium concentration of the initial solutions were varied by using water and $CaCl_2$, NaCl, NaOH, $Ca(OH)_2$ solutions at different concentrations. After the addition of C_3S in the different aqueous solutions, a sharp rise in the conductivity occurs due to the dissolution of C_3S . Then, the conductivity keeps stable during the induction period and the precipitation of C-S-H occurs. At the end of the plateau, the conductivity starts increasing

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due to the acceleration of C_3S hydration. In fact, the stoichiometric ratio Ca/Si of C_3S when dissolving ($Ca/Si=3$) is higher than the one of $C-S-H$ when precipitating ($Ca/Si < 2$): there is an accumulation of calcium hydroxide in solution which increases the conductivity until portlandite precipitates.

From Figure 4, one can realize hexitols in water, $NaCl$ solutions at 44 mmol/L and $CaCl_2$ solutions at 22 mmol/L do not have noteworthy effect on the hydration of C_3S whereas they lengthen the induction period during C_3S hydration in $Ca(OH)_2$ solutions at 11 and 22 mmol/L and $NaOH$ solutions at 44 mmol/L. Hence, whatever the calcium concentration in initial solutions at low pH (≈ 7), there is no retarding effect induced by alditols on C_3S hydration whereas a delay is generated at higher pH.

It can be noted that D-galactitol is the best retarder of C_3S hydration in 11 mmol/L $Ca(OH)_2$ solutions and is followed by D-mannitol and D-glucitol which have similar retarding effects. On the other hand, in 22 mmol/L $Ca(OH)_2$ solutions, D-glucitol is the best retarder and D-mannitol is the less retarding molecules, D-galactitol being between them. The relative order of retardation changes depending on the concentration of $Ca(OH)_2$. Nevertheless, when comparing the impacts of the molecules on C_3S hydration in $Ca(OH)_2$ solutions at 11 and 22 mmol/L, both the calcium concentration and the pH vary so their retarding effects can not be related to their interaction with calcium and/or hydroxide ions.

To do so, the influence of the calcium concentration on the retardation of C_3S hydration caused by alditols is identified at a given pH and vice-versa. D-galactitol retards more the hydration of C_3S in 44 mmol/L $NaOH$ solution than the two other hexitols whereas no retardation is observed in $NaCl$ solutions at 44 mmol/L. D-galactitol is then particularly sensitive to pH in solutions exempted of calcium ions. When comparing the retardation induced by the sugar alcohols in $Ca(OH)_2$ solutions at 22 mmol/L and $NaOH$ solutions at 44 mmol/L, one can observe that D-glucitol has an enhanced retarding effectiveness in the first solution mentioned for a given and high pH (≈ 12.5). It reveals that D-glucitol is especially sensitive to calcium ions at high pH. On the other hand, this molecule is pretty much not sensitive to calcium ions at lower pH (≈ 7) as the other alditols (solutions at 22 mmol/L of $CaCl_2$).

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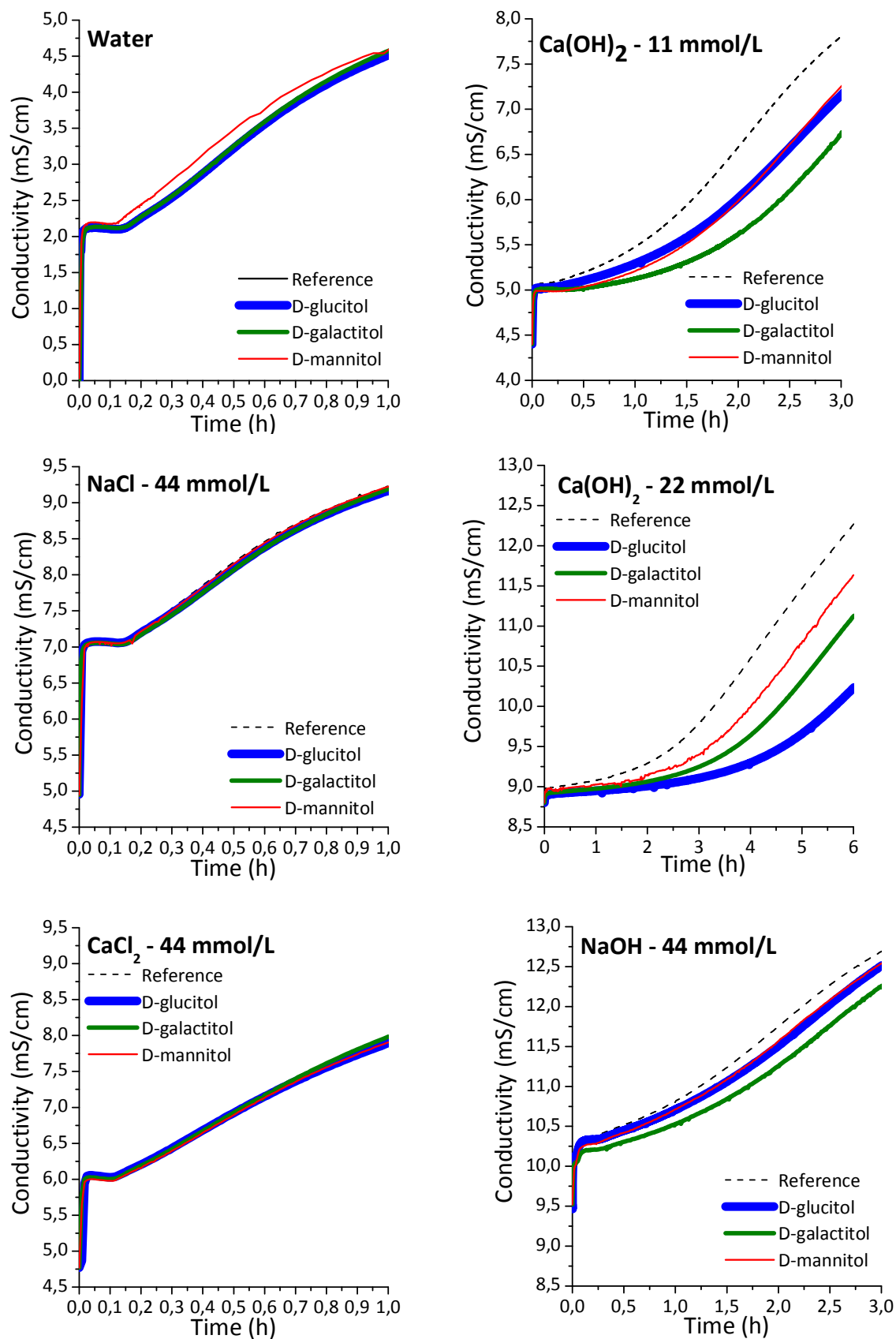


Figure 4: Conductivity monitored during the hydration of C₃S suspensions in initial solutions at different pH and calcium concentrations with and without hexitols (7.5 mmol/L), L/S=100.

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3.3. Impacts of hexitols on the dissolution-precipitation process of C_3S hydration

3.3.1. Effects of alditols on the pure dissolution of C_3S

The pure dissolution of C_3S with and without D-glucitol, D-galactitol and D-mannitol (7.5 mmol/L) in 11 mmol/L $Ca(OH)_2$ solutions was followed to identify their effects on the initial rate of C_3S dissolution. The comparison of their impacts on the silicates concentration over time is presented in Figure 5. In presence of D-mannitol in the C_3S suspension, the silicates concentration is similar to the one of the reference for a given time. With D-galactitol and D-glucitol, the concentrations of silicate ions of the C_3S suspensions are even more important than for the reference sample. These molecules are then supposed to increase the dissolution rate of C_3S by complexing with calcium, silicate and/or hydroxide ions in solution. Hence, the pure dissolution of C_3S in 11 mmol/L $Ca(OH)_2$ solutions is not limited by the polyols studied but is even enhanced in presence of the strongest retarders that are D-glucitol and D-galactitol.

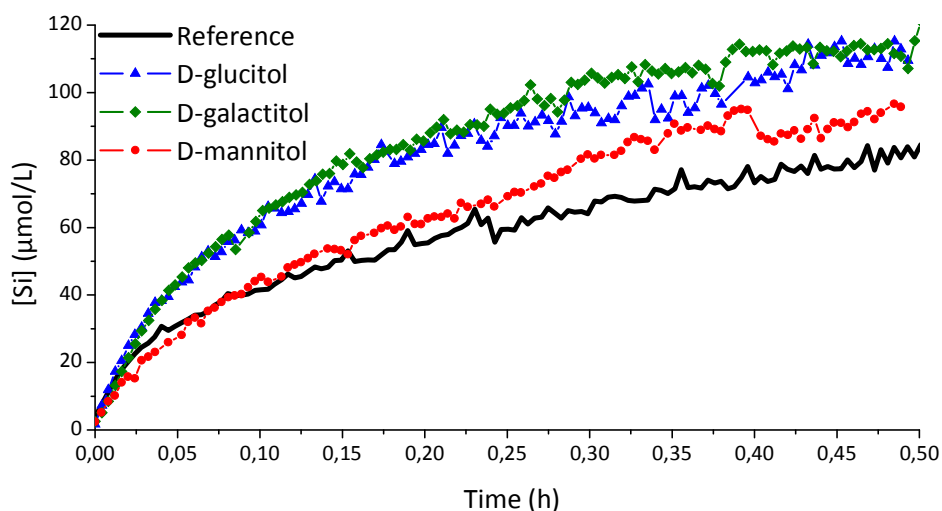


Figure 5: Evolution of the silicates concentration over time during the pure dissolution of C_3S in suspensions with and without hexitols (7.5 mmol/L), $[Ca(OH)_2]=11$ mmol/L and $L/S=10\ 000$.

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3.3.2. Effects of hexitols on the precipitation of C-S-H during C_3S hydration

The hydration of C_3S started in water was followed by measuring the silicates concentration of the suspensions over time with and without sugar alcohols present, Figure 6.

Once C_3S is added to the aqueous solutions, the concentration of silicates immediately increases due to the dissolution of C_3S and reaches a maximum value. Then, it keeps decreasing due to the precipitation of C-S-H consuming silicates which is faster than the dissolution of C_3S . The precipitation of C-S-H can be described as a primary and secondary nucleation. The primary heterogeneous nucleation refers to the spontaneous formation of C-S-H at the surface of C_3S when the critical super-saturation with respect to the hydrate is reached in solution. The secondary heterogeneous nucleation corresponds to the precipitation of new C-S-H at the surface of initial nuclei. Indeed the true growth of C-S-H nuclei is very limited.

Just after the concentration of silicates reaches its maximum value, no plateau of the silicates concentration is observed but a drop of the concentration is identified with and without the molecules due to the primary nucleation of C-S-H [25]. This result indicates that there is no apparent effect of alditols on the primary nucleation of C-S-H in the conditions of the study. However, after 4 min of hydration, the silicates concentrations of the suspensions of C_3S with sugar alcohols decrease slowly compare to the one of the reference. Comparable effects on the silicates concentration over time were identified during the hydration of C_3S in suspension with retarding organic molecules such as D-gluconate, cellulose ethers and a polycarboxylate functionalized latex [19-21]. This important concentration of silicates could be interpreted as a slowing down effect caused by the organics on the secondary nucleation of C-S-H or/and it might be related to the complexation of the molecules with silicate, calcium and/or hydroxide ions present in solution.

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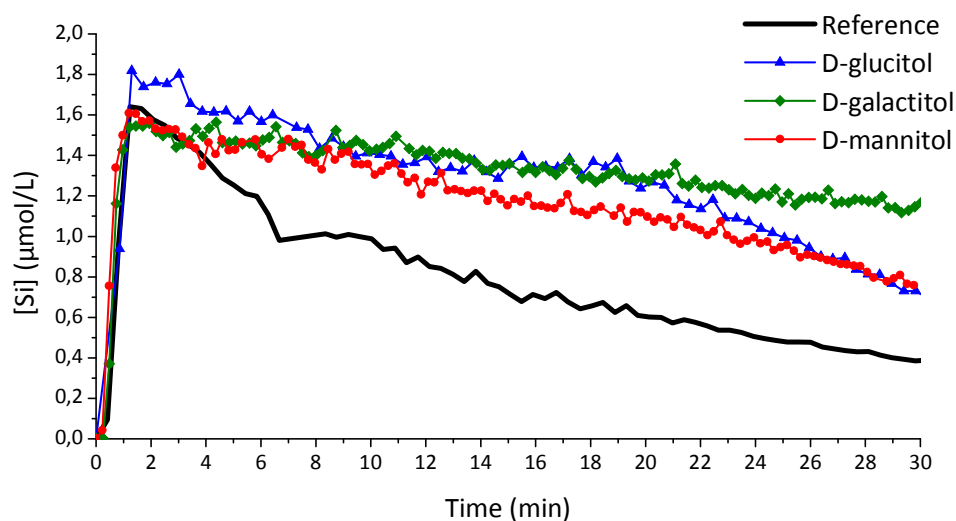


Figure 6: Evolution of the silicates concentration during the hydration of C_3S suspensions started in water as a function of the time in presence of hexitols (7.5 mmol/L), $\text{L/S}=100$.

3.3.3. Effects of a delayed addition of C-S-H on the hydration of C_3S suspensions with D-glucitol

Already made C-S-H were added to C_3S hydrated in saturated lime solutions with D-glucitol (7.5 mmol/L) at 30 min of hydration. The conductimetric curves monitored during the hydration of C_3S with D-glucitol in presence of an increasing amount of C-S-H are compared in Figure 7.

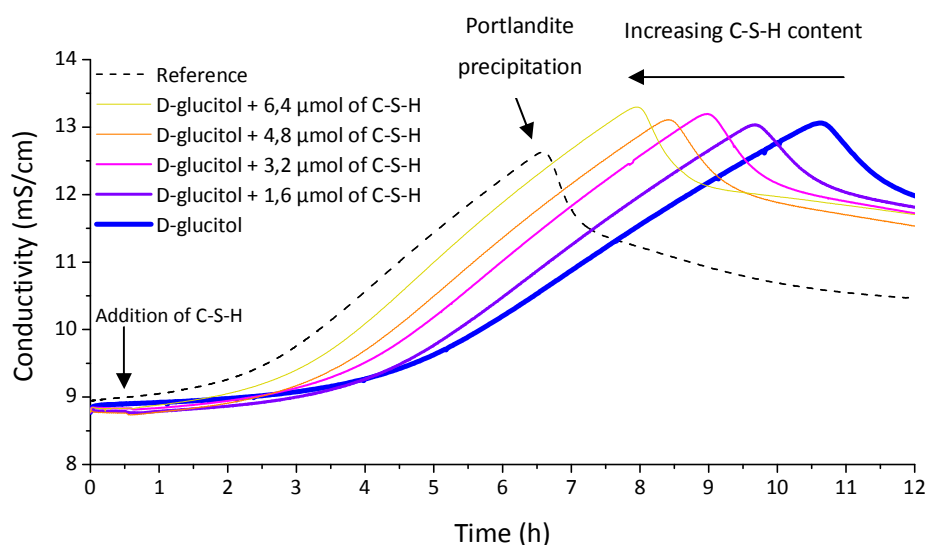


Figure 7: Delayed addition of C-S-H to C_3S suspensions in presence of 7.5 mmol/L of D-glucitol, $[\text{Ca}(\text{OH})_2]=22$ mmol/L and $\text{L/S}=100$.

