Doctoral Thesis

Controlling cement hydration through the molecular structure of comb copolymer superplasticizers

Author(s):
Marchon, Delphine

Publication Date:
2016

Permanent Link:
https://doi.org/10.3929/ethz-a-010798278

Rights / License:
In Copyright - Non-Commercial Use Permitted

This page was generated automatically upon download from the ETH Zurich Research Collection. For more information please consult the Terms of use.
CONTROLLING CEMENT HYDRATION THROUGH THE MOLECULAR STRUCTURE OF COMB COPOLYMER SUPERPLASTICIZERS

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

presented by

DELPHINE MARCHON

M.Sc. Materials Science and Engineering, EPFL Lausanne

born on 31.01.1985
from Vuisternens-en-Ogoz, Switzerland

accepted on the recommendation of

Prof Dr Robert J. Flatt, examiner
Prof Dr Jean-Baptiste d'Espinose de Lacaillerie, co-examiner
Prof Dr Paul Bowen, co-examiner
Dr Patrick Juilland, co-examiner

2016
Acknowledgements

This thesis was realised in the group of Physical Chemistry of Building Materials (PCBM) at ETH Zurich and sponsored by Sika Technology AG.

First, I would like to thank the jury members of my thesis for reviewing this work: Prof. Robert J. Flatt from ETH Zurich, Prof. Jean-Baptiste d’Espinose de Lacaillerie from ESPCI Paris, Prof. Paul Bowen from EPFL and Dr. Patrick Juillard from Sika Technology AG. I am also thankful to Prof. Mario Fontana from ETH Zurich who was the Chairman of this jury.

Second, I would like to express my gratitude to all the people who helped me over the last years in the work leading to this dissertation.

Primarily, I would like to thank my supervisor, Prof. Robert J. Flatt, who gave me the opportunity to work on what he considered at that time as the Holy Grail in the field of chemical admixtures. He trusted me, guided me all along this challenging task and, most importantly, he was a constant source of inspiration and motivation. Si cette thèse a conduit à autant de succès, c’est grâce aux très nombreuses heures de brain time que tu m’as allouées et à ta patience légendaire. Encore merci, et au prochain Graal !

I was particularly fortunate to work and/or spend my time with the current and previous members of PCBM: Giulia Gelardi, Paula Bran, Dr Prannoy Suraneni, Sara Mantellato, Dr Marta Palacios, Dr Tim Wangler, Prof Francesco Caruso, Dr Thibault Demoulin, Ylenia Praticò, Matteo Stefanoni, Lex Reiter, Kornel Kovacs, Marc Schultheiss, Heinz Richner, Yurena Segui Femenias, Ana Vallejo Vitaller, Andrea Louys, Nicolas Ruffray, Ena Lloret, Elizaveta Pustovgar, Denise Altermatt, Gaby Peschke, Asel Maria Aguilar, Carolina Boschmann, Prof Ueli Angst, Oliver Glauser, Dr Ratan Mishra, Dr Daniel Sanz, Dr Wei Cai, Andi Reusser, Köbi Scherrer, Prof Jean-Baptiste d’Espinose de Lacaillerie, Dr Nicolas Roussel and Prof Bernhard Elsener.
I especially want to thank Marta for her support in the lab, as well as in the debriefing of the meetings with Robert. She is Mama Marta because she taught me so much in these past years; she always cared about my work and my life. I also want to thank her for smiling at me during the presentations in conferences, workshops, defences, etc.

A special thanks to Andrea and Heinz for their unconditional help and patience. This lab would not stand without them.

A deep gratitude to Francesco, because he did not lose his patience when training me and Thibault for *Magic of Chemistry*, and particularly because he corrected this manuscript even if he was in bed with a strong fever.

To the best officemates I have ever had: Giulia, Paula and Prannoy. It is for sure that, in one way or another, you and the good atmosphere we had in our messy office contributed to the success of this work. Together with Thibault, Ylenia and Matteo, I was very lucky to have you, especially in the not so easy last months of the thesis, for all the moments we shared watching movies, running, travelling, *Super Konding*, cooking (ok, letting you cook), etc.

Ylenia, thank you for your unconditional motivation to meet/have a drink/dinner/watch a movie and for your warm welcome at your place. Without you and your inseparable camera, we would not have memories of the great moments we all have spent together.

I would like to thank you, Paula, for your patience when correcting my poor English and, most of all, because we share the same love for San Francisco and dogs. When I will be on my own in California or lost somewhere else, please cheer me up by sending videos of Jimmy and co., pandas or whatever you will consider appropriate.

A special thanks to Matteo; firstly, for your patience before being able to play tennis. And also because you showed me how beautiful Italy is and how to appreciate happy sarcasm (among other things, such as how to open a bottle of wine).

Thibault, parce qu'on partage plus qu'une langue maternelle et un appartement chaotique. J'apprécie ton humour absurde mais frais, tes goûts musicaux jovialement mélancoliques et nos échanges littéraires peu scientifiques. À la prochaine émission avec Jean d'Ormesson (à défaut de discussions métaphysiques qui durent toute la nuit).
Giulia, writing a book, road tripping in Canada, mumbling great songs or becoming paranoid are among the very numerous moments that I am grateful to have shared with you. You are my back vocals-, dress-, window-, map-mate. And above all: ... more and from before.

I was particularly honoured and grateful for the opportunity to work with the groups of Construction Materials and New Polymers at Sika Technology AG in Zurich. A special thanks to Dr Emmanuel Gallucci, Dr Patrick Juilland, Dr Lukas Frunz and Dr Arnd Eberhardt for everything they taught me, for their help and support and for the highly appreciated scientific discussions. And to Denise, for her help and for having let me “borrow” things from the lab.

Un merci tout particulier à Patrick qui certes m’a supervisée et conseillée tout le long de cette thèse mais avec qui je partage également le même goût de la neige et de la littérature.

I want to thank all the motivated and motivating undergraduate students I had the pleasure to supervise during these 4 years: Lex, Jang, Christophe, Jean-Yves, Marie and Raphaëlle. A special thanks to Lex, because I am not sure who taught what to whom... and most of all because he wore his suit at least twice specially for me.

I would like to thank Fabian Rüdy, the graphic designer who perfectly interpreted my abstract imagination and produced great work.

Je tiens également à remercier mes amis de Bulle, de Lausanne, de Morzine-en-Autriche et d’ailleurs pour leur soutien sans déflection et parce qu’ils sont les meilleurs. Un énorme merci à Amélie et Niels qui répondent toujours présent quand j’ai besoin de changer d’air. Et surtout pour comparer mes superplastifiants à des spaghettis. À Alexis et ses parents, pour m’avoir encouragée et soutenue durant toutes ces années.

Et finalement, à mes parents et à mon frère, pour leur amour, leur confiance, leur soutien et ce qu’ils ont sacrifié sans me le dire pour que j’arrive là.
Graphical abstract

Visual summary of the main thesis objective and approach. The comb copolymer superplasticizers (top) are well known to delay cement hydration (middle). This is studied as a function of their molecular structure (top). This has involved detailed study of the phase evolution (bottom) to extract a model allowing a rational optimisation of comb copolymers for enhanced performance through molecular design. More details about this figure are given in Chapter 1, where it is reproduced.
Abstract

Superplasticizers are polymeric dispersants widely used in concrete technology. Among them, comb shaped polycarboxylate ethers (PCEs) are the most efficient, but they typically delay the reactions involved in cement hydration. This leads to lower mechanical strength of concrete or cement paste at early age, which can be a limiting factor, in particular with respect to the development of cements with a reduced environmental impact.

Up to now, the mechanism through which hydration is delayed remained unclear and no general relation had been established between the molecular structure of PCEs and the induced retardation. This can be attributed to the inherent complexity of cement hydration, being a multi-component system with different coupled reactions, together with interactions between organic compounds and mineral phases.

In this thesis, with the use of comb copolymers with targeted and controlled molecular structural variations and a well-characterised model cement with tricalcium silicates, aluminates and calcium sulfates, it was possible for the first time to quantify the role of molecular structure of PCEs on the reactivity of a cementitious system.

In particular, it was shown that the induced delay on silicate hydration depends on local interactions between the adsorbed polymer backbone and the mineral surface leading to the blocking of hydration mechanisms. This effect could be well described in a first principle model that provides the ability to predict retardation on the basis of molecular structure.
Abstract

Furthermore, thanks to the well-defined model cement and PCEs, we could quantitatively elucidate the role that aluminates play on the performance of PCEs. More specifically, it was shown that ettringite acts as a “sink” for PCEs, limiting the retardation of silicate hydration unless a sufficient amount of PCEs is added to completely cover the ettringite surface. The quantification of these effects also defines the importance of the extent to which PCEs modify ettringite nucleation.

Finally, it was possible to show how, above a certain dosage of PCEs, the dynamic reactive balance between aluminates, silicates and sulfates can be perturbed leading to massive retardation. A lot of speculations had been voiced about this process, in particular for cements of low environmental impact, but it could never be studied in a systematic way before.

In summary, in this thesis and for the first time, the effect of PCEs on the reactivity of a cementitious system is explained and quantified on a molecular and sub-molecular level. This introduces a promising approach to the molecular design of organic additives to quantitatively control the reactivity of coupled chemical systems such as cement.
Zusammenfassung


Der Mechanismus der Verzögerung der Zementhydratation war bis jetzt unklar. Auch eine allgemeine Beziehung zwischen der molekularen Struktur der PCEs und der hervorgerufenen Verzögerung war nicht bekannt. Dies kann der inhärenten Komplexität der Zementhydratation zugeschrieben werden: Zement ist ein Vielkomponentensystem, dessen Hydratation aus einem komplexen Geflecht von unterschiedlichen, gekoppelten Reaktionen zwischen verschiedenen mineralischen Phasen besteht, welche zudem von organischen Verbindungen beeinflusst werden.

In dieser Doktorarbeit war es zum ersten Mal möglich, den Einfluss der molekularen Struktur der PCEs auf die Reaktivität eines zementösen Systems zu quantifizieren. Möglich war dies dank der Verwendung von Kammcopolymeren mit gezielten und kontrollierten Variationen ihrer molekularen Struktur und eines gut charakterisierten Modell-Zements, welcher Tricalciumsilikate, Aluminate und Calciumsulfate enthält.

Insbesondere wurde gezeigt, dass die induzierte Verzögerung der Silikatreaktion von lokalen Interaktionen zwischen dem adsorbierten PCE und der mineralischen Oberfläche abhängt, was zur Blockierung des Hydratationsmechanismus führt. Dieser Effekt konnte mit einem Grundlagenmodell beschrieben werden, das es
ermöglicht, die verzögernde Wirkung auf Grund der molekularen Struktur vorherzusagen.

Zudem konnten wir dank den wohldefinierten Modell-Zementen und PCEs den Einfluss der Aluminate auf die Performance der PCEs quantifizieren. Wir konnten zeigen, dass PCEs bevorzugt auf Ettringit adsorbieren, was deren Einfluss auf die Silikate limitiert. PCEs beeinflussen die Silikathydratation erst oberhalb der für komplette Bedeckung der Ettringitoberfläche notwendigen Menge. Die Quantifizierung dieser Effekte zeigt die Wichtigkeit der Tatsache, dass und zu welchem Ausmass PCEs die Ettringit Keimbildung beeinflussen.

Schliesslich konnten wir zeigen, wie oberhalb einer bestimmten PCE Menge die dynamischen, reaktiven Gleichgewichte zwischen Aluminaten, Silikaten und Sulfaten gestört werden. Über diesen Prozess wurde schon länger, speziell im Zusammenhang von Zementen mit vermindertem Umwelteinfluss, viel spekuliert, aber er konnte bisher nie auf systematische Weise untersucht werden.

Somit beschreibt, erklärt und quantifiziert diese Doktorarbeit zum ersten Mal die Effekte von PCEs auf die Reaktivität eines zementösen Systems auf molekularer Ebene. Dies ermöglicht einen vielversprechenden Ansatz in Richtung molekulares Design von organischen Additiven, die quantitativ die Reaktivität von gekoppelten chemischen Systemen, wie z.B. Zement, kontrollieren.
Résumé

Les superplastifiants sont des dispersants polymériques largement utilisés dans l'industrie du béton. Parmi ces adjuvants, les copolymères peigne d'éther de polycarboxylate (abrégés PCE) sont les plus efficaces en terme de dispersion mais retardent invariablement les réactions d'hydratation du ciment. Par ce retard, les résistances mécaniques du béton au jeune âge sont diminuées, ce qui peut être un facteur limitant en particulier dans le développement de ciments avec un impact environnemental réduit.

Jusqu'à présent, les mécanismes conduisant au retard d'hydratation ne sont pas clairement expliqués et aucune relation générale entre la structure moléculaire des PCEs et le retard qu'ils induisent n'a été établie. Ceci peut être attribué à la complexité intrinsèque du ciment, lequel est un système à plusieurs composants, et de son hydration impliquant différentes réactions couplées entre des constituants organiques et des phases minérales.

Grâce à l'utilisation de polymères dont les structures ont été soigneusement contrôlées et à une caractérisation minutieuse d'un ciment modèle composé de silicate tricalcique, aluminate tricalcique et de sulfate de calcium, cette thèse a permis de quantifier pour la première fois le rôle de la structure moléculaire des PCEs sur la réactivité d'un système cimentaire.

En particulier, il est démontré que le retard introduit sur l'hydratation de la phase silicate dépend d'interactions locales entre la surface du minéral et la chaîne principale du polymère adsorbé conduisant au blocage des mécanismes d'hydratation. Cet effet est également décrit à l'aide d'un modèle de principes fondamentaux qui permet de prédire le retard sur la base de la structure moléculaire.
De plus, l’utilisation du ciment modèle et des polymères, tous soigneusement caractérisés, a permis de comprendre quantitativement le rôle des aluminates sur la performance des PCEs. Plus exactement, cette étude montre que l’affinité des PCEs pour l’ettringite limite le retard jusqu’à ce que cette phase soit complètement recouverte et que l’excédent de polymère puisse s’adsorber sur les silicates et induire le retard. La quantification de cet effet par rapport à la surface d’occupation des polymères permet de mieux appréhender leur influence quant à la modification de la nucléation d’ettringite qu’ils engendrent.

Finalement, cette étude montre comment une grande quantité de PCEs, une fois passé un dosage critique, cause un retard massif en perturbant l’équilibre dynamique des réactions entre silicates, aluminates et sulfates. Beaucoup de spéculations ont été formulées sur ce phénomène qui n’a par contre jamais été étudié de façon systématique.

En résumé, cette thèse explique et quantifie pour la première fois l’effet des PCEs et de leur structure sur la réactivité d’un système cimentaire à un niveau moléculaire et sub-moléculaire. Cette étude ouvre la voie vers le design moléculaire d’adjuvants organiques pour quantitativement contrôler la réactivité de systèmes chimiques complexes comme le ciment.
Contents

Acknowledgements .................................................................................................................................................. iii
Graphical abstract ..................................................................................................................................................... vii
Abstract .................................................................................................................................................................... viii
Zusammenfassung ........................................................................................................................................................ x
Résumé ......................................................................................................................................................................... xii
Contents ...................................................................................................................................................................... xv
List of Figures .............................................................................................................................................................. xviii
List of Tables ............................................................................................................................................................... xxi
Glossary ......................................................................................................................................................................... xxiii

Chapter 1  Introduction .................................................................................................................................................. 1
  1.1 General introduction ............................................................................................................................................ 1
  1.2 Objective of the thesis .......................................................................................................................................... 6
  1.3 Structure of the manuscript ............................................................................................................................... 7

Chapter 2  State of the Art ........................................................................................................................................ 9
  2.1 Hydration of cement .......................................................................................................................................... 10
    2.1.1 Hydration of C₃A ......................................................................................................................................... 10
    2.1.2 Hydration of alite ........................................................................................................................................ 13
    2.1.3 Hydration of ordinary Portland cement ................................................................................................. 23
  2.2 PCE superplasticizers ......................................................................................................................................... 27
    2.2.1 Molecular architecture of PCEs ................................................................................................................. 27
    2.2.2 Conformation of PCEs in solution ............................................................................................................. 29
  2.3 Adsorption ........................................................................................................................................................... 31
    2.3.1 Adsorption and fluidity ............................................................................................................................... 32
    2.3.2 Adsorption isotherms ............................................................................................................................... 34
    2.3.3 Molecular structure and adsorption ......................................................................................................... 40
    2.3.4 Dynamic exchanges between surface and solution ................................................................................... 44
    2.3.5 Consumption (ineffective adsorption) ...................................................................................................... 47
2.4 Impact of PCEs on cement hydration ................................................................. 52
  2.4.1 Mechanisms of retardation ............................................................................. 53
  2.4.2 Hydration retardation by PCEs ..................................................................... 62
  2.4.3 Conclusion .................................................................................................... 65

Chapter 3 Materials and Methods ........................................................................... 67
  3.1 Materials .............................................................................................................. 67
    3.1.1 Model clinker ................................................................................................ 67
    3.1.2 Hemihydrate ............................................................................................... 70
    3.1.3 Pure C₃S ...................................................................................................... 71
    3.1.4 Ordinary Portland cement .......................................................................... 72
    3.1.5 PCEs synthesis and characterisation .......................................................... 73
  3.2 Methods .............................................................................................................. 75
    3.2.1 Preparation of the paste ............................................................................. 75
    3.2.2 Calorimetric measurements ....................................................................... 76
    3.2.3 Flow spread test ......................................................................................... 76
    3.2.4 Study of pore solution ................................................................................ 77
    3.2.5 Stopping hydration .................................................................................... 78
    3.2.6 BET specific surface area measurements ............................................... 79
    3.2.7 Thermogravimetric analysis ..................................................................... 79
    3.2.8 X-Ray Diffraction .................................................................................... 79
    3.2.9 Rietveld refinement and phases quantification with external standard ....... 80

Chapter 4 Quantification Method from XRD Analysis .............................................. 83
  4.1 Introduction ........................................................................................................ 83
  4.2 Phase assemblage evolution during C₃S hydration ........................................... 84
  4.3 Calculation of the heat flow from phase quantification ...................................... 89
  4.4 Conclusion ......................................................................................................... 91

Chapter 5 Impact of PCEs on Model Cement Hydration ........................................ 93
  5.1 Introduction ...................................................................................................... 94
  5.2 Characterisation of the model cement ............................................................... 98
    5.2.1 Reproduction of Tenoutasse’s test .............................................................. 98
    5.2.2 Phase assemblage of the metastable system ............................................ 99
  5.3 Phases evolution of hydrating model cement with PCEs .................................. 104
    5.3.1 General observations of addition mode on the heat release .................... 104
    5.3.2 Phases assemblage evolution of hydrating model cement with PCEs ..... 106
    5.3.3 Evolution of the phases involved in tricalcium silicate reaction ............... 108
5.3.4 Evolution of the phases involved in tricalcium aluminate reaction ............... 111
5.4 Effect of the PCEs addition mode and structure on silicate hydration ............... 120
  5.4.1 Delayed addition .......................................................................................... 120
  5.4.2 Direct addition ............................................................................................ 124
  5.4.3 Mechanistic origin of the silicate hydration delay ...................................... 131
  5.4.4 Model rationalisation .................................................................................. 135
5.5 Conclusion ......................................................................................................... 140

Chapter 6 Impact of PCEs on Pure C₃S Hydration .................................................. 141
  6.1 Introduction ...................................................................................................... 141
  6.2 Effect of the PCEs on the phases assemblage evolution .................................. 142
    6.2.1 General features of the heat release ......................................................... 144
    6.2.2 Evolution of C₃S content ......................................................................... 145
    6.2.3 Evolution of hydrates content and composition ....................................... 147
    6.2.4 Calculation of the heat release from XRD on pure C₃S with PCEs ............. 150
  6.3 Effect of PCEs dosage and structure on the measured heat release ............... 154
    6.3.1 General impact on heat release ............................................................... 154
    6.3.2 Apparent impact on dissolution, nucleation and growth ......................... 158
  6.4 Effect of PCEs dosage and charge density on retardation of C₃S hydration ....... 159
    6.4.1 Critical dosage for pure C₃S hydration retardation ................................. 162
    6.4.2 Relative change of slope of C₃S retardation ............................................ 166
  6.5 Conclusion ...................................................................................................... 167

Chapter 7 Conclusion and Outlook ............................................................................ 169
  7.1 Main outcome .................................................................................................. 169
  7.2 Importance of the model system ................................................................... 171
  7.3 Future work .................................................................................................... 172
    7.3.1 Effect of PCEs on silicates ..................................................................... 172
    7.3.2 Effect of PCEs on aluminates ................................................................. 172
  7.4 Outlook .......................................................................................................... 173

References .............................................................................................................. 179
Appendix .................................................................................................................. 195
Curriculum Vitae .................................................................................................... 211
List of Figures

Figure 1.1. Impact of comb copolymer on the hydration kinetics of cement ......................... 3

Figure 2.1. Heat release during hydration of C₃A with gypsum ........................................ 12
Figure 2.2. Illustration of the different stages of alite hydration ........................................ 14
Figure 2.3. Example of dissolution rate of alite ................................................................. 16
Figure 2.4. Impact of the addition of C-S-H seeds on hydration kinetics of C₃S .................... 19
Figure 2.5. Schematic illustration of hydration process (seeding) ..................................... 22
Figure 2.6. Heat release of an ordinary Portland cement .................................................... 24
Figure 2.7. Isothermal calorimetry of 80% C₃S and 20% C₃A with gypsum ...................... 25
Figure 2.8. Schematic representation of PCEs polymerisation ........................................... 28
Figure 2.9. Phase diagram for comb homopolymer ......................................................... 29
Figure 2.10. Critical dosages with respect to the dispersing ability .................................. 32
Figure 2.11. Adsorption data of different lignosulfonate polymers ..................................... 38
Figure 2.12. Adsorption data of different polycarboxylate polymers ................................. 39
Figure 2.13. Schematic representation of a comb copolymer in solution ......................... 42
Figure 2.14. Illustration of the effect of sulfates on the performance of a PCE ................... 46
Figure 2.15. TEM image of a PCE/hydrocalumite composite ........................................... 49
Figure 2.16. Illustration of the effect of addition time on setting times of OPC ............... 52
Figure 2.17. Isothermal calorimetry showing the effect of a PCE and PNS ....................... 53
Figure 2.18. Dissolution of C₃S with two carboxylated latexes .......................................... 56
Figure 2.19. Ca²⁺ evolution from reaction of CaCl₂ and Na₂SiO₃ polyacrylate ..................... 58
Figure 2.20. Isothermal calorimetry on cement with different types of PCEs .................... 60
Figure 2.21. Impact of PCEs on yield stress, adsorption, calorimetry of OPC .................. 64

Figure 3.1. Particles size distribution of the model clinker and hemihydrate ....................... 68
Figure 3.2. SEM images of model clinker grains ............................................................... 69
Figure 3.3. XRD patterns of pure C₃S, model clinker and cements ................................... 70
Figure 3.4. Particles size distribution of the pure tricalcium silicate phase ......................... 71
Figure 3.5. Particles size distribution of cem1 and cem2 .................................................. 73
Figure 3.6. Description of the PCEs structural parameters, N, n, P and C/E ..................... 74
Figure 3.7. Principle of the phases quantification method .................................................. 82

Figure 4.1. Heat flow and phase assemblage of pure C₃S hydration ................................. 85
Figure 4.2. Evolution of ΔC₃S/ΔCH and Ca/Si ratio of the C-S-H in pure C₃S ................. 87
List of Figures

Figure 4.3. Heat flow of the pure C₃S and C-S-H evolution.................................88
Figure 4.4. Measured and calculated heat release of pure C₃S hydration................91

Figure 5.1. Heat flow of an OPC with different dosages of PCE .........................95
Figure 5.2. Representation of hydration of model clinker with hemihydrate ..................97
Figure 5.3. Heat release of the model clinker vs dosages of hemihydrate ....................99
Figure 5.4. Phase evolution during hydration of model cement without PCE. ...........101
Figure 5.5. Mass ratio ΔC₃S/ΔCH during hydration of the model cement...............102
Figure 5.6. Influence of the PCE addition mode on model cement hydration ............105
Figure 5.7. Effect of PCE addition mode on phase evolution of model cement .............107
Figure 5.8. Evolution of C₃S during hydration of the model cement with PCE ............109
Figure 5.9. Evolution of CH during hydration of the model cement with PCE .............109
Figure 5.10. ΔC₃S/ΔCH during cement model hydration with PCE .......................110
Figure 5.11. Hemihydrate evolution during cement model hydration with PCE ..........111
Figure 5.12. Evolution of gypsum during cement model hydration with PCE .............113
Figure 5.13. Evolution of ettringite during model cement hydration with PCE ..........115
Figure 5.14. SEM images of the model cement with and without polymer ...............116
Figure 5.15. Evolution of the specific surface area of the model cement ..................118
Figure 5.16. Evolution of C₃A during model cement hydration with PCE .................119
Figure 5.17. Retardation of hydration of model cement in delayed addition, master curve......122
Figure 5.18. Master curve of retardation for oversulfated model cement ................123
Figure 5.19. Master curve of retardation for an OPC ........................................123
Figure 5.20. Influence of n in the heat flow of the model cement .........................124
Figure 5.21. Retardation of hydration of model cement in delayed addition .............125
Figure 5.22. Specific surface area of model cement with PCE direct addition .............126
Figure 5.23. Dependance of retardation on the structure in direct addition ................128
Figure 5.24. Retardation of model cement hydration with PCE 1PMA1000 ...............131
Figure 5.25. Dissolution rate of C₃S with PCEs .............................................133
Figure 5.26. Heat flows of annealed C₃S and C₃S with PCE ..............................135
Figure 5.27. Molecular and sub-molecular scale effects of an adsorbed comb-copolymer....139