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One can first observe that the time at which the conductivity starts to increase (at the end of the plateau of conductivity) is reduced in presence of increasing C-S-H contents, Figure 7. Hence, the acceleration of C_3S hydration occurs earlier when adding new C-S-H in presence of D-glucitol. Moreover, the values of the maximum conductivity revealing the composition of the solution reached before portlandite starts precipitating are really similar in presence of D-glucitol whatever the amount of C-S-H added to C_3S suspensions (around 13.1 mS/cm). However, the value of the maximum conductivity is higher in presence of D-glucitol than without (around 12.6 mS/cm). It means that the molecules modify the ionic composition of the C_3S suspension and that the supersaturation with respect to portlandite reached is similar whatever the amount of new C-S-H added. These results let us suggest that the ionic composition of the solution corresponding to the supersaturation with respect to portlandite is the consequence of the interaction(s) of D-glucitol which occurred before the addition of new C-S-H. These interactions can be a complexation with some ions in solution, an adsorption at the surface of C_3S and/or on C-S-H precipitated on C_3S .

4. Discussion

The retarding effectiveness of hexitols on the hydration of C_3S pastes depends on the stereochemistry of their hydroxyl groups: D-glucitol > D-galactitol > D-mannitol. The role played by the pH and the calcium concentration on the delay generated by hexitols on the hydration of C_3S was pointed out suggesting an interaction of the molecules with calcium and hydroxide ions. It is known that hexitols form calcium complexes in aqueous solution and D-glucitol is often stated as the strongest calcium complexing hexitol [26-30]. Some authors also underlined that an interaction of hexitols with hydroxide ions may exist [30] and that hydroxide ions favour the complex formation of D-glucitol with calcium ions [27].

The configurations of the hydroxyl groups carried by the hexitols studied are described in Figure 8 thanks to their Fischer projections. Angyal proposed different effectiveness of the complexing sites depending on the configuration of the molecules [31]: threo-threo-erythro > threo-erythro-threo > erythro-threo-erythro. Consequently, the retarding effect caused by hexitols on C_3S hydration follows the complexing sites

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effectiveness proposed by Angyal. It was shown that the relative retarding effects of alditols on the hydration of C_3S pastes and of C_3S suspensions in saturated lime solutions are similar. In fact, when hydrating C_3S in paste, the solution which is initially water becomes rapidly saturated with respect to calcium hydroxide and allows us to assume that comparable interactions of the molecules with calcium and hydroxide exist in these two systems.

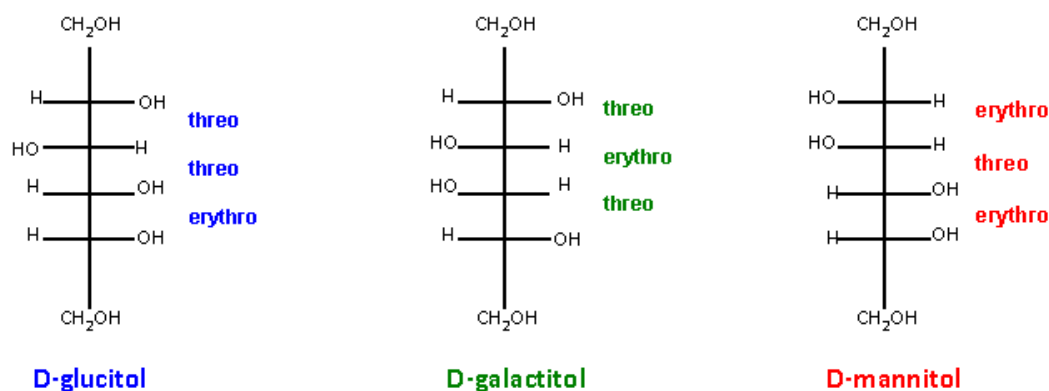


Figure 8: Fischer projections of hexitols. “Threo” stands for two hydroxyl groups on opposite sides and “erythro” stands for two hydroxyl groups on the same side of the carbon chain.

This study revealed that alditols retard the hydration of C_3S without reducing its dissolution rate. Several authors which investigated the effect of different retarders such as yellow dextrin, cellulose ethers and hydroxypropylguars on the pure dissolution of cement or C_3S also found that there was no limitation of the dissolution process caused by these molecules [4,6,19]. D-gluconate which also delays C_3S hydration was shown to slow down the pure dissolution of the anhydrous compound but not to inhibit it. This way, the impact of the molecules on the dissolution of C_3S does not seem to be at the origin of their retarding effect but may enhance it. Finally, hexitols are supposed to retard C_3S hydration by impeding the precipitation of C-S-H due to an interaction of the molecules with ions in solution and/or to an interaction with C-S-H [30]. In fact, a slow decrease of the silicates concentrations was identified in solution during the hydration of C_3S started in water in presence of hexitols (Figure 6) whereas no retardation of C_3S hydration was noticed by conductimetric measurements (Figure 4). Then, these important silicates concentrations result from the complexation of hexitols with silicate, calcium and/or hydroxide ions in solution. Moreover, it is known that D-glucitol and D-mannitol adsorb on C-S-H in systems at equilibrium [30] so these molecules may interact with C-S-H present at the surface of C_3S during its hydration and disturb their growth.

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The increase of the length of the induction period, of the time and amount of C-S-H at the maximum hydration rate of C_3S might also be related with an effect of alditols on the precipitation of C-S-H. In fact, for a given lime concentration, it was shown that when hydrating C_3S with a low amount of C-S-H initial nuclei on C_3S , the length of the induction period, the time and advancement for which the deceleration of C_3S hydration occurs is increased compare to C_3S with a high initial quantity of C-S-H [32]. In presence of hexitols, the induction period seems to be lengthened due to initial C-S-H nuclei which can not grow and other C-S-H nuclei are assumed to precipitate somewhere else on C_3S and so on. Given that the solution becomes less and less super-saturated with respect to C-S-H, the precipitation of new C-S-H nuclei is slowed down. Now, the influence of the interactions of hexitols with some ions in solution and/or with C-S-H nuclei on the formation of new C-S-H should be investigated more in details.

5. Conclusions

The retarding effectiveness of hexitols (D-glucitol, D-galactitol and D-mannitol) on C_3S hydration was related to their affinity with hydroxide and calcium ions present in solution. Moreover, the impacts of these organic molecules on the dissolution-precipitation process of C_3S hydration were investigated.

The study reveals that alditols delay the acceleration of C_3S hydration and enhance the degree of hydration when the maximum rate of C_3S hydration is reached depending on the stereochemistry of their hydroxyl groups: D-glucitol > D-galactitol > D-mannitol. The retardation on the hydration of C_3S induced by hexitols depends on their sensitivity to both hydroxide and calcium ions in solution but their relative retarding effectiveness in paste is controlled by their affinity with calcium ions. It is also pointed out that the delay generated by alditols does not come from an effect of these organic molecules on the dissolution of C_3S but is assumed to result from a disruption of the precipitation of C-S-H.

III.3. Effets des hexitols sur l'hydratation du silicate tricalcique

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III.4. Impacts des hexitols sur l'hydratation du mélange aluminat tricalcique-sulfate de calcium

Impacts of hexitols on the hydration of a tricalcium aluminate-calcium sulfate mixture

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Abstract

The effects of hexitols which are stereoisomers (D-glucitol, D-galactitol and D-mannitol) on the hydration of a tricalcium aluminate-calcium sulfate mixture with calcium hydroxide in paste were assessed and compared. The interactions of the molecules in solution and at the solid-liquid interface were studied by following the ionic and organic composition of the solution during the hydration of the mineral mixture in suspension in saturated calcium hydroxide solutions.

The impact of the concentration of D-glucitol and D-galactitol on the precipitation rate of ettringite was found to be non-monotonic whereas D-mannitol always accelerates the formation of ettringite in the range of concentrations studied. Nevertheless, whatever the influence of these sugar alcohols on the precipitation rate of ettringite, they slow down the formation of AFm. Moreover, these organic molecules were found to complex with ions in solution and to adsorb on both ettringite and AFm but to different extent depending on their stereochemistry.

Keywords: sugar, aluminate, adsorption, complexation, hydration

III.4. Impacts des hexitols sur l'hydratation du mélange aluminat tricalcique-sulfate de calcium

1. Introduction

Ordinary Portland Cement (OPC) is composed of silicate (C_3S and C_2S), aluminate (C_3A and C_4AF) and sulfate ($CaSO_4 \cdot x H_2O$) phases. Despite the fact C_3A is the most reactive mineral phase of OPC, the hydration kinetics of OPC are governed by the hydration of the silicate phases. The rapid reaction of C_3A is regulated by the presence of sulfate phases [1] and has an important influence on the early hydration of OPC pastes. Hence, the reactivity of C_3A with sulfate phases appears as an important parameter controlling the workability of OPC pastes. When added to OPC, some water reducing admixtures such as lignosulfonates, cellulose ethers, polysaccharides, saccharides and some of their derivatives were found to retard the hydration of its silicate phases [2-8]. However, the retarding effects generated by several carbohydrates on the hydration of the silicate phases of OPC were revealed to change depending on its content of aluminate phases suggesting possible interactions of the molecules with these compounds and/or their hydrates [2-4].

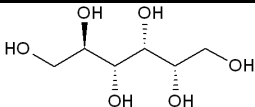
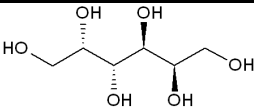
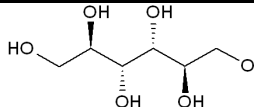
The hydration kinetics of C_3A with and without the presence of calcium sulfate phases were also observed to be affected by the presence of setting retarders. The hydration of pure C_3A resulting in the precipitation of calcium hydroaluminates was shown to be retarded by the presence of lignosulfonates, glucose, D-gluconate and cellulose ethers [9-11]. During the hydration of C_3A and calcium sulfate in saturated calcium hydroxide solutions and of C_3A in cement, the formation of ettringite was found to be accelerated by lignosulfonates but retarded by polysaccharides, cellulose ethers and glucose [10,12,13]. Hence, some setting retarders disturb the hydration of C_3A but their interactions are still not well elucidated and prevent us to control their impact on the hydration of the silicate compounds of OPC.

Some sugars were shown to have a reduced effect on the setting time of the silicate phases of OPC pastes compare to the one generated during the hydration of pure C_3S suggesting possible interactions of these molecules with aluminate phases and/or their hydrates [4]. Hence, the purpose of the present paper is to investigate the effects and interactions of hexitols which are sugar derivatives on the hydration of C_3A and calcium sulfate phases (called aluminate-sulfate mixture in this study) in presence of saturated calcium hydroxide solutions which simply mimic the pore solution composition of OPC

III.4. Impacts des hexitols sur l'hydratation du mélange aluminat tricalcique-sulfate de calcium

pastes during the hydration of its silicate phases. The organic molecules studied called D-glucitol, D-galactitol and D-mannitol are stereoisomers, see Table 1 for their structure.

Table 1: Chemical structures of the stereoisomers studied.

D-glucitol	D-galactitol	D-mannitol
		

To proceed, the influence of hexitols on the hydration kinetics of the aluminate-sulfate mixture with calcium hydroxide in paste were first assessed by isothermal calorimetry. Secondly, the impacts of these polyols on the ionic composition of aluminate-sulfate suspensions in saturated calcium hydroxide solutions were studied by conductivity and Inductively Coupled Plasma - Atomic Emission Spectroscopy. In parallel, their adsorption was investigated by Total Organic Carbon measurements and their effects on the morphology of hydrates were revealed by Scanning Electron Microscopy. Finally, the relations between the influence of the organic molecules on the hydration rate of the aluminate-sulfate mixture with calcium hydroxide, their adsorption and ionic complexation in solution are discussed.

2. Experimental procedure

2.1. Materials

The water used to prepare the pastes, suspensions and solutions was both distilled and deionised.

The molecules studied were D-glucitol ($\geq 98\%$), D-galactitol ($\geq 99\%$) and D-mannitol ($\geq 98\%$), all as a powder form (Sigma Aldrich).

The aluminate-sulfate mixture used is composed of C_3A , gypsum and hemihydrate and came from Lafarge. Its characteristics are shown in Table 2. Calcium hydroxide was obtained from Merck and was added at 1 % to the aluminate-sulfate mixture to hydrate the aluminate-sulfate mixture in saturated calcium hydroxide solutions.

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Table 2: Physical parameter and chemical compositions of the aluminate-sulfate mixture.

Specific surface area (m ² /g)	0.34 ⁺
Cubic aluminate (%)	80
Gypsum (%)	5
Hemihydrate (%)	15

⁺ Calculated from particle size distribution assuming that the density of particles is homogeneous with the size, that the particles are spherical and considering a density of 3 030 kg/m³ for the mixture.

Calcium oxide was obtained after decarbonation of calcium carbonate (98.5-100 %, VWR AnalaR NORMAPUR) at 1000 °C for 24 h. Saturated calcium hydroxide suspensions were made by adding an excess of freshly decarbonated calcium oxide in water kept at 25 °C in a thermoregulated bath during minimum a day. Finally, they were filtered to produce saturated calcium hydroxide (0.1 µm cellulose ether, Millipore filter).

2.2. Methods

2.2.1. Methods of preparation

2.2.1.a. Preparation of the pastes

10 mg of calcium hydroxide was added to 0.99 g of the aluminate-sulfate mixture in order to buffer the solution during its hydration. 1 g of the final mixture was mixed with 1 mL of aqueous solutions with and without sugar alcohols (Liquid to Solid ratio, L/S=1). These pastes were stirred for 2 min at 3200 rpm in different ampoules.

2.2.1.b. Preparation of the suspensions

The suspensions were made by adding 2.5 g of the aluminate-sulfate mixture to 250 mL of saturated calcium hydroxide solutions with different concentrations of alditols (L/S=100).

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2.2.1.c. Preparation of the samples for analysis

Some samples of the aluminate-sulfate mixture in suspension were taken over time to identify the feature of the solids and solutions. These samples were poured through a filter (0.1 μm cellulose ethers, Merck Millipore) in plastic Büchner funnels connected to a vacuum pump before the analysis of the obtained residues and filtrates.

The filtrates were analyzed to identify their concentrations of ions and organic molecules in solution. The residues left on the filter after filtering the suspensions but also the pastes used for the calorimetric experiments were dried to reveal the nature and morphology of the phases present. The solids were first washed with water-ethanol (50/50) and then with pure ethanol in Büchner funnels related to a vacuum pump in order to remove the free water present and finally evaporate the left ethanol. Sintered glass Büchner funnels were used for the pastes (Por.4, Robu or Pyrex) whereas plastic Büchner funnels were used for the suspensions to dry their residues after filtration.

2.2.2. Methods of characterization

2.2.2.a. Study of the hydration of the aluminate-sulfate mixture in paste and suspension

The hydration of the aluminate-sulfate mixture was followed by using calorimetric and conductimetric measurements of the pastes and of the suspensions respectively in presence of different concentrations of hexitols in saturated calcium hydroxide solutions.

Immediately after stirring the pastes of the aluminate-sulfate mixture with calcium hydroxide in the ampoules, the latter were capped and inserted in the isothermal calorimeter (TAM AIR) where the heat flow was monitored at 23 °C.

The continuous acquisition of the conductivity of the aluminate-sulfate suspensions hydrated in saturated calcium hydroxide solutions was made with a 856 conductivity module (Metrohm) and a XE161 conductivity electrode (Radiometer analytical). The suspensions were stirred under a continuous nitrogen gas atmosphere in thermoregulated cells at 25 °C.

2.2.2.b. Measurement of the ionic concentrations in solution

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The pH of the filtrates was measured thanks to a pH meter (Consort C931) and a Schott Instruments electrode. The concentrations of the species present in the filtrates which contain calcium, aluminium and sulfur were measured by using Inductively Coupled Plasma – Atomic Emission Spectroscopy (Vista Pro, Varian). The filtrates were acidified with a small and known amount of hydrochloric acid (37 %, Analar Normapur, VWR) before being analyzed.

2.2.2.c. Adsorption measurement of hexitols

The adsorption of the organic molecules was calculated by using the depletion method. The concentration of the remaining molecules present in the filtrates was determined by measuring their Total Organic Carbon (Shimadzu TOC analyser V_{CPN}). A small and known quantity of orthophosphoric acid (85 %, Analar Normapur, VWR) was added to the filtrates to remove the possible inorganic carbon before their analysis with the TOC device.

2.2.2.d. Identification of the mineral phases

The powders were analyzed by X-Ray Diffraction (XRD) to identify the nature of the phases present. The XRD data was recorded using a D8 Advance with a position sensitive Vantec detector ranging from 2θ equals from 3 to 80° (Bruker) and a Cu-K α radiation ($\lambda=1.54056 \text{ \AA}$).

2.2.2.e. Morphological analysis of the phases

The morphology of the phases present in the powders was identified by using the Scanning Electron Microscopy (SEM). A pinch of the dried solids was added in absolute ethanol ($\geq 99.5 \%$, Sigma Aldrich) and dispersed with an ultrasonic device. A drop of the ethanol dispersions was poured on a silicon substrate. Then, the samples were coated with 5 nm of carbon. Finally, the images of the powders were taken with a JEOL JSM-7600F Field Emission Gun - Scanning Electron Microscope (FEG-SEM).

3. Results

III.4. Impacts des hexitols sur l'hydratation du mélange aluminat tricalcique-sulfate de calcium

3.1. Effects of hexitols on the hydration of the aluminate-sulfate mixture in paste

The calorimetric curves obtained during the hydration of the aluminate-sulfate mixture with calcium hydroxide in presence of different concentrations of polyols are shown in Figure 1. The concentrations of the organic molecules were varied from 0 to maximum 75 mmol/L depending on the hexitols in order to be able to identify and compare their effects on the different periods of the hydration of the aluminate-sulfate mixture in paste.

The first exothermic peak of heat flow observed during the first hour of hydration for the reference sample in Figure 1 points out the dissolution of the anhydrous compounds which leads to the precipitation of calcium sulfo-aluminates. At 1 h of hydration, XRD characterizations of the dried pastes revealed the presence of C_3A , gypsum and ettringite, a calcium aluminate trisulfate (AFt phase). The second exothermic peak indicates the dissolution of C_3A when ettringite stops precipitating [1]. The following period is characterized by the formation of monosulfate and calcium hydroaluminates (AFm phases) which were observed by XRD at 47 h of hydration. D-galactitol and D-glucitol lead to similar effects on the hydration of the aluminate-sulfate mixture with calcium hydroxide whereas D-mannitol has a different impact as a function of its concentration, Figure 1. Therefore, the influence of D-galactitol and D-glucitol will be discussed simultaneously depending on their range of concentrations whereas the one of D-mannitol will be described separately.

- Up to 30 mmol/L of D-galactitol and D-glucitol, Figure 1:

These two polyols delay the time of occurrence of the second exothermic peak of heat flow up to 30 mmol/L. This effect is more pronounced in presence of D-glucitol. Hence, it suggests that D-galactitol and more particularly D-glucitol slow down the precipitation of ettringite in this range of concentrations. These sugar alcohols also reduce the intensity of the second peak of heat flow with increasing concentrations in solution revealing that the maximum hydration rate of C_3A is reduced by their presence. Moreover, a third exothermic peak with a lower intensity than the second one appears from 20.25 mmol/L of D-galactitol and from 30 mmol/L of D-glucitol. It points out a phenomenon resulting in the massive formation of AFm. For the reference sample, the third peak is not observed probably

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because the second and third peaks are so close together that they can not be distinguished. It can also be noticed that the time of occurrence of this third peak in presence of D-galactitol and D-glucitol is retarded with increasing concentrations of these organic molecules compare to the time of occurrence of the second peak. This effect is stronger in presence of D-galactitol than with D-glucitol in solution. Hence, these molecules and in particular D-galactitol also slow down the precipitation of AFm.

Finally, in this range of concentrations, D-glucitol especially slows down the formation of ettringite compare to D-galactitol whereas for the precipitation of AFm, the contrary is observed.

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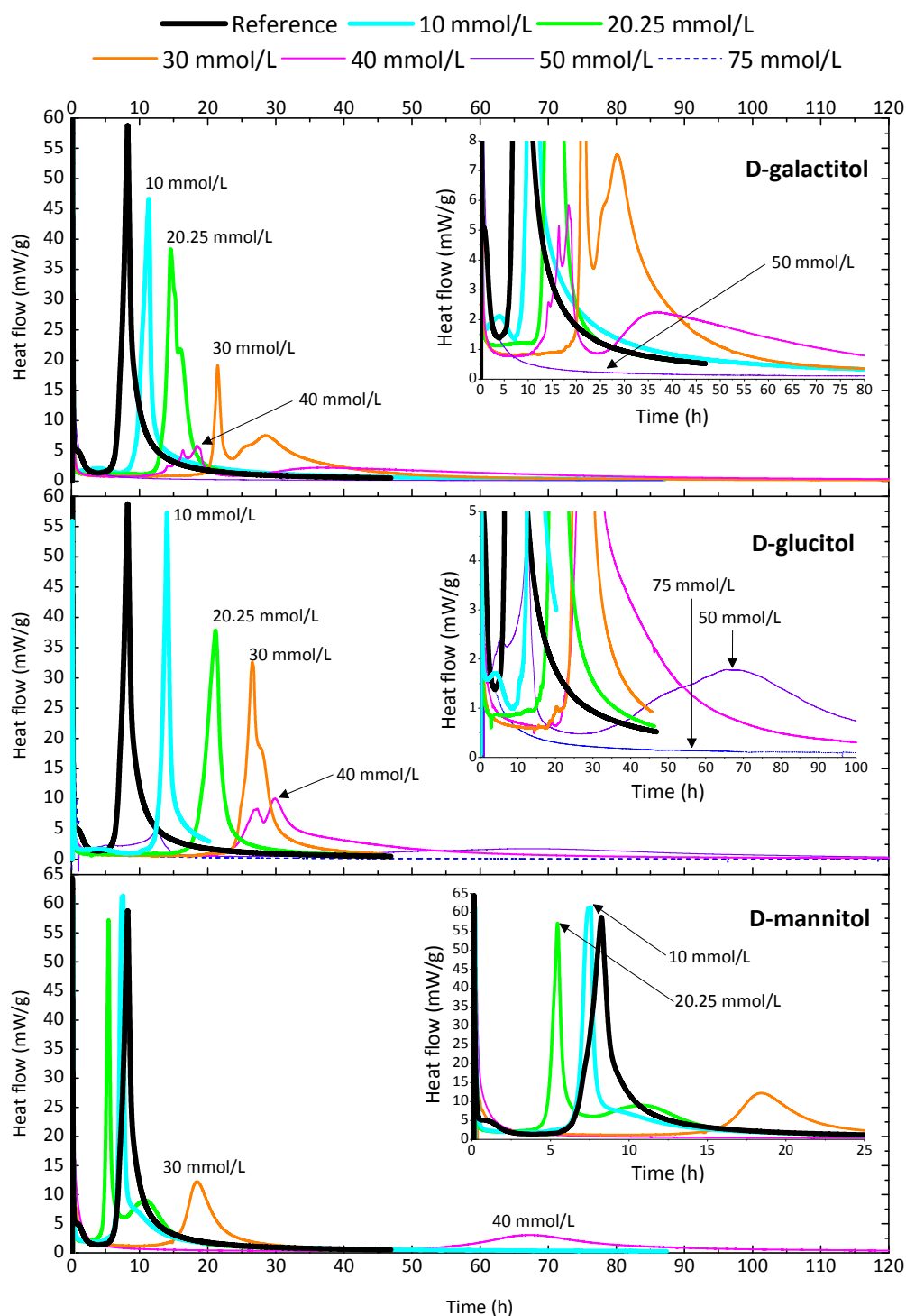


Figure 1: Hydration of the aluminat-sulfate mixture with calcium hydroxide in presence of different concentrations of hexitols followed by calorimetric measurements, L/S=1.

III.4. Impacts des hexitols sur l'hydratation du mélange aluminat tricalcique-sulfate de calcium

- Above 30 mmol/L of D-galactitol and D-glucitol, Figure 1:

The time of occurrence and the intensity of the second peak of heat flow are strongly reduced in presence of concentrations of these two hexitols above 30 mmol/L compare to the ones induced at lower concentrations. As far as the third exothermic peak of heat flow is concerned, its time of occurrence is extensively increased by the presence of the sugar alcohols compare to the time of occurrence of the second peak above 30 mmol/L of molecules. With 50 mmol/L of D-galactitol and 75 mmol/L of D-glucitol, no second and third peaks are identified on the calorimetric curves until 80 h. XRD diffractograms of the dried pastes revealed that at 1 h of hydration, there were less gypsum and more ettringite in the pastes with these concentrations of alditols than without (not shown). This result means that they strongly accelerate the formation of ettringite for these concentrations.

Hence, the formation of ettringite is less slowed down and even accelerated by this range of concentrations of D-galactitol and D-glucitol. However, the formation of AFm is particularly slowed down by the two organic compounds. In these conditions, D-galactitol especially reduces the time needed to precipitate ettringite and slows down the formation of AFm in regards to D-glucitol.

- Up to 40 mmol/L of D-mannitol, Figure 1:

As can be seen up to 20.25 mmol/L of D-mannitol, an increasing concentration of this molecule reduces the time needed to reach the second exothermic peak of heat flow. For 30 mmol/L of D-mannitol and above, this second peak is not even identified on the calorimetric curves. In fact, as for D-galactitol (50 mmol/L) and D-glucitol (75 mmol/L), XRD diffractograms of the dried pastes showed that at 1 h of hydration, there were less gypsum and more ettringite in the paste with 30 mmol/L of D-mannitol than in the reference sample (not shown). Hence, this molecule also accelerates the formation of ettringite. Moreover, D-mannitol extends the time required to reach the third exothermic peak of heat flow when increasing its concentrations: the formation of AFm is also slowed down by this polyol.

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To sum up, D-galactitol and D-glucitol slow down the precipitation of ettringite up to 30 mmol/L whereas above this concentration its formation is less retarded and even accelerated. D-mannitol is the strongest accelerator of the precipitation of ettringite up to the maximum concentration studied for this molecule (40 mmol/L). Whatever the hexitols studied, their presence slows down the precipitation of AFm. These modifications of the hydration rate of the aluminate-sulfate mixture might result from an effect of these organic molecules on the dissolution of the anhydrous phases and/or on the precipitation of the hydrates.

3.2. Impacts of alditols on the ionic composition of the aluminate-sulfate mixture in suspension

3.2.1. Effects of increasing concentrations of D-mannitol

The evolution of the conductivity, pH and ionic concentrations of the aluminate-sulfate mixture in saturated calcium hydroxide solutions are shown in Figure 2 in presence of different concentrations of D-mannitol (0, 0.50, 0.75 and 1 mmol/L). These concentrations of D-mannitol were chosen to distinguish the impact of the molecules on the different steps of the hydration of the aluminate-sulfate mixture in suspension during a day.

For the reference sample, during the first minutes of hydration, the conductivity increases due to the release of calcium, aluminate, sulfate and hydroxide ions resulting from the dissolution of the anhydrous phases. Then, a plateau of conductivity occurs due to a constant pH and calcium concentration while the concentration of sulfate ions decreases. Due to the diluted system used ($L/S=100$), the solution is under-saturated with respect to gypsum so the precipitation of aluminate hydrates consumes sulfate ions present in solution and then lowers down their concentration. C_3A and ettringite were observed at 1 h of hydration by XRD of the dried suspension (not shown). At 4 h 30, no sulfate ion is observed in solution and a narrow peak of conductivity is identified revealing a fast dissolution of C_3A . After this peak, the conductivity decreases indicating that there is no more solid reservoir of C_3A in suspension and that the further hydrates precipitate by consuming the left ions present in solution. Finally, the conductivity keeps constant when the solution reaches the solubility of the hydrates.

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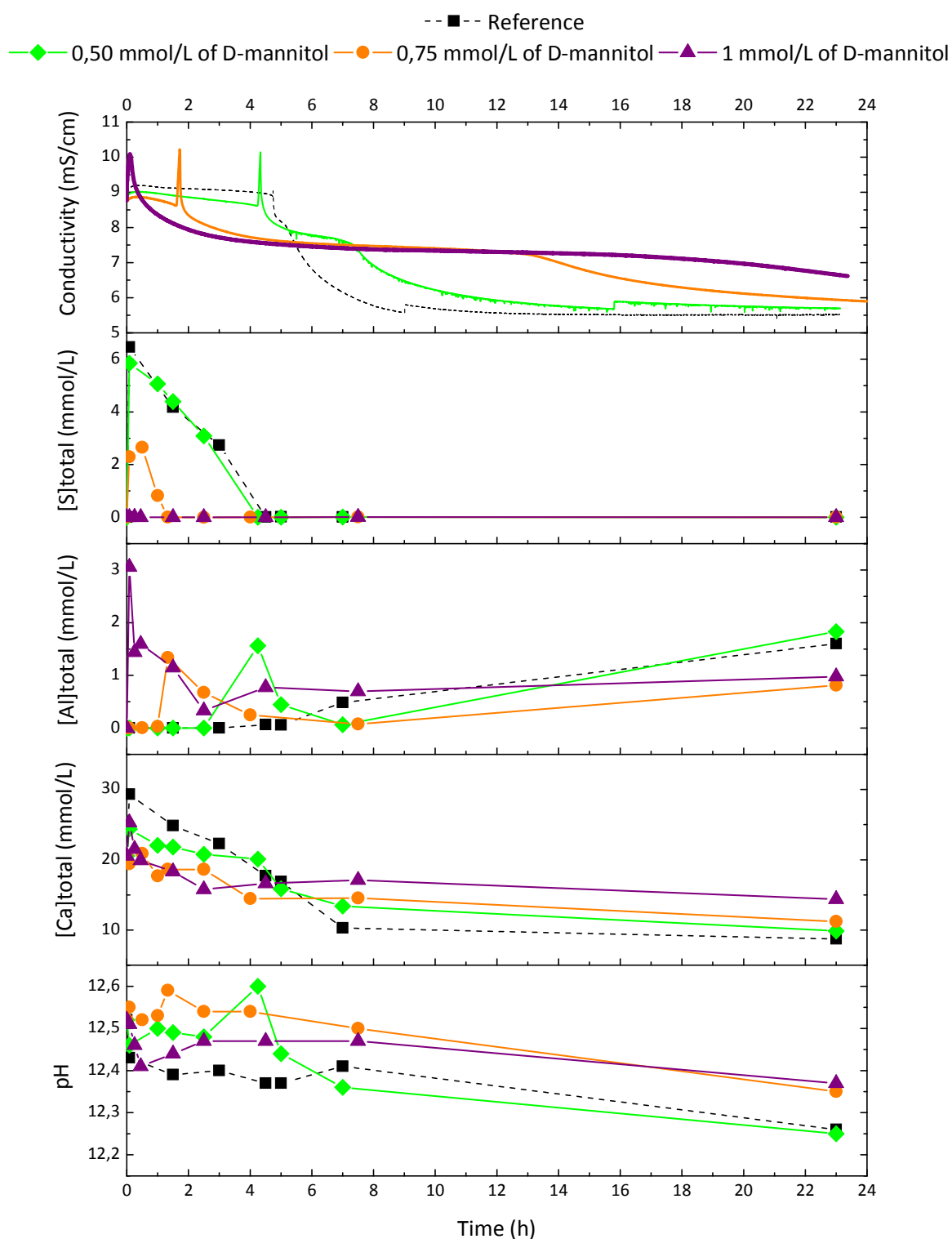


Figure 2: Evolution of the conductivity, pH and ionic concentrations of the aluminate-sulfate suspensions in presence of different concentrations of D-mannitol, $[\text{Ca}(\text{OH})_2]=22$ mmol/L and $\text{L/S}=100$. Lines are only guides for the eyes.