Figure 6.1. Effect of the PCE addition mode on phase assemblage of pure C₃S ............143
Figure 6.2. Evolution of C₃S during C₃S hydration with PCE ..............................145
Figure 6.3. Evolution of “other” phases during C₃S hydration with PCE ..................147
Figure 6.4. Evolution of portlandite during C₃S hydration with PCE .....................148
Figure 6.5. Evolution of ΔC₃S/ΔCH during C₃S hydration with PCE ......................149
Figure 6.6. Measured and calculated heat of C₃S with PCE direct addition ..........151
Figure 6.7. Measured and calculated heat of C₃S with PCE delayed addition ............152
Figure 6.8. Effect of 3PMA1000 on the heat release of pure C₃S ..........................156
List of Figures

Figure 6.9. Effect of 6PMA1000 on the heat release of pure C3S .............................................................. 156
Figure 6.10. Effect of 3PMA3000 on the heat release of pure C3S .......................................................... 156
Figure 6.11. Effect of 6PMA3000 on the heat release of pure C3S .......................................................... 157
Figure 6.12. Effect of 1PMA1000 on the heat release of pure C3S .......................................................... 157
Figure 6.13. Retardation of the maximum heat of pure C3S with PCEs ..................................................... 160
Figure 6.14. Minimum dosage and the slopes $m_{dir}$ and $m_{del}$ .............................................................. 161
Figure 6.15. Ratios of minimum dosages and slopes with respect to $q/SPCE$ ............................................ 161
Figure 6.16. Covered surface corresponding to $\Delta c_0$ function of $q/SPCE$ ................................................ 164
Figure 6.17. Minimum dosage $\Delta c_0$ function of $q/SPCE$ ................................................................. 166
Figure 6.18. Relative change of slope vs surface charge density $q/SPCE$ ................................................ 167

Figure 7.1. Abacus of retardation ratios function of $N_1/N_2$ ratio .......................................................... 175

Figure A.1.1. XRD patterns of pure C3S and model clinker ................................................................. 195
Figure A.2.1. Phase evolution during hydration of model cement .......................................................... 197
Figure A.2.2. Influence of 3PMA3000 on the hydration of the model cement ........................................ 197
Figure A.2.3. Influence of 6PMA1000 on the hydration of the model cement ........................................ 197
Figure A.2.4. Influence of 6PMA3000 on the hydration of the model cement ........................................ 197
Figure A.2.5. Influence of 1PMA1000 on the hydration of the model cement ........................................ 198
Figure A.2.6. Master curve of retardation for an ordinary Portland cement ............................................. 199
Figure A.3.1. Evolution of portlandite during hydration of pure C3S with PCE ....................................... 200
Figure A.3.2. Evolution of the estimated Ca/Si ratio of the C-S-H .......................................................... 201
Figure A.3.3. Evolution of the C-S-H content during pure C3S hydration .............................................. 202
Figure A.4.1. Flow spread diameter function of the amount of adsorbed PCE ........................................ 204
Figure A.4.2. Slope of the spread diameter vs PCE adsorption vs $P/N$ ............................................... 206
Figure A.4.3. Adsorbed PCE function of the initial dosage ................................................................. 207
List of Tables

Table 3.1. Chemical composition of the model clinker in % (w/w) ......................................................... 68
Table 3.2. Chemical composition of the pure tricalcium silicate in % (w/w) ........................................ 72
Table 3.3. Mineralogical composition of cem1 and cem2. ................................................................. 72
Table 3.4. Characteristics of the comb-shaped copolymers............................................................... 75
Table 3.5. Selected spectral lines used for the pore solution analysis................................................. 78
Table 3.6. Structure models used for the Rietveld refinement............................................................ 80

Table 4.1. Enthalpy of formation of reactants and products of C₃S hydration................................. 90

Table 5.1. Sulfur concentration in pore solution of model cement with PCE........................................ 112

Table 6.1. Enthalpy of dissolution of C₃S and portlandite................................................................. 153
Table 6.2. Minimum dosage Δc₀ and its corresponding surface occupation........................................ 163

Table A.2.1. Ions concentration in pore solution of the model cement.............................................. 198
**Glossary**

**Cement notation**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Calcium oxide, CaO</td>
</tr>
<tr>
<td>S</td>
<td>Silicon dioxide, SiO$_2$</td>
</tr>
<tr>
<td>A</td>
<td>Aluminium oxide, Al$_2$O$_3$</td>
</tr>
<tr>
<td>F</td>
<td>Iron oxide, Fe$_2$O$_3$</td>
</tr>
<tr>
<td>$</td>
<td>Sulfur trioxide, SO$_3$</td>
</tr>
<tr>
<td>H</td>
<td>Water, H$_2$O</td>
</tr>
<tr>
<td>C$_3$S</td>
<td>Tricalcium silicate</td>
</tr>
<tr>
<td>C$_2$S</td>
<td>Dicalcium silicate</td>
</tr>
<tr>
<td>C$_3$A</td>
<td>Tricalcium aluminate</td>
</tr>
<tr>
<td>C$_4$AF</td>
<td>Calcium alumino-ferrite</td>
</tr>
<tr>
<td>C-S-H</td>
<td>Calcium-silicate hydrates</td>
</tr>
<tr>
<td>CH</td>
<td>Portlandite / calcium hydroxide Ca(OH)$_2$</td>
</tr>
<tr>
<td>AFt</td>
<td>Ettringite / trisulfo aluminoferrite</td>
</tr>
<tr>
<td>AFm</td>
<td>Monosulfoalumino ferrite</td>
</tr>
</tbody>
</table>

**Acronyms**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>Ordinary Portland cement</td>
</tr>
<tr>
<td>SCM</td>
<td>Supplementary cementitious material</td>
</tr>
<tr>
<td>PCE</td>
<td>Polycarboxylate ether</td>
</tr>
<tr>
<td>LS</td>
<td>Lignosulfonate</td>
</tr>
<tr>
<td>PNS</td>
<td>Polynaphthalene sulfonate</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>FBW</td>
<td>Flexible backbone worm</td>
</tr>
<tr>
<td>SC</td>
<td>Side chain</td>
</tr>
<tr>
<td>BB</td>
<td>Backbone</td>
</tr>
<tr>
<td>C/E</td>
<td>Carboxylate to ester ratio</td>
</tr>
<tr>
<td>P</td>
<td>Side chain length</td>
</tr>
<tr>
<td>N</td>
<td>Number of monomers in BB for one SC</td>
</tr>
<tr>
<td>n</td>
<td>Number of SCs for one molecule</td>
</tr>
<tr>
<td>w/c, w/s</td>
<td>Water to cement or solid ratio</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma - optical emission spectrometry</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle size distribution</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
</tbody>
</table>
Chapter 1
Introduction

Part of this chapter is based on the introduction of a paper accepted as feature article in the Journal of the American Ceramic Society:

Molecular and sub-molecular scale effects of comb-copolymers on tricalcium silicate reactivity: Towards molecular design


The elements of that introduction used in the present chapter were written by Ms Marchon under the guidance of Prof Flatt.

1.1 General introduction

Many chemical admixtures are known to delay cement hydration. It is an intentional effect for retarders, but for many other admixtures it is mostly an undesired side effect. Preventing it represents a very important industrial objective, which is difficult to achieve because the underlying mechanisms are poorly understood and by no means quantified. This can be explained by the inherent complexity of the problem. Indeed, this involves coupled chemical reactions in a multi component system, for which reaction rates are additionally affected by specific interactions between organic compounds and mineral surfaces. Therefore, studying the impact that chemical admixtures can have on cement hydration represents a challenging subject, which, as explained below, also addresses basic scientific questions common to numerous fields of materials science.
From a general point of view, the hydration of cement can be considered as being controlled by reactive inorganic solid-liquid interfaces. These are at the origin of the remarkable properties of cement, the binder in concrete, which is by far the most used man-made material with a yearly worldwide production of 3.5 billion tonnes\(^2\). Such solid-liquid interfaces also involve reaction mechanisms common to biological or natural processes, such as bone growth\(^3\)–\(^5\) or degradation of constructions\(^6\),\(^7\).

Moreover, the reactions taking place at these interfaces are also prime candidates for being modified by molecular additives, and this has attracted a lot of attention in research to improve existing processes\(^8\), create new materials\(^9\),\(^10\) and devise new therapeutic treatments as for bone disease\(^11\). Nevertheless, as recently stated for polymer nanocomposites, the molecular design of organic compounds to reach targeted properties is a field that “still remains in infancy”\(^12\).

In a broad sense, this doctoral thesis examines the question of how organic compounds can modify the reactivity of a multicomponent inorganic reactive system. More specifically, it is focused on how superplasticizers, also called high range water reducers, affect cement hydration. The superplasticizers considered in this thesis are comb copolymers that offer large variations in their molecular structure\(^13\),\(^14\) (Figure 1.1a-c). The model cement used consists of a synthetic clinker composed of calcium silicates and aluminates mixed with sulfates. This combination of model cement and polymers represents a clean and well-controlled system to study competitive processes involving adsorption, dissolution, nucleation and growth as it occurs during cement hydration. Developing and characterising the model system allowed us to understand how comb copolymers affect cement hydration. It also led us to establish a predictive model of retardation as a function of molecular structure that is not only effective in our model cement, but also in real industrial cements.
Figure 1.1. Impact of polycarboxylate ester (PCE) comb copolymer on the hydration kinetics of cement. a) Schematic representation of a comb-copolymer. The backbone is represented in blue and the side chains in yellow. b) Schematic representation of a PCE in terms of repeat units. $n$ represents the number of side chains in one molecule. $C/E$ represents the number of carboxylate functions $C$ per ester group $E$ through which a side chain with $P$ the number of ethylene oxide monomers is grafted. c) Chemical structure of the type of PCE used in this study (methacrylic backbone and PEG side chains). d) Example of heat release rate evolution during cement hydration and its modification by a PCE. The slope of the acceleration period is however not changed, which is highlighted by the parallel bands of the coloured strip. e) Schematic representation of the fact that hydration reactions convert anhydrous phases to hydrates with a time delay $\Delta t$ that is affected by the PCEs dosage ($c_{PCE}$) and structural parameters ($C/E, n, P$).
The chosen comb copolymers are extensively used as dispersants in numerous materials, with a yearly production of about 2 million tonnes for concrete only. These dispersants make it possible to enhance the workability thanks to their large structural variations that have an impact on rheology. This is particularly important for blended cements that are considered as the most effective solution for reducing the environmental impact of cement production, which currently represents between 5 and 8% of the CO₂ world emissions. Indeed, in these cements, the clinker is partially replaced by supplementary cementitious materials (SCMs), such as fly ash, slag and silica fume, or by calcined clay or limestone, which is generally detrimental to early strength. Standard concrete technology tries to correct for this by reducing the water content of concrete and adjusting the rheology by increasing the superplasticizer dosage. However, by slowing down cement hydration, superplasticizers almost unavoidably lead to lower mechanical strength at early age, which is counter-productive and poses serious and increasing problems for the development of cements with lower environmental impact.

This retardation of hydration that superplasticizers generally cause (Figure 1.1d) remains largely unexplained, whether in terms of the nature of the involved mechanisms or the influence of molecular architecture. This is not facilitated by the fact that there are still many open questions concerning cement hydration, even in absence of organic admixtures. Nevertheless, in the last decades substantial progresses have been made in understanding some important hydration mechanisms, such as the dissolution of the main anhydrous phase or the growth of the main hydrates. Additionally, important developments have been made in terms of characterisation methods.

When organic admixtures are added, the level of complexity of the system increases, which largely explains the difficulty in understanding related effects. It is a challenging and exciting question that numerous studies have tried to tackle. However, among the works dedicated to comb-shaped copolymers, the molecular structures of the PCEs and/or the cement characteristics are often insufficiently defined. This compromises not only the understanding of how retardation relates to the molecular architecture of PCEs, but prevents any definition of how to control
retardation through targeted changes in polymer synthesis and/or product formulation. Industrial developments in this area are therefore in great need of mechanistic insight into the problem at stake.

A challenge in achieving this is that hydrating cement is a multimineral system with coupled mechanisms. To simplify the problem, studies usually target one pure phase (generally, alite) and/or concentrate on a single hydration mechanism, which requires ideal and unrealistic conditions, such as high dilutions with different ionic strengths than those found in cement paste and concrete.\textsuperscript{37-42} Although the studies performed on pure phases are essential to understand fundamental mechanisms, they neglect the influence of the other cement phases. Therefore, there is a lack of fundamental knowledge concerning the effect of the PCE architecture on the interaction between the main cement phases. More specifically, it is necessary to define a model cement that is more representative of real cements, yet easier to characterise and that facilitates the study of how PCEs, in such a multi-component system, affect the hydration of tricalcium silicate. In fact, tricalcium silicate is the most important component in cementitious materials and its hydration products confer final strength and durability to these materials.\textsuperscript{36,43-45} This is why the study of the hydration kinetics of such a phase, in a reliable model system, represents a focal point of interest in this thesis.

In summary, the impact of PCEs on the hydration of cement is a subject of major industrial relevance since it is presently a limiting factor for the development of cements with a reduced environmental impact. It is also an extremely challenging subject from a scientific point of view. To date, and despite more than half a century of research on the question, molecular level effects are still not explained. We have attributed this in large part to an inadequate selection of model materials, both in terms of the cement and of the organic admixture. In this thesis, thanks to specific choices and developments on this front, it has been possible for the first time to quantify the impact of the molecular structure of the admixture on cement hydration and to propose predictive models that can be reliably applied to industrial cement.
1.2 Objective of the thesis

The objective of this study is to determine how comb-shaped copolymers affect the hydration of cement. In particular, it places a specific focus on the so-called “aluminate-sulfate-silicate” balance, which is a fundamental phenomenon that arises directly from the multimineral nature of cementitious systems, and can lead to strong retardations of the main phase of the system, tricalcium silicate.

A model cement was conceived and produced to study this question in a broader sense. This is based on a model clinker, composed of 80% (w/w) tricalcium silicate and 20% (w/w) tricalcium aluminate. \(^{46,47}\) To prevent the rapid hydration of the aluminate, hemihydrate is added, mimicking common practice in cement. \(^{43,44}\) This model cement is close enough to reality to give useable conclusions but simple enough to understand the main principles governing cement hydration.

What this thesis examines more specifically is how the reactivity of this coupled chemical system is modified in relation to the molecular structure, dosage and addition mode of comb copolymer superplasticizers. These polymers have also been selected to offer all the features needed to understand the mechanisms involved.

Through carefully chosen experiments, we separate the contributions of the various processes, emphasising under what conditions and why organic additives modify the hydration of the most important cement component. These experiments involve:

- Precise synthesis and characterisation of the model cement and the polymers;
- Well controlled protocols for preparing hydrating pastes, extracting pore solution and stopping hydration without damaging the sensitive phases;
- The control of the overall hydration mainly by calorimetry, X-ray diffraction, thermogravimetry analysis, specific surface area measurements and pore solution analysis;
- The development and validation of a reliable quantification method to follow the evolution of the main phases during hydration.
1.3 Structure of the manuscript

This manuscript is structured as follows:

Chapter 2 presents the state of the art. It is separated in 4 main parts dealing with: cement hydration, comb-shaped polycarboxylate superplasticizers, adsorption of superplasticizers and a review on the retardation of cement hydration caused by organic admixtures. These sections are based on three chapters written as first author for the peer-reviewed book *Science and Technology of Concrete Admixtures*.35,48,49

Chapter 3 gives an overview of the different materials and methods used throughout the thesis. In particular, a description of the model cement conceived to tackle the scientific challenges of this thesis is given. Also, a purposely-developed procedure for quantifying its phase evolution during hydration is presented. This overcomes the fundamental limitations that standard approaches encounter. Additionally the used superplasticizers are here presented. On this front, it is important to emphasise that the used copolymers are produced by grafting rather than copolymerization, because this leads to polymers with a more homogenous structure that can be more reliably characterised.

Chapter 4 describes the validation of the phase quantification method developed in this thesis by combining thermogravimetry with XRD measurements and Rietveld refinement with an external standard. The work presented here is carried out on pure hydrating tricalcium silicate used as a model system for cement. This choice is dictated by the fact that in both cases the main difficulty in phase quantification using XRD lies in the simultaneous presence of two amorphous phases, water and calcium silicate hydrate. The results validate the approach and represent an important achievement as this procedure is used in the characterisation of the model cement (Chapter 5). In particular, it allows a close pursuit of the evolution of the main phases during hydration, discriminating possible mechanisms and providing the necessary insight to better understand the changes induced by the polymer.
Chapter 5 represents the core of this thesis. It focuses on the hydration of the model cement containing the main phases, silicate, aluminate and sulfate, and its perturbation by the PCEs. The chapter begins with a study on the phase assemblage evolution with and without PCEs. The second part of the chapter deals with the analysis of the silicate hydration retardation with respect to PCEs addition mode, dosage and molecular structure. Here we have been able to quantitatively explain the role of molecular structure and the nature of the rate-determining mechanism. More importantly, we have found that the role of the molecular structure is identical in industrial cement, demonstrating the relevance of our model cement. These results are what we consider the most substantial contribution to the field. The corresponding results are contained in a paper accepted as feature article in the Journal of the American Ceramic Society¹.

Chapter 6 analyses the effect of PCEs on the hydration of pure tricalcium silicate. This is often used as a model phase for cement hydration. However, we show that the dependence of retardation on molecular structure is different, so that our model cement is a much more reliable system to endorse. This chapter examines the roles of dosage, polymer structure and addition time on retardation. Important relations are established, but not deepened since they are not representative of what happens in industrial cement.

Chapter 7 presents the general conclusions and outlook of this thesis. The conclusions are presented in a very concise way, while the outlook section is developed in more detail. This concerns the prospects opened by this thesis in terms of molecular design, something that can be considered as the “Holy Grail” of research and development in the field of chemical admixtures.
Chapter 2
State of the Art

This chapter is based on three chapters written as first author for the book *Science and Technology of Concrete Admixtures*:\textsuperscript{35,48,49}

Section 2.1 of the present chapter is based on *Chapter 8 – Mechanisms of cement hydration*,\textsuperscript{48} entirely written by Ms Marchon under the guidance of Prof Flatt.

Section 2.3 of the present chapter is based on *Chapter 10 – Adsorption of chemical admixtures*.\textsuperscript{49} The contribution involved Ms Marchon, Ms Mantellato and Prof Flatt. Ms Marchon wrote the subsections 2.3.4 and 2.3.5. She also co-wrote the subsections 2.3.2 and 2.3.3 with Ms Mantellato. Additionally, as she extensively edited the whole book chapter for consistency of the various contributions, she also did so in the previously mentioned section 2.3.4. and 2.3.5.

Section 2.4 of the present chapter is based on *Chapter 12 – Impact of chemical admixtures on cement hydration*,\textsuperscript{35} entirely written by Ms Marchon under the guidance of Prof Flatt.
2.1 Hydration of cement

Ordinary Portland cement (OPC) is a material composed of four main phases to which a small amount of calcium sulfate (in former times, as essentially gypsum and, at present, as a mixture of different forms of calcium sulfate) has been added.\textsuperscript{43,50} These four main phases are: alite, an impure form of C\textsubscript{3}S, belite, an impure form of C\textsubscript{2}S, and an interstitial phase composed of tricalcium aluminate (C\textsubscript{3}A) and tetracalcium aluminoferrite (C\textsubscript{4}AF) more or less crystallised, depending essentially on the composition of the raw meal, the maximum temperature in the firing zone and its final quenching after its passage in the firing zone. Depending on the type of final grinding, some gypsum can be partially dehydrated into calcium sulfate hemihydrate or even totally dehydrated to form a calcium sulfate phase improperly called anhydrite in the industry.

OPC hydration involves processes of dissolution and precipitation in a complex chemical system resulting in the formation of different hydrates. This leads to the setting and the hardening of cement. The products of silicates hydration are a gel of calcium silicate hydrate (C-S-H) and a crystalline phase of calcium hydroxide, portlandite (CH). The hydration reactions between the aluminates and the calcium sulfate lead to the formation of two different families of phases that are called trisulfoaluminoferrite hydrates (AFt), in which the most important is ettringite, and monosulfoaluminoferrite hydrates (AFm), which are all composed of positively charged platelets of calcium and aluminium on octahedral coordination with oxygen. The AFm phases differ by their counterion intercalated between the platelets: sulfate (the phase is called monosulfoaluminate), hydroxide (hydrocalumite), carbonate (monocarboaluminate), carbonate and hydroxyl (hemicarboaluminate) and chloride (Friedel’s salt).

2.1.1 Hydration of C\textsubscript{3}A

As C\textsubscript{3}A is the most reactive phase in cement, its role in (very) early hydration is important and concerns both mechanical properties as well as rheological
performances. In absence of sulfates, $C_3A$ reacts quickly with water and leads to a rapid and unintended setting called “flash set”. This is due to the precipitation on clinker surface of irregular hexagonal platelets of calcium aluminates hydrates, $C_4AH_{19}$ or $C_4AH_{13}$ (depending on the water activity) and $C_2AH_8$, both of them converting finally to a cubic hydrogarnet, $C_3AH_{6.43,51,52}$

To avoid this rapid setting and therefore to keep a needed period of workability before the setting, calcium sulfate is added to the clinker during production to control $C_3A$ hydration. In presence of sulfates (here gypsum), the hydration of $C_3A$ leads to the precipitation of ettringite:

$$C_3A + 3C\text{SH}_2 + 26H \rightarrow C_6A\text{S}_3H_{32} \tag{2.1}$$

Depending on the degree of supersaturation, ettringite presents different morphologies. This can vary from short hexagonal prisms to long needles.$^{53,54}$ Ettringite is stable as long as sulfates are still available in the system. Provided that ettringite is forming, the concentration of aluminium in the pore solution is kept at low levels. This has important implications on the hydration of $C_3S$, as discussed later.

Once the sulfate depletion point is reached, ettringite reacts with the remaining $C_3A$ to form monosulfoaluminate:

$$2C_3A + C_6A\text{S}_3H_{32} + 4H \rightarrow 3C_4A\text{S}H_{12} \tag{2.2}$$

The hydration of $C_3A$ in presence of sulfates is exothermic and isothermal calorimetry allows following the process and dividing it in three main stages (Figure 2.1).$^{46,55}$
The high heat release in stage I represents the dissolution of anhydrous phases and the rapid precipitation of ettringite. This reaction is quite short and directly followed by a deceleration, which is not yet fully understood. This could be due to the formation of a protective membrane of ettringite or AFm phases, but more likely to the adsorption of sulfates on active sites of C₃A with the effect of slowing down its dissolution. Both hypotheses are subject of debate. In the case of the protective membrane, Scrivener et al. mentioned that the ettringite morphology in needles could not provide a dense barrier layer that would slow down in a sufficient way hydration of cement. Furthermore, AFm precipitation has been observed in both systems with or without calcium sulfates. The fact that only the system with sulfates shows a rapid deceleration is therefore in contradiction with the protective layer composed of AFm.

During period II (Figure 2.1), although the heat release demonstrates that the reaction rate is low, a decrease of the conductivity in the middle of this stage (consequence of a consumption of sulfate and calcium ions) shows that ettringite is still forming.

The onset of the period III starts when sulfate ions are no more present in solution. At this point, a second sharp exothermic peak occurs, that is attributed to C₃A dissolution as well as to a faster precipitation of ettringite. During stage III, monosulfoaluminate precipitates from the reaction between ettringite and C₃A.
The source and the content of sulfates in the system have their importance, as they control the time of occurrence of the depletion point and therefore the length of the stage II, the nature of the aluminates phases forming as well as their morphology. At low content of gypsum, an amorphous coating on C\textsubscript{3}A particles has been observed and attributed to an AFm type phase.\textsuperscript{54} These reportedly form because normal hydration of aluminates cannot be totally prevented by a too low degree of sulfatation. In contrast, at high gypsum content, only ettringite formation has been reported.\textsuperscript{65} At intermediate gypsum content, at early age, normal precipitation of ettringite as well as formation of hydrocalumite (which converts slowly to a solid solution with monosulfoaluminate) have been observed.\textsuperscript{55,63,65} However, when hemihydrate is used as sulfate carrier, the initial precipitation of hydroxy-AFm is not observed due to the higher solubility of hemihydrate that releases sulfate ions faster.\textsuperscript{66} It has to be mentioned that these situations essentially occur in model systems and can be different in cement because of the presence of soluble alkali sulfates coming from clinker production.

### 2.1.2 Hydration of alite

Although C\textsubscript{3}A is the most reactive phase, OPC hydration kinetics is dominated by alite hydration, as it is the main component of cement (50-70%).

#### 2.1.2.1 Chemistry and stages of alite hydration

As said above, alite is a tricalcium silicate with impurities, such as aluminium, magnesium, iron or sodium. Its hydration leads to the precipitation of C-S-H, an amorphous or poorly crystalline phase with variable stoichiometry, which is responsible of the strength development of the cement, and portlandite (CH), a crystalline phase:

\[
\text{C}_3\text{S} + (3\text{-x}+n) \text{H}_2\text{O} \rightarrow \text{C}_x\text{-S-H}_n \ + \ (3\text{-x}) \text{CH} \tag{2.3}
\]

n represents the water to silicate ratio in C-S-H. The CaO to SiO\textsubscript{2} ratio varies between 1.2 and 2.1.
The hydration of alite can be divided in five to six periods, as described by Gartner et al. in Figure 2.2. These stages are interpreted in relation to different rate limiting mechanisms that are discussed in the following subsections. Many of their aspects are however still debated and this does not make the task of understanding the impact of chemical admixtures on hydration easier. Therefore, we have attempted to summarise the main points of view present in the literature to provide a broader base for interpreting the retardation from chemical admixtures. In particular, we dedicate a special effort to the dissolution stage, which is of particular importance to chemical admixtures.