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In presence of D-mannitol, one can observe in Figure 2 that the time of occurrence of the exhaustion of sulfate ions and so of the peak of conductivity caused by the dissolution of C_3A is reduced with increasing concentrations of the polyol. Hence, D-mannitol accelerates the consumption of sulfate ions in solution and so, the formation of ettringite as observed in paste (Figure 1). Moreover, the intensity of the peaks of conductivity and their corresponding concentrations of aluminate, calcium and hydroxide ions are also more important with D-mannitol than without. Hence, this alditol enhances the dissolution of C_3A . One can also realize that in presence of D-mannitol the peaks of conductivity are larger than the one distinguished in the reference sample meaning that the precipitation of AFm is impeded. After the exhaustion of sulfate ions in solution, D-mannitol slows down the decrease of the conductivity: a plateau occurs in this part of the conductimetric curve whereas it is slightly observable for the reference sample. This plateau of conductivity is particularly lengthened with increasing concentrations of D-mannitol meaning that the precipitation of AFm is slowed down. Then, the conductivity finally drops and reaches a final plateau at the end of the hydration of the mixture.

3.2.2. Influence of the stereochemistry of hexitols

The conductimetric studies made during the hydration of the aluminate-sulfate mixture in saturated calcium hydroxide solutions are exposed in Figure 3 in presence of the different hexitols at 0.75 mmol/L.

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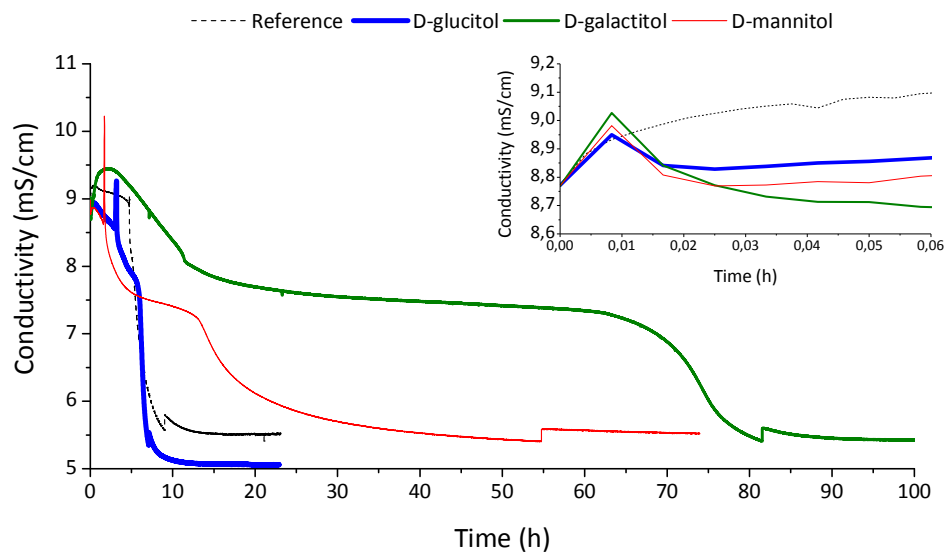


Figure 3 : Conductivity measurements over time of the aluminate-sulfate suspensions with hexitols (0.75 mmol/L), $[Ca(OH)_2]=22$ mmol/L and L/S=100.

During the first minutes of hydration (see the zoomed view in Figure 3), the conductivity increases due to the dissolution of the anhydrous phases and suddenly decreases in presence of the polyols whereas for the reference sample it keeps increasing. This drop of conductivity is particularly enhanced in presence of D-galactitol followed by D-mannitol and then by D-glucitol. It suggests that the dissolution of the anhydrous phases is slowed down and/or that the precipitation rate of hydrates is increased and that, depending on the sugar alcohol.

Later on, one can observe that hexitols generate different effects on the hydration of the aluminate-sulfate mixture and especially D-galactitol, Figure 3. D-glucitol and D-mannitol affect the time of occurrence of the peak of conductivity revealing the fast dissolution of C_3A in solution whereas in presence of D-galactitol an initial bump of conductivity which lasts approximately 11 h is identified. These peaks of conductivity occur at 1 h 40 for D-mannitol and at 3 h for D-glucitol whereas it occurs at 4 h 30 for the reference sample. Consequently, D-glucitol also accelerates the precipitation of ettringite but D-mannitol is the best accelerator at this concentration. D-glucitol increases the intensity of this peak of conductivity but to a lower extent than D-mannitol. The former seems to have a lower accelerating effect on the dissolution of C_3A than the latter. After these peaks of conductivity observed in presence of D-glucitol and D-mannitol and after the bump of conductivity identified with D-galactitol, a drop of the conductivity is observed in presence of the

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different organic molecules. This period is followed by a plateau of conductivity with different lengths depending on the hexitols present in solution (D-galactitol > D-mannitol > D-glucitol > Reference) and finally the conductivity decreases until the end of the reaction. Consequently, these sugar alcohols slow down the formation of AFm but differently depending on the stereochemistry of their hydroxyl groups.

The effect of D-galactitol at 0.75 mmol/L on the ionic composition of the aluminate-sulfate suspension is detailed in Figure 4. The strong increase of the conductivity generated by its addition can be related to important concentrations of calcium, aluminate and hydroxide ions compare to the ones found in the reference sample up to 11 h of hydration. The dissolution of the anhydrous phases is then particularly favoured by D-galactitol. Moreover, from 30 min (the first point measured) to 23 h of hydration, there is no sulfate in solution. At 1 h of hydration, C₃A and ettringite were revealed on the XRD characterization of the dried suspension (not shown). It means that at that time, ettringite has completely precipitated whereas this hydrate stops forming at 4 h 30 for the reference. Consequently, D-galactitol accelerates the formation of ettringite and its accelerating effect is even more important than the one of D-mannitol in the conditions of the study.

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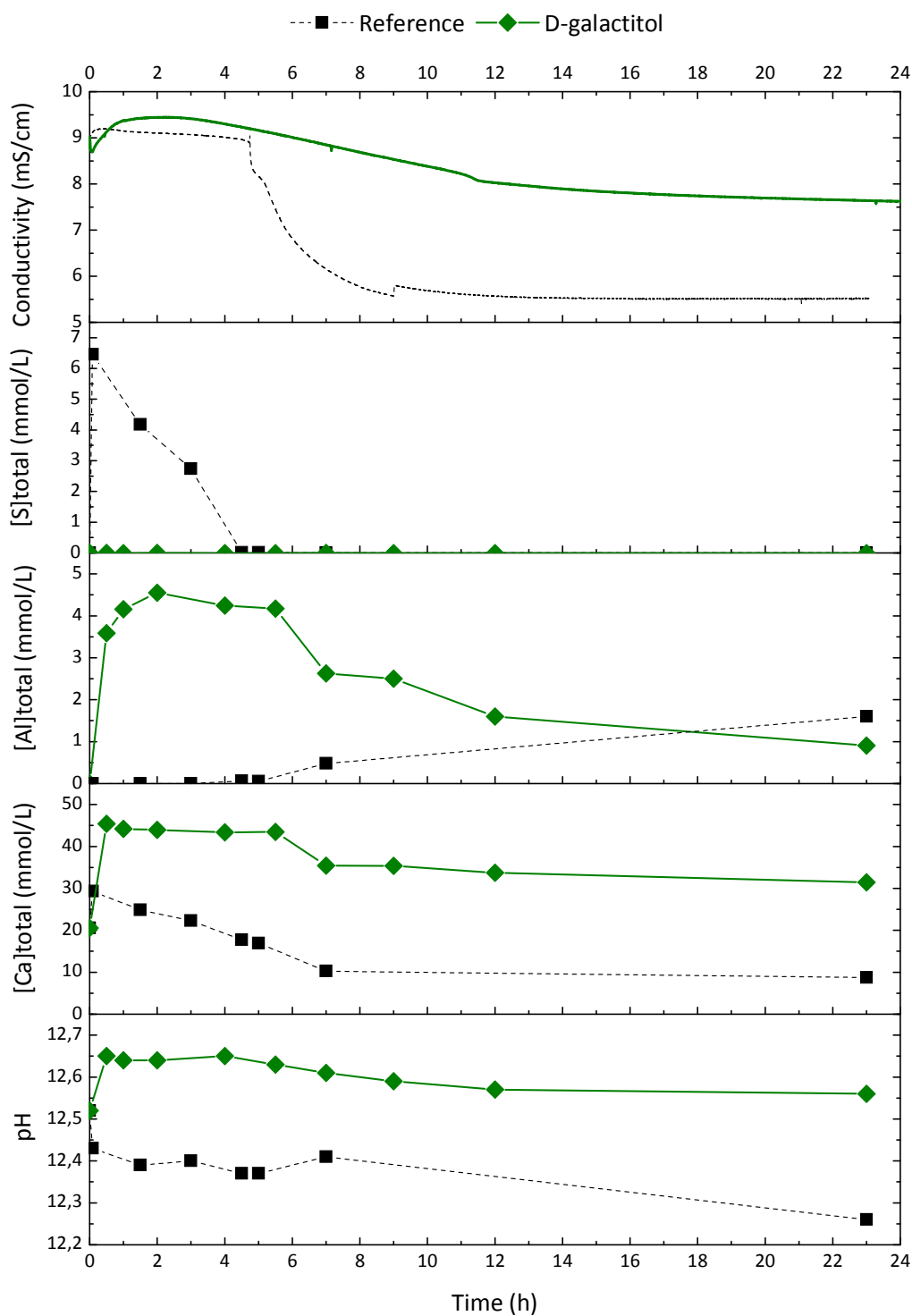


Figure 4: Evolution of the conductivity and of the ionic concentrations during the hydration of the aluminat-sulfate suspensions with and without D-galactitol (0.75 mmol/L), $[\text{Ca}(\text{OH})_2]=22$ mmol/L and $L/S=100$. Lines are only guides for the eyes.

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3.3. Adsorption of hexitols during the hydration of the aluminate-sulfate mixture in suspension

The evolution of the conductivity and of the adsorbed content of hexitols during the hydration of the aluminate-sulfate mixture in saturated calcium hydroxide solutions is presented in Figure 5. The adsorption of polyols on the hydrating aluminate-sulfate mixture is noticed to increase over time. Given that hexitols were shown to accelerate the dissolution of C_3A , it can be assumed that there is a low or no adsorption of the molecules on the anhydrous phase limiting its dissolution. Consequently, these organic molecules are supposed to be particularly consumed by the aluminate-sulfate hydrates.

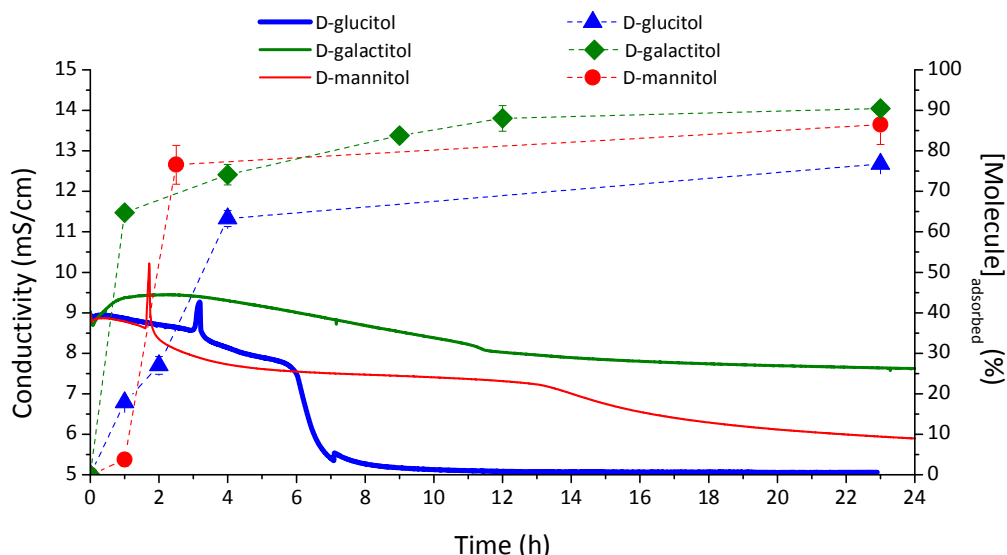


Figure 5: Evolution of the conductivity of the aluminate-sulfate suspensions in presence of hexitols (0.75 mmol/L) and of the adsorbed amount of the molecules depending on the time, $[Ca(OH)_2]=22$ mmol/L and $L/S=100$. Dash lines are only guides for the eyes.

At 1 h of hydration, there is 4 % of D-mannitol and 18 % of D-glucitol adsorbed on the hydrating aluminate-sulfate mixture. Moreover, the adsorption of D-glucitol increases during the precipitation of ettringite and reaches 29 % after 2 h of hydration. Given that D-mannitol accelerates more the precipitation of ettringite than D-glucitol, at 1 h of hydration there is more ettringite in the system with D-mannitol whereas it is the less adsorbing molecule. It can be concluded that D-glucitol adsorbs more on ettringite than D-mannitol. For D-galactitol, at 1 h of hydration there is 65 % of the molecules adsorbed on the hydrates of the aluminate-sulfate mixture. At that time of hydration, ettringite and AFm were

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identified by XRD in the dried suspension. Due to the presence of different hydrates, the decrease of the concentration of D-galactitol in the suspension can not be attributed to the adsorption of the molecule on a specific hydrate. At the end of the hydration, when all the AFm have precipitated, there is approximately 91 % of D-mannitol and D-galactitol adsorbed whereas there is 77 % of D-glucitol adsorbed on hydrates (not shown). However, D-mannitol adsorbs less on ettringite than D-glucitol, so it can be deduced from the final adsorptions that D-mannitol adsorbs more on AFm than D-glucitol.

3.4. Impacts of sugar alcohols on the morphology of aluminate-sulfate hydrates

SEM images of the aluminate-sulfate mixture at 1 h of hydration in saturated calcium hydroxide solutions and at the end of the hydration were performed, Figure 6. At 1 h of hydration, ettringite needles are mainly observed, Figure 6-a. They are more elongated and thinner in presence of the strongest accelerators of the precipitation of ettringite that are D-galactitol and D-mannitol than the ones which are formed in presence of D-glucitol and in the reference sample. At the end of the hydration of the aluminate-sulfate mixture, Figure 6-b indicates that there are fluffy AFm in presence of D-mannitol whereas with D-galactitol, D-glucitol and for the reference sample, they are flat but with different shapes. In the reference sample, AFm have the known hexagonal shape whereas the ones formed in presence of D-galactitol have a disc shape: it seems that the original hexagonal crystals get bend angles. The presence of D-glucitol generates AFm with a triangular shape: one can suggest that every other angle of the original hexagonal crystals was eliminated.