![Illustration of the different stages of alite hydration following the Ca\textsuperscript{2+} concentration evolution and the associated heat release. Adapted from Gartner et al.](image)

**Figure 2.2. Illustration of the different stages of alite hydration following the Ca\textsuperscript{2+} concentration evolution and the associated heat release. Adapted from Gartner et al.**

### 2.1.2.2 Stages 0 and I: initial dissolution

The first peak during stage 0 is due to the dissolution of alite that is highly exothermic. This period lasts only a few minutes and is followed by a first deceleration in stage I and by a period of low reaction rates in stage II, which is called induction period. The reasons for the first deceleration are not fully understood and various controversial hypotheses are discussed.
Protective membrane

The first one involves a protective membrane of hydrates on alite surface that prevents further dissolution and therefore slows down hydration reactions. This layer of metastable hydrates would either convert to a more permeable stable hydrate\textsuperscript{68,69} or would break due to osmotic pressure, explaining the end of the induction period. By comparing solution concentrations of pore solution, Gartner and Jennings\textsuperscript{70} proposed that a first metastable C-S-H with a higher solubility and protective properties precipitates on C\textsubscript{3}S surface. This metastable C-S-H would undergo a solid-state transformation into a more stable but permeable C-S-H with a lower solubility causing the end of the induction period. Although NMR and X-ray photoelectron spectroscopy (XPS) measurements\textsuperscript{71–73} show the formation of an intermediate phase with different characteristics than the final C-S-H, no direct and visual evidence of such a continuous and impermeable layer has been observed.

Dissolution control

Recently, a theory based on crystal dissolution from geochemistry and applied to C\textsubscript{3}S hydration has been used to explain the first deceleration and the induction period.\textsuperscript{28–30,74,75} This theory implies that the dissolution mechanisms depend on the solution concentrations, and thus the degree of saturation.

Two main regimes of dissolution can be observed (Figure 2.3). At very high undersaturation level (low values of ln(\(\Pi\))), two-dimensional vacancy islands can nucleate on the surface with or without the help of impurities. This surface pitting and the following step retreat have been shown to control the dissolution. In a very recent study, Juillard and Gallucci\textsuperscript{29} determined an activation energy of 26 kJ mol\(^{-1}\) to this fast dissolution mechanism (Mechanism II in Figure 2.3), attributed to the process of etch opening. In support of this theory, several studies have reported more extensive pitting and more extensive heterogeneous dissolution characteristics on alite surface in conditions of high undersaturation.\textsuperscript{28–30}

At low undersaturation levels and close to equilibrium (values of ln(\(\Pi\)) higher than -64 in Figure 2.3), the mechanism of dissolution (Mechanism I) is slower and seems to be dominated by the step retreat of previously opened etch pits or pre-existing
roughness. In this case, the history and physical characteristics of the alite surface plays an important role as the rate of dissolution depends on how easily atoms are removed and therefore on the surfacial crystallographic characteristics and density of defects. Although the dissolution in low undersaturation is dominated by step retreat and that topographical analysis gives evidences of more homogeneous dissolution characteristics, the formation of etch pits at low undersaturation cannot be excluded as recently observed by Juillard and Gallucci\textsuperscript{29} However, they remain small and therefore play a minor role in the dissolution.

Figure 2.3. Example of dissolution rate of alite showing the two different mechanisms involved and their associated apparent activation energies of dissolution as a function of the undersaturation degree. As the undersaturation tends towards zero, the rate-determining dissolution step changes as shown by the change in the apparent activation energy. Mechanism II represents a fast dissolution regime most probably controlled by etch pits formation and step retreat and mechanism I a slower regime essentially controlled by step retreat. Reproduced from Juillard and Gallucci.\textsuperscript{29}

Two different studies, one performed on ground powder and the other one on polished cross-section of polycrystalline alite, led to very similar rate of dissolution
although the experimental conditions were completely different. In both cases, the transition to the slow dissolution rates occurs at the same undersaturation ($\ln(\Pi)$ of -64). This threshold is associated to a change of the interface between the surface and the liquid occurring at a pH of around 12.25. It might come from a higher deprotonation of the aqueous silicate groups at the surface that leads to the adsorption of more Ca-ions stabilising the dissolution of the surface.\(^{29}\)

The density of defect plays a significant role as shown by calorimetric measurements performed on alite annealed at 650 °C. This annealing removes defects on the surface and leads to longer induction period.\(^{76}\) However, there is a lack of knowledge concerning the characterisation and quantification of defects that would allow determining their exact role and quantifying their contribution in the energy associated to the dissolution.

The change of dissolution mechanism from creation of etch pits to slow release of ions from preformed steps provides a satisfying explanation for the deceleration and the induction period where the building up of calcium and silicate in solution increases the saturation degree. Following this hypothesis, the onset of the acceleration period (i.e. the end of the induction one) would occur when reaching the supersaturation needed to precipitate portlandite. Portlandite formation would increase the degree of undersaturation with respect to C-S-H, renew C₃S dissolution and therefore offer a greater driving force for C-S-H precipitation.\(^{77,78}\) However, limitations of the slow dissolution step hypothesis have been mentioned by Gartner\(^{79}\) because of a discrepancy between the effective solution concentration when the dissolution rate decreases and the theoretical values of C₃S solubility calculated from thermodynamics. But, as explained by Scrivener and Nonat,\(^{45}\) this probably comes from the solubility of alite, determined by its bulk surface, which is different in its hydrolyzed state in water. Indeed, the nature of tricalcium silicate surface in water is strongly dependent on the presence of the silanol groups of which the protonation is influenced by the pH as mentioned above. The deprotonation of the surface would lead to a substantial change of interfacial properties due to the ionic charge and the possibly resulting formation of complexes with Ca-ions.\(^{30}\)
Physical parameters of the surface have a great importance regarding the dissolution process and kinetics. The most important ones are the particle size distribution and the specific surface area. The finer the cement powder, the higher is the specific surface and the higher is its reactivity. Other parameters include the density of defects,\textsuperscript{\textregistered} crystal orientation,\textsuperscript{\textregistered} fracture surface or damages coming from the grinding process.

2.1.2.3 Stage II: the induction period

For some authors the induction period (stage II in Figure 2.2) corresponds to a latent time until a critical event as nucleation or polymerization of silicates takes place. The event would mark the end of the period of low chemical activity and the onset of the acceleration period. For others, the induction period is just the time in which a process of reducing rate (dissolution) is matched by a process of increasing rate (growth).

From this last perspective, the fast drop of silicate concentration already at the beginning of hydration proves that C-S-H nuclei form in the very first minutes after immersion in water and control the hydration kinetics.\textsuperscript{\textregistered}\textsuperscript{\textreg} During the induction period, C-S-H nuclei still form and, once they reach a certain critical size, start to grow, which represents the start of the acceleration period. The importance of the available surfaces provided initially by the nuclei for further growth has been shown by the study of Thomas et al.,\textsuperscript{\textreg} where stable C-S-H seeds added in hydrating C\textsubscript{3}S accelerate notably the hydration by shifting the onset of the acceleration period to earlier times and increasing the slope of the main peak (Figure 2.4).
This means that a certain amount of surface has to be reached to observe the significant precipitation of hydrates linked to the onset. This would imply that the induction and the acceleration periods are controlled by the nucleation and growth of hydrates, which is of course coupled with C₃S dissolution through ionic concentrations in the aqueous phase. Although this hypothesis might explain what is going on during the induction period and the start of the acceleration period, it does not explain the first rapid deceleration. Moreover, as for other views on hydration, direct experimental evidence is lacking to support this hypothesis.

2.1.2.4 Stage III : the acceleration period

As seen above, during the first periods, concentrations of calcium and silicate increase until reaching a critical supersaturation level at which hydrates can nucleate and then grow. Stage III in Figure 2.2 represents the acceleration period where the main peak of the heat release corresponds to a massive precipitation of C₃S-H and CH responsible for setting and hardening. Although it has never been experimentally proven, the predominant view is that in this period a heterogeneous
nucleation and growth of hydrated controls the rate of hydration, which is assumed to be dependent on the C-S-H surface area. However, results of recent experimental and modelling studies seriously question this theory. This starts with the calculation of an apparent activation energy of dissolution (described above in subsection 2.1.2.2) that is very similar to the ones measured by calorimetric methods for C₃S and cement. Furthermore, in a recent study based on the analysis of solution composition, it is proposed that dissolution might fully control C₃S hydration. Looking at the literature advocating the role of nucleation and growth, it can be seen that conclusions mainly rely on different fits to equations describing nucleation and growth. As the equations can fit the data, it is concluded that nucleation and growth is the limiting factor. However, those approaches overlook dissolution. In contrast, approaches only looking at dissolution can also fit the data, which leads the corresponding papers to conclude that dissolution is the rate limiting reaction. Therefore, simple models cannot be used to determine rate limiting steps. To the best of my knowledge, the most significant experimental evidence is the one of activation energy mentioned above and that suggest dissolution to be the rate limiting step.

**Structure of C-S-H**

As mentioned above, C-S-H is poorly crystalline and is composed of sheets of calcium and oxygen surrounded by chains of tetrahedral silica, forming the main layers that are separated by water interlayers. It is generally accepted that the C-S-H atomic structure is close to the ones of tobermorite and/or jennite, two crystalline phases that however have different calcium to silicon ratio than C-S-H. Nevertheless, the growth mechanism of C-S-H and its morphology are still a subject of much debate. Two structural developments have been described: aggregation of nanoparticles and large and defective sheets of silicate.

In the first case, C-S-H particles would grow until reaching a maximum size of some nanometers, but also provide new surfaces for further heterogeneous nucleation or agglomerate with other previously formed nanoparticles. The cohesive nature of these nanoplatelets would arise from ionic correlation forces.
In the second case, Gartner\textsuperscript{96} assumed that the initially nucleated C-S-H particles have a tobermorite-like structure mostly consisting of only one layer, which grows as a 2D product by addition of silicate chains with regularly crystallised regions and others containing defects that present a certain curvature. A second sheet is assumed to nucleate on the perfect region of the first sheet. This second layer grows along the perfect region until reaching the curvature caused by the defects where it separates and continues growing in an independent way. This process leads to well organised nanocrystalline tobermorite-like structures surrounded by amorphous regions. This type of growth with branched nanoparticles might explain the cohesive characteristics of C-S-H.

Besides the uncertainty about the way C-S-H develops in a nano-scale, it also presents two types of more macroscopic morphology depending on where they develop. The first one is the outer product that develops from the grain to the pore space and presents a fibrillar and directional morphology. The second one is the inner product, which forms in the volume originally filled by the anhydrous phase and presents a more compact and homogeneous morphology.\textsuperscript{32,98,99}

Concrete durability is dependent on the microstructure of the hydrated cement paste, and thus on the development and growth process of C-S-H. As mentioned earlier, Thomas et al.\textsuperscript{84} showed that the addition of C-S-H seeds not only increases C\textsubscript{3}S or cement hydration rate by providing more surface, but also promotes hydrates precipitation in the capillary pore space, which is usually not possible in non-seeded systems (Figure 2.5). According to the authors, evidences of the occurrence of these two different processes can be observed on the calorimetric curves of Figure 2.4 where a shoulder appears before the main hydration peak of seeded systems and increases with the amount of added seeds. In the same study, SEM images performed on 28 days old hydrated C\textsubscript{3}S clearly show that the seeding provides a more uniform microstructure with a better distribution of the hydrates and less pores. This means that promoting a more homogeneous growth of hydrates impacts positively the microstructure by decreasing the capillary porosity. We can therefore expect that this should lead to better durability properties at equivalent mechanical strengths at least at the cement paste level. However, this benefit could be (strongly)
attenuated in concrete as it is a composite material with big inclusions that lead to inhomogeneities such as interfacial transition zone (ITZ) or microcracks, which play an important role in the ions transport and therefore in the durability properties of the concrete. Experimental investigation of this hypothesis would be an interesting subject to examine with important possible practical implications.

Figure 2.5. Schematic illustration of hydration process a few minutes (a) or several hours (b) after mixing a paste without seeding. The hydration product nucleates on particles surface and grows towards the pore space. After some hours, the thickness of the hydration product limits further grows, which leads to a high volume of capillary porosity. With the seeding, hydration products precipitate on particles surface and on C-S-H seeds after some minutes (c), which leads to less porosity after some hours (d). Reproduced from Thomas et al.84

2.1.2.5 The deceleration period

More recently, STEM (scanning transmission electron microscopy) images of early hydrated C₃S have confirmed that C-S-H grows as needles with a well defined shape outside the grains.32 The needles form on the C₃S surface until reaching a complete coverage that always corresponds to the maximum of the heat release regardless of the impingement degree (and therefore the water content and the volume still free of hydrates). In the same study, to explain the deceleration of hydration leading to the stage IV in Figure 2.2, Bazzoni proposed a transition from outer product to inner
product growth. Instead of having new needles precipitating on previously formed ones, C-S-H would precipitate at the interface between anhydrous grains and the originally formed needles, leading to another slower growth mechanism. This hypothesis shows a similarity with the model developed in Dijon where the authors proposed that C-S-H precipitates and grows both parallel and perpendicular to the surface of the particles until full coverage is reached.\textsuperscript{82,83} At that point the main hydration peak is reached and the model of Dijon assumes that C-S-H growth then only proceeds perpendicularly to the surface (outwards) on previously formed C-S-H. In this case, the lower rate of hydration is explained by a slower diffusion of ions through the hydrates. A transition to a diffusion regime because of denser hydrates layer has always been proposed for the deceleration but has never met all the conditions to explain the experimental observations.

Finally, the lower heat release of stage V is usually attributed to a limited transport process through the densifying microstructure. However, recent findings and proposed models already discussed above contradict this hypothesis: similar activation energy throughout the acceleration and deceleration periods of hydration, reduction in the reactive surface area due to etch pits coalescence, etc (Nicoleau, Bullard Scherer, Thomas, juilland).\textsuperscript{29,75,100} All these works tend towards either a dissolution control or a mix control between nucleation, growth and dissolution.

2.1.3 Hydration of ordinary Portland cement

2.1.3.1 Stages of cement hydration

As already mentioned, Portland cement is composed mainly of silicates and a small amount of aluminates. Therefore, its heat release presents characteristics from the hydration of those anhydrous phases and can also be divided in five steps corresponding mainly to alite (or C\textsubscript{3}S) hydration (Figure 2.6).
As for alite, the first exothermic peak in stage I is due to the wetting of the cement surface and to a fast dissolution of the anhydrous phases. Furthermore, in the very first minutes, ettringite precipitates due to the high reactivity of the aluminates and the availability of calcium sulfate. This sharp peak is followed by the sudden slowdown of the reaction and the induction period (stage II). As discussed earlier, the second main peak corresponds to the precipitation of the main products of the silicates hydration (stage III). The reaction then slows down. This second deceleration can be seen in period IV. During this deceleration, a second peak occurs that represents the sulfate depletion point and, as explained earlier, corresponds to a faster precipitation of ettringite and a higher dissolution of $C_3A$. The last stage (V) is a period of low activity due to the slow diffusion of species in the hardened material and includes a third peak corresponding to the formation of AFm from the reaction between ettringite and $C_3A$.

2.1.3.2 Silicate – aluminate – sulfate balance

To understand all the mechanisms involved during cement hydration, studying the fundamental mechanisms with pure phases is a first step. However, it is also necessary to study the interaction between the different phases that might induce
other reactions or kinetics as in pure phases systems. Lerch\textsuperscript{101} and later Tenoutasse\textsuperscript{102} illustrated in particular the importance of the balance between the silicates, the aluminates and the sulfates (Figure 2.7).

![Figure 2.7. Isothermal calorimetry obtained on mixtures of 80\% C\textsubscript{3}S and 20\% C\textsubscript{3}A in presence of variable amounts of gypsum (given in the insert). Adapted from Tenoutasse.\textsuperscript{102}](image)

In a system with 80\% (w/w) of pure C\textsubscript{3}S and 20\% (w/w) of C\textsubscript{3}A, Tenoutasse showed that in absence of sulfates, the aluminates hydration largely suppresses the silicate hydration. However, as gypsum is added, the extent of C\textsubscript{3}S hydration also increases. This addition also delays the sulfate depletion point. At a certain dosage (about 4\% in the case shown in Figure 2.7), there is an inversion of both peaks, so that the sulfate depletion point occurs right after the main silicate peak. From this dosage on, adding more sulfates further delays the sulfate depletion point but does not influence the silicate peak.

The explanation for this is thought to lie in the availability of aluminium ions in the pore solution. Several studies have indeed shown that they negatively impact C\textsubscript{3}S hydration\textsuperscript{47,64,103,104} A longer induction period has been observed by Odler and Schüppstuhl\textsuperscript{103} after the addition of aluminium in the system. More recently, Minard\textsuperscript{46} and Quennoz\textsuperscript{64} observed that either the addition of aluminium ions in the
pore solution or the release of ions from the dissolution of aluminium containing
alite decreases the extent of $C_3S$ hydration.$^{47}$

The addition of sulfates results in the consumption of free aluminium ions through
the precipitation of ettringite. The low solubility of this mineral further contributes
to reducing the concentration of aluminium ions in the aqueous phase, thereby
preventing them from negatively affecting alite hydration. Here again a number of
open questions subsist. For example, the detailed mechanism through which
aluminium affects alite hydration is still debated. One of the explanations proposed
is that released aluminium ions precipitate as C-A-S-H particles, which cannot act as
seeds for further C-S-H growth.$^{104}$

On another hand, studies performed on silica-containing materials, such as quartz or
amorphous silicates, showed that the adsorption of aluminium on their surface
prevents their dissolution.$^{105-108}$ Therefore, we must also consider that in cement it
may be aluminium adsorption rather than C-A-S-H formation that is responsible for
reduced dissolution. In fact, Nicoleau et al. more recently showed that aluminate
ions do not physically adsorb but covalently bind onto silicates surface, which
strongly inhibits $C_3S$ dissolution.$^{75}$ Although the condensation of these alumino-
silicate species is favoured at moderate alkaline conditions, which can be met only in
the very first minutes of cement hydration, the authors mentioned that their
stabilization is possible at higher pH thanks to the presence of calcium ions.

Most importantly is that the role of aluminium on cement hydration cannot be
neglected. Moreover its significance increases as more and more supplementary
cementitious materials (which generally involve a high content of aluminium) are
used in modern and more environmentally friendly concrete.
2.2 PCE superplasticizers

Polycarboxylate ether (PCE) superplasticizers, also defined as high-range water reducers, are comb-shaped copolymers that modify the rheological behaviour of fresh concrete. Developed in the 1980s, they became one of the most used admixtures in concrete technology thanks to their easily modified molecular architecture and their high efficiency, allowing keeping a good workability at low water to cement ratio using low dosage of admixtures.

2.2.1 Molecular architecture of PCEs

PCE molecules generally consist of a backbone with carboxylate functions and lateral side chains (usually composed of polyethylene glycol, Figure 1.1 a-c). The carboxylic groups provide negative charges to the backbones in basic solutions, which promotes their adsorption thanks to the charge reversal of the alite surface at high pH.\textsuperscript{109} The non-adsorbing side chains induce steric repulsion, responsible of the dispersive effect.\textsuperscript{14,110} One of the main advantages of using PCEs is that the molecular structure can be modified to target the expected performances in adsorption as well as in dispersion. This can be achieved by varying the length of the backbone ($n$ in Figure 1.1), the length ($P$), density ($C/E$) and distribution of the side chains along the backbone as well as the chemical nature of the monomers and the bonds between the backbone and the side chains.

Two syntheses are used to produce PCEs.\textsuperscript{13} The first one is the free radical copolymerization of monomers bearing the carboxylic functions with macromonomers that are previously formed from the synthesis of carboxylates with side chains (Figure 2.8). This procedure is promoted in industry as it is simple and cost-effective. However, it leads to a high degree of polydispersity regarding the statistical distribution of the side chains as well as the length of the backbone. The second synthesis is the analogous esterification (or amidation, depending on the nature of the bonds between the side chains and the backbone) of side chains on previously polymerized backbone. This allows having a better distribution of the
side chains and PCEs with low polydispersity, as the length of the backbone is controlled.

![Diagram of Free radical copolymerization and Polymer analogous esterification]

**Figure 2.8. Schematic representation of the two main routes for synthesizing an acrylic (R=H) or methacrylic-based (R=CH₃) PCE.**¹³

As mentioned earlier, the properties of PCEs vary with the nature of their monomers and bonds between the side chains and the backbones. For example, a PCE synthesized with acrylic acid monomers in the backbone and ester bonds will undergo hydrolysis of the side chains in alkaline medium, leading to PCEs with higher charges densities and therefore to better adsorption efficiency over time. In the opposite, when better stability of PCEs is required, the methyl group of methacrylic acid monomers or the use of other linkage with the side chains, such as amid, imide or ether bonds, will prevent the hydrolysis of the side chains and offer more stable polymers. Furthermore, introducing in the backbone other monomers or macromonomers can modify PCEs adsorption ability by either changing either the flexibility of the backbone or the sensitivity of the PCEs to competitive adsorption.¹¹,¹² These are simple examples of how the properties of a PCE change
with the chemical nature of its components and only represent a small overview of what can be done.\textsuperscript{13,14}

2.2.2 Conformation of PCEs in solution

As mentioned above, comb copolymers can be described as the assemblage of \( n \) repeating structural units, each containing \( C/E+1 \) (or \( N \)) monomers in the backbone and one side chain of \( P \) monomers (Figure 1.1b). Gay and Raphaël proposed that the conformation of such polymers in solution depends on the relative values of those three structural parameters and can be grouped into five classes as illustrated in Figure 2.9.\textsuperscript{113,114} Most of the polymers studied in that work belong to the FBW (Flexible Backbone Worm) where the polymer can be viewed as an ideal chain of cores, each having a radius of gyration of \( R_c \). Gay and Raphaël derived scaling laws that describe the size of these cores and the radius of gyration of such polymers as a function of their structural parameters \( n, P \) and \( N \).

![Figure 2.9. Phase diagram for comb homopolymer according to Gay and Raphaël and adapted by Flatt et al.\textsuperscript{113,114} The different domains are the following: decorated chains (DC), flexible backbone worm (FBW), stretched backbone worm (SBW), stretched backbone star (SBS) and flexible backbone star (FBS). \( R_c \) is the core size and \( R_p \) is the side chain size.](image-url)
More recently, this approach was extended for a FBW comb copolymer, representing common PCEs that have side chains significantly shorter than the backbone. Flatt et al. expressed the radius of gyration for comb-shaped copolymers with backbone and side chains monomers having different size:\textsuperscript{114}

\[
R = \left( \left( \frac{a_N}{a_P} \right)^2 \frac{1 - 2\chi}{2} \right)^{1/5} a_P N^{2/5} N^{1/5} N^{3/5} \tag{2.4}
\]

where \(a_N\) and \(a_P\) are the size of the backbone and side-chain monomers respectively. For methacrylic acid monomer, \(a_N = 0.25\) nm and for PEG \(a_P = 0.36\) nm. \(\chi\) is the Flory parameter and is equal to 0.37 for PEG.
2.3 Adsorption

The working mechanisms of numerous chemical admixtures involve the adsorption of water-soluble compounds at a solid-liquid interface. This is in particular the case for water reducers and high range water reducers. If we consider a given dispersant, its impact on fluidity increases with dosage, provided that the admixture continues to adsorb on the surface of the solid particles to disperse. In fact, it is especially the adsorbed fraction of the dispersant that is responsible for the effect on fluidity. Depending on the admixture type and its dosage, there may or not be an equilibrium established between fraction of admixtures adsorbed and those remaining in solution. The nature of this relation is most often reported in the form of adsorption isotherms, which are covered in section 2.3.2.

In addition to the nature of the surface, this relation is profoundly affected by the chemical nature of the dispersant. While it is difficult to establish general relations owing to the variety of chemical compositions and structures available, we outline some general chemical features of dispersants that affect their adsorption in section 2.3.3.

Molecules with a low affinity to the surface may desorb if the conditions are changed (section 2.3.4). This may be by replacing the solution with water\textsuperscript{115,116} or by modifying the ionic composition of the solution by increasing the sulfate or hydroxyl ions concentrations.\textsuperscript{117,118} Admixtures may therefore be subject to competitive adsorption that can reduce their performance.

Other factors that reduce the performance of admixtures can involve an apparent increase rather than a reduction in adsorption (section 2.3.5). Most of these are due to artifacts linked to the standard way of solution depletion method used to measure adsorption. Indeed, in this approach, adsorption is determined by measuring the difference between the amount of admixture added and its fraction remaining in solution after a given time. However, if admixtures are consumed by precipitation or intercalation, their apparent adsorption increases. The amount of admixture adsorbed and acting as dispersant may increase, remain equal or even decrease. The
later situation happens if the admixtures are more effectively precipitated or intercalated, so that the surface coverage of particles to be dispersed decreases.\textsuperscript{119} A similar situation may occur if the admixtures modify the process of nucleation and growth of aluminates, causing an increase in the solid-liquid interfacial area.\textsuperscript{120}

2.3.1 Adsorption and fluidity

2.3.1.1 Initial fluidity

The adsorption increases with polymer dosage until the surface of the solid particles is completely covered. At the same time the fluidity increases and approaches a maximum level that is dictated by the adsorbed conformation of the polymer and the saturation of the surface (Figure 2.10).\textsuperscript{121,122}

![Figure 2.10. Critical and saturation dosages with respect to the dispersing ability. Adapted from Hanehara and Yamada.\textsuperscript{122}](image)

The polymer affinity for the surface has a critical effect on the amount of polymer that must be added before the surface is covered. For example, a polymer with a low affinity for the surface will have to be added in large amounts because a large fraction of it remains in solution rather than being adsorbed. This has led authors to
define the so-called saturation dosage, above which a further addition of polymer does not affect much the fluidity.

Another concept that is found in the literature in regard to polymer dosage is the critical dosage. This is defined as the dosage above which a dispersion effect is noticed. The results obtained from testing this dosage are however extremely dependent on the experimental conditions, such as the w/c ratio (or volume fraction), the type of cement and the type and the chemical structure of the polymer.

2.3.1.2 Fluidity retention

Vickers et al. demonstrated that the loss of fluidity depends on the amount of polymer remaining in solution.\textsuperscript{123} This might be explained considering that a reserve of polymer is available in solution to adsorb on newly formed hydrates.\textsuperscript{124} The question of why polymers that do not initially adsorb would adsorb later in time has two answers. The first is that if there is equilibrium between the solid particles surface and the solution, the distribution of polymers between both depends on the ratio of the surface area to the solution volume. Consequently, if more surface is created, at least one part of the non-adsorbed polymers will move onto the newly created surface, even if the original surface is not fully covered. The second reason is that during the initial 1-2 hours of hydration, most of the hydrates formed are aluminates for which the polymers have a higher affinity, as seen above. Therefore, we could consider that aluminates may initially be at full surface coverage, but not silicates. As long as polymers are available in solution they would extensively adsorb on the aluminates while remaining in equilibrium with partially covered silicate surfaces.

Apart from this, another general consideration is that the workability is lost much faster in systems reaching only partial surface coverage than that with a full surface coverage.\textsuperscript{125} The explanation lies rather in the ability of adsorbed admixtures to modify the chemical kinetics of cement hydration and the associated creation of new surfaces that are detrimental to workability. It probably also includes the possibility that partially covered particles have to let polymers rearrange themselves on their surface, creating contact points having stronger cohesive forces.
2.3.2 Adsorption isotherms

2.3.2.1 Basic phenomenology of adsorption

Adsorption data are most often reported in terms of adsorption isotherms by plotting the amount of adsorbed polymer with respect to the amount remaining in solution. This procedure makes most sense if equilibrium is established between the surface and the solution. In what follows we discuss basic characteristics of adsorption isotherms before discussing possible models for it.

Many theoretical approaches to adsorption isotherms predict that, at low surface and solution concentrations, the adsorbed amount should be proportional to the concentration in solution. However, these approaches may differ substantially with respect to the extent of this linear zone.

The slope in this initial regime represents an adsorption equilibrium constant, $K$, which depends on the free energy of the adsorbate-solvent, adsorbate-surface of the adsorbent and surface-solvent interactions. This implies that, for polymers, the change in configurational entropy between solution and surface, which depends on the molecular structure of the polymer, plays an important role. For linear chains various expressions have been proposed.

For compounds with sufficient affinity for the surface, increasing dosages mainly enrich the surface, while the concentration in solution remains dilute. Rising concentrations at the surface cause the adsorbed polymer to enter a semi-dilute regime in which the adsorbates start to have excluded volume interactions. In this situation polymers reorganize themselves on the surface to minimize the system free energy. The extent of conformational change that they may undergo in this stage depends on the adsorption energy (high values allowing more adsorption). The state of minimal energy corresponds to the so-called adsorption plateau, a regime in which the adsorbed amount becomes independent of the concentration in solution.
2.3.2.2 Simple adsorption isotherm models

As explained above, at low concentrations, adsorption includes a linear range in which the adsorbed amount and the solution concentrations are proportional. Additionally, at higher solution concentrations the adsorbed amount eventually reaches a plateau. These represent two basic features that any adsorption isotherm must capture.

This is for example the case of the Langmuir adsorption isotherm and explains the very popular use of this model.\textsuperscript{126} However, this does not guarantee that it adequately accounts for data in the intermediate regime. In order to better emphasise this, we present an alternative derivation of this relation and then an analogous one that is probably more adequate for polymers.

We begin by considering a chemical reaction in which an adsorbate \( A \) reacts reversibly with a free site \( S \) to form an occupied surface site \( SA \).

\[
S + A \rightleftharpoons SA
\]

For this chemical reaction, we can write an equilibrium constant \( K \), as:

\[
K = \frac{[SA]}{[S][A]}
\]

where \([A]\) is the activity of the adsorbate in solution, \([S]\) is the activity of the free surface site and \([SA]\) is the activity of the occupied surface site.

Considering an ideal mixing situation, \([S]\) and \([SA]\) may be represented by surface fractions. In absence of other substances, we have:

\[
[SA] + [S] = 1
\]

Substitution of (2.7) into (2.6) leads to the first expression of the Langmuir isotherm:

\[
[SA] = \frac{K [A]}{1 + K[A]}
\]
This equation is generally transformed to account for the maximum adsorbed amount and is written as:

\[ m_{SA} = \frac{m_{SA}^\infty K c_A}{1 + K c_A} \quad (2.9) \]

where \( m_{SA} \) is the adsorbed mass, \( m_{SA}^\infty \) is the adsorbed mass at the plateau and \( c_A \) is the concentration in solution.

As explained in the previous section the plateau for polymer adsorption depends on their ability to organize themselves in a compact way on the surface. This is affected by their adsorption energy. For linear chains, the adsorbed mass at the plateau \( m_{SA}^\infty \) increases with the cubic root of the adsorption energy.\(^{128}\) Although this dependence is much lower than for \( K \), which varies as the exponential of adsorption energy, it is not negligible. Equation (2.9) is therefore somewhat misleading as it suggests that only \( K \) would depend on it. Reducing the adsorption energy should therefore affect the plateau.

However, there are other more important issues that one may consider before applying this equation to polymer adsorption. We present a simple modification of the above derivation, to illustrate one matter of concern.

We now consider a situation in which \( x \) sites \( S \) get occupied by one polymer \( P \). Equation (2.5), (2.6) and (2.7) becomes:

\[ xS + P \rightleftharpoons S_xP \quad (2.10) \]

\[ K = \frac{[S_xP]}{[S]^x[P]} \quad (2.11) \]

\[ [S_xP] + [S] = 1 \quad (2.12) \]

Combining (2.11) and (2.12), we write:

\[ [P] = \frac{[S_xP]}{K(1 - [S_xP])^x} \quad (2.13) \]

36
The important point here is that the relation between amounts adsorbed and in solution depends on $x$. It can be shown that the equilibrium constant $K$ however has an even stronger dependence on $x$. Consequently, the initial slope of the adsorption isotherm is initially much steeper, but would then curve over at larger concentrations in solution to reach the true adsorption plateau.

However, this model probably puts an over proportional weight on the activity of the free sites. Indeed, for polymer adsorption it may be more realistic to consider that on the surface covered by an adsorbed polymer, only a fraction of surface sites are occupied. In such situation, the free site activity may remain unity (or constant in case of competitive adsorption with small species) over a large range of concentration. In this case (2.6) may be rewritten as:

$$K \equiv \frac{[SA]}{[A]} \quad (2.14)$$

In the next sub-section we examine experimental data for the adsorption of superplasticizers to determine the extent to which one or the other of these predictions may hold.

### 2.3.2.3 Linear zone of adsorption isotherms of superplasticizers

Studies on the adsorption of superplasticizers often show that the fraction of adsorbed polymer remains constant as dosage increases. Moreover, this fraction can be quite different from unity over a large range of dosages. This large linear zone can be interpreted in two ways. First, it may be a result of polydispersity, with only one fraction of the polymers adsorbing strongly and the other barely adsorbing. Second, as explained previously, it may be due to the fact that the free site activity remains roughly constant because the number of sites occupied in the surface covered by a polymer is small. In the later case, the proportionality between adsorption and dosage is a result of the equilibrium expressed in (2.14).

To better identify situations in which adsorption is proportional to dosage, it can be helpful to also plot adsorption versus dosage. In this case, the same units should be used on both scales, for example polymer mass with respect to solid (mass of
surface). An example for lignosulfonates (LS) dispersants is illustrated in Figure 2.11.\textsuperscript{131} It clearly shows that the initial part of the adsorption is linear with dosage. A more careful analysis shows that the initial slopes are not all identical and slightly lower than unity (0.82–0.98). This implies that during this initial stage only a fixed fraction of the polymer is adsorbed (82 to 98%), which most probably results from the polydispersity in size and/or molecular structure. On the same graph, it can also be observed that above this linear zone, some polymers are at their plateau, while others continue to adsorb gradually with increasing dosage.

A similar situation is shown in Figure 2.12 for various polycarboxylate ether (PCE) dispersants.\textsuperscript{131} In that case also, there is a distinct initial linear zone as a function of dosage. However, here the slopes are substantially lower and more differentiated (0.37 – 0.58). In this graph, it should be noted that the polymer PCP-3 does not reach a plateau. This is probably a result of precipitation as discussed in section 2.3.5.1.

Figure 2.11. Adsorption data of different lignosulfonate polymers plotted as a function of the added polymer amount. Adapted from Houst et al.\textsuperscript{131}
Chapter 2 – State of the Art

The amount of polymer adsorbed at the end of the linear zone is far beyond what would be expected if a Langmuir type isotherm were followed (true isotherms not shown here). For LS, it could be argued that owing to the high fraction of polymers adsorbed, a relation of the form given in (2.13) may apply. A consequence of this would be that true equilibrium would be very difficult to reach at the plateau. However, we cannot exclude that (2.14) applies.

For PCEs however, only a rather limited fraction of the polymer adsorbs in the linear regime. One possible reason for this could be polydispersity. Indeed, superplasticizers show typically a polydispersed structure, meaning that they contain many fractions of different molecular weights and/or structure. It is therefore possible for a certain discrimination to take place during adsorption between these different fractions.\textsuperscript{132}

However, in absence of polydispersity effects, we would infer that (2.13) does not apply. Rather, we would conclude to the existence of an extended linear zone resulting from a constant activity of the free sites, so that (2.14) applies. To distinguish between both situations it would be necessary to compare adsorption

Figure 2.12. Adsorption data of different polycarboxylate polymers plotted as a function of the added polymer amount. Adapted from Houst et al.\textsuperscript{131}
data obtained in suspensions of which the solid to liquid ratios would be varied. Plate\textsuperscript{15} has carried out such experiments and his results support the reversibility of PCE adsorption above a certain adsorption threshold.

2.3.2.4 Specific issues in studying adsorption on cementitious systems

An important issue in measuring adsorption isotherms of polymers is to know whether true equilibrium has been reached. At high surface coverage, the rearrangement of polymer will take time, particularly if their adsorption energy is high. In cementitious systems the problem is exacerbated by the fact that the surface area changes with time owing to chemical reaction so that only limited contact times may be used.

Another issue in cementitious systems is that polymers are not expected to adsorb uniformly on the different phases present in cement. Indeed, several studies performed on pure cement clinker phases and hydration products showed that superplasticizers adsorb preferably on aluminates phases, which have a positively charged surface (ettringite having the highest affinity), than on silicates with a negatively charged surface, although a charge reversal taking place on silicates phase surface still provides an apparent positive charge.\textsuperscript{133–135} These studies show the importance of understanding the behaviour of superplasticizers when facing each cement phase for controlling fluidity of cement paste and concrete.

2.3.3 Molecular structure and adsorption

2.3.3.1 Adsorption of superplasticizers

Molecular mass plays an important role in PCE superplasticizers adsorption, regardless of their molecular nature.\textsuperscript{136,137} Adjusting molecular mass is therefore a way to modify the performance of a superplasticizer. For synthetic polymers it can be done by modifying synthesis conditions, such as concentrations of monomers and chain transfer agents, as well as temperature and reaction time, among others. Additionally, as mentioned earlier, one should also consider that superplasticizers
are polydispersed in size and structure so that a certain discrimination can take place during adsorption.\textsuperscript{132}

On the basis of the synthetic nature of PCEs, one can in principle change the chemistry of the backbone and its length, the amount of ionic group with respect to the side chains, expressed as carboxylic to ester (C/E) ratio or grafting density, the length of side chains etc., depending on the performance desired. All these factors affect the adsorption, which in turn affects the rheological properties as evidenced in numerous papers.\textsuperscript{121,125,136,138–141}

In section 2.2.2, the conformation of a comb-shaped copolymer in solution and more specifically its radius of gyration have been defined in equation (2.4) with the structural parameters $P$, $N$ and $n$ (Figure 1.1b) and the size of the different monomers in the backbone or in the side chains.\textsuperscript{114} As illustrated in Figure 2.13, the conformation is represented in solution as a chain of blobs (the size of which relates to the previously mentioned parameters). The conformation of such a comp-shaped copolymer adsorbed on a particle of cement can be derived in a similar way by using a chain of hemispheres on a surface (see also Figure 2.13). The radius of these hemispheres is noted $R_{AC}$ and is defined as:

$$R_{AC} = \left(2\sqrt{2}(1 - 2\chi) \frac{a_P}{a_N}\right)^{1/5} a_P P^{7/10} N^{-1/10}$$  \hspace{1cm} (2.15)

where $a_N$ and $a_P$ are the size of the monomers in the backbone and in the side chains, respectively, $P$ the number of monomers in the side chain and $N$ the number of monomers in the backbone for one side chain. The surface $S$ occupied by each molecule on a particle can be then calculated from:

$$S_A = \frac{\pi}{\sqrt{2}} a_N a_P \left(2\sqrt{2}(1 - 2\chi) \frac{a_P}{a_N}\right)^{2/5} P^{9/10} N^{3/10} n$$  \hspace{1cm} (2.16)
The most important parameter during adsorption is the density of ionic groups in the backbone. Indeed, PCEs adsorption increases with the density of ionic groups on the backbone.$^{121,142}$ Interestingly, independent studies from Regnaud et al.$^{142}$ and Winnefeld et al.$^{138}$ suggest that adsorption drops strongly below a $C/E$ ratio of 2, regardless of the side chains length.$^{14}$

The strong effect of the ionic charge can be understood to some extent using the first principle equilibrium constant proposed by Marchon et al.$^{118}$ In that study, the authors considered that the charges are competing with other ions on the surface that are present in much larger amounts. To support this approximation, we consider that in the area occupied by a PCE, the density of functional groups is:

$$\sigma_A = \frac{n(N - 1)}{S_A}$$  \hspace{1cm} (2.17)

A first simple approximation for the charge density on the surface $\sigma_s$ is to consider that there is one charge in an area given by the $a_p a_N$. The ratio of charge densities between the surface and the adsorbing function of the polymer is then:
\[
\frac{\sigma_S}{\sigma_A} = \frac{\pi}{\sqrt{2}} \left(2\sqrt{2}(1 - 2\chi) \frac{a_P}{a_N}\right)^{2/5} P^{9/10} N^{3/10} (N - 1)
\]

This shows that the charge density ratio increases almost linearly with \(P\). Its dependence on \(N\) is less trivial, but in first order would decrease with its 7/10 power (approximating the denominator \(N-1\) to \(N\)). Higher values of \(N\) therefore decrease this ratio, which is expected since this directly increases the number of functional groups. Nevertheless, the dependence is not linear. In quantitative terms we can consider polymethacrylate based PCEs with PEG side chains for which we have \(a_P = 0.36\), \(a_N = 0.25\) nm and \(\chi = 0.37\). Taking typical values of \(P = 23\) and \(N = 4\), we get a charge density ratio of about 20. Therefore in the surface occupied by a PCE, we expect that only about 5\% of the surface charges will be occupied by the functional groups. While this approximation depends a lot on our estimate of \(\sigma_S\) the main conclusion should remain. In particular it implies that the surface occupancy of charges does not need to be considered and leads to an adsorption isotherm of the form given in (2.14) (equation 6 in Marchon et al.\(^{118}\)).

To estimate the adsorption equilibrium constant as a function of PCE molecular structure, Marchon et al. considered the balance between adsorption and desorption rates of functional groups.\(^{118}\) More specifically, they defined the rate constant for these processes respectively as \(k_A^a\) and \(k_A^d\). For each of these constants they proposed the following relations to the structural parameters of the polymer:

\[
k_A^a \propto \frac{n(N-1)z}{S_A} \frac{1}{n} = \frac{(N-1)z}{S_A}
\]

\[
k_A^d \propto \frac{S_A}{n(N-1)z}
\]

where \(z\) is the number of charges carried by each monomer in the backbone and \(S_A\) the surface occupied by the molecule proportional to \(P^{9/10} N^{3/10} n\) as seen in equation (2.16).
The adsorption kinetic rate constant is proportional to $n(N - 1)z/S_A$, which represents the surface charge density of the adsorbed molecule, and inversely proportional to the number of side chains $n$ to take into account the steric hindrance induced by the side chains. The desorption rate constant is inversely proportional to the surface charge density.

The adsorption equilibrium constant is then obtained as the ratio between both constants:

$$K_A = \frac{k_A^a}{k_A^d} \propto \frac{z^2(N - 1)^2}{nP^{9/5}N^3/5}$$

(2.21)

With this adsorption equilibrium constant, it is possible to link the structural parameter of a polymer with its adsorption ability.

### 2.3.4 Dynamic exchanges between surface and solution

#### 2.3.4.1 Reversibility of adsorption

The adsorption of admixtures at interfaces represents a reversible process in which various admixtures will have different affinities for the surfaces. Moreover, just as adsorption depends on surface coverage so does desorption. For example, if the aqueous phase of a suspension containing a large amount of admixtures both in solution and at the solid-liquid interface is replaced by pure water, part of the admixtures will desorb. However, with lower amounts of admixtures in the systems, these will mainly be adsorbed at the surface, and will therefore not or barely desorb if the solution is replaced by pure water. Such effects are well known and have also been measured with superplasticizers in cement suspensions.\textsuperscript{115,116}

The fundamental reason for this behaviour is that adsorbed admixtures are not immobile on the surface. In particular, at high surface coverage, the equilibrium with the surface is dynamic. This was shown by Pefferkorn et al.\textsuperscript{143} They adsorbed labeled polymers on particles and subsequently replaced the continuous phase with solution containing identical unlabeled polymers. By measuring the labeled
polymers, they showed that radioactive decay is proportional both to the coverage by labeled polymers, $\Gamma^*$, and to the bulk concentration of unlabeled polymers, $c_b$. There is therefore a faster exchange of polymers when their concentration in solution is high and a much lower one otherwise. This explains why it is very difficult to completely desorb polymers by repeated washing with pure solvent.\textsuperscript{144} An interesting aspect of this result is also that at high polymer dosages, owing to polymer mobility, the system has the capacity to rearrange polymers at the surface and evolve towards a true equilibrium full surface coverage. However, the kinetics of this process may be slow, even more so for polymers with a high affinity for the surface.

The above finding emphasises an important fact: adsorbed polymers are not irreversibly fixed. They can be replaced by similar polymers, but more generally also by other species. This brings us to the notion of competitive adsorption that is dealt with in the next section.

2.3.4.2 Competitive adsorption

One of the reasons for some cement-superplasticizer incompatibilities comes from soluble sulfates contained in the cement.\textsuperscript{145} More generally, the performance of superplasticizers can be perturbed by various ionic species, leading to a dramatic loss of the dispersive effect due to competitive adsorption. Hydroxides,\textsuperscript{118,146} sulfate ions,\textsuperscript{117} citrates and tartrates\textsuperscript{147} or other polymeric admixtures\textsuperscript{148} are among the chemical species competing for the solid surface with superplasticizers and thus reducing their adsorption.

When dealing with competitive adsorption, it is important to consider that not only the initial slope $K$ but also the plateau are affected by adsorption energy. Additionally, when extracting data from adsorption isotherms, the choice of the model will obviously affect the result.

Yamada et al.\textsuperscript{117} showed the competitive adsorption between PCEs and sulfates. By alternatively changing the concentration of sulfate ions in solution with the addition
of CaSO₄ and Na₂SO₄, the authors showed the reversibility of the PCEs adsorption (Figure 2.14 left) and its effect on the rheology (Figure 2.14 right).

![Figure 2.14](image)

**Figure 2.14.** Illustration of the effect of sulfates on the performance of a PCE superplasticizer in cycles involving alternative additions of CaCl₂ and Na₂SO₄. Left: adsorbed PCE as a function of sulfates concentration in the aqueous phase. Right: relative flow area from paste flow tests as a function of sulfates concentration in the aqueous phase. Reproduced from Yamada et al.¹¹⁷

Later, the correlation between the sulfate sensitivity and the structural parameters of the polymer has been demonstrated on cement pastes with different PCEs.¹⁴⁹ By using a similar test to change sulfates content, the sulfate sensitivity of the PCEs was found to be proportional to \( P/N^2 \). With a theoretical approach, Flatt et al. refined the dependence of the sensitivity with a molecular structure dependent parameter called Sulfate Sensitivity Parameter (SSP) and given by: \( P^{4/5} N^{3/5}(N-1)^{-2} \).¹⁵⁰

More recently, a study about alkaline activation of superplasticized blended cement focused on the sensitivity of PCEs to hydroxides.¹¹⁸ By neutralizing the hydroxides with HCl, the authors were able to show that the loss of PCEs dispersive effect in an activated system with NaOH is not due to a possible hydrolysis of the side chains but to a competitive adsorption. Moreover, the sensitivity of PCEs to the presence of additional alkalis could be related to changes in the adsorption equilibrium constant given in equation (2.21). This criterion is particularly useful to determine easily the adsorption behaviour of a molecular structure in extreme conditions, such as
alkaline activated systems, where strong incompatibilities between the PCE superplasticizers and the ionic species in solution have been observed.\textsuperscript{146}

2.3.5 Consumption (ineffective adsorption)

2.3.5.1 Precipitation

In regard to the efficiency of dispersants, we are interested in molecules that are adsorbed and reduce the maximum attractive interparticle force.\textsuperscript{110} If admixtures precipitate with hydrates to form new organo-mineral phases, they will not be active as dispersants.

If such precipitation takes place on particle surfaces, it will create a layer of which the dielectric properties will contribute to the overall Van der Waals forces. As a rule of thumb, the lower the density of this layer, the lower will be its contribution to Van der Waals force. However, unless it is several nanometers thick, one can expect a low-density layer to get compressed under the action of Van der Waals forces between particles on which they have formed. They would do so until they cannot get more compressed, at which point the attraction between particles will result from a combination of the dielectric properties of both the layer and the particles. Such surface precipitates may therefore be beneficial in reducing the magnitude of the Van der Waals force, but the extent to which they can do so is most probably limited. If precipitation occurs in the bulk solution, the impact on rheological properties should in general be low, unless a gel network were to be formed.

However, such precipitation reactions may have an important role on hydration kinetics. Indeed, the precipitation of admixtures on surfaces can most likely slow down diffusion, in particular if it takes place around high-energy sites.\textsuperscript{35,48} Precipitation in the bulk of the solution might have an indirect effect. Indeed, it will deplete the solution from some ions and thereby increase the driving force for dissolution.

An indication of precipitation can be seen if adsorption measurements do not reach a plateau, even at very high dosages, as shown in Figure 2.12 with the PCE polymer
PCP-3. This indicates that “normal” adsorption is not taking place. However, it does not indicate the nature of the compound forming or its location (solution or surface).

2.3.5.2 Organo-aluminates

One type of precipitate that can form is an organo-aluminate phase.\textsuperscript{151–154} As explained in the section 2.1.1, a product of the hydration of aluminates is composed of positively charged platelets with counter ions intercalated between them. An organo-aluminate phase is a layered double hydroxide between the layers of which polymers are intercalated compensating only in part the surface charge balanced otherwise by hydroxides.\textsuperscript{155}

The conceptual model concerning the impact of the formation of this phase is that polymers would be trapped within it and incapable of dispersing cement particles.\textsuperscript{119} Various observations were used to postulate the existence of such a process:

1. Delayed addition of superplasticizers generally leads to much better fluidity, even if this is only done less than a minute after water addition.
2. Atomic force microscopy measurements by Uchikawa et al. suggested the presence of a steric layer much larger than the polymer size (10 to 100 times).\textsuperscript{156} Their measurements therefore rather point to the formation of a gel on the clinker surfaces rather than simple steric hindrance from adsorbed polymers.
3. Addition of sulfates tends to reduce polymer adsorption, but improves the fluidity for polymers that are sensitive to the addition time.\textsuperscript{157}

Since then the possibility of forming such phases has been demonstrated by different approaches. These involve: reacting C\textsubscript{3}A in water and in presence of PCEs,\textsuperscript{153,154} precipitation by mixing a solution of sodium aluminate and polymer with a solution of calcium hydroxide, adding the polymer to a suspension of previously precipitated hydrocalumite.\textsuperscript{151}

Thermal analysis, XRD, NMR and TEM have all concluded to the formation of such phases in absence of sulfates. It has been found that layers of organo-aluminates do
An example for a polymethacrylate PCE is shown in Figure 2.15. In that case the layer spacing is between 7 and 10 nm. The authors of that study found that small angle X-ray scattering gave small angle peaks also compatible with such distances. In fact, these would correspond to polymers adsorbed through their backbones and having coiled side chains. Further evidence in support of the coiled conformation has been provided by NMR transfer of polarization measurements. Moreover, the layer spacing shows a scaling exponent with respect to the side chain length that is the same as that of coils.

The conclusion concerning the coiled conformation of the side chains and the relatively large interlayer spacing raise a serious question concerning the stability of such lamellar phases. Indeed, at such distances, it is difficult to understand which cohesion forces would hold the layers together as the polymers ought rather to be acting as steric dispersants. One possible explanation is that platelets are in fact dispersed and align during sample preparation. This would be consistent with a
coherence length determined from low angle X-ray scattering that suggest the average number of stacked layers only to be between 3 and 4.\textsuperscript{151}

Another important observation concerning this organo-aluminate phase is that it is destabilised in presence of sulfates at the expense either of monosulfate or ettringite.\textsuperscript{151,158} In the experiments of Giraudeau et al., the conversion was shown to take place through a process of dissolution, nucleation and growth.\textsuperscript{151} More importantly, an induction time before conversion was observed and dependent on the nature of the PCE. More ionic PCEs tend to lead to longer induction times.