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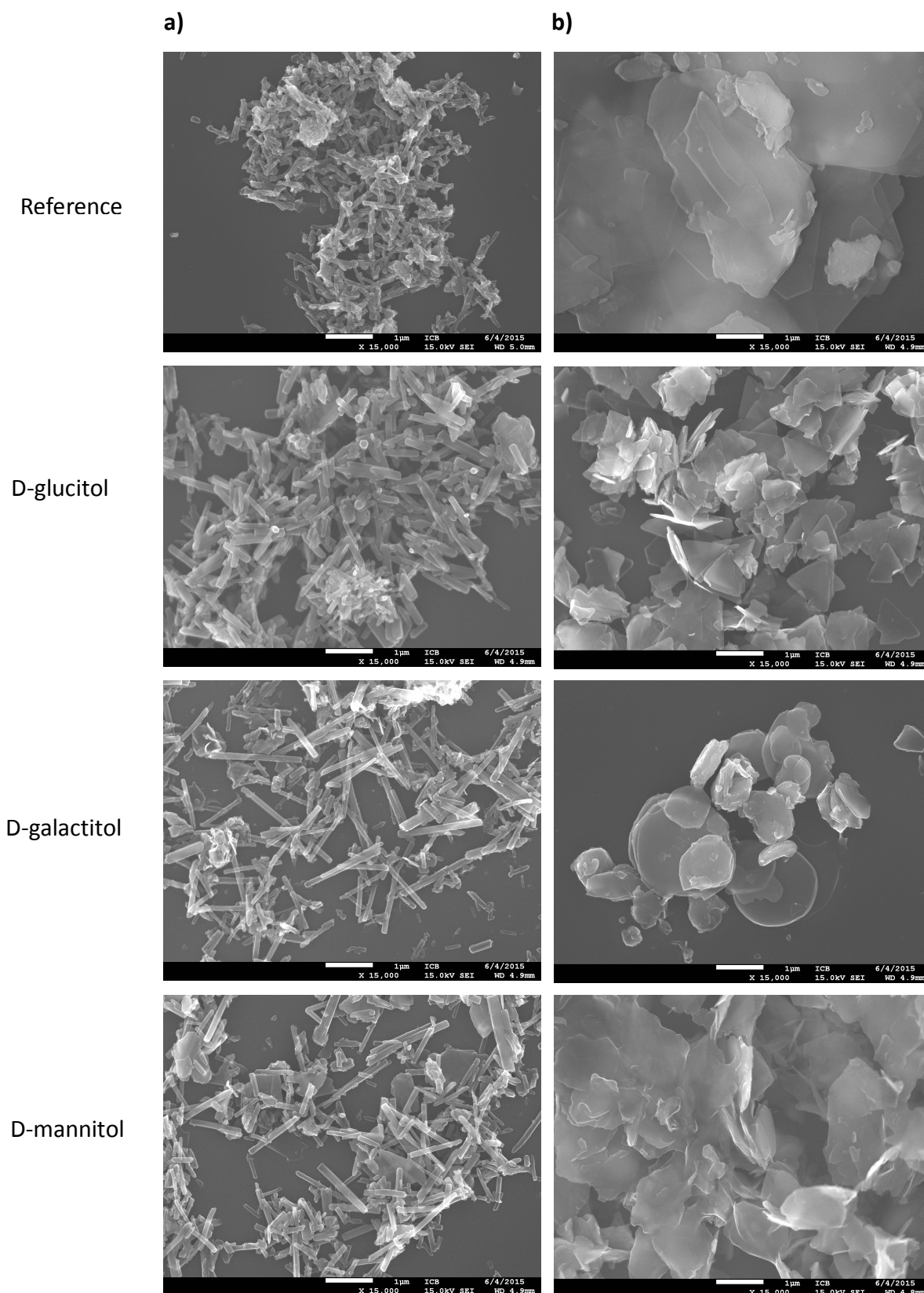


Figure 6: SEM images of the dried suspensions of the aluminate-sulfate mixture in saturated calcium hydroxide solutions with hexitols (0.75 mmol/L) at a) 1 h of hydration and b) the end of hydration.

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4. Discussion

The retarding and accelerating effects of hexitols on the precipitation of ettringite are compared in Table 3 depending on their concentration and on their corresponding weight % in paste and in suspension.

Table 3: Comparison of the effects of hexitols on the precipitation rate of ettringite during the hydration of the aluminate-sulfate mixture in suspension and in paste (R stands for the retarding effect generated by the organic molecules on the precipitation of ettringite and A for their accelerating effect).

	Paste						Suspension
Concentration (mmol/L)	10	20.25	30	40	50	75	0.75
L/S	1	1	1	1	1	1	100
weight %	0.18	0.37	0.55	0.73	0.91	1.37	1.37
D-glucitol	R	R	R	R	R	A	A
D-galactitol	R	R	R	R	R	A	A
D-mannitol	A	A	A	A	A	A	A

Whatever the weight % of the alditols studied, D-mannitol was found to accelerate the precipitation of ettringite when hydrating the aluminate-sulfate mixture, Table 3. Below 1.37 weight % of molecules, D-glucitol and D-galactitol were shown to slow down the precipitation of ettringite whereas at 1.37 weight % of molecules, they have an accelerating effect on its precipitation. Therefore, the impacts of D-glucitol and D-galactitol on the precipitation rate of ettringite are non-monotonic depending on their concentrations in solution. Moreover, it can be noticed that hexitols accelerate the precipitation of ettringite at 1.37 weight % of molecules when hydrating the mixture in paste and in suspension whereas the concentration of organic molecules in the former is 100 times more important than the one of the latter. This result suggests that in presence of a high amount of hexitols in solution, the concentration of the organic molecules does not govern the enhancement of the precipitation rate of ettringite but that the number of molecules present in solution with respect to the amount of solid might play a role. The interactions of hexitols in solution might be at the origin of their accelerating effect on the precipitation of ettringite.

In fact, it was shown that D-mannitol and D-glucitol increase the dissolution rate of C_3A after the exhaustion of sulfate ions during the hydration of the aluminate-sulfate mixture in suspension. It might be enhanced by a complexation between the organic

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molecules and some ions in solution which would low down the under-saturation with respect to C_3A . Indeed, hexitols are known to complex with calcium and hydroxide ions [14] but also with aluminate ions in solution [15]. It was also revealed that D-mannitol affects more the dissolution rate of C_3A and the precipitation rate of ettringite than D-glucitol. Finally, the accelerating effect of these organic molecules on the precipitation of ettringite might be related to their increase of the dissolution rate of C_3A .

On top of that, D-glucitol was shown to have a higher adsorption on ettringite than D-mannitol. On the other hand, D-mannitol was revealed to be particularly adsorbed on AFm and to especially impede their formation compare to D-glucitol. Finally, the amount of organic molecules which is not adsorbed on ettringite is assumed to be able to slow down the next hydration: the precipitation of AFm. The adsorption of hexitols on specific sites of AFm may explain their impacts on the morphology of these hydrates observed in this study.

Concerning the retarding and accelerating effects of D-glucitol and D-galactitol on the precipitation of ettringite, they might be explained by two interactions of the molecules which would be in competition: the adsorption of the molecules on ettringite and their ionic complexation in solution. However, due to the adsorption of the molecules on hydrates which occurs simultaneously with their complexation with ions in solution, it prevents any useful conclusions being drawn on their respective effect on the hydration of the aluminate-sulfate mixture with calcium hydroxide. To avoid the kinetic effects, the adsorption of hexitols on hydrates and their ionic complexation should be studied in systems at equilibrium. The impact of these hexitols on the super-saturation with respect to ettringite and on the under-saturation with respect to C_3A could also be investigated more in details. The difficulty being the identification of the different complexes formed in solution and their corresponding formation constant which are necessary to calculate the super and under-saturation degrees with respect to the hydrated and anhydrous phases respectively.

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5. Conclusions

Hexitols modify the hydration of the aluminate-sulfate mixture with calcium hydroxide but affect differently the formation of ettringite and AFm depending on the stereochemistry of their hydroxyl groups. The effects of D-glucitol and D-galactitol on the precipitation of ettringite are non-monotonic: they slow down the formation of this hydrate until a respective threshold concentration and then accelerate it whereas D-mannitol always accelerates its formation in the conditions of the study. Whatever the effect of these organic molecules on the precipitation of ettringite, the formation of AFm is slowed down.

These alditols form complexes in solution and adsorb on the hydrates (ettringite and AFm) but differently depending on their stereochemistry. These interactions might be at the origin of their slowing down and accelerating effects on the precipitation of ettringite. The precipitation rate of AFm which is decreased was related to the adsorption of the organic compounds on this hydrate. This adsorption possibly explains the morphological changes of AFm.

Acknowledgements

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III.5. Pouvoir retardateur des hexitols sur l'hydratation des phases silicates du ciment : interaction avec les phases aluminate et sulfate

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

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Abstract

The interactions of retarding organic molecules with the silicate, aluminate and sulfate phases of Ordinary Portland Cement are still not well identified and understood. Hence, 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.

Keywords: adsorption, aluminate, cement, complexation, retardation, stereochemistry

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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.

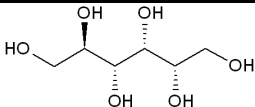
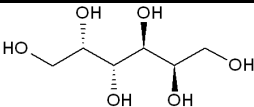
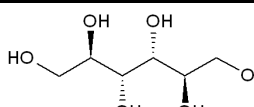
The retarding effect generated by several polysaccharides (dextrin, starch) and saccharides derivatives (D-gluconate, D-glucitol) on the hydration of OPC were reported to be sensitive to its composition and particularly to its aluminate content [1,4,8]. Several setting retarders were also shown to be adsorbed on aluminate hydrates [1,10,11]. 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

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on the hydration of pure C_3S already studied in a previous paper [9] 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.

Table 1: Chemical structures of the molecules studied.

D-glucitol	D-galactitol	D-mannitol
		

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 studied were D-glucitol ($\geq 98\%$), D-galactitol ($\geq 99\%$) and D-mannitol ($\geq 98\%$) 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 the study, the C_3A -gypsum-hemihydrate

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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 % without changing the sulfate ratio.

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
Mono. alite (%)	66.1	-	-
Tric. alite (%)	0.0	100.0	-
Belite (%)	24.2	-	-
Ferrite (%)	0.4	-	-
Cub. aluminate (%)	2.0	-	80.0
Ortho. aluminate (%)	0.7	-	-
Lime (%)	0.3	-	-
Gypsum (%)	0.2	-	5.0
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 : 3 210 kg/m^3 and C_3A : 3 030 kg/m^3).

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).

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

2.2.1.a. Definition of the retardation generated by hexitols on the hydration of C_3S and cement

Figure 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) compare to their respective reference without additive as can be seen for D-glucitol, Figure 1. However, the molecules lengthen the induction period during the hydration of C_3S and cement pastes

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compare 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 Figure 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.

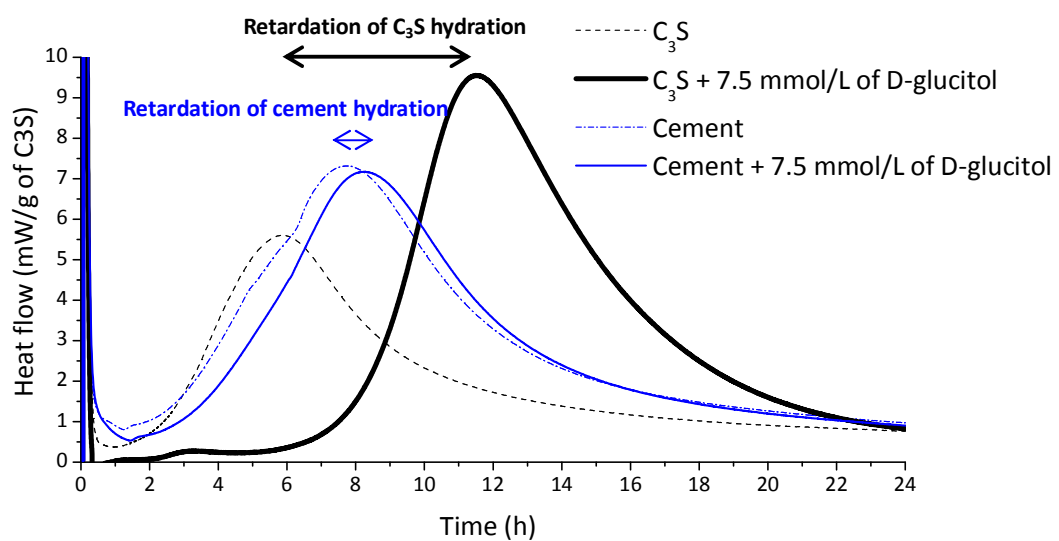


Figure 1: Calorimetric curves monitored during the hydration of C_3S and cement pastes with and without D-glucitol (7.5 mmol/L), L/S=0.4.

2.2.1.b. Definition of the time ending the induction period when hydrating cement with different C_3A contents with and without alditols

Figure 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 equals to the one found at the intersection between the slope of the calorimetric curve during the acceleration period and the x-axis as shown in Figure 2. Using this method, the concentration of the

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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 %.

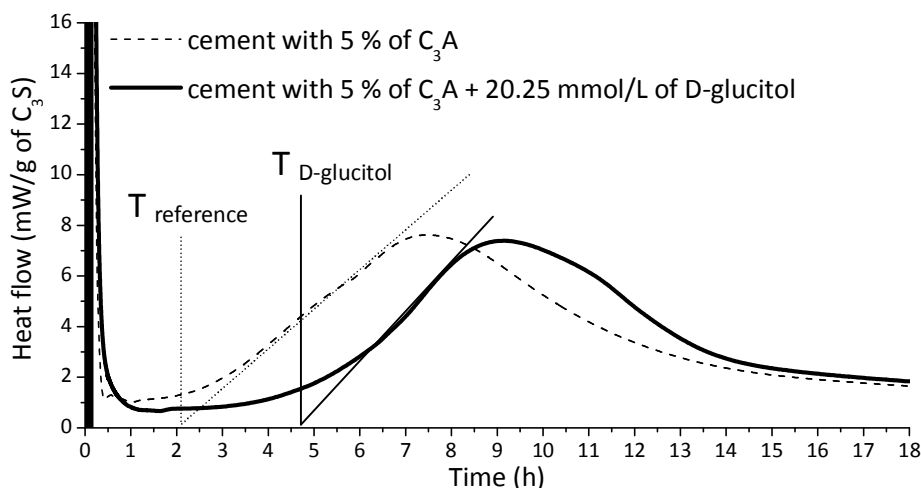


Figure 2: Calorimetric curves obtained during the hydration of cement with 5 % of C_3A , with and without the presence of D-glucitol (20.3 mmol/L), $L/S=0.4$.

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}).

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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.

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 μ m 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 Figure 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, Figure 3. In contrast, the retarding effect induced by these organics on the hydration of the silicate phases of cement starts to be strongly enhanced

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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 compare 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].

It can also be observed in Figure 3 that D-glucitol is the most retarding organic molecule in both C_3S and cement pastes compare 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.