Such observations point to the crucial role of sulfates in determining whether or not organo-aluminates may form.\textsuperscript{159} Mixing process may also play a role in this phenomenon as it affects ion concentration at particle surfaces. Indeed, if organo-aluminates are given a chance to form, they may remain stable beyond the mixing time and consequently affect rheological properties and their evolution. If they are immediately destabilised, they probably play an important role in the nucleation of ettringite as discussed in the next subsection.

2.3.5.3 Change of specific surface

As explained by Yamada,\textsuperscript{160} one may expect that the extent of dispersion that can be reached strongly depends on the specific surface of the system. This basic principle has far reaching implications. One of them is methodological. It concerns mainly the sample preparation for BET measurements of hydrates.

A second implication is that any replacement of a component by one having a higher specific surface will in most cases lead to a lower surface coverage (unless a large excess of polymer is used initially). Additionally, even if the surface coverage remained the same, the reduction in average particle size would also be detrimental to yield stress.

The case of organominerals defined in the previous section can in fact be understood from the perspective of an increase in specific surface. This would be internal if one has true intercalation and external otherwise. However, the result is the same. A particularly interesting aspect of the case of organominerals is that their amount
and surface results from hydration reactions. Such reactions can be modified by the presence of chemical admixtures as explained in the section 2.4. For example it is well known that the morphology of ettringite can be altered in presence of superplasticizers. At equivalent amounts of ettringite, the surface area of a given system is increased and the surface coverage decreased. Consequently, the way in which admixtures impact early hydration reaction also impacts their rheology. This may or may not also impact later hydration, but there is no direct relation.

Finally, a last source of large surface areas in cementitious materials can be clay minerals, more specifically swelling clay minerals. In the later case both external and internal surfaces must be considered.
2.4 Impact of PCEs on cement hydration

Many chemical admixtures are known to retard cement hydration. In the case of “retarders” this is an intentional effect, but for many other admixtures it is mostly an undesired side effect. In this section, we deal in a general way with the mechanisms that affect hydration in order to encompass the behaviour of most chemical admixtures and especially PCE superplasticizers.

In general, retardation by chemical admixtures depends not only on their dosage, chemical nature, molecular architecture, the time of admixture addition (Figure 2.16), but also on the characteristics of the cement, such as its mineralogical composition, fineness and sulfate availability. Additionally, commercial admixtures are often formulated products that can contain multiple components. For example, in addition to polymeric dispersants, commercial superplasticizers may also contain defoamers, accelerators, viscosity modifying admixtures, all of which can modify the extent of retardation.

![Figure 2.16. Illustration of the effect of addition time on setting times (initial and final) of normal Portland cement for different admixtures. Adapted from Hanehara and Yamada.163](image)

In calorimetric measurements, retardation is typically seen to prolong the induction period. However, the effect on hydration is not always only to delay the onset of the
main hydration peak. For example, chemical admixtures can also change the slope of the acceleration period, as well as the maximum heat release (i.e. the height of the main peak) and/or displace the sulfate depletion peak. Such changes can lead to a totally different calorimetric signature of the hydration process as illustrated in Figure 1.1 and Figure 2.17 for two different superplasticizers. This implies that complex interactions between chemical admixtures and cement are taking place during hydration and that they can substantially modify the rates of the dissolution, nucleation and/or growth of various phases. These changes may also modify the nature of the step that is rate limiting for cement hydration, something addressed later in this chapter.

![Figure 2.17. Example of isothermal calorimetry showing the effect of a PCE and PNS superplasticizer on a mortar with ordinary Portland cement. The difference in the shapes of the curve is in particular noted. Reproduced from Robeyst et al.164](image)

### 2.4.1 Mechanisms of retardation

The above examples illustrate how a set of admixtures, differing in chemical nature and molecular structure, impact in variable ways cement hydration. Although they are subject of many studies, the mechanisms through which they modify hydration
remain unclear.\textsuperscript{27,165} The different hypotheses that have been formulated to explain this are:

- Complexation of calcium ions
- Slowing down of dissolution of anhydrous phases
- Disrupting nucleation of hydration
- Perturbation of the aluminate-silicate-sulfate balance.

Each of these situations is discussed in a separate sub-section.

\subsection{2.4.1.1 Complexation of calcium ions in solution}

Chemical admixtures interact with ionic species in solution (in particular calcium ion) and this may slow down the building up of the supersaturation needed for hydrates nucleation. It is well known that in a clean system (i.e. pure solution of polymers with generally one type of salt), organic admixtures can form complexes with ions in different ways, whose stability depends on the nature of the chemical function, the metallic ion involved as well as the environment conditions.\textsuperscript{166}

In the case of PCE superplasticizers, the first one, mentioned in several studies about interactions between polyoxyethylene and cations,\textsuperscript{167–169} is similar to the ion complexation of crown ethers, where the cation is immobilised inside the polyether ring through ion-dipole interactions with ether oxygen atoms. The second type of possible complexation of PCEs has been mentioned by Plank et al.\textsuperscript{39} In this case the carboxylate functions of the backbone form a mono- or bidentate ligand with Ca-ions depending on the side chains density.

Different studies show evidences of a formation of complexes between highly charged carboxylate polymers and Ca-ions during either C\textsubscript{3}S hydration or C-S-H nucleation.\textsuperscript{42,170} However, the amount of calcium mobilised by such complexes is limited by the low dosage of retarding molecules introduced in the system and the number of charges really involved in the complexing phenomenon. In addition, the complexation stability in solution of PCEs and other admixtures, such as phosphonates or sugars, which also present substantial chelating ability, are too low to significantly influence the calcium concentration to explain the possible strong
retardation.\textsuperscript{170-174} Furthermore, as Thomas and Birchall mentioned in the case of sugars, where, for example, the most retarding ones have the lowest binding ability, no direct correspondence has been found between the complexation ability and the retarding effect.\textsuperscript{175} The specific case of sugars is discussed more extensively in\textsuperscript{35}.

Therefore, although relatively simple, this argument does appear to provide a reasonable ground to disregard the role of calcium complexation on the retardation of cement hydration, at least until further evidence is brought to this debate.

2.4.1.2 Inhibition of the dissolution of anhydrous phases

Chemical admixtures may act on dissolution of anhydrous phases through adsorption, reducing the rate of ion release into solution. By electric conductivity measurements, Comparet observed that PCE superplasticizers delay the increase of conductivity coming from the dissolution of the anhydrous C\textsubscript{3}S and the free growth of C-S-H.\textsuperscript{170} He concluded that PCEs may strongly slow down C\textsubscript{3}S dissolution with a probable additional effect on growth of hydrates, even blocking it for the polymers with the highest charge density. This is further shown by Nicoleau and Pourchet et al. who observed that latexes composed of a core copolymer of styrene and butadiene with carboxylate groups on the surface slow down strongly the silicate reaction after adsorption (Figure 2.18).\textsuperscript{37,38} This conclusion was reached on the basis of measuring the concentration of calcium and silicon by ICP-OES measurements during the dissolution of C\textsubscript{3}S in a very diluted lime saturated solution containing the latexes.
Figure 2.18. Dissolution of 1.5 mg of C₃S in 200 mL of 11 mmol/L lime saturated solution in presence of 0.4 g of two carboxylated latexes, POLYAC1 and POLYAC2. These latexes are composed of a core copolymer of styrene and butadiene with carboxylate groups on the surface. Adapted from Nicoleau.37

It is worth to note that, in both cases, the experiments were performed in lime saturated and very diluted systems with a high admixture dosage, not representative of the real conditions in early age hydration of cement paste. However, the results show clearly that carboxylate additives can strongly decrease the dissolution rate of C₃S as well as the primary C-S-H nucleation, which leads us to the next hypothesis.

2.4.1.3 Inhibition of nucleation and/or growth of hydrates

Chemical admixtures can influence and modify nucleation and growth of minerals.176,177 In the case of C₃S and cement hydration, several studies have implied that chemical admixtures act on precipitation and growth of hydrates interfering with it in various ways. These may include the poisoning of nuclei or the prevention of growth through adsorption onto nuclei or particles,42,175,178 the alteration of dissolution kinetics due to the dispersive effect of superplasticizers,40,41,179 the blocking of the normally favoured crystal growth directions, etc. To illustrate the first case, several studies have suggested that the retardation ability of sucrose for example comes from the poisoning of portlandite nucleation.175,178 If portlandite precipitation is suppressed, C₃S dissolution cannot be resumed, as the degree of
saturation of the solution does not change, which does not allow C-S-H precipitation and leads to the prolongation of the induction period.\textsuperscript{77}

In the case of PCE superplasticizers, as a model system for studying the effect of such polymers on the precipitation of cement hydrates, several studies have dealt with the precipitation of CaCO\textsubscript{3} in presence of linear and comb-shaped polycarboxylates.\textsuperscript{180-182} In a first study, Rieger et al.\textsuperscript{180} showed that amorphous CaCO\textsubscript{3} precursors, which normally dissolve and recrystallize as calcite, are fixed in a network consisting of linear carboxylate chains bridged by Ca\textsuperscript{2+}, avoiding the dissolution of the precursors and their recrystallization. Falini et al.\textsuperscript{181} mentioned that carboxylate admixtures not only inhibit CaCO\textsubscript{3} precipitation in the case of high dosages but also modify growth, size and morphology of the crystals, depending on the length and density of the side chains. This has also been confirmed by Keller et al.\textsuperscript{182}, who mentioned that CaCO\textsubscript{3} nuclei are distributed along the polymer backbone through complexation of Ca-ions by the carboxylic groups. In this case, the authors concluded that, in presence of PCEs, mesocrystals form via self-assembly of the PCE-stabilised initial calcite nanocrystals.

A similar mechanism occurring during C-S-H precipitation and involving the calcium ions could explain the delay of C\textsubscript{3}S hydration. Indeed, it has been proposed that, during the first step of C-S-H nucleation, Ca-ions trigger the oligomerization of the silicates and bridge these oligomers to form larger agglomerates.\textsuperscript{42} In presence of PCEs, hydrate precursors could be adsorbed to negatively charged sites on the polymer via Ca\textsuperscript{2+} bridging and thus be stabilised against agglomeration, which would penalize C-S-H nucleation. This has been suggested by Picker who used calcium titration to study the effect of highly charged polyacrylate acid chains on the nucleation of C-S-H from a solution of Na\textsubscript{2}SiO\textsubscript{3} and CaCl\textsubscript{2}.\textsuperscript{42} His results show that, first, the polymer modifies the prenucleation slope (point 1 in Figure 2.19), indicating a change of interaction between the calcium and the silicate species. Then, the first nucleation point (point 2) is delayed and occurs at higher supersaturation. The primary particles are probably stabilised by the polymer but cannot assimilate all the additional Ca-ions (point 3). Then the calcium potential drops indicating a
secondary formation of C-S-H particles via a possible heterogeneous nucleation process on primary formed nuclei (point 4).

![Figure 2.19. Evolution of free Ca\(^{2+}\) during addition of CaCl\(_2\) solution into Na\(_2\)SiO\(_3\) in absence (reference) and in presence of a highly charged polyacrylate (PAA 450000). Reproduced from Picker.\(^{42}\)](image)

This last study offers useful insight into possible reasons for the retardation of cement hydration. However, it only targeted C-S-H precipitation in pure conditions and does not explain why, with a common dosage of PCEs (containing a concentration of carboxylate groups much lower than in that study), the delay can increase up to hours, if not days, in superplasticized cement pastes where a part of the molecules can adsorb not only on C-S-H but also on other hydrates as well as anhydrous phases. In short, it is our opinion that the multicomponent nature of the cement cannot be neglected. This leads us to the last hypothesis concerning retardation.

### 2.4.1.4 Perturbation of the silicate-aluminate-sulfate balance

*Superplasticizers can cause a drastic delay by perturbing the aluminate-silicate-sulfate balance.* In contrast to most of the other mechanisms, this process is considered to
be particularly difficult to predict,\textsuperscript{27} which probably comes from an expected non-linear dependence on the polymer dosage. It can also appear suddenly in cements having apparently similar compositions to others in which retardation is not problematic.

In our opinion, when it occurs, this mechanism of retardation is one of the most problematic because it can create a highly non-linear and therefore non-predictable increase in retardation. It is also one of the least well-studied and understood processes. For this reason we dedicate a certain effort in presenting the current state-of-the-art on the subject in order to expose the various mechanisms proposed to explain its occurrence.

As a basis for this mode of retardation, we can state that an additional level of complexity is added when the main cement phases, silicates, aluminates and sulfates, are taken into account simultaneously. This is not negligible regarding the fact that superplasticizers adsorption is not the same on all phases. Therefore, although studies performed on pure C\textsubscript{3}S with superplasticizers are useful to understand their effect on fundamental mechanisms, data on the behaviour of admixtures in systems containing silicates, aluminates and sulfates are needed to better understand the massive retardation than can occasionally arise in such cases. This requires studying the importance of the balance between silicates, aluminates and sulfates, as explained in section 2.1.3.2 and illustrated by the works of Lerch or Tenoutasse.\textsuperscript{101,102} As for these works, studying the effect of superplasticizers on a cement model rather than on Portland cement allows separating the influence of important parameters that cannot be differentiated and controlled in normal Portland cement, such as the amount and type of alkalis and sulfate carriers.

Adding superplasticizers in such coupled chemical systems makes for a complex and challenging topic. Indeed, in addition to the noticeable delay of C\textsubscript{3}S hydration, whose dependence with aluminates reactions has been discussed in section 2.1.2, water reducers and superplasticizers can modify the interaction between the aluminates and the sulfates. Evidence has shown that they disturb aluminates reaction by perturbing for example ettringite formation or the transition to
monosulfoaluminate.\textsuperscript{161,170,174,183-186} An important feature of many of these studies is that the C\textsubscript{3}A hydration consumes a part of the added chemical admixture, for example either by increasing the specific surface or, intercalating the admixtures in organomineral phases (see section 2.3.5).

The perturbation of the balance between the main phases during cement hydration illustrates itself by a change in the shape and the occurrence time of the so-called sulfate depletion peak. For example, in a study about the interaction of PCEs with cements containing different C\textsubscript{3}A amounts, a strong impact on the sulfate depletion peak of the cement with the highest content of C\textsubscript{3}A can be observed.\textsuperscript{187} In particular as shown in the example of Figure 2.20, in presence of the PCEs, it is no more possible to distinguish between the main hydration peak and the sulfate depletion one.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{iso thermal_calorimetry.png}
\caption{Isothermal calorimetry on cement paste containing different types of PCEs. The first number gives the number of EO units in the side chains, while the second gives the grafting ratio. Reproduced from Zingg et al.\textsuperscript{187}}
\end{figure}
This has also been observed in other studies where, in presence of superplasticizers, the sulfate depletion peak seems to be shifted to earlier times with respect to silicate hydration.\textsuperscript{171,188–190} The merging of both peaks results in a narrower main peak and a change in the maximum of the heat release. This change in the heat release would imply that there is either a faster consumption of sulfates or a change in their availability. Indeed, as mentioned above, studies focused on the effect of superplasticizers on aluminate reactions in cement have shown that the admixtures can affect ettringite precipitation and consequently reactions involving sulfates.\textsuperscript{161,162,170,174,183–186,188,191}

Various mechanisms have been proposed to explain this as summarised below.

1. A first hypothesis would be that the adsorption of PCEs on the sulfate carriers hinders or slows down its dissolution.\textsuperscript{162} The rate of sulfate supply can therefore no more keep \( \text{C}_3\text{A} \) dissolution under control creating a type of false set, which could also be called a “false” sulfate depletion point (the system behaves as if no more sulfates were available, while they still are).

2. A second explanation proposed is that the better dispersion of the anhydrous particles in presence of PCEs enhances the dissolution of \( \text{C}_3\text{A} \) leading to faster sulfates consumption.\textsuperscript{188} An observation favouring this interpretation is that ettringite precipitation tends to be enhanced in presence of PCEs.\textsuperscript{188,191}

3. However, the enhanced precipitation of ettringite mainly occurs in the first minutes of hydration and this leads us to the third hypothesis, which is that PCEs would enhance ettringite nucleation.\textsuperscript{170} This would provide a large surface area for growth, leading to a faster consumption of sulfates, and thus to an earlier true sulfate depletion point. Although this increase of ettringite has been observed several times, the reasons for that are not well understood.

It should finally also be noted that any of the above mechanisms may result in a modification of ettringite morphology in presence of PCEs. For example, the adsorption of molecules on ettringite may either hinder further growth or affect the growth rate of specific crystallographic planes.\textsuperscript{162,192} Additionally, PCE adsorption on nuclei would change the saturation degree and consequently the nucleation rate of
ettringite. Beyond these rather general statements, there does not appear to be a clearer picture in literature regarding the way in which PCEs modify the morphology of ettringite in relation to their dosage and/or molecular structure.

As mentioned above, the cases in which the chemical admixtures cause a massive silicate retardation by perturbing the aluminate-silicate-sulfate balance are a very problematic situation, although not a very frequent one. This does not mean however that the interaction of chemical admixtures and the aluminate phases can be neglected. Indeed, it has been shown that the content of C₃A and alkalis in cement has an important effect on retardation in presence of superplasticizers. In these studies, the authors pointed out that the strong adsorption of PCEs on aluminates reduces the amount of PCEs that remain available to delay the C₃S hydration. This means that, for a given dosage, cements with a higher content of aluminates should suffer less retardation. In this context, the challenge is to determine the proportion of polymer interacting with aluminates and in which way, and how the molecular structure controls this. To the best of our knowledge this remains an important challenge for research on the subject.

2.4.2 Hydration retardation by PCEs

2.4.2.1 Role of the molecular architecture of PCEs

Comparative studies show that, at equal dosages, among all the superplasticizers, PCEs tend to be the most retarding (with the exception of lignosulfonates†).\textsuperscript{163,170,195} As explained above, this retardation is believed to originate from the adsorption of PCEs on one of the phases in the system (reactant or product).

Qualitatively, we can expect that the same molecular structure features will affect adsorption on all these phases, although the extent of adsorption should differ. If this is the case, we can benefit from adsorption studies performed at early age in the

\footnote{† Lignosulfonates are rather to be considered as mid range water reducers. Taken alone they can induce substantial retardation. This can be incremented by residual sugars.}
context of the study of the rheological performance of superplasticizers in relation to their molecular structure.

As explained above, the extent of adsorption is one of the most important parameters for the dispersive effect of superplasticizers. In the case of PCEs, adsorption is mostly influenced by the length of the backbone and the side chains as well as by the grafting density.\textsuperscript{118} Winnefeld et al. show that a higher charge density of the polymer (number of charges per unit mass) leads to a higher consumption of the polymer (i.e. a better adsorption) and to a lower yield stress of the superplasticized cement paste (i.e. a better dispersion), as shown in Figure 2.21.\textsuperscript{193} In the same study, the authors show that the polymers that adsorb most extensively (those with the highest charge density) induce the longest induction period and the latest start of acceleration period (experiments performed with a 0.3% dosage of each polymer).

Concerning the relative influence of the length of the side chains and the grafting density, several studies show that shorter side chains with constant $C/E$ ratio as well as increasing $C/E$ ratio with constant side chain length lead to an increase of the retarding effect.\textsuperscript{38,121,170,193} This is not surprising as, in both cases, the density of carboxylate functions by weight of polymer increases leading to a more effective adsorption and probably longer retardation. In this regard, it would make sense to express the polymer dosage either as a function of the number of carboxylic groups introduced or of the concentration of carboxylate groups per molecule rather than a mass percentage of polymer with respect to cement.\textsuperscript{140} However, adsorption is a complex process that depends on non-trivial combinations of molecular structure parameters so that single variable explanations are rather unlikely to be successful. In contrast combinations thereof relating for example to adsorption energy may have a greater chance of success.\textsuperscript{118}
2.4.2.2 Role of the chemical composition

Besides the molecular architecture of the PCEs, the nature of the monomers in the backbone and the side chains is also important. For example, it has been observed that a polymer composed of backbones with methacrylate monomers without side chains shows the highest impact on cement hydration, as is expected from a polymer with the highest possible charge density.\textsuperscript{193,196}

However, Eusebio et al. show that a backbone only composed of polyacrylate acid monomers does not influence the hydration of $\text{C}_3\text{S}$.\textsuperscript{192} It is tempting to explain this difference by the precipitation of a poorly soluble calcium salt of polyacrylic acid that would prevent this polymer from negatively impacting cement hydration.
However, similar differences between acrylate- and methacrylate-based have also been reported for PCEs that are much more soluble than their pure backbones.\textsuperscript{197} Regnaud et al. studied the hydration of Portland cements with different alkali and tricalcium aluminate contents.\textsuperscript{194} They reported that the delay caused by the methacrylate-based PCEs depends on the amount of initially adsorbed polymers, while the retardation caused by the acrylate-based PCEs depends on the amount of polymer remaining in the pore solution. They concluded that in the first case, the adsorbed methacrylate-based PCEs act on the initial \( C_3S \) dissolution, while in the second case, the non-adsorbed acrylate-based PCEs act mainly on nucleation of C-S-H. However, they do observe differences in behaviour between both polymers when the level of alkalis or the amount of \( C_3A \) is changed.

At this point in time, it is worth recalling that acrylate based PCEs undergo a progressive cleavage of their side chains in alkaline media, while those of methacrylates are much more stable (see section 2.2.1). While this can be beneficial in terms of formulation to control the flow retention,\textsuperscript{198} it poses problems when studying the impact that the PCEs with an acrylic backbone have on hydration. Indeed their ionic charge increases over time, which must certainly affect their adsorption and impact on hydration.

### 2.4.3 Conclusion

The retardation of cement hydration due to admixtures is a complex problem of a coupled system. Although this has been the subject of many studies involving all the types of superplasticizers, important aspects have not been carefully addressed and are still not fully understood.

*The exact mechanism through which adsorbed molecules can delay the hydration.* Three fundamental hypotheses have been described: complexation with Ca-ions, decreased rate of dissolution and perturbation of nucleation and growth. Although evidence (from studies generally performed on pure phases) exists for most of these hypotheses, questions subsist about their relative importance and possible
interactions. Resolving such issues is of course dependent on the general understanding of cement hydration basics that also host their number of remaining open questions.

*The destabilization of the silicate-aluminate-sulfate balance.* It is clear that admixtures affect aluminates hydration, which in consequence disturbs silicates hydration. However, the way they act is not yet fully understood. To address this issue, more information about the different adsorption behaviours of admixtures on aluminates or silicates are needed, as well as the role of the resulting change of specific surface of aluminate hydrates. Indeed, superplasticizers are becoming indispensable in numerous applications, many of which will increasingly suffer from limited early strength in systems using highly blended cements. Therefore understanding the relation between molecular structure and retardation is an important subject where fundamental insights can be used to design products with a great market potential.
Chapter 3
Materials and Methods

3.1 Materials

3.1.1 Model clinker

Model clinker was produced from a homogenised mixture of high grade (99% pure) quartz powder (SiO₂), calcium carbonate (CaCO₃), aluminium oxide (Al₂O₃) and magnesium oxide (MgO) (Sigma-Aldrich) in the molar ratio of 1: 3.428: 0.219: 0.064. The powder was blended in a shaker-mixer (Turbula T2F, WAB) for 24 h and then pressed into pellets of about 10 g and 3 cm of diameter using a hydraulic press (VLP-Series, Enerpac). The pellets were heated up from 25°C to 1600 °C for 5 h, then sintered at 1600 °C for 8 h in a high temperature furnace (Nabertherm LHT 08/16) and finally rapidly quenched with compressed air on a cold steel plate.

The sintered pellets of model clinker were first broken with an agate mortar and pestle into small parts of some millimeters, then coarsely ground with a vibratory disk mill (Retsch) at 700 rpm for 45 s and milled into finer powder with a planetary mill (Pulverisette 5, Fritsch) at 400 rpm for 4 min using zirconia beads to obtain a particle size distribution similar to the one of an ordinary Portland cement, as shown in Figure 3.1 (measured in isopropanol with a Malvern MasterSizer S diffractometer).

The Dₓ₅₀ for the model clinker is 9.92 μm and its BET specific surface area is 1.009 ± 0.006 m²/g, as measured by nitrogen adsorption technique (Micromeritics Tristar II)
3020) after degassing in \( \text{N}_2 \) flow for 1 h at 100 °C (VacPrep 061, Micromeritics). The powder was then homogenised in the shaker-mixer for 12 h, sampled by the coning and quartering method and stored in dessicator.

![Graph](image)  

**Figure 3.1.** Particles size distribution of the model clinker and hemihydrate.

Table 3.1 shows the chemical composition determined by XRF measurements (WD-XRF PANalytical AXIOS). The mass attenuation coefficients (MAC) of the model clinker was calculated from its oxides content: 97.82 cm\(^2\)/g.

**Table 3.1. Chemical composition of the model clinker in % (w/w)**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>CaO</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>MgO</th>
<th>TiO(_2)</th>
<th>P(_2)O(_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% (w/w)</td>
<td>70.01</td>
<td>21.04</td>
<td>8.07</td>
<td>0.04</td>
<td>0.86</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>
The final product is composed of 80.5% (w/w) of triclinic tricalcium silicate, 18.4% (w/w) of cubic tricalcium aluminate and less than 2% (w/w) of impurities (calcium carbonate, dolomite and portlandite). The composition was measured and quantified by XRD (D8 Advance, Bruker AXS) and Rietveld refinement (with the software DIFFRAC.SUITE TOPAS). Figure 3.2 shows a large grain of model clinker with the particles of $C_3S$ (light grey) embedded in $C_3A$ (dark grey).