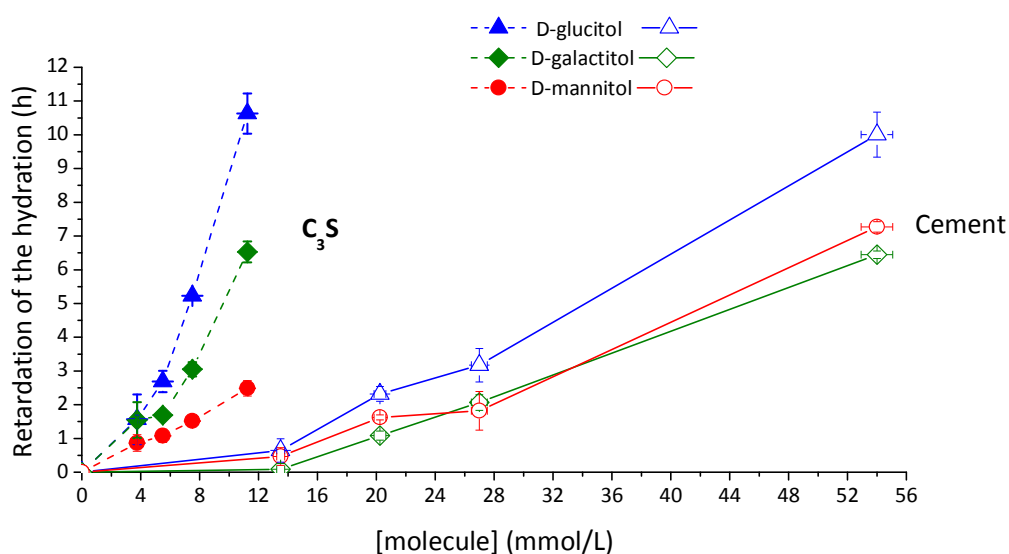


Figure 3: Retarding effects caused by hexitols on the hydration of the silicate phases of cement and of C_3S depending on the concentrations of the organic molecules, L/S =0.4.

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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 Figure 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, Figure 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.

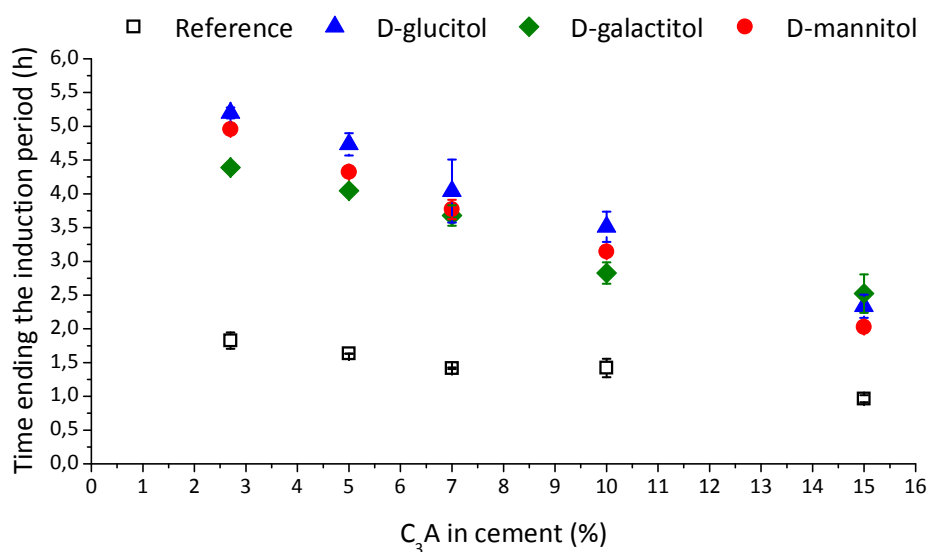


Figure 4: Evolution of the time ending the induction period from the calorimetric curves as a function of the percentage of C_3A in white cement pastes with and without hexitols (20.3 mmol/L), L/S=0.4.

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3.3. Adsorption of hexitols on hydrating cement

Figure 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. The value of the adsorption corresponds to the amount of molecules adsorbed 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 Figure 5 indicates that there are different adsorption behaviors depending on the stereochemistry of the hydroxyl groups carried by hexitols. The adsorption 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 adsorption 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, Figure 5. Hence, D-glucitol has the most important affinity with the anhydrous and/or hydrated component(s) of white cement compare to the two other polyols.

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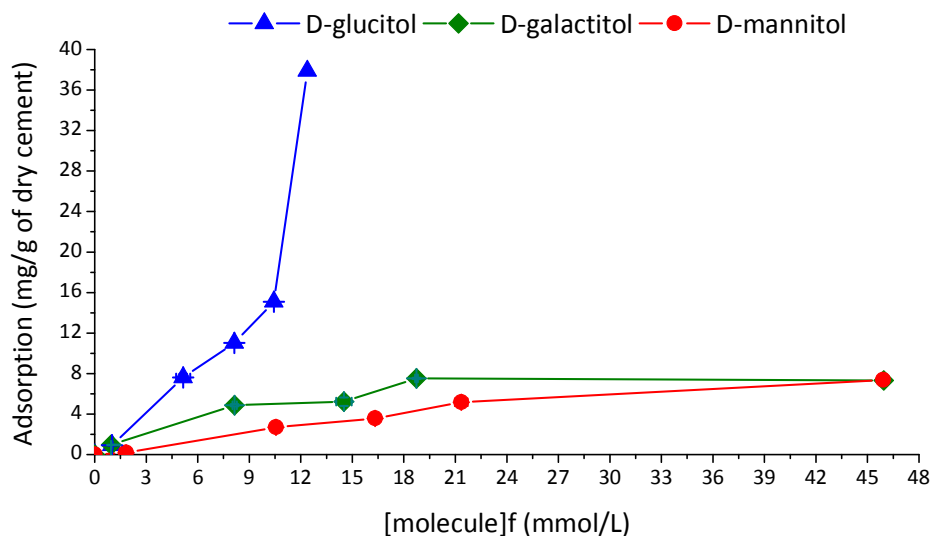


Figure 5: Pseudo adsorption isotherm of sugar alcohols on hydrating white cement during the induction period, $[\text{Ca}(\text{OH})_2]=22 \text{ mmol/L}$ and $\text{L/S}=5$.

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 mmol/L) in saturated lime solutions is presented in Figure 6 depending on the time.

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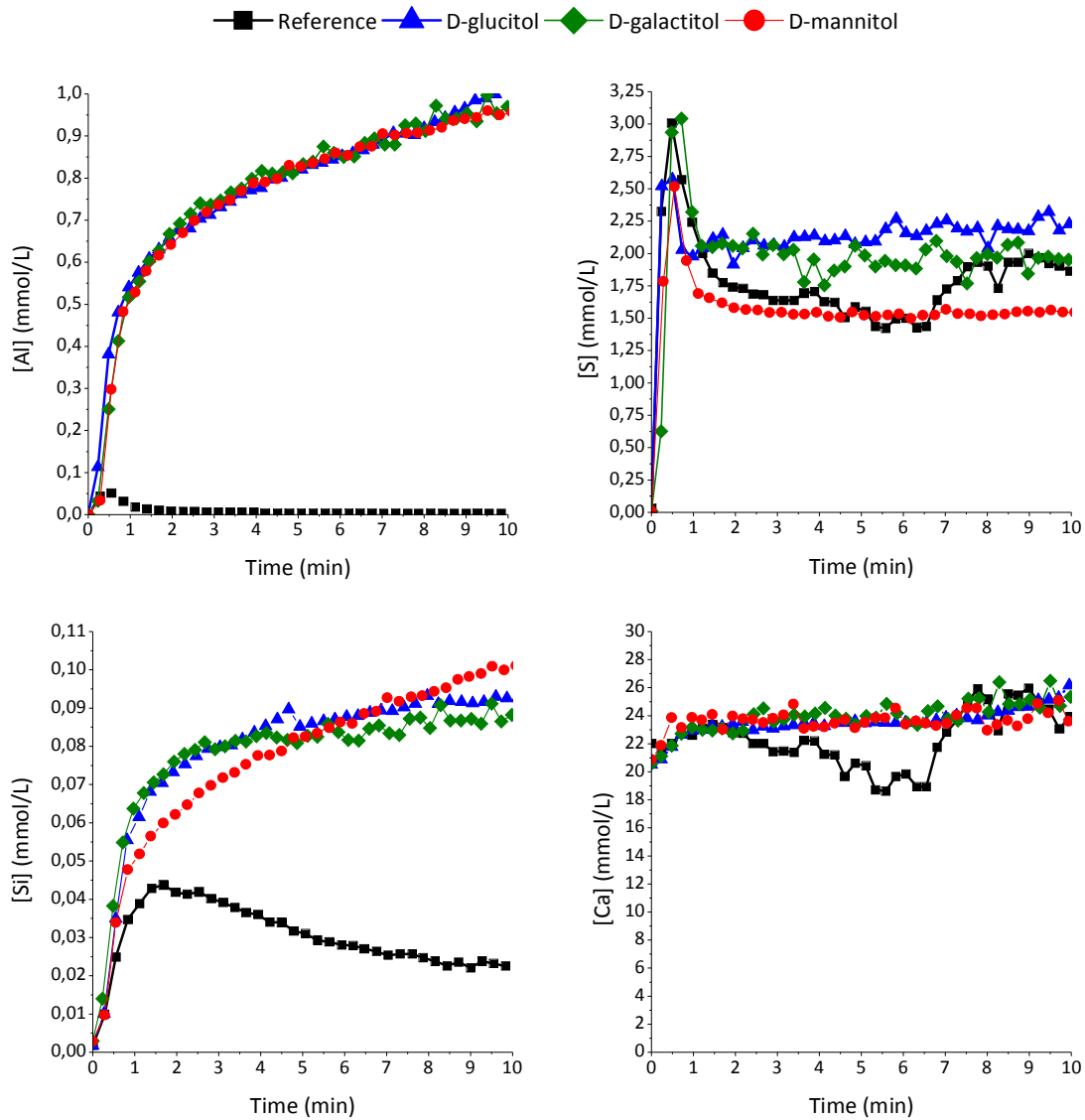


Figure 6: Evolution of the ionic concentrations during the hydration of white cement suspensions with and without hexitols (20.3 mmol/L), $[\text{Ca}(\text{OH})_2]=22$ mmol/L and $\text{L/S}=100$.

For the reference sample without additive, the concentrations of aluminate and sulfate ions reach their maximum at 30 sec of hydration revealing the precipitation of ettringite when the ionic composition of the solution reaches the critic super-saturation with respect to the hydrate, Figure 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 keeps pretty much constant up to 10 min of hydration: a stationary state is

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established. The presence of the sugar alcohols studied increases similarly the concentrations of aluminate ions over time which reach 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.

Finally, this study points out that hexitols strongly enhance the concentration of aluminate ions during the hydration of cement in suspension compare 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 in the cement suspensions, Figure 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 [11-13].

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 cement suspension without additive and then decreases due to the nucleation and growth of C-S-H, Figure 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 increase. For the cement suspension with D-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.

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3.4.2. Comparison of the concentrations of silicates present in cement and C_3S suspensions in presence of hexitols

The evolution of the concentration of silicate ions during the hydration of pure C_3S and cement in suspension with and without sugar alcohols are compared in Figure 7. For C_3S 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 D-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 C_3S suspensions with and without hexitols (not shown). The important concentration of silicate ions observed with D-galactitol in the C_3S 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 D-mannitol and D-glucitol.

After the maximum concentrations of silicates are reached in the C_3S suspensions, the one of the reference sample starts decreasing whereas it keeps constant in presence of D-glucitol, Figure 7. In presence of D-mannitol and D-galactitol, it barely decreases. Given that the concentrations of silicates do 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 C_3S than during the hydration of the silicate phases of cement, Figure 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.

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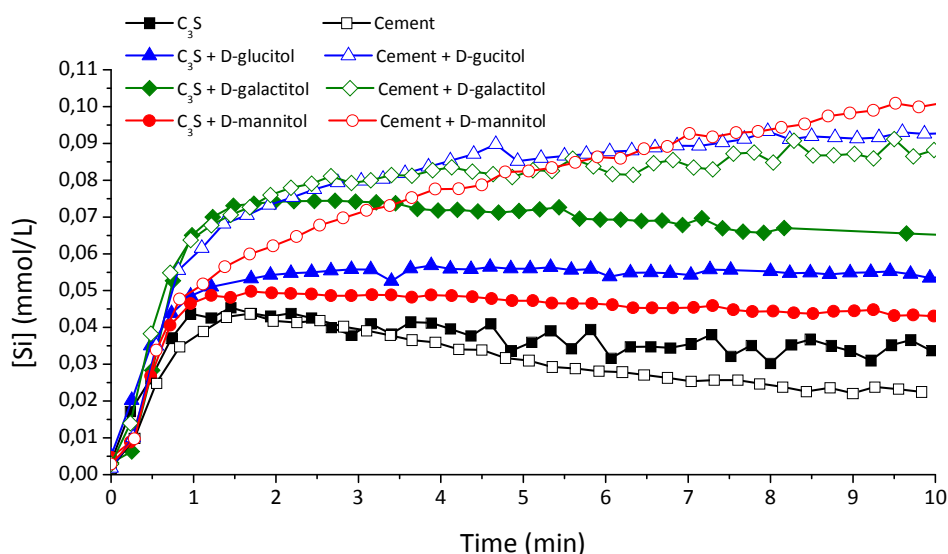


Figure 7: Comparison of the evolution of the silicate concentration over time during the hydration of C_3S and cement suspensions with and without hexitols (20.3 mmol/L), $[Ca(OH)_2]=22$ mmol/L and $L/S=100$.

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 C_3A 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 Figure 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 Figure 3. The values of the adsorption of hexitols on hydrating cement correspond to the ones revealed in the pseudo adsorption isotherm in Figure 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, Figure 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 D-mannitol. This result allows us to suppose that the retardation is not only related to the adsorption of the

III.5. Pouvoir retardateur des hexitols sur l'hydratation des phases silicates du ciment : interaction avec les phases aluminates et sulfate

organic molecules on hydrating cement and/or that they adsorb on different phases present in cement.

In two previous studies, we have shown that hexitols adsorb on ettringite and AFm [11] but also on C-S-H as indicated for D-mannitol and D-glucitol [12]. However, D-glucitol was found to have a favored adsorption on both C-S-H in systems at equilibrium and ettringite during the hydration of an aluminate-sulfate mixture compare to D-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 low down 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 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 deeply studied.

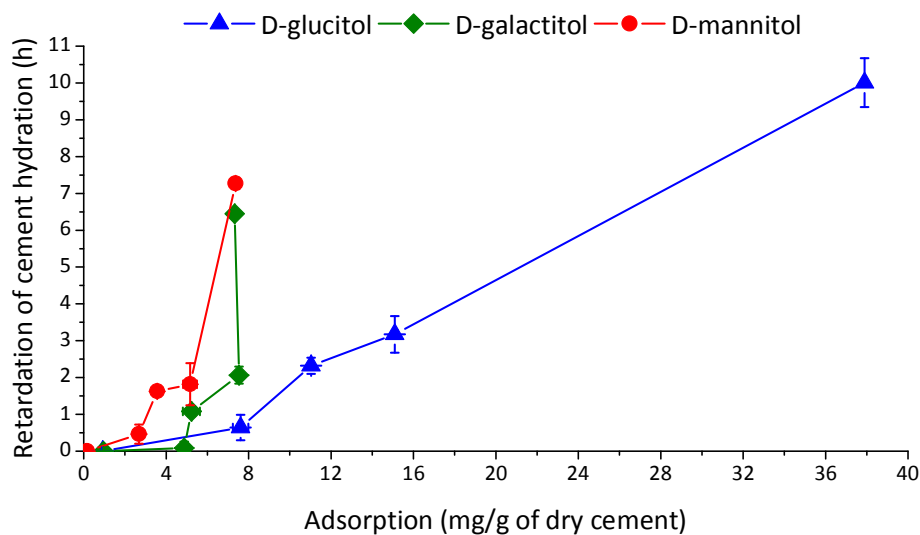


Figure 8: Retardation of the hydration of the silicate phases of cement in paste induced by hexitols depending on their adsorption on hydrating cement during the induction period.