![Figure 3.2. SEM images of model clinker grains. The light grey phase is $C_3S$ surrounded by $C_3A$ (dark grey).](image)

Figure 3.3 shows the type of polymorphism of the tricalcium silicate present in the model clinker, in the pure $C_3S$ and in both cements used in this study and described later in this chapter. Although magnesium was used in the synthesis of the model clinker to obtain a monoclinic $C_3S$, its tricalcium silicate shows a triclinic polymorph that is similar to the triclinic T2 found in $C_3S$ with impurities, such as zinc. Pure $C_3S$ is a triclinic polymorphism T1 and alite in the cements is a monoclinic polymorphism M3.
3.1.2 Hemihydrate

Hemihydrate was obtained from partial dehydration of gypsum (Acros Organics, 98% pure) in an oven at 110 °C for 16 h. Gypsum was preliminary sieved under 20 μm. Hemihydrate particle size distribution is shown in Figure 3.1. Its $D_{50}$ is 7.20 μm and its BET specific surface area $11.06 \pm 0.06$ m$^2$/g after degassing in N$_2$ flow for 16 h at 40°C.
3.1.3 Pure C₃S

Pure tricalcium silicate was produced from a homogenised mixture of high grade (99% pure) quartz powder (SiO₂), calcium carbonate (CaCO₃) (Sigma-Aldrich) in the molar ratio of 1:3. The synthesis, grinding, sampling and storage followed the same protocols as for the model clinker. However, a second sintering cycle was needed to avoid contamination of C₂S and free lime.

Figure 3.4 shows the particle size distribution of the C₃S with bimodal characteristics. Its Dᵥ₅₀ is 4.73 μm and its BET specific surface area is 1.41 ± 0.01 m²/g after degassing in N₂ flow for 1 h at 100°C.

![Figure 3.4. Particles size distribution of the pure tricalcium silicate phase](image)

Table 3.2 shows the chemical composition of the C₃S measured by XRF measurements. The mass attenuation coefficients (MAC) of the C₃S was calculated from its oxides content: 102.60 cm²/g. The final product contains less than 1% (w/w) of impurities (dicalcium silicate, quartz and portlandite) and is triclinic (Figure 3.3, Figure A.1.1 in the Appendix).
Table 3.2. Chemical composition of the pure tricalcium silicate in % (w/w)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>TiO₂</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>% (w/w)</td>
<td>74.68</td>
<td>25.54</td>
<td>0.15</td>
<td>0.08</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

3.1.4 Ordinary Portland cement

Two different batches of the same cement CEM I 42.5 (Normo 4 from Holcim) called cem1 and cem2 were used in this study. Their XRD patterns for C₃S polymorphism show a monoclinic polymorphism M3 in Figure 3.3 and their mineralogical composition is summarised in Table 3.3. Their particle size distribution is shown in Figure 3.5. The Dᵥ50 and BET specific surface areas are 17.70 μm and 0.79 ± 0.02 m²/g for cem1 and 17.44 μm and 0.82 ± 0.02 m²/g for cem2.

Table 3.3. Mineralogical composition of cem1 and cem2 in % (w/w) obtained by XRD measurements and Rietveld refinement.

<table>
<thead>
<tr>
<th>Cement phases</th>
<th>cem1</th>
<th>cem2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite</td>
<td>69.4</td>
<td>68.7</td>
</tr>
<tr>
<td>C₂S</td>
<td>5.8</td>
<td>5.5</td>
</tr>
<tr>
<td>Cubic C₃A</td>
<td>2.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Orthorhombic C₃A</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>C₄AF</td>
<td>9.9</td>
<td>10.9</td>
</tr>
<tr>
<td>Periclase</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Gypsum</td>
<td>2.3</td>
<td>3.9</td>
</tr>
<tr>
<td>Hemihydrate</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Calcite</td>
<td>3.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.5</td>
<td>1.9</td>
</tr>
</tbody>
</table>
3.1.5 PCEs synthesis and characterisation

The characteristics of the PCEs used in this study are summarised in Figure 1.1 and Table 3.4. They were all synthesized by esterification of methyl polyethylene glycol side chains (BASF) on previously polymerized backbones of about 5300 g/mol with methacrylic acid monomers (custom-made by BASF). The carboxylate to ether (C/E) ratio indicates the grafting density of the side chains and was determined by the quantification of the side chains that did not react with the backbones during esterification by Ultra High Performance Liquid Chromatography (Acquity UPLC, Waters). The polymers were then ultrafiltered (Labscale TFF System, Merck Millipore, with a membrane Pellicon XL Biomax 5kDa) to remove residual monomers, side chains and salts.

As shown in Figure 1.1 and Figure 3.6, PCEs structural characteristics are described by different parameters: $n$, C/E, $N$ and $P$. $n$ is the number of units or the number of
side chains for one molecule and was calculated from the molar mass $M_w$ determined by size exclusion chromatography with an Agilent 1260 Infinity system (Agilent Technologies). The eluent was $Na_2HPO_4$ 0.067 mol/L at a flow rate of 1 mL/min. $C/E$ is the number of monomers in the backbone for a single side chain that contains $P$ monomers of ethylene oxide ($P$ simply representing the length of one side chain). $N$ ($= C/E + 1$) is the total number of monomers in the backbone for a single unit. As the length of the backbone is the same for all the polymers, $N\cdot n$ remains constant.

![Diagram](image)

Figure 3.6. Description of the PCEs structural parameters, $N$, $n$, $P$ and $C/E$. $C/E$ represents the number of carboxylate functions, $C$, per ester group, $E$, through which a side chain with $P$, the number of ethylene oxide monomers, is grafted (left). $N$ ($= C/E + 1$) is the number of monomers in the backbone for one side chain (right). $n$ represents the number of side chains in one molecule.

The surface $S_{PCE}$ occupied by a single adsorbed molecule is calculated from equation (2.16):

$$S_A = \frac{\pi}{\sqrt{2}} a_N a_P \left(2\sqrt{2} \left(1 - 2\chi \frac{a_P}{a_N}\right)^{2/5} \right) p^{9/10} N^{3/10} n$$

(2.16)

where $a_N$ and $a_P$ are the sizes of the backbone and the side-chain monomers respectively. For methacrylic acid monomer, $a_N = 0.25$ nm, whereas, for PEG $a_P = 0.36$ nm. $\chi$ is the Flory parameter and is equal to 0.37 for PEG.
Chapter 3 – Materials and Methods

Table 3.4. Characteristics of the comb-shaped copolymers. \( n \) is the number of units or the number of side chains for a single molecule. \( C/E \) is the number of monomers in the backbone for a single side chain that contains \( P \) monomers of ethylene oxide (\( P \) simply representing the length of one side chain). \( S_{PCE} \) is the surface occupied by a single adsorbed molecule calculated with equation (2.16). \( K \) is the adsorption equilibrium constant (equation (2.21)). \#COO\(^-\) is the content of carboxylate groups in mmol for 1 g of dry polymer. \( c^* \) is the measured critical dosage of COO\(^-\) at which retardation increases massively with direct addition of the PCE (see section 5.4.2).

<table>
<thead>
<tr>
<th>PCE</th>
<th>( n )</th>
<th>( C/E ) ratio</th>
<th>SC length [g/mol]</th>
<th>( P )</th>
<th>( S_{PCE} ) [nm(^2)/molecule]</th>
<th>( K ) ( \times 10^5 )</th>
<th>#COO(^-) [mmol/g PCE]</th>
<th>( c^* ) [μmol/g solid]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1PMA1000</td>
<td>26.8</td>
<td>1.3</td>
<td>1000</td>
<td>23</td>
<td>118</td>
<td>14</td>
<td>1.02</td>
<td>-</td>
</tr>
<tr>
<td>2PMA1000</td>
<td>20.3</td>
<td>2</td>
<td>1000</td>
<td>23</td>
<td>97</td>
<td>37</td>
<td>1.59</td>
<td>-</td>
</tr>
<tr>
<td>3PMA1000</td>
<td>14.8</td>
<td>3.2</td>
<td>1000</td>
<td>23</td>
<td>77</td>
<td>106</td>
<td>2.26</td>
<td>1.13</td>
</tr>
<tr>
<td>6PMA1000</td>
<td>8.4</td>
<td>6.3</td>
<td>1000</td>
<td>23</td>
<td>52</td>
<td>516</td>
<td>3.61</td>
<td>1.08</td>
</tr>
<tr>
<td>3PMA3000</td>
<td>13.9</td>
<td>3.4</td>
<td>3000</td>
<td>68</td>
<td>198</td>
<td>17</td>
<td>1.01</td>
<td>0.51</td>
</tr>
<tr>
<td>6PMA3000</td>
<td>8.3</td>
<td>6.4</td>
<td>3000</td>
<td>68</td>
<td>138</td>
<td>74</td>
<td>1.68</td>
<td>1.01</td>
</tr>
</tbody>
</table>

3.2 Methods

3.2.1 Preparation of the paste

In this study, to properly handle the different storage conditions between the model clinker and the hemihydrate and to control their content ratio, they were mixed together after the grinding and right before the preparation of the paste to avoid pre-hydration.

Model clinker and hemihydrate (the mixture is called model cement) were first homogenised by hand in an agate mortar and a pestle for 10 min. Then, the homogenised powder was mixed with ultrapure water (UPW, \( \rho = 18.2 \) MΩ cm, TOC around 1-2 ppb, by a Milli-Q A+ water purification system from Millipore, Merck & Cie) with a water to cement ratio (w/c) of 0.4 at 200 rpm for 30 s and 800 rpm for 2 min with a vertical mixer (Eurostar power control visc with a 4-bladed propeller
The PCE was added either directly in the water before mixing (direct addition) or in the paste 5 min after mixing (delayed addition). The paste was then remixed at 800 rpm for 1 min.

$C_3S$ and cement pastes were mixed in the same way but with a w/c ratio of 0.35 and 0.3, respectively.

When the paste was used at later time of hydration for specific measurements (XRD/BET), small samples of 3 to 6 g were isolated in sealed plastic bags and immersed in a water bath at 23°C.

### 3.2.2 Calorimetric measurements

Calorimetric measurements were performed on 5 g of the final paste in an isothermal calorimeter TAM Air (TA Instruments) at 23 °C. The time delay $\Delta t$ caused by polymers was determined by the difference of occurrence of the maximum of the silicate peak with the reference without polymer. This is a justified approach since, as shown in Figure 1.1, the used polymer does not modify the first part of the main hydration peak. Taking the difference between the maxima is therefore a representative but also convenient way of determining retardation.

### 3.2.3 Flow spread test

The flow spread test is a simple and traditional test to measure the fluidity of a paste and determine its yield stress. A cylinder placed on a flat glass plate with a smooth surface was filled with the cement paste one minute after the mixing. The cylinder used had a volume of 99 cm$^3$. It was then lifted up one minute later to let the paste flow. Two perpendicular diameters of the spread were measured.
3.2.4 Study of pore solution

Pore solution was extracted from the model cement or cement pastes with a stainless steel pressure filter holder through a nylon 0.45 μm membrane filter (Sartorius Stedim Biotech) connected to a high pressure air circuit (4 bar). The pore solution was then filtered in a plastic syringe through a disposable syringe 0.45 μm filter (CHROMAFIL Xtra H-PTFE-45/35, Macherey-Nagel).

3.2.4.1 TOC analysis

The so-called depletion method was used to quantify the amount of adsorbed PCE. For total organic carbon (TOC) measurements, a part of the filtered solution was diluted with ultrapure water to reach the calibration range of the TOC analyser (Shimadzu TOC-V CSH). The diluted pore solution was then analysed in the next minutes as it becomes unstable over time. TOC content of the reference paste without polymer was measured and subtracted from the analysis of the samples with polymer.

3.2.4.2 Inductively coupled plasma – optical emission spectrometry (ICP-OES)

For ICP measurements, the filtered pore solution (see above) was first diluted 1:10 by mass with HNO₃ 2% (w/w) in ultrapure water to measure the concentration of Al and Si. A part of this solution was then further diluted 1:20 by mass to quantify the concentration of Ca and S. The samples were stored in the fridge at 4 °C and analysed within one week with a Thermo Scientific iCAP 6300 Dual View ICP-OES (Thermo Fisher Scientific) with a CETAC ASX-260 autosampler (CETAC).

Table 3.5 summarises the selected spectral lines used for the quantification of the different elements. Further details for the characteristics of the instrument and the complete quantification protocol are described in 204.
Table 3.5. Selected spectral lines used for the pore solution analysis of the model cement.

<table>
<thead>
<tr>
<th>Element</th>
<th>Plasma viewing</th>
<th>Spectral line (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>axial</td>
<td>167.079, 396.152</td>
</tr>
<tr>
<td>Ca</td>
<td>axial</td>
<td>315.887, 317.993, 318.128</td>
</tr>
<tr>
<td>S</td>
<td>axial</td>
<td>182.034, 182.624</td>
</tr>
<tr>
<td>Si</td>
<td>axial</td>
<td>251.611, 288.158</td>
</tr>
</tbody>
</table>

3.2.5 Stopping hydration

For BET specific surface area, XRD and TGA measurements, hydration was stopped by solvent exchange (for the model cement) or freeze-drying (for C₃S pastes). Freeze-drying should not be used for samples bearing aluminate and sulfate phases as these phases are easily damaged by the high vacuum.

The solvent exchange was carried out by using cold isopropanol (5°C) in a ratio of 20 mL for 1 g of paste. The paste was mixed with the alcohol for 1 min. With such a short contact time and low temperature, ettringite needles are not damaged and adsorption of isopropanol is drastically reduced, which allows better quantification and comparison.²⁰⁵ For hardened pastes, the samples were previously ground to fine powder with a mortar. The solution was then filtered through a polyamide filter (pore size of 0.45 μm, Sartorius Stedim) and the collected powder was then dried for 4 days in a desiccator. The desiccator was maintained under a low vacuum of 700 mbar and about 35% RH (vapor pressure of calcium chloride solution).

C₃S paste hydration was stopped by freeze drying with an Alpha 1-6 freeze-dryer (from Christ) at -55°C and <0.1 mbar for 24 h. The plastic bags containing the paste were previously immersed in liquid nitrogen for 20 min.

The dried powder was then gently homogenised gently in a mortar prior to the different measurements.
3.2.6 BET specific surface area measurements

The specific surface area measurements were performed using a BET multi-point (6 points isotherm) nitrogen physisorption device (Micromeritics Tristar II 3020) on the previously stopped samples. Before the measurement, the samples were degassed in an external degassing station (VacPrep 061, Micromeritics) at 40°C with N₂ flow for 16 h.

3.2.7 Thermogravimetric analysis

The amount of bound water in collected samples after stopping hydration was determined by thermogravimetric analysis (TGA) on a TA Instrument TGA Q50. Around 15 mg of material was placed in the platinum crucible and heated from 25 °C up to 1000 °C at a rate of 10 °C/min under a 60mL/min flow of dry N₂.

The amount of water in the samples was assumed to be the total loss of weight between 25 °C and 500 °C (which corresponds to the end of the loss of weight of the portlandite).

3.2.8 X-Ray Diffraction

The anhydrous powders as well as the evolution of the phases during hydration were characterised by X-ray diffraction using a Bruker D8 Advance diffractometer with a CuKα radiation (λ = 1.54 Å) at 40 kV and 40 mA in a Bragg-Brentano geometry with a 280 mm goniometer radius, a 0.3° fixed divergence slit (FDS) angle, a primary and secondary Soller slit (4.1°), nickel filter and a LYNXEYE detector. Data were collected from 7° to 65° with a step size of 0.01533° and 1 s per step.
3.2.9 Rietveld refinement and phases quantification with external standard

Rietveld refinement was performed using the software DIFFRAC.SUITE TOPAS 4.2. Table 3.6 shows the structure models used for the characterisation of the anhydrous powders (model clinker, hemihydrate and pure C$_3$S) and their composition after hydration.

Table 3.6. Structure models used for the Rietveld refinement

<table>
<thead>
<tr>
<th>Phases</th>
<th>Code ICSD</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$S - triclinic</td>
<td>04331</td>
<td>Golovastikov$^{206}$</td>
</tr>
<tr>
<td>C$_3$S - monoclinic</td>
<td>64759</td>
<td>Nishi et al.$^{207}$</td>
</tr>
<tr>
<td>C$_3$A - cubic</td>
<td>1841</td>
<td>Mondal and Jeffery$^{208}$</td>
</tr>
<tr>
<td>C$_3$A - orthorhombic</td>
<td>100220</td>
<td>Nishi and Takeuchi$^{209}$</td>
</tr>
<tr>
<td>Gypsum</td>
<td>27221</td>
<td>Pedersen and Semmingsen$^{210}$</td>
</tr>
<tr>
<td>Bassanite</td>
<td>-</td>
<td>Bezou et al.$^{211}$</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>16382</td>
<td>Kirfel and Will$^{212}$</td>
</tr>
<tr>
<td>Calcite</td>
<td>80869</td>
<td>Maslen et al.$^{213}$</td>
</tr>
<tr>
<td>Portlandite</td>
<td>-</td>
<td>Desgranges et al.$^{214}$</td>
</tr>
<tr>
<td>Dolomite</td>
<td>-</td>
<td>Effenberger et al.$^{215}$</td>
</tr>
<tr>
<td>Ettringite</td>
<td>155395</td>
<td>Goetz-Neunhoeffer and Neubauer$^{216}$</td>
</tr>
<tr>
<td>Quartz</td>
<td>174</td>
<td>Le Page and Donnay$^{217}$</td>
</tr>
<tr>
<td>Periclase</td>
<td>-</td>
<td>Hazen$^{218}$</td>
</tr>
</tbody>
</table>

The external standard method was used to quantify absolute phase contents of the hydrated samples following a methodology developed elsewhere$^{33,34,219}$ for in-situ XRD measurements of hydrating samples. The method was adapted in this work for stopped samples and is summarised in Figure 3.7 for the case of pure C$_3$S.

The absolute weight fraction of the different crystalline phases, initially quantified by Rietveld refinement, is calculated from the equation (3.1):
\[ W_i = \frac{s_i \rho_i V_i^2 \mu_{\text{sample}}}{D} \] (3.1)

where \( s_i \) is the Rietveld scale factor of phase \( i \), \( \rho_i \) and \( V_i \) its density and unit-cell volume respectively, \( \mu_{\text{sample}} \) is the mass attenuation coefficient of the sample. Its value is calculated using a simple mixing law from the bound water weight fraction remaining after stopping hydration and determined by TGA and the mass attenuation coefficient of the anhydrous powder calculated from its oxides content:

\[ \mu_{\text{sample}} = w_{H_2O} \cdot \mu_{H_2O} + (100 - w_{H_2O}) \cdot \mu_{\text{anhydr}} \] (3.2)

\( D \) in equation (3.1) is an instrumental parameter and takes into account the diffractometer configuration, the radiation performance and the conditions of data acquisition. It is calculated with the refined parameters of the external standard, which was pure silicon (silicon powder 640d for powder diffraction, NIST) and measured in the same conditions as the investigated samples:

\[ D = \frac{s_{\text{sil}} \rho_{\text{sil}} V_{\text{sil}}^2 \mu_{\text{sil}}}{c_{\text{sil}}} \] (3.3)

\( s_{\text{sil}} \), \( \rho_{\text{sil}} \), \( V_{\text{sil}} \) and \( \mu_{\text{sil}} \) are the scale factor, the density, the unit-cell volume and the mass attenuation coefficient of the silicon, respectively. As pure silicon was used, \( c_{\text{sil}} \) is equal to 100%. Because the scale factor depends on the performance of the X-ray tube that changes over time,\(^\text{34}\) XRD measurements were performed on the external standard every three samples, to which the corresponding \( D \) parameter was used to quantify their phase content. The error of quantification coming from the Rietveld refinement and calibration on the external standard is considered to be around 1\% (w/w), which is quite substantial in the first hours of hydration, considering the low amount of formed hydrates, but not critical at later ages.

At the end, the composition is scaled a first time to 100 \% to quantify the amount of other phases, such as the amorphous phases or the ones not directly quantified, and a second time to include the amount of free water that was removed in the stopping hydration step. This is simply done by substracting the bound water from the total
water used to make the paste. In the case of the pure C₃S, the composition of the “other” phases is for a large part C-S-H, but it also includes impurities and errors coming from the non-ideal fitting of the XRD pattern. The content of impurities and the errors of fitting were not considered as negligible but as low enough so that the fraction of “other” phases gives a reasonable information about the evolution of C-S-H content. However, in the case of the model cement, some phases, such as the AFm phases, could not be refined and were therefore included in the content of “other” phases. In this case, it was not possible to obtain direct information about the C-S-H content.

Figure 3.7. Principle of the phases quantification method explained in the case of a pure C₃S paste after having stopped the hydration.
Chapter 4
Quantification Method from XRD Analysis

The content of this chapter is presently not included in any publication or draft publication. However, in combination with Chapter 6, it is planned to write at least one ISI journal paper.

4.1 Introduction

Pure tricalcium silicate was used in this study to set up the protocol for a reliable quantification of the phases during hydration using XRD measurements and Rietveld refinement with an external standard (see Chapter 3 for more details about the methods of stopping hydration and quantification).

In contrast to ordinary Portland cement, which is a complex multi-component system with calcium silicate, aluminate and sulfate phases as well as alkalis and other impurities, pure C₃S offers a simple and ideal system with only one phase that reacts with water and two hydration products, which simplifies considerably the data analysis. However, as for cement, hydrating C₃S pastes contain two amorphous phases, water and C-S-H, which substantially complicate phase quantification by XRD and thermodynamic calculations.

This chapter presents the validation of the different protocol steps elaborated to achieve proper quantification of phases in such systems. It includes the analysis of
the phase assemblage evolution during hydration of pure C₃S and the calculation of the heat release associated to the reacted amount of anhydrous phase. The positive outcome enables us to apply this method to study the effect of PCEs on a model cement (Chapter 5) and on pure C₃S (Chapter 6).

4.2 Phase assemblage evolution during C₃S hydration

The heat release measured by calorimetry and the phase evolution determined by XRD during the hydration of pure C₃S are shown in Figure 4.1. The initial weight fraction of C₃S before mixing with water is 74.1% (w/w) for a water to solid (w/s) ratio of 0.35. The dissolution of C₃S starts to be clearly visible after three hours of hydration (i.e. right after the beginning of the acceleration period), which corresponds also to an increase of the portlandite content. It later seems to decrease, after the maximum of the main peak, as the system enters in the deceleration period, which is consistent with other studies.³³,³⁴,⁶⁴,¹⁸⁸ It has to be noticed that the dashed lines between the two last points (8 and 24 h) are only a guideline and do not represent the real evolution of the phases during the deceleration period. Quantification during this period was not performed since the retardation due to PCEs only really concerns the time before the maximum of the main silicate peak.

The weight fraction of “Others” represents the content of amorphous phases, other crystalline phases that might not have been quantified and the quantification error resulting from any misfitting of the XRD patterns. It is simply the subtraction of C₃S, portlandite and the free water from 100%. As long as the system is well known (C₃S, portlandite and calcium carbonate, which is present in a very small amount and not shown in the results, in our case), the fraction of “Others” can provide a rough estimate of the C-S-H content, which cannot be directly quantified by XRD measurements. While this is only an approximation and should be remembered as such, we will show evidence later in this chapter that it does seem to provide a rather good estimate of the expected C-S-H content.
Figure 4.1. Heat flow and evolution of the phase assemblage during the first hours of pure C₃S hydration measured by XRD. The dashed line between the two last points is only an eye guideline and do not represent the real evolution of the phases.

Figure 4.2 shows the ratio between the amount of C₃S dissolved and the portandite precipitated. According to the commonly used stoichiometry for C₃S hydration, shown in equation (4.1), 1 mole of C₃S should lead to the formation of 1.33 moles of portlandite. This corresponds to a mass ratio ΔC₃S/ΔCH of 2.32.

\[
C_3S + 3.43H_2O \rightarrow C_{1.67}SH_{2.1} + 1.33Ca(OH)_2
\]  \hspace{1cm} (4.1)

The values of this ratio in the very first hours are not shown because the error of quantification is larger than the calculated amounts. Beyond those couple hours, we observe a first strong increase of ΔC₃S/ΔCH up to a time corresponding to the maximum heat flow. Then the value of ΔC₃S/ΔCH, which reaches 2.28 at 24 hours, very closely approaches the one of 2.32 expected from the above stoichiometry.

The initially lower values of ΔC₃S/ΔCH mean that, during the first hours and following equation (4.1), the amount of portlandite that precipitates is too high with
respect to the C₃S dissolved. In other words, it suggests that initially, the C-S-H formed would have a lower Ca/Si ratio than the 1.67 in equation (4.1). In our pure C₃S samples this value increases with time as shown in Figure 4.2 to reach the value of 1.65 at 24 h. In this plot the Ca/Si ratios of C-S-H were determined from the mass balance of the calcium between the amounts of C₃S dissolved and those of portlandite precipitated, considering that all the Si-ions are in the C-S-H and neglecting the amount of the ions concentration in solution. The increase of Ca/Si that we find is however in contradiction with the decrease in the first hours of pure C₃S hydration observed by Bazzoni with energy dispersive X-ray spectrometry (EDX) measurements.³² It also contrasts with the initial decrease that we report for our model clinker in Chapter 5 and values observed for cement.³⁴,¹⁸⁸
Chapter 4 – Quantification Method from XRD Analysis

Figure 4.2. Heat flow of the pure C₃S, evolution of the ratio between the total mass of C₃S reacted and the total mass of CH formed (ΔC₃S/ΔCH) and the respective Ca/Si ratio of the C-S-H formed. Values of ΔC₃S/ΔCH are directly calculated from XRD measurements. The Ca/Si ratio of C-S-H was determined from the mass balance of the calcium between the amounts of C₃S dissolved and portlandite precipitated considering that all the Si ions were in the C-S-H. The values of both ratios in the very first hours are not shown because the error of quantification is larger than the calculated amounts. The empty points of ΔC₃S/ΔCH represent values that are still sensitive to the error of quantification.

Using the solid-solution model of C-S-H described by Kulik for different Ca/Si ratios,²²⁰ it is possible to determine by extrapolation the amount of water molecules we should have in the C-S-H of our samples for each Ca/Si reported in Figure 4.2, as long as they are in the range of the poles of the solid-solution model. This allows calculating the mass of C-S-H that should be present in the samples and comparing it to the one called “Others” and estimated from the XRD measurements. Figure 4.3 shows that these values are very similar, although systematically slightly higher for “Others”. This indicates that the simple estimation of phase noted “Others” offers a very decent estimation of the C-S-H content in our system.
Figure 4.3. Heat flow of the pure C₃S and C-S-H evolution calculated either from the estimation of “Others” (orange circles) or from the Ca/Si ratios (Figure 4.2) using C-S-H solid-solution model from Kulik²²⁰ for the water content (green diamond). The mass of “Others” represents the content of amorphous phases, other cristalline phases that might not have been quantified and the quantification error resulting from any misfitting of the XRD patterns. It is simply the subtraction of C₃S, portlandite and the free water from 100 % scaled with the known mass of C₃S initially used in the paste. Data show that this provides a very good estimated of the C-S-H content.

What is certain is that our results indicate that in the very first hours of hydration, and almost up to the maximum of the main peak, the hydration products formed do not follow the stoichiometry of equation (4.1). In the context of this thesis, the consequences of this may however not be critical. Indeed, to examine the impact of PCEs on C₃S hydration we are most interested in knowing at which rate C₃S hydrates. Therefore, the stoichiometry of equation (4.1) only matters in as much as it may affect our quantification of the amount of reacted C₃S at any point in time. This is why in the next section, we attempt to quantify this extent of reaction independently, using calorimetry, something specifically made possible by the use of C₃S as a model system.
4.3 Calculation of the heat flow from phase quantification

The cumulative heat release and the heat flow of the pure C₃S was calculated from the XRD/Rietveld refinement shown above. For this, we calculated the enthalpy of hydration of C₃S, using the enthalpies of formation of reactants and products listed in Table 4.1. Although we demonstrated low but increasing values of ΔC₃S/ΔCH and consequently that Ca/Si ratios vary in C-S-H during the first hours of hydration, we considered here equation (4.1) and assumed that the jennite-type C-S-H with a Ca/Si ratio of 1.67 is formed. This choice was made first because this ratio is close to the one estimated at 24 hours (Figure 4.2) and second because it is also in the range of ratios (1.5-2) often observed for C₃S or ordinary Portland cement at equilibrium (i.e. at later age of hydration). Furthermore, it is well defined in literature with respect to its thermodynamics properties. Additionally, using the enthalpies of formation of ions in solution, also shown in Table 4.1, we calculated the heat of dissolution of C₃S. This value is very close to its heat of hydration (-142 versus -118 kJ/mol), so that the exact stoichiometry of the products does not much affect the enthalpy of hydration. For our purpose this is very useful, since it implies that calorimetry measurements should provide a relatively accurate measurement of the amount of C₃S reacting, even if the stoichiometry of equation (4.1) is not rigorously respected as suggested in Figure 4.2.
Table 4.1. Enthalpy of formation of reactants and products of C₃S hydration reaction.²²⁷ Equation (4.1) was used to calculate the hydration enthalpy of C₃S.

<table>
<thead>
<tr>
<th>Phase/species</th>
<th>ΔfH⁰ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>-543</td>
</tr>
<tr>
<td>OH⁻</td>
<td>-230</td>
</tr>
<tr>
<td>SiO₃²⁻</td>
<td>-1098</td>
</tr>
<tr>
<td>C₃S</td>
<td>-2931</td>
</tr>
<tr>
<td>H₂O</td>
<td>-286</td>
</tr>
<tr>
<td>C₁.₆₇⁻S-H₂.₁ (Jennite type)</td>
<td>-2723</td>
</tr>
<tr>
<td>Portlandite</td>
<td>-985</td>
</tr>
</tbody>
</table>

Using the above determined enthalpy of hydration, we use our XRD quantification to calculate the heat expected to be released over time. This is plotted in Figure 4.4 (squares) along with the cumulative heat (left) and the heat flow (right) directly measured by calorimetry. Because the first minutes of calorimetry measurements are perturbed by the difference of temperature coming from the sample and the calorimeter as well as its opening, Figure 4.4 (left) also shows the cumulated heat after subtracting the heat released during the 20 first minutes (discontinuous line). Except for the point at 24 hours for which the heat is overestimated, the heats measured by calorimetry and inferred from XRD perfectly match. Importantly, we note that the issue of shifting data in relation to the initially released heat disappears when considering the rate of heat release (derivative). This is why, as shown in Figure 4.4 (right), we also get a very good agreement between the calorimetry measurements of heat flow and the corresponding values inferred from XRD phase quantification. All in all, this supports the validity of the quantification method we developed.
Having said this, it is important to recall that the calculation of the heat flow is done assuming that all the reactions of C₃S hydration (C₃S dissolution, portlandite and C-S-H precipitation) are concurrent and follow the stoichiometry of equation (4.1). As explained earlier with Figure 4.2, this is not the case as the ΔC₃S/ΔCH ratio is not constant but rather strongly increases in the first hours to reach only later the stoichiometric value. However, as was also already stated, the heat released during hydration of C₃S is mostly due to the dissolution of C₃S that is highly exothermic. Therefore, the stoichiometry of the reaction is only a second order factor that improves accuracy but is not essential to quantifying the amount of heat that a given amount of C₃S can release due to hydration.

### 4.4 Conclusion

This chapter focused on a reliable quantification by XRD analysis and Rietveld refinement with an external standard on pastes of C₃S of which the hydration was previously stopped. Importantly, all samples of which the hydration was stopped were stored separately in small sealed containers in an isothermal bath. This was essential to guarantee similar hydration conditions in those samples as the ones in
the isothermal calorimeter. As mentioned in Chapter 3, many studies in the literature overlook this aspect, which explains many reported discrepancies between XRD measurements and calorimetry.

Using that procedure, it has been shown that the calculation of the heat flow obtained from the hydration of C₃S that reacted matched the calorimetric curves very well up to the maximum of the main peak. This is very important in the context of this thesis, since this period precisely corresponds to the most relevant one to analyse when dealing with systems retarded by organic admixtures. Therefore, this chapter validates the protocol of phase quantification that is subsequently used to study the hydration of a model cement (Chapter 5) and pure C₃S (Chapter 6) in presence of comb-shaped polycarboxylates superplasticizers.
Chapter 5
Impact of PCEs on Model Cement Hydration

Part of this chapter is based on a paper accepted as feature article in the Journal of the American Ceramic Society:¹

Molecular and sub-molecular scale effects of comb-copolymers on tricalcium silicate reactivity: Towards molecular design

by D. Marchon, P. Juilland, E. Gallucci, L. Frunz, R.J. Flatt.

To the exception of the data in Figure 5.25 and Figure 5.26, all experiments were performed by Ms Marchon. The design of these experiments, in particular the concept for the model system used, the novel approach for the phase quantification as well as the writing of the paper is attributed to Ms Marchon. She received guidance in different forms from the different co-authors who were following her project. Dr Gallucci and Dr Juilland mainly contributed by provided data for Figure 5.25 and Figure 5.26 and by targeted feedback on the section discussing dissolution kinetics. Dr Frunz contributed to the decision on the types of polymers to be used and was responsible for their synthesis. All co-authors were involved in the discussion of the results and critical feedback on the paper. Figure 5.2, Figure 5.17, Figure 5.21 and Figure 5.27 were produced by Mr Fabian Rüdy, a professional illustrator. He received detailed instructions from Ms Marchon who was intensely involved in the iterative process that led to the desired final appearance of these figures.
5.1 Introduction

As introduced earlier, one of the most important questions that still has to be addressed and constitutes the main objective of this work is how the reactivity of the coupled chemical system that is cement hydrating is modified in relation to the molecular structure, dosage and addition mode of comb copolymers, as illustrated in Figure 5.1.

To mimic the interaction between the main and most reactive cement phases, a model cement, composed of silicate, aluminate and sulfate phases, was designed and used. It is close enough to reality to give useable conclusions but simple enough to understand main principles regarding cement hydration. In particular, it contains a model clinker with around 80% (w/w) of tricalcium silicate and 20% (w/w) of tricalcium aluminate and a small amount of hemihydrate (CaSO₄·½H₂O) added as sulfates carrier to prevent the too fast hydration of the aluminate phase. Chapter 3 provides details about the model clinker synthesis and its characterisation.
Figure 5.1. Heat flow of an ordinary Portland cement (cem1) with different dosages % (w/w) of the comb-shaped copolymer 3PMA1000 added in a delayed mode. The varying shape of these curves reflects differences in how the most important reactions are modified by the PCE. This is visible by the increase of the delay of hydration with the dosage of the PCE and perturbation of the time of occurrence of the sulfate depletion peak with respect to the maximum of the silicate peak, leading to their merging at high polymer content (0.4%).

The hydration of this system is summarised in Figure 5.2. In contact with water, the reactants dissolve building up ion concentrations in the aqueous phase. The reaction of dissolution is marked $D_i$ with $i$ referring to the phase concerned by the specific reaction. Once the supersaturation needed to precipitate a product is reached, it nucleates ($N_i$) and grows ($G_i$)\(^{82,96,228-231}\). During the first minutes, the main hydration product is ettringite (phase number 4 with composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$ also noted $C_6A$\(_3$\(_{32}$)), which is formed by the reaction between tricalcium aluminate, hemihydrate and water. It is followed by the precipitation of portlandite (phase 5 with $\text{Ca(OH)}_2$ noted CH) and calcium silicate hydrate (phase 6, a calcium silicate hydrate of variable composition noted $C$-$S$-$H$). These two phases are formed as a result of the hydration of the tricalcium silicate.
Through carefully chosen experiments we separate the contributions of the various processes, emphasising under what conditions and why organic additives modify them. More specifically, we focus on understanding the hydration delay of tricalcium silicate, which is the most important component in cementitious materials since its hydration products confer final strength and durability to these materials.\textsuperscript{36,43,44}

For this to be possible a proper quantification of the phase evolution over time is essential. This is presented in the section 5.3, discussing the various aspects of this challenging problem, after defining our model cement in 5.2. The main outcome of 5.3 is first to demonstrate that our experimental approach leads to a reliable phase quantification. Second, it shows substantial differences concerning the formation of ettringite, which play an important role in our discussion of the retarding effects of PCEs. Third, it supports our interpretation of calorimetry curves, allowing us to effectively locate the main hydration peak of tricalcium silicate hydration, even in cases when it is rather attenuated. With this in hand the following subsection 5.4 goes more directly into the impact of PCEs on retardation and proposes a mechanism explaining all effects observed.
Figure 5.2. Schematic representation of the reaction in water of hemihydrate (phase 1) and model clinker that contains 20% (w/w) tricalcium aluminate (2) and 80% (w/w) alite (3). Reaction products are ettringite (4), portlandite (5) and calcium silicate hydrate (6). The reactions of dissolution, nucleation and growth are respectively marked as D_i, N_i, G_i, with i referring to the phase concerned. The discontinuous line indicates that aluminate ions may influence the dissolution reaction of silicates, which is something that the dispersant can affect indirectly.
5.2 Characterisation of the model cement

5.2.1 Reproduction of Tenoutasse’s test

As Tenoutasse demonstrated with a mixture of pure $C_3S$ and $C_3A$, the balance between the silicate, aluminate and sulfate phases is one of the most important aspect during cement hydration (see Figure 2.7 in section 2.1.3.2). For this study, rather than using a mixture of pure phases, we employed a model clinker mixed with hemihydrate with particle size distribution close to cement to better mimic it. The hydration of this model clinker with different amounts of hemihydrate is shown in Figure 5.3 based on isothermal calorimetry measurements. As for Tenoutasse, in absence of sulfates, the tricalcium silicate hydration is strongly decreased and delayed. With the addition of low dosages of hemihydrate, the sulfate depletion point, also called aluminate peak, is delayed. However, at this low sulfate contents (3 and 4 % (w/w) of hemihydrate) and in contrast to Tenoutasse’s observations, $C_3S$ hydration is not enhanced but rather slightly delayed. This might come from the fact that first, we are not dealing with “free” particles of pure phases but with a system where the $C_3S$ particles are partially embedded in the aluminate phase and that second, we have different particle size distributions to that used by Tenoutasse.

The behaviour of our system matches again Tenoutasse’s observations from 4.5 % (w/w) of hemihydrate, where the aluminate peak is delayed and $C_3S$ hydration is enhanced and occurs earlier in time. At 5% of hemihydrate, both peaks are clearly inversed, the sulfate depletion point occurring right after the silicate peak as it is generally observed during ordinary Portland cement hydration. This state is called metastable and is the one that will be analysed in presence of PCEs later in this chapter. At higher sulfate dosages, the aluminate peak is further delayed but the time of occurrence of the silicate peak is not affected. This system is called oversulfated.

The successful reproduction of Tenoutasse’s test showed us the expected behaviour of the model clinker in presence of hemihydrate during hydration and allowed us to
find the perfect sulfate dosage for a metastable system (5% of hemihydrate). Therefore, we could obtain a system representing a very important characteristic of cement and also particularly adequate to determine if PCEs can or cannot modify the aluminate-silicate-sulfate balance.

![Figure 5.3. Heat release of the model clinker with different contents of hemihydrate in % (w/w) (given in the insert). The circles indicate the time of occurrence of the silicates peak for each system.](image)

5.2.2 Phase assemblage of the metastable system

XRD and Rietveld refinement with an external standard (see Chapter 3 for more details about the method of quantification) were used to follow the phase evolution during the first hours of hydration. Figure 5.4 shows the comparison between the heat release of the model cement, i.e. model clinker in the metastable state (with 5% (w/w) of hemihydrate) and the evolution of its main phases, C₃S, C₃A, hemihydrate, gypsum, ettringite, and portlandite during the first hours (up to 25 h) of hydration.
The first observations concern the dissolution of the reactant phases. Hemihydrate (green triangles) dissolves very fast in the first two hours leading to the precipitation of gypsum (pink diamonds). The precipitation and dissolution of gypsum correspond perfectly to the first peak of the heat release at 2 h (indicated by the black arrow). This is confirmed by ICP-OES measurements showing that before the small peak the concentration of sulfur in the pore solution is 51.2 mM and after 19.8, which is close to gypsum solubility at 17.6 mM. Furthermore, its precipitation seems to disturb the formation of ettringite (orange stars), which remains constant as long as the content of gypsum increases in the system, but increases again when the gypsum content decreases. This dissolution of gypsum seems constant until it completely disappears after 7 h, which corresponds exactly to the sulfate depletion point on the calorimetric curve. As observed elsewhere, this seems to correspond to an acceleration of ettringite precipitation.
Figure 5.4. Quantification of phase evolution during hydration of model clinker with 5% (w/w) of hemihydrate without PCE. The heat release shows that we are in the presence of a metastable system where the sulfate depletion point, also called the aluminate peak, occurs right after the maximum of the silicate peak, which is shown by the vertical dashed line. The black arrow indicates the small peak attributed to the formation of gypsum, which perfectly corresponds to the XRD analysis (pink diamond).

A closer look at the data from Figure 5.4 shows that C₃S dissolution accelerates at 3 h when the main peak of the heat release starts (Figure A.2.1 in the Appendix). Later, after the maximum of the main peak and the aluminate peak, during the deceleration period, the rate of C₃S consumption decreases. This represents a normal evolution as it is consistent with what was reported for pure C₃S in the previous chapter. However, in the opposite of that case, for which an increase of the mass ratio ΔC₃S/ΔCH (Figure 4.2) had been found, our model cement shows that this ratio is very high in the first minutes and then decreases, with a strong deceleration after the maximum of the main peak (Figure 5.5). This means that, according to equation (4.1), at the beginning of hydration, the amount of C₃S reacting is higher than the amount of portlandite precipitated. This is coherent with the fact that the tricalcium silicate has to dissolve first to build up the ion...
concentration and to reach the supersaturation degree needed to precipitate portlandite. Furthermore, the fact that Ca-ions are also consumed for gypsum and ettringite precipitation might as well contribute to the lower amount of portlandite compared to C₃S reacted. In addition to this, there is also a possibility that the Ca/Si ratio of C-S-H is higher, which would reduce the amount of portlandite that can form. At 27 hours, the ratio ΔC₃S/ΔCH is equal to 3.39, which is substantially higher than the 2.32 expected from equation (4.1). The important difference with pure C₃S hydration confirms that the concurrent reaction of aluminates cannot be neglected when studying the retardation of silicate hydration induced by organic admixtures.

Figure 5.5. Heat flow and evolution of the mass ratio ΔC₃S/ΔCH during the first hours of model cement hydration calculated from XRD measurements.

Figure 5.4 also shows that C₃A dissolves quickly in the first minutes, which is accompanied by a fast precipitation of ettringite. Then the consumption of C₃A becomes very slow until the depletion point at 7.35 h, when it accelerates drastically before a second slow down in the deceleration period. Another important
observation from Figure 5.4 is that the sulfate depletion point occurring at 7.35 h according to the heat release measurement correlates exactly with the highest content of ettringite and the accelerated dissolution of C₃A. This is expected, but observing this as accurately was only possible because of the experimental protocol that we developed. Furthermore, the absolute weight fraction of C₃A that dissolved up to the depletion point (1.9 %) is close to the theoretical amount needed for that amount of C₃A (2.11 %) to react with all the sulfates present in the system to form ettringite, according to :

\[ C₃A + 3\text{CaSO}_4\cdot2\text{H}_2\text{O} + 26\text{H}_2\text{O} \rightarrow C₆₄\text{A}_8\text{O}_3\text{H}_₃₂ \] (5.1)

The theoretical amount of ettringite that should form before the depletion point if all the sulfates were used for its precipitation is 9.79 %. At 7 h, the content of ettringite is only 8.1 %. This difference might come from the fact that we did not measure the ettringite content exactly at the depletion point, but 20 minutes earlier. If the precipitation of ettringite is accelerated when the content of sulfates decreases drastically in solution (i.e. when gypsum is completely dissolved and therefore cannot provide more sulfates), 46,64,188 20 minutes might be a reasonable time to approach the expected amount of ettringite. At this point, about 12 % (w/w) of the total sulfates content is found neither in gypsum nor ettringite. This sulfate content might be in the pore solution or adsorbed on C-S-H for example and can potentially be used for more ettringite precipitation. 232,233

It should also be mentioned, that an important phase is missing in this assemblage: the monosulfoaluminate phase (or AFm). It was indeed found in XRD measurements after the depletion point but its peaks could not be well fitted by Rietveld refinement, which affects the quality of our phase quantification.

Except for the AFm phase, all the correlations explained above prove that the storage of the hydrating samples (in the bath at the same temperature as the calorimeter), the protocole for stopping hydration and the Rietveld refinement with an external standard are suitable for a reliable quantification of the phases of our system. A very important outcome of this was to enhance our confidence in the
interpretation of heat flow measurements to determine in particular the location of the silicate hydration peak.

5.3 Phases evolution of hydrating model cement with PCEs

5.3.1 General observations of addition mode on the heat release

Before analysing the evolution of the phases in model cement with PCEs, it is important to observe the differences in the heat release. A typical observation in normal Portland cement, as illustrated in Figure 1.1 and Figure 5.1 for polycarboxylate ether comb copolymers (PCEs), is that, beside the obvious delay of occurrence of the main hydration peak, many organic additives also change its shape by differently affecting the hydration rates of aluminate and silicate phases. Quantifying this is essential to understand the impact of these molecular additives and is relatively easier to do with our model reactive system.

Quite surprisingly, while the maximum of the silicate peak systematically occurs later, the aluminate peak is moved to earlier times if the polymer is present in the mixing water (Figure 5.6a), whereas it is delayed if the polymer is added shortly (5 minutes) after mixing (Figure 5.6b). This difference comes from the ability of these polymers to modify the fastest reactions occurring after contact with water, namely the dissolution of hemihydrate (D1 in Figure 5.2), the dissolution of tricalcium aluminate (D2) and the nucleation of ettringite (N4). In particular, they can increase the amount and surface of the ettringite formed, provided they are present in the mixing water, as developed in the next subsection.
Figure 5.6. Influence of the addition mode of a PCE on the hydration of the model cement initially in the metastable state (with 5% (w/w) hemihydrate). The comb copolymer is 3PMA1000, having C/E equal to 3, a backbone containing methacrylic acid monomers and a molar mass of the side chain of 1000 g/mol. a) direct addition and b) delayed addition. The circles indicate the time of occurrence of the silicates peak for each system. The arrows represent the resulting shift of the silicates and aluminates peaks due to the presence of the polymer. The influence of other PCEs are shown in Figure A.2.2 to Figure A.2.5 in the Appendix.
5.3.2 Phases assemblage evolution of hydrating model cement with PCEs

Figure 5.7 shows the overall phase assemblage evolution during hydration of the model cement for each addition mode of 0.1% (w/w) 3PMA1000. An important information is that, for both addition modes, there is a strong decrease of C_3A content occurring after the consumption of 2% C_3A (w/w), which also corresponds to the highest content of ettringite and to the complete consumption of gypsum. More importantly, the time at which this occurs corresponds exactly to the sulfate depletion point measured by calorimetry.

The evolution of each individual phase in the systems with PCE is compared with the reference in the next subsection (Figure 5.8 to Figure 5.13).
Figure 5.7. Effect of direct (top) and delayed (below) addition of 0.1 % (w/w) 3PMA1000 on the heat flow and evolution of the phase assemblage measured by XRD during the first hours of hydration of the model cement initially in the metastable state (with 5% (w/w) hemihydrate). The dashed lines indicate the maximum of the silicate peak.
5.3.3 Evolution of the phases involved in tricalcium silicate reaction

The extent of retardation between direct and delayed addition can be evaluated from the evolution of C₃S and portlandite (Figure 5.8 and Figure 5.9 respectively). Both modes of addition induce retardation, but it is slightly stronger in delayed addition. In this case, after the first intensive dissolution that occurs in the very first minutes, the content of C₃S shows a marked plateau until the onset of the acceleration period at around 6 hours. The C₃S content then decreases strongly before the normal slowing down during the deceleration period. This seems to be coherent with the evolution of portlandite for which the formation significantly increases after the onset of the acceleration period (Figure 5.9). Another important observation is that overall, the evolution of both phases in the system with delayed addition seems to be similar to the reference, although being retarded.

In the case of direct addition, the evolution of C₃S provides a good estimation of the onset of the acceleration period, which in this specific case cannot be determined from the heat flow curve because the sulfate depletion point occurs at the same time. The phase analysis shows that after an initial fast consumption, the C₃S content shows a plateau until 4 hours, after which it decreases strongly. This occurs exactly at the same time as the sulfate depletion, confirming the reason for which peak position identification cannot be done by calorimetry for this sample. Later, the decrease in C₃S content becomes constant until the maximum of the main peak at around 11 hours (marked by the vertical dashed line in Figure 5.7, top). Although this final evolution is qualitatively similar to the reference paste, the rate at which C₃S content decreases is lower. This is coherent with the fact that the main peak is less intense and broader than for either the reference paste or the delayed addition system. In other words, this indicates that here the retardation is not only due to the polymer but also and mainly to the hydration of the aluminate phase coming after the sulfate depletion point, which leads to a different mechanism of retardation.
Figure 5.8. Evolution of the amount of C₃S during hydration of the model cement as determined by quantitative XRD measurements and Rietveld refinement in absence and presence of 0.1 % (w/w) of 3PMA1000 added in a direct and delayed mode.

Figure 5.9. Evolution of the amount of portlandite during hydration of the model cement as determined by quantitative XRD measurements and Rietveld refinement in absence and presence of 0.1 % (w/w) of 3PMA1000 added in a direct and delayed mode.
Figure 5.10 shows the evolution of the mass ratio, $\Delta C_3S/\Delta CH$, for all systems. They all show an initial decrease from very high values until a strong change of slope after the maximum of the main peak. Although the direct addition shows a different rate of hydration regarding the heat flow curve and the dissolution of $C_3S$, its $\Delta C_3S/\Delta CH$ ratio remains similar to the reference paste. In the case of the delayed addition system, its ratio is systematically higher, indicating that in general less portlandite formed with respect to the amount of $C_3S$ reacted according to equation (4.1).

![Figure 5.10. Evolution of the mass ratio, $\Delta C_3S/\Delta CH$, during hydration of the reference cement model paste (no PCE) and the pastes with direct and delayed addition of 0.1 % (w/w) of 3PMA1000.]
5.3.4 Evolution of the phases involved in tricalcium aluminate reaction

Figure 5.11 to Figure 5.16 show the evolution of the phases involved in the hydration reaction of aluminates. First, in all cases, hemihydrate dissolves very fast during the first minutes of hydration but at a slightly lower rate for the delayed addition (Figure 5.11). In contrast, the direct addition seems to accelerate its dissolution. However, this concerns very low amounts of hemihydrate and considering the error coming from the quantification (about 1 % (w/w)), we cannot fully trust these small differences found between the addition modes.

![Graph showing the evolution of hemihydrate during hydration](image)

**Figure 5.11.** Evolution of the amount of hemihydrate during hydration of the model cement as determined by quantitative XRD measurements and Rietveld refinement in absence and presence of 0.1 % (w/w) of 3PMA1000 added in a direct and delayed mode.

As explained in section 5.2.2 in the reference paste, the fast dissolution of hemihydrate allows to reach the supersaturation needed to precipitate gypsum. This is visible in the heat flow by the small peak around 2.5 hours and further proved by
Table 5.1 that shows the concentration of sulfur in the pore solution before and after this small peak. The sulfur concentration after the peak is indeed very close to gypsum solubility, which is 17.6 mM. We take this concentration as an indication because in this system we cannot quantify calcium activity in presence of PCEs, which prevents a rigorous solubility product from being calculated. The addition of the PCE most probably decreases the supersaturation with respect to gypsum since the sulfate concentration goes from 51.2 mM (for the reference without PCE) to around 40 mM. This suggests that either hemihydrate dissolution is hindered or ettringite formation is enhanced. However, none of these effects prevents gypsum from forming, as indicated by the drop of the concentration to 17 and 19.6 mM for the direct and the delayed addition respectively.