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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 complex ions 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

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CHAPITRE IV : DISCUSSION

Pouvoir retardateur des molécules organiques sur l'hydratation du C_3S : relation avec leur adsorption sur le C-S-H et leur complexation ionique en solution

L'étude de la vitesse d'hydratation du C_3S en présence de molécules organiques telles que des dérivés de sucres, des carboxylates et des amino-carboxylates, sulfonates et phosphonates présentée dans l'Article 1 a montré que ces dernières retardent l'accélération de la croissance des C-S-H et augmentent le degré d'hydratation à partir duquel il y a une décélération de l'hydratation du C_3S . Comme d'autres molécules organiques, ces composés retardent dans un premier l'hydratation du C_3S puis l'accélèrent [1,2]. La Figure 10 compare les pouvoirs retardateurs de certaines molécules organiques étudiées dans l'Article 1 sur l'hydratation du C_3S . Ce pouvoir retardateur correspond au coefficient directeur de la droite $y=ax$ décrivant l'évolution du retard induit par les molécules organiques sur l'hydratation du C_3S en fonction de leur concentration en solution. Malgré le fait que l'évolution du retard en fonction de la concentration en molécules organiques ne soit pas toujours parfaitement décrite par cette équation linéaire, cette dernière permet d'obtenir un nombre unique caractéristique du pouvoir retardateur d'un composé organique qui peut être aisément comparé à celui d'autres composés.

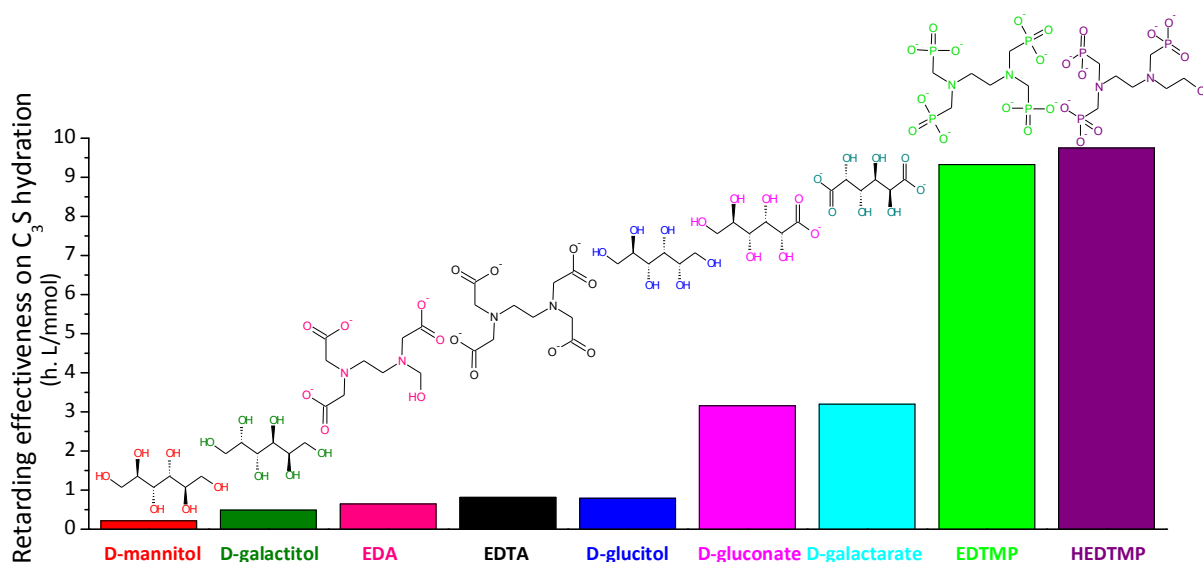


Figure 10 : Comparaison des pouvoirs retardateurs de différentes molécules organiques sur l'hydratation du C_3S .

Il peut être observé que les molécules organiques les plus chargées, les tri et tétra amino-phosphonates (HEDTMP et EDTMP), ont des pouvoirs retardateurs plus importants sur l'hydratation du C_3S que les autres molécules étudiées, Figure 10. Cependant, ce pouvoir

retardateur ne dépend pas seulement de la charge portée par les composés organiques. En effet, les charges portées par les tri et tétra amino-phosphonates (respectivement six et huit) sont différentes alors que ces molécules organiques ont des pouvoirs retardateurs similaires sur l'hydratation du C_3S . De même, des anions de sucres acides comportant une (D-gluconate) ou deux charges (D-galactarate) ont des pouvoirs retardateurs plus élevés que les tri et tétra amino-carboxylates (EDA et EDTA) qui en portent respectivement trois et quatre. Des composés organiques initialement neutres comme les hexitols (D-mannitol, D-galactitol et D-glucitol) induisent eux aussi des retards sur l'hydratation du C_3S qui diffèrent selon la stéréochimie de leurs groupes hydroxyles. Ainsi, le pouvoir retardateur d'une molécule organique sur l'hydratation du C_3S n'est pas uniquement fonction de sa charge mais varie aussi selon ses groupes fonctionnels et la stéréochimie de ses groupes hydroxyles.

Dans l'Article 2, il a été révélé que les molécules organiques retardant l'hydratation du C_3S s'adsorbent sur le C-S-H et complexent de manière spécifique les ions calcium en solution. Une relation linéaire a été trouvée entre le pouvoir complexant des molécules organiques avec les ions calcium en solution et leur affinité avec le C-S-H à haut rapport Ca/Si suggérant une interaction avec les ions calcium présents à sa surface. La Figure 11 représente l'évolution du pouvoir retardateur de différentes molécules organiques sur l'hydratation du C_3S en fonction de leur affinité avec les ions calcium à la surface du C-S-H ou en solution.

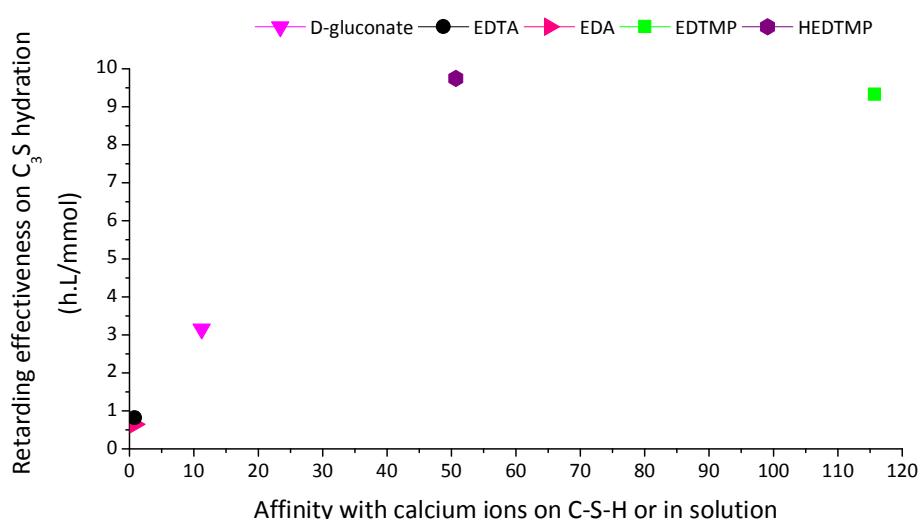


Figure 11 : Evolution du pouvoir retardateur de différentes molécules organiques sur l'hydratation du C_3S en fonction de leur affinité pour les ions calcium à la surface du C-S-H à haut rapport Ca/Si ou en solution.

Il peut être observé que plus l'affinité des molécules organiques avec les ions calcium est grande, plus elles ont un pouvoir retardateur prononcé sur l'hydratation du C_3S , Figure 11. Cependant, le retard induit n'est pas uniquement fonction de leur pouvoir complexant avec les ions calcium en solution ou à la surface des C-S-H. En effet, le tri (HEDTMP) et le tétra amino-phosphonates (EDTMP) entraînent des retards similaires sur l'hydratation du C_3S alors que le pouvoir complexant avec les ions calcium ou l'affinité de la première molécule avec le C-S-H est plus de deux fois plus faible que celui de la dernière. De plus, il a été remarqué que les molécules organiques qui retardent le plus l'hydratation du C_3S complexent aussi les ions silicates et hydroxyde en solution comme le D-gluconate, l'HEDTMP et l'EDTMP (Article 2). Cependant, des composés organiques tels que les amino-carboxylates (EDA et EDTA) ne complexent pas les ions silicates mais génèrent tout de même un retard sur l'hydratation du C_3S . Un constat similaire a été fait avec le sucre [3]. Ainsi, la complexation des molécules organiques avec les ions silicates n'est pas uniquement à l'origine du retard mais semble l'amplifier.

Il est important de noter que durant l'hydratation du C_3S , les composés organiques vont à la fois complexer les ions en solution et s'adsorber à la surface du C-S-H. Le pouvoir complexant des molécules avec les ions calcium et leur adsorption sur les C-S-H étant des grandeurs thermodynamiques mesurées à l'équilibre, leur vitesse relative n'est pas connue. Il s'agirait donc d'identifier l'impact de l'adsorption des molécules sur le C-S-H sur la vitesse d'hydratation du C_3S d'un côté et celui de la complexation ionique en solution de l'autre ainsi que leur vitesse relative. La difficulté majeure étant que même si une de ces interactions n'est pas à l'origine du retard, elle peut en changer l'intensité. En effet, ces différentes interactions sont constamment couplées car les molécules organiques qui sont complexées en solution ne peuvent être présentes à la surface des C-S-H et inversement. Ainsi, le retard de l'hydratation du C_3S est la conséquence des interactions des molécules à l'origine ou non de cet effet et de leur vitesse relative.

Origine du retard : impacts des hexitols sur la dissolution du C_3S et la précipitation des C-S-H

Les interactions des molécules organiques à l'origine du retard de l'hydratation du C_3S étant difficile à identifier, les effets des hexitols qui sont des molécules particulièrement intéressantes car très similaires, sur les différentes étapes de l'hydratation, c'est-à-dire sur la dissolution du C_3S et la précipitation des C-S-H ont été plus particulièrement étudiés dans l'Article 3. Il a été montré que les hexitols retardent l'hydratation du C_3S sans toutefois affecter sa dissolution pure dans une solution d'hydroxyde de calcium à 11 mmol/L ce qui est représentatif de la concentration ionique à un instant de l'hydratation. Cela a aussi été observé en présence d'éthers de cellulose [4]. Par conséquent, un blocage de la dissolution du C_3S n'est pas à l'origine du retard induit par les molécules organiques sur l'hydratation de l'anhydre.

De plus, l'Article 2 a mis en évidence que les molécules organiques qui retardent l'hydratation du C_3S s'adsorbent sur le C-S-H. Cette interaction à la surface des hydrates pourrait ainsi perturber leur croissance et ainsi retarder l'hydratation du C_3S . En revanche, d'autres retardateurs de prise comme un polycarboxylate et le D-gluconate entraînent un ralentissement de la dissolution du C_3S [5-7]. La vitesse de précipitation des C-S-H étant égale à celle de la dissolution du C_3S , si cette dernière est abaissée par la présence des molécules organiques, la première le sera aussi et vice-versa. Si en plus d'affecter de manière directe la croissance des C-S-H, des composés organiques limitent la dissolution du C_3S , la précipitation des hydrates sera d'autant plus ralentie.

Il conviendrait donc de mesurer systématiquement la vitesse de dissolution pure du C_3S en présence des différentes molécules organiques étudiées dans ce travail et de les comparer. Il faudrait également étudier séparément l'influence de ces mêmes composés organiques sur la vitesse de précipitation du C-S-H ce qui est moins facile à réaliser expérimentalement dans des conditions représentatives de l'hydratation.

Il existe cependant une autre possibilité d'identifier la réaction sur laquelle les molécules agissent le plus. En effet, durant l'hydratation du C_3S , la vitesse de dissolution de cet anhydre et la vitesse de précipitation du C-S-H sont maintenues égales par l'évolution de la sous-saturation par rapport à l'anhydre (β_{C_3S}) et de la sursaturation par rapport à l'hydrate (β_{C-S-H}) [8] qui sont décrites par comme suivant :

$$\beta_X = PAI/K_{sp} X$$

Où PAI est le Produit d'Activité Ionique de la solution et K_{sp} le produit de solubilité de la phase X.

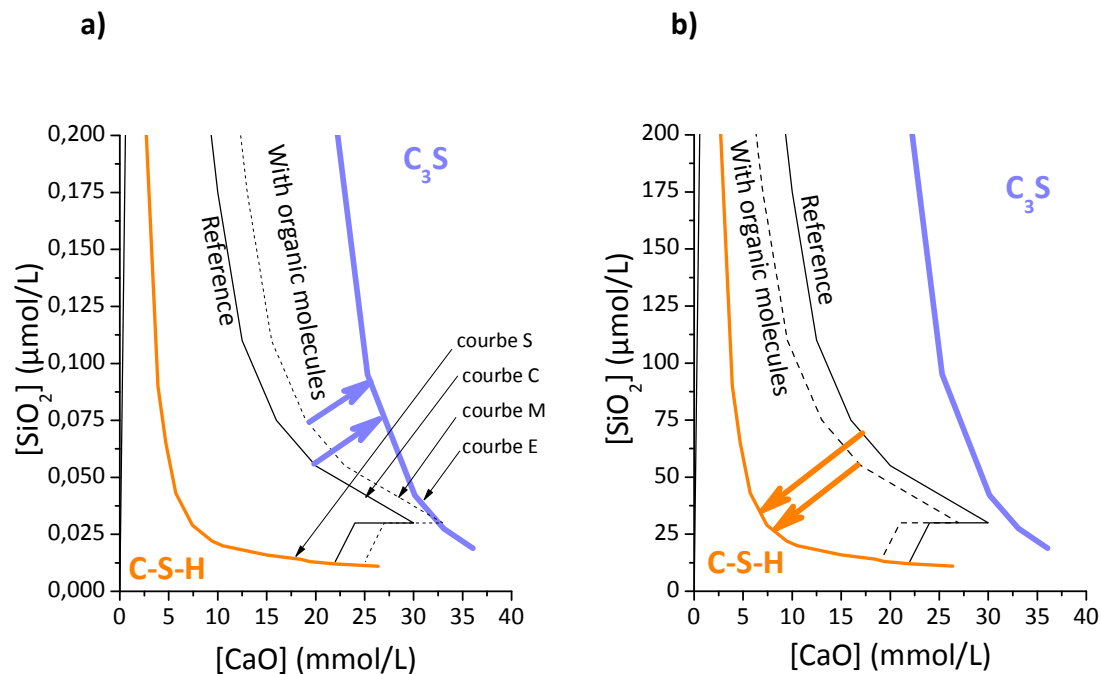


Figure 12 : Diagramme chaux-silice-eau donnant l'exemple de l'évolution de la composition ionique de la solution (courbe M) lorsque a) la précipitation du C-S-H est principalement limitée et b) la dissolution du C_3S est majoritairement limitée par la présence des molécules organiques. La courbe C décrit les concentrations en solution pendant l'hydratation du C_3S en absence de molécule organique. La courbe S représente la courbe de solubilité du C-S-H et la courbe E celle de la solubilité du C_3S .

La position de la courbe C sur la Figure 12 représente la composition de la solution pendant l'hydratation du C_3S en absence de tout ajout dans le diagramme chaux-silice-eau. Si l'ajout d'un composé organique déplace cette courbe de telle sorte que la sous-saturation par rapport à l'anhydre est diminuée et par conséquent que la sursaturation par rapport à l'hydrate est augmentée (Figure 12-a), la présence de la molécule organique affecte plus particulièrement la vitesse de précipitation du C-S-H. Si au contraire, la courbe est déplacée dans l'autre sens (Figure 12-b), la molécule organique ralentit plus particulièrement la dissolution du C_3S . Ainsi, de manière à identifier si les composés organiques affectent de manière plus prononcée la dissolution du C_3S ou la précipitation du C-S-H, il faudrait calculer les β_{C_3S} et β_{C-S-H} lors de l'hydratation du C_3S . Ces sous et sursaturations étant proportionnelles au Produit d'Activité Ionique, les activités en ions calcium, silicates et hydroxyde doivent être connues. Or, la mesure de concentration ionique en solution donne la concentration totale en ions, comprenant celle en ions libres et celle en ions complexés par les composés organiques. Cependant, à cause de la formation de complexes entre certaines molécules et les ions silicates, calcium et/ou hydroxyde dont nous ne connaissons actuellement pas toutes les constantes de complexation, les activités de ces espèces ne peuvent être calculées. Ainsi, cette méthode pourrait être employée pour déterminer si la réaction de dissolution du C_3S ou celle de la précipitation du C-S-H est majoritairement affectée par la présence des molécules organiques si toutes leurs constantes de complexation avec les ions calcium, silicates et/ou hydroxyde étaient connues.

Interaction des hexitols avec la phase aluminatée du ciment : influence sur le retard de l'hydratation des phases silicatées

L'étude portant sur l'effet des hexitols sur l'hydratation du ciment (Article 5) et des ses composés constitutifs a révélé que ces polyols modifient non seulement la vitesse d'hydratation de ses phases silicatées (Articles 3) mais aussi celle de ses phases aluminatée (C_3A) et sulfates (Article 4). Il a été observé que la vitesse de précipitation de l'ettringite évolue de façon non monotone en fonction de la concentration en D-galactitol et du D-glucitol (Article 5). Ces deux molécules retardent la précipitation jusqu'à une concentration seuil respective puis l'accélèrent alors que le troisième hexitol étudié, le D-mannitol, l'accélère toujours dans les conditions de l'étude. Ces retards et accélérations concernant la précipitation de l'ettringite provoqués par le D-galactitol et le D-glucitol ont été expliqués par une compétition entre l'adsorption de ces molécules à sa surface et leur complexation avec les ions en solution. L'adsorption des hexitols sur l'ettringite est supposée ralentir sa précipitation alors que la complexation ionique en solution accélérerait sa précipitation. En effet, la formation de complexes en solution avec les ions calcium, hydroxyde et/ou aluminatée pourrait augmenter la sous-saturation par rapport au C_3A et donc accélérer sa dissolution.

Cependant durant l'hydratation des phases aluminatée et sulfates, l'impact des interactions des sucres alcools en solution et à la surface de l'ettringite qui sont simultanées, dépend aussi de leur vitesse relative. Ainsi, cette dernière pourrait être déterminée en mesurant les concentrations ioniques en solution et l'adsorption des hexitols sur l'hydrate en faisant varier le temps de contact entre les molécules organiques en solution et de l'ettringite en suspension. A l'équilibre, l'adsorption des hexitols sur l'ettringite et leur complexation avec les ions calcium, hydroxyde et/ou aluminatée en solution pourraient être étudiées. L'identification des divers complexes présents en solution à l'équilibre ainsi que leur constante de formation permettrait de calculer le Produit d'Activité Ionique de la solution et par conséquent de vérifier si la complexation ionique en solution augmente ou non la sous-saturation par rapport au C_3A .

Par ailleurs, il a été remarqué dans l'Article 5 que le retard induit par les hexitols sur l'hydratation des phases silicates du ciment diminue en augmentant la proportion de sa phase aluminatée. De plus, cette réduction du retard généré sur l'hydratation des phases silicates du ciment diffère selon la stéréochimie des groupes alcools portés par les hexitols. Le D-glucitol entraîne une réduction plus importante du retard de l'hydratation des phases silicates du ciment au D-mannitol. Or, l'Article 4 a montré que le D-glucitol s'adsorbe de manière plus importante sur l'ettringite que le D-mannitol. Il apparaît donc que plus l'adsorption des hexitols sur l'ettringite est importante plus le retard généré par les composés organiques sur l'hydratation des phases silicates du ciment est réduit. L'adsorption des molécules organiques sur l'ettringite abaisse la concentration des composés organiques capables de perturber la suite de l'hydratation des phases du ciment. La complexation des hexitols avec les ions aluminatés en solution semble favoriser la dissolution des phases silicates du ciment et pourrait ainsi participer à la réduction du retard généré par les molécules organiques, Articles 5.

Nous avons vu à travers ces diverses études que les hexitols changent la vitesse d'hydratation des différents composés minéraux du ciment, s'adsorbent sur leurs hydrates (C-S-H, ettringite et AFm) et complexent des ions en solution. A cause des vitesses relatives de ces interactions à la surface des différents hydrates et en solution avec les divers ions, il est toutefois compliqué de différencier celles qui sont à l'origine du retard de l'hydratation des phases silicates du ciment de celles qui sont cinétiquement favorisées.

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CONCLUSIONS

Ces travaux de thèse avaient pour objectif de comprendre pourquoi et comment des molécules organiques modifient l'hydratation de composés cimentaires. Les molécules organiques utilisées étaient simples de type hexitols, anions de sucres acides, carboxylates, amino-sulfonates, -carboxylates et -phosphonates de manière à modifier pas à pas leurs groupes fonctionnels, leur charge et stéréochimie. Leur effet retard induit sur l'hydratation du C_3S , composé responsable des propriétés finales du Ciment Portland Ordinaire (CPO), a été relié à leurs caractéristiques ainsi qu'à leurs interactions avec le C-S-H et les ions en solution. L'impact des composés organiques sur la dissolution du C_3S et la précipitation du C-S-H se déroulant durant l'hydratation de l'anhydre a été étudié en présence d'hexitols. Les effets de ces polyols sur l'hydratation d'un mélange aluminat-sulfate de calcium ainsi que leurs interactions avec les aluminates de calcium hydratés et les ions en solution ont été révélés. Ces dernières ont été corrélées au retard généré par les hexitols sur l'hydratation des phases silicates du CPO.

L'étude du retard entraîné par des petites molécules organiques sur l'hydratation du C_3S a mis en évidence que leur effet est plus prononcé pour les plus chargées d'entre elles mais qu'il ne dépend pas uniquement de leur charge. La nature de leurs groupes fonctionnels ainsi que la stéréochimie de leurs groupes hydroxyles jouent aussi un rôle. En effet, pour une concentration équivalente en anion, les composés organiques portant des groupes sulfonates ou carboxylates provoquent des retards similaires sur l'hydratation du C_3S mais ceux-ci sont inférieurs aux retards induits par les molécules organiques possédant des groupes phosphonates. De plus, le nombre de paires de groupes hydroxyles en configuration thréo (groupes hydroxyles positionnés de part et d'autre de la chaîne carbonée sur la représentation de Fischer) et plus particulièrement les paires qui sont adjacentes, augmente le retard généré par les sucres alcools et les anions de sucres acides.

De manière à relier le retard à la complexation ionique des molécules organiques en solution et/ou à leur adsorption sur les produits d'hydratation du C_3S tout en s'affranchissant de sa dynamique, l'étude de ces interactions a été réalisée dans des suspensions de portlandite et de C-S-H à l'équilibre. Les composés organiques retardateurs

s'adsorbent sur le C-S-H et complexent les ions calciums en solution de manière spécifique. Certains complexent aussi les ions hydroxyde et/ou silicates. Il a été observé que l'affinité des molécules organiques pour le C-S-H à haut rapport Ca/Si augmente avec le pouvoir qu'elles ont à complexer les ions calcium en solution, laissant suggérer une interaction de celles-ci avec les ions calcium présents à la surface des hydrates. Par ailleurs, l'effet retard entraîné sur l'hydratation du C_3S s'intensifie avec le pouvoir complexant des composés organiques avec les ions calcium (en solution ou à la surface des C-S-H) mais il n'en est pas uniquement fonction. La formation de complexes avec les ions silicates et/ou hydroxyde en solution est aussi présumée participer au retard engendré par les molécules organiques. Une compétition entre la présence des molécules organiques complexées en solution et à la surface du C-S-H semble aussi jouer un rôle indirect en changeant l'intensité des interactions à l'origine du retard lors de l'hydratation du C_3S .

Les interactions des molécules organiques provoquant un retard sur l'hydratation du C_3S étant difficilement identifiables, leurs conséquences sur son processus de dissolution-précipitation ont été observés par des études en suspensions diluées en présence des hexitols. Le retard de l'hydratation du C_3S induit par les hexitols n'est pas relié à une diminution de la vitesse de dissolution de l'anhydre. Ces polyols sont ainsi présumés ralentir la précipitation des C-S-H en adsorbant notamment à leur surface et/ou en diminuant le degré de sursaturation par rapport à l'hydrate. De plus, les hexitols modifient la vitesse de l'hydratation du mélange aluminat-sulfate de calcium : la précipitation de l'ettringite peut être ralentie ou accélérée en fonction de la stéréochimie des groupes hydroxyles des composés organiques et de leur concentration alors que la formation des AFm est toujours freinée en leur présence. L'accélération de la précipitation de l'ettringite a pu être reliée à une importante complexation ionique en solution et à une faible adsorption des hexitols sur cet hydrate. Il semblerait qu'il existe une compétition entre la complexation des molécules organiques avec les ions en solution et leur adsorption sur l'ettringite changeant ainsi la quantité de composés organiques capables de ralentir la précipitation des AFm.

En résumé, les hexitols affectent l'hydratation du C_3S d'un côté et du mélange aluminat-sulfate de calcium de l'autre. Ils s'adsorbent sur les différents hydrates formés (C-S-H, ettringite et AFm) et interagissent avec les ions calcium, hydroxyde, aluminates et silicates (uniquement pour le D-glucitol). Pour les deux systèmes modèles respectivement, il

a pu être mis en évidence qu'une certaine compétition entre l'adsorption des molécules organiques à la surface des hydrates et leur complexation ionique en solution existait. Ainsi, de manière à identifier quel est l'effet des interactions privilégiées durant l'hydratation d'un système réel, le ciment, le retard causé par les hexitols sur l'hydratation des phases silicates du ciment a été étudié. Il en résulte que le retard entraîné par ces molécules organiques sur l'hydratation des phases silicates du ciment diminue avec la proportion de phase aluminatée présente. Cette réduction du retard a été reliée à l'adsorption des hexitols sur l'ettringite et à leur complexation avec les ions aluminatés en solution.

Pour aller plus loin, de manière à identifier les processus de l'hydratation du C_3S qui sont particulièrement affectés par les composés organiques retardateurs, les vitesses de dissolution pure de l'anhydre et de précipitation des C-S-H pourraient être mesurées en leur présence de manière séparée. La sous-saturation par rapport au C_3S et la sursaturation par rapport au C-S-H pourraient aussi être calculées de manière à révéler si la dissolution de l'anhydre ou la précipitation des hydrates est principalement ralentie durant l'hydratation du C_3S . Néanmoins, toutes les constantes de complexation des molécules avec les ions calcium, hydroxyde et silicates doivent être connues pour mener à bien ces méthodes. Le plus aisé étant de commencer avec des molécules organiques ne complexant que les ions calcium et dont la constante de complexation a souvent été étudiée dans la littérature telle que l'EDTA par exemple.

Abstract

The current limited knowledge on the interactions between organic admixtures and mineral phases as well as their influence on the hydration mechanisms of the Ordinary Portland Cement (OPC) represents a real limitation in the development of new organic products with improved and controlled properties. Here, this study intended to understand why and how organic admixtures modify the setting time of OPC by progressively varying the characteristics of simple organic molecules such as their charge, functional groups (hydroxyl, hydroxy-carboxylate, carboxylate, sulfonate and phosphonate) and the stereochemistry of their hydroxyl groups.

The different retardations induced by the organic molecules studied on the hydration of the mineral compound responsible of the final properties of OPC, tricalcium silicate, were related to the characteristics of the organic admixtures. The interactions of these organic compounds such as their adsorption on calcium silicate hydrate (C-S-H) and their complexation with calcium, hydroxide and/or silicate ions in solution were identified in systems at equilibrium and correlated to the retarding effect generated by the organic molecules on the hydration of tricalcium silicate.

The impact of hexitols which differ from one another in the stereochemistry of their hydroxyl groups on the dissolution-precipitation process of the hydration of tricalcium silicate was studied. The influence of these polyols on the hydration of a calcium aluminate and calcium sulfate mixture was explained by their adsorption on ettringite and AFm as well as by their ionic complexation in solution. Finally, this study focused on the consequences of the interactions of hexitols with ettringite and aluminate ions in solution on the hydration of the silicate phases present in OPC.

Keywords: hydration, cement, organic admixture, adsorption, complexation

Résumé

Le manque de connaissance sur les interactions existantes entre les adjuvants organiques et les phases minérales ainsi que leur influence sur les mécanismes d'hydratation du Ciment Portland Ordinaire (CPO) limite le développement de nouvelles molécules organiques avec des propriétés améliorées et contrôlées. Ici, le but de ces travaux était de comprendre pourquoi et comment des adjuvants organiques modifient le temps de prise du CPO en faisant varier progressivement les caractéristiques de molécules organiques simples comme leur charge, leurs groupes fonctionnels (hydroxyle, hydroxy-carboxylate, carboxylate, sulfonate et phosphonate) et la stéréochimie de leurs groupes hydroxyles.

Les différents retards induits par les molécules organiques étudiées sur l'hydratation du composé minéral responsable des propriétés finales du CPO, le silicate tricalcique, ont été reliés aux caractéristiques des composés organiques. Les interactions de ces derniers dont leur adsorption sur du silicate de calcium hydraté (C-S-H) ainsi que leur complexation avec les ions calcium, hydroxyde et/ou silicates en solution ont été identifiées dans des systèmes à l'équilibre et corrélées au retard généré par les molécules organiques sur l'hydratation du silicate tricalcique.

L'impact des hexitols qui varient uniquement en fonction de la stéréochimie de leurs groupes hydroxyles sur le processus de dissolution-précipitation de l'hydratation du silicate tricalcique a été étudié. L'influence de ces polyols sur l'hydratation d'un mélange aluminat-sulfate de calcium a été expliquée par leur adsorption sur l'ettringite, les AFm et par leur complexation ionique en solution. Pour finir, cette étude s'est focalisée sur les conséquences des interactions des hexitols avec l'ettringite et les ions aluminat en solution sur l'hydratation des phases silicates présentes dans le CPO.

Mots clés : hydratation, ciment, adjuvant organique, adsorption, complexation