<table>
<thead>
<tr>
<th>Hydrating system</th>
<th>Extraction time</th>
<th>[S] mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>No PCE</td>
<td>27 min (before gypsum)</td>
<td>51.2</td>
</tr>
<tr>
<td>No PCE</td>
<td>2 h (after gypsum)</td>
<td>19.8</td>
</tr>
<tr>
<td>Direct addition</td>
<td>30 min (before gypsum)</td>
<td>41.8</td>
</tr>
<tr>
<td>Direct addition</td>
<td>2 h (after gypsum)</td>
<td>17.0</td>
</tr>
<tr>
<td>Delayed addition</td>
<td>37 min (before gypsum)</td>
<td>38.4</td>
</tr>
<tr>
<td>Delayed addition</td>
<td>3 h (after gypsum)</td>
<td>19.6</td>
</tr>
</tbody>
</table>

There is however an effect on the amount of gypsum precipitated, which is reflected by the lower peaks on the heat flow curves, and further confirmed by Figure 5.12 that shows the evolution of gypsum content in all systems. In direct addition, only a very low gypsum content was detected by XRD measurements, which is not surprising regarding the substantial precipitation of ettringite induced by the PCE (Figure 5.13). As already shown elsewhere (see section 2.4), the PCE favours the nucleation of ettringite leading to a high initial formation of this mineral that
consumes faster the sulfates supplied in solution by the dissolving hemihydrate. In consequence, although gypsum is nucleated in all cases, the initially favoured formation of ettringite implies that lower amounts of gypsum are precipitated in direct addition.

In delayed addition, the slower dissolution of hemihydrate observed in Figure 5.11 seems to correspond to the delayed precipitation of gypsum with respect to the reference. In this case, as the precipitation of ettringite is not favoured (Figure 5.13), gypsum precipitation is not prevented but rather delayed. After a maximum content lower than the reference, it then dissolves in a similar constant way until the depletion point. This suggests that gypsum precipitation is shifted at later time rather than being significantly reduced when the PCE is added in a delayed mode.

Figure 5.12. Evolution of the amount of gypsum during hydration of the model cement as determined by quantitative XRD measurements and Rietveld refinement in absence and presence of 0.1 % (w/w) of 3PMA1000 added in a direct and delayed mode.
With respect to the ettringite content, in the case of delayed addition, the polymer cannot favour its nucleation in the very first minutes but rather seems to decrease its formation as shown in Figure 5.13. This leads to a lower content of ettringite over time up to the sulfate depletion point and raises the question of the location of the sulfates. Indeed, if less gypsum and ettringite are precipitated before the sulfate depletion point and a similar concentration of sulfur is measured in the pore solution after the peak of gypsum, then some sulfates are « missing ». While around 12 and 9 % (w/w) of the total sulfates content are not used in gypsum or consumed in ettringite right before the sulfate depletion point for the reference and the direct addition system respectively, around 21 % (w/w) is still “missing” in the case of delayed addition. An early precipitation of AFm that could be stabilised by PCEs can already be excluded as no AFm phases were found on XRD patterns for all the systems before the depletion point. Additionally NMR measurements not reported here also did not identify the presence of AFm phases. Therefore, either the missing sulfates were lost during the filtration and extraction of the pore solution, possibly because of some complex and or aggregates involving the polymer and other ions including sulfates. However, they also could be consumed by adsorption on another phase, such as C-S-H.232,233
Figure 5.13. Evolution of the amount of ettringite during hydration of the model cement as determined by quantitative XRD measurements and Rietveld refinement in absence and presence of 0.1% (w/w) of 3PMA1000 added in a direct and delayed mode.

A direct visualization of the effect of the addition mode on ettringite formation is shown in Figure 5.14 with SEM images performed on the three samples stopped after 2 hours of hydration. In the reference paste (Figure 5.14 a), the particles of ettringite are found on the anhydrous surface in the shape of thick needles of about half a micrometer long. In direct addition (Figure 5.14 b), the ettringite needles are clearly more numerous and agglomerated (probably put down on the surface when the water is removed) but slightly smaller than in the reference paste. However, in the delayed addition case, the ettringite particles are more difficult to find as they are smaller and do not have a clear hexagonal needle-shape.
Figure 5.14. SEM images in secondary electron mode of the model cement without polymer (a), with direct (b) and delayed (c) addition of 0.1% (w/w) 3PMA1000 stopped after 2 h of hydration.
Another way to quantify the change in precipitation of ettringite in presence of PCE is to measure the BET specific surface area of the hydrating sample (Figure 5.22) at early ages. Indeed, as this is the most abundant phase formed in those periods, most changes in specific surface area are expected to come from the amount and/or specific surface area of the ettringite precipitated. In direct addition case, the presence of the polymer when ettringite nucleates modifies this process and increases the specific surface area by about 50%. In delayed addition, only a slight decrease was observed in the first minutes compared to the reference system without polymer. All these observations follow the same trends of the content of ettringite shown in Figure 5.13, indicating that while the specific surface area of ettringite does appear changed in presence of the polymer (Figure 5.14) the main fact of the changes of the sample specific surface area is the amount of ettringite formed.
Figure 5.15. Evolution of the specific surface area over time of the reactive system. The empty square indicates the specific surface of the anhydrous powder. The full squares show the one of the model clinker with 5% (w/w) hemihydrate without PCE. Circles and triangles show the changes in specific surface when 0.1% (w/w) of the polymer 3PMA1000 is respectively added in the mixing water (direct addition) or added as a concentrated solution 5 minutes after mixing the reactive system with water (delayed addition).

Finally, the comparison of $C_3A$ evolution between the different addition modes is not only coherent with the heat flow, where the rapid dissolution occurs at the same time as the sulfate depletion, but also with the initial evolution of ettringite in Figure 5.13. In particular the lowest $C_3A$ content corresponds to the highest precipitation of ettringite. Interestingly, for all the cases, the total amount of $C_3A$ reacted right before the depletion point is very close to the theoretical one needed to consume all the sulfates introduced in the system by precipitation of ettringite according to equation (5.1) and this although the corresponding content of ettringite was not quite reached, as mentioned earlier. In the case of the reference paste and the direct addition system, 90 and 98% (w/w) of the theoretical amount of ettringite that
should have formed with respect to the $C_3A$ reacted, while only 76 % (w/w) was obtained for the delayed addition.

Despite that minor discrepancy, we can state and emphasise once again that the results presented in this section strongly support our phase analysis protocol. In the context of the impact of PCEs discussed in the following sections, this provides invaluable information in identifying possible working mechanisms, in particular concerning the role of aluminates in this complex problem.

![Figure 5.16. Evolution of the amount of $C_3A$ during hydration of the model cement as determined by quantitative XRD measurements and Rietveld refinement in absence and presence of 0.1 % (w/w) of 3PMA1000 added in a direct and delayed mode.](image-url)
5.4 Effect of the PCEs addition mode and structure on silicate hydration

5.4.1 Delayed addition

Nucleation and growth of ettringite is extremely rapid, with a time scale on the order of seconds rather than minutes. Therefore, in delayed addition, most of the ettringite crystals have precipitated by the time the PCE is added, so that neither nucleation (N4) nor growth (G4) of ettringite are perturbed. This considerably simplifies the analysis and is why we first discuss this situation.

As shown in Figure 5.17 (top left), the time delay ($\Delta t$), for the silicate hydration increases linearly with the number of carboxylate groups $x_0$ introduced in the system:

$$x_0 = n_{RU}^{\text{tot}} \frac{C}{E}$$

(5.2)

where $n_{RU}^{\text{tot}} = \frac{c_{PCE}}{M_{RU}}$ is the total number of repeat units, $c_{PCE}$ is PCE dosage by mass and $M_{RU}$ is the molar mass of a repeat unit given by:

$$M_{RU} = P \cdot M_{SC} + \left( \frac{C}{E} + 1 \right) \cdot M_{BB}$$

(5.3)

with $M_{SC}$ and $M_{BB}$ respectively the molar masses of side chain and backbone monomers (here ethylene oxide and methacrylic acid).

Additionally, the slopes of $\Delta t$ versus $x_0$ are also dependent on $C/E$. A careful examination of the slopes led us to find that they are proportional to $\frac{\left( \frac{C}{E} \right)^{1/2}}{\left( \frac{C}{E} + 1 \right)^{3/2}}$. This leads to a very simple relation between retardation, $\Delta t$, the total number of repeat units and a function of the repeat unit charge density:

$$\Delta t \propto n_{RU}^{\text{tot}} \cdot \left( \frac{C}{E} \right)^{3/2} \left( \frac{C}{E} + 1 \right)^{3/2}$$

(5.4)
This perfectly collapses all our results on a single master curve, accounting for the impact of all PCEs and dosages tested (Figure 5.17 bottom left). Its generality is confirmed on a system with a different proportion of hemihydrate (6.5% of hemihydrate, which represents an oversulfated system in Figure 5.18) and real cements in Figure 5.19 for cem1 and Figure A.2.6 in the Appendix for cem2. It is worth noting that equation (5.4) does not include a dependence on the length of the polymer backbone, which is consistent with results shown in Figure 5.20, where two polymers having the same characteristics as 3PMA1000 (C/E ratio and side chain length) but with different backbone length (n equal to 6 and 38) induce exactly the same retardation. A mechanistic interpretation of the origin of this equation is developed in the sub-section 5.4.4.
Figure 5.17. Impact of various PCEs on the hydration of the model cement. The top left graph shows a linear increase of retardation, $\Delta t$, with the number of carboxylate groups introduced. The slopes $\gamma_{SP}$ of the corresponding linear regressions do not depend on the side chain length. The slopes are found to vary as $\left( \frac{C/E}{C/E+1} \right)^{3/2}$ (right). This expression allows representing all data in the master curve at the bottom of this figure using equation (5.4). It shows that retardation is proportional to the number of repeat units $\frac{c_{PCE}}{M_{RU}}$ and to a function of the polymer structure given by $\left( \frac{C/E}{C/E+1} \right)^{3/2}$. 
Figure 5.18. Master curve of retardation of the maximum of the silicate peak as a function of PCE structure and dosage obtained for the model clinker with 6.5% (w/w) of hemihydrate, which represents an oversulfated state.

Figure 5.19. Master curve of retardation of the maximum of the silicate peak as a function of PCE structure and dosage obtained for an ordinary Portland cement (cem1). The deviation observed at high dosages of the PCE 1PMA1000 is expected to be due to the low adsorption equilibrium constant of this polymer causing it to have an adsorption that would be much more sensitive to the alkali sulfates salt present in cement but not in our reactive system.
Figure 5.20. Heat flow of the model clinker with 5% (w/w) hemihydrate with two polymers having the same C/E ratio (3) and side chain length (1000 g/mol) but different number of repeat unit $n$. In the first case, $n$ is around 38 and in the second case, $n$ is around 6. The similarities of occurrence and shape of curves show that the perturbation induced by the PCE is not dependent on the length of the backbone represented by $n$.

5.4.2 Direct addition

When the polymer is present in the mixing water (Figure 5.6a), its impact on hydration is fundamentally different from delayed addition (Figure 5.6b). Also, the retardation induced is no more a linear function of dosage (Figure 5.21 compared to Figure 5.17). In direct addition, we find that before a critical dosage $c^*$, there is no or little impact on silicate hydration. This represents a convenient dosage by which we normalized each data series in Figure 5.21 to better compare the impact of different polymers. It highlights the zone of low retardation below $c^*$ and better shows above $c^*$ an extremely sharp transition to an important retardation with a plateau starting at a second critical dosage, which is denoted $c^{**}$. 

124
Our interpretation of this non-linear behavior is summarized by the inserts in Figure 5.21. It finds its origin in specific surface area changes that are caused by the polymer's presence during the nucleation of initial hydrates\textsuperscript{235}. This effect depends both on polymer structure and dosage, as illustrated in Figure 5.22, and concerns ettringite, which is the phase that mostly precipitates in our model cement in the first minutes.

**Figure 5.21.** Retardation in case of direct addition of PCEs. Up to a first critical concentration $c^*$ ($c/c^* = 1$), almost no retardation occurs since almost all the polymer added is mobilised on ettringite (zone I). At $c^*$, all the surface of precipitated ettringite is occupied by all the added polymer, leaving the silicate still largely free of polymer (zone II). Above $c^*$, the created surface of ettringite is not sufficient to adsorb all the polymer, so that PCEs also adsorb on the silicates and retardation increases with dosage up to $c^{**}$ (zone III). At a second critical concentration $c^{**}$, the silicate retardation reaches a plateau controlled by aluminate ions and typical of an undersulfated system. In this case, new calcium aluminate hydrates (AFm), which adsorb strongly the PCEs, form in the same time or instead of ettringite (zone IV). For the purpose of the illustration, only the silicate phase is represented for the reactants rather than the combination of model clinker grains and hemihydrate, as the silicate phase is the most abundant and the one of which the retardation is considered.
Figure 5.22. Evolution of the specific surface area of the reactive system with 5% (w/w) hemihydrate after 10 minutes with the direct addition of different dosages of PCEs. At $c^*$, which corresponds to the onset of retardation (that differs from a PCE to another one, see Table 3.4), the results show that the polymers influence differently the specific surface area. This means that the favoured nucleation of ettringite is dependent on the structure of the polymers. Above $c^*$, the specific surface area increases with the dosage. At $c^{**}$, which represents the end of the transition of the balanced system to an unbalanced or undersulfated one, specific surface area created by the polymers are quite similar. The measured specific surface of the sample in absence of polymer but after the same hydration time is included as reference and shown for each concentration range for better comparison with the samples containing polymers.

The situation at $c=c^*$ is particularly interesting from a quantitative point of view. Indeed, we find that the surface area of initially precipitated hydrates corresponds within +/-20% to the one that each polymer can cover at $c=c^*$ (Figure 5.21, insert II). This surface is obtained by multiplying the number of PCE molecules at $c=c^*$ by the surface $S_A$ occupied by an individual polymer. The later can be described by a self-excluding chain of half spheres, as illustrated in Figure 5.27 (bottom), and is given by the following scaling relation:

$$S_A = \frac{\pi}{\sqrt{2}} a_N a_P \left(2\sqrt{2}(1 - 2\chi) \frac{a_P}{a_N}\right)^{2/5} P^{9/10}(C/E + 1)^{3/10} n$$  \hspace{1cm} (5.5)
where \( a_N \) and \( a_P \) are the size of the monomers in the backbone and in the side chains, respectively (here 0.25 and 0.36 nm). \( \chi \) is the Flory parameter (0.37 at 25\(^\circ\)C for PEG\(^{20}\)).

Therefore, up to \( c^* \), almost all polymers must adsorb on ettringite and almost none remain available to retard silicate hydration, which is illustrated by inserts I and II (Figure 5.21).

Above \( c^* \) but below \( c^{**} \), silicate retardation increases with dosage. The surface of ettringite continues to increase as more PCEs are added (Figure 5.22). However, it does not increase enough to mobilize all the additionally added PCEs. Therefore, some PCEs remain available to inhibit the hydration of tricalcium silicate. In line with the results presented in the next section, we believe that retardation most probably involves the hindering of tricalcium silicate dissolution by PCEs adsorbed on its surface, which is illustrated in insert III (Figure 5.21).

Between \( c^* \) and \( c^{**} \), the amount of PCE repeat units causing the retardation of silicate hydration can be written as: \( (n_{RU}^{\text{tot}} - n_{RU}^{\text{Eff}}) \), where \( n_{RU}^{\text{tot}} \) and \( n_{RU}^{\text{Eff}} \) are the number of repeat units respectively dosed in the system and adsorbed on ettringite. Building on our result at \( c=c^* \), we can estimate \( n_{RU}^{\text{Eff}} \) from \( S_{\text{A}} \ n \) and the measured surface of initially precipitated hydrates, \( S_{\text{Eff}} \):

\[
n_{RU}^{\text{Eff}} = n \frac{S_{\text{Eff}}}{S_{\text{A}}} \tag{5.6}
\]

With this, retardation between \( c^* \) and \( c^{**} \) is found to qualitatively match the trend for delayed addition with a proportionality to the number of repeat units and to the same function of polymer structure as in equation (5.4):

\[
\Delta t_{\text{Eff}}^{\text{direct}} \propto (n_{RU}^{\text{tot}} - n_{RU}^{\text{Eff}}) \cdot \left( \frac{C/E}{C/E + 1} \right)^{3/2} \tag{5.7}
\]

As shown in Figure 5.23, the data do not fit quite as well, but the general trend is nevertheless well captured considering the higher level of uncertainties in this case.
Overall, this points to the fact that the same mechanism is at play for retarding silicate hydration in both addition modes.

Figure 5.23. Confirmation that between $c^*$ and $c^{**}$, retardation increases with the same dependence on molecular structure as for delayed addition. The y-axis show the slope of retardation versus number of repeat units from the polymer expected to reach the silicates in direct addition. This is determined using measurements of specific surface between $c^*$ and $c^{**}$ and first determining the amount of polymer repeat units expected to be adsorbed on ettringite. The difference of this value with respect to the dosed amount is used to report the values of gamma reported here. These are plotted as a function of C/E defined in the main text (as also illustrated in Figure 5.17). The line shows the linear regression over the four points shown with filled symbols. The open symbol corresponds to the point having the largest slope. This is associated with a much larger experimental error and is the reason why we do not consider it in the regression.

The dosage $c^{**}$ represents the transition to an “unbalanced” or undersulfated system and the start of a retardation plateau (Figure 5.21). It corresponds to a situation where, by strongly affecting one chemical reaction, an organic compound can completely upset the reactivity of a coupled chemical system. Understanding the
details of this situation however requires specific notions of cement chemistry for which some background must first be given. To explain this, we consider the relative reaction rates of the silicate, aluminate and sulfate phases, which is one of the most important aspects during cement hydration. We recall the milestone work by Tenoutasse,\textsuperscript{102} who, by using a mixture of pure tricalcium silicate and aluminate with gypsum, showed that below a critical gypsum dosage, the silicate peak gets massively retarded, but that it occurs at a fixed time above that dosage (Figure 2.7 and Figure 5.3). Systems having at least this critical gypsum content are defined as “balanced” and the others as “unbalanced” or undersulfated. The later situations show a massive retardation of the silicate peak that is a major issue in practice.

The delay of silicate hydration at too low sulfate content results from a higher concentration of aluminate ions in solution.\textsuperscript{47,103,236} In contrast, with a sufficient amount of calcium sulfates most aluminate ions are consumed by ettringite precipitation while additional sulfate ions inhibit tricalcium aluminate dissolution, allowing the silicate to hydrate normally (Figure 5.2).\textsuperscript{43,44} Our model cements correspond to such “well-balanced” situations. However, if we prepare them by deliberately including too low amounts of calcium sulfate hemi-hydrate, we get a substantial retardation of which the magnitude is identical to the plateau observed in Figure 5.21 above $c^\ast\ast$.

Therefore, we infer that the transition to the retardation plateau seen in Figure 5.21 corresponds to systems becoming “unbalanced” because of a too high PCE dosage. The possibility of chemical admixtures to cause this has been mentioned in the literature\textsuperscript{47,96}, but was never studied systematically despite its major practical implications. Referring to the main reactions described in Figure 5.2, this is due to polymers favouring ettringite nucleation, increasing its amount (Figure 5.13) and specific surface area (Figure 5.15) in the first minutes.\textsuperscript{120} This accelerates the dissolution of hemihydrate (D1 in Figure 5.2) and leads to a faster depletion of the sulfate carrier. After that, tricalcium aluminate dissolution (D2) accelerates and aluminate ions accumulate in solution, causing systems to become “unbalanced” if the silicate peak has not yet occurred.
At $c^\circ$, specific surfaces are found to be high and roughly identical (Figure 5.22), most probably due to the onset of the formation of calcium aluminate hydrates (noted AFm) typical of undersulfated systems. These phases are known to strongly adsorb and/or intercalate comb-copolymers$^{119,151,153}$ and should therefore be capable to adsorb all PCEs, leaving silicates to only be retarded by aluminate ions$^{47,75,103,236}$ (insert IV, Figure 5.21). This explains why a similar retardation as polymer free undersulfated systems is observed.

This behaviour is observed for polymers that modify the nucleation of ettringite. In contrast, a polymer with a low adsorption equilibrium constant as the 1PMA1000, only causes a gradual increase of retardation with dosage, similar to delayed addition (Figure 5.24 and Figure A.2.5). According to Marchon et al.,$^{118}$ this could result from a higher sensitivity to competitive adsorption with sulfates that prevent the polymer from adsorbing on ettringite.
5.4.3 Mechanistic origin of the silicate hydration delay

We previously showed that the polymers available to cause silicate retardation do so with a similar dependence on molecular structure in both addition modes, suggesting that the same mechanism is involved. It implies that its origin can be equally well studied in either addition mode. However, we focus our attention on the delayed addition in what follows since it is simpler.

In delayed addition, we clearly find that PCEs shift the silicate peak to later times, without changing its initial shape (left side of the peak, called the acceleration period). This is visible in Figure 1.1 and Figure 5.1. It suggests that PCEs delay a critical event, after which the system behaves similarly, only somewhat later. Among the various competing mechanisms that may explain this, the most probable one
concerns a reduced dissolution (D3, Figure 5.2) or an inhibition of the nucleation of hydrates (N5 and N6).

In the light of recent research, an inhibition of silicate dissolution probably offers the most credible explanation. Indeed, already in absence of PCEs, the rate limiting step of cement hydration seems to be dissolution, as proposed by Nicoleau et al.\textsuperscript{237} following the evolution of saturation index during hydration. Very importantly also, the activation energy of cement hydration is the same as that of tricalcium silicate dissolution\textsuperscript{29,87,238}. Additionally, it was shown that, in presence of PCEs, hydration kinetics of tricalcium silicate have a reduced frequency factor of the Arrhenius law, but the same activation energy.\textsuperscript{239} This means that the same rate-limiting step, namely tricalcium silicate dissolution, most probably controls hydration in presence of PCEs. These recent findings support preliminary observations on the role of latexes bearing carboxylate groups on dissolution of hydrating tricalcium silicate\textsuperscript{38}.

Here we present direct experimental evidence that silicate dissolution can be substantially reduced by PCEs. This was done using a flow through reactor providing high dilutions that prevent hydrates from precipitating, which makes it possible to study dissolution alone\textsuperscript{29}. Dissolution rates are highly dependent on undersaturation, which is affected by ion complexation. Therefore, it is only possible to properly assess the impact of organic compounds on dissolution by reporting rates in terms of the ionic activity product $\Pi$ of the dissolving compound. This requires a rather tedious determination of ion activities, which is why it has not been done so far for cementitious systems. The ion activity products reported in Figure 5.25 offer a good approximation of the real values, thereby making it possible to reliably take into account complexation by organic compound during the dissolution of a tricalcium silicate (containing impurities and most commonly called alite). This is particularly important for real systems with low water content, such as the pastes used in this study, since their lower dilutions substantially reduce undersaturation, leading to values of $\ln(\Pi)$ in the range of -60 or above. As shown in Figure 5.25, in presence of PCEs, dissolution rates of tricalcium silicate are then reduced by one to two orders of magnitude. It can also be noted that dissolution rates tend towards different limiting undersaturations. On the basis of dissolution
measurements without polymers it has been proposed that this value represents an apparent solubility of the dissolving surface\textsuperscript{30}. The results in Figure 5.25 may therefore indicate that the polymer is changing the properties of the solid-liquid interface, more specifically reducing its apparent solubility. This is compatible with the assertion that the polymer reduces the dissolution rate. However, as the concept of “apparent solubility” is ill-defined from a chemical point of view, we will not further elaborate on such considerations in this paper.

Figure 5.25. Dissolution rate \( r \) measured on impure tricalcium silicate in a flow through dissolution cell allowing to maintain sufficiently dilute conditions to prevent hydrates precipitation\textsuperscript{29}. The dissolution rates measured are reported as a function of the ionic activity product \( \Pi \) of tricalcium silicate determined by solution composition measurements and Debye Hückel-based ion activity calculations, accounting also for calcium complexation by the PCE (data provided by Dr Patrick Juilland and Dr Emmanuel Gallucci, Sika Technology AG).

The fact that low dosages of polymers may so effectively block the dissolution of a reactive phase may be understood from the perspective of blocking surface reactive areas. These are areas of higher density of kinks, such as for example corners and
etch pits, which are the most reactive areas present on surfaces.\textsuperscript{240} The opening of etch pits at crystallographic defects represents one of the major processes of mineral dissolution.\textsuperscript{74,241} This was first ascertained in geochemistry and has recently gained a lot of attention in cement research.\textsuperscript{28–30,237,242} The culprit of this theory is that dissolution pits play an important role in creating new kink sites, thereby increasing the dissolution rate that predominantly takes place through step retreat from those kinks until a steady state is reached.\textsuperscript{74} With respect to the present study, the most noteworthy aspect is that compounds adsorbing at kinks are particularly detrimental to dissolution as they not only decrease the number of steps able to retreat, but also probably block the retreat of subsequent steps.\textsuperscript{243}

This interpretation is supported by the fact that the hydration delay induced by a PCE on pure tricalcium silicate can be matched to the one caused by annealing this material, as shown in Figure 5.26. Indeed, annealing is a process that relaxes subsurface crystallographic defects, reducing the density of natural kink sites.\textsuperscript{32} The similarity that both samples show in terms of delay and hydration kinetic pattern very strongly suggests that polymers, exactly like annealing, have a preferred impact on the most reactive dissolution areas. Therefore, we infer that dissolution is the rate limiting step for silicate hydration and that PCEs delay it by blocking reactive dissolution areas that would otherwise develop as dissolution pits and retreating steps.
5.4.4 Model rationalisation

The inhibition of tricalcium silicate dissolution by PCEs must involve their adsorption on this phase, providing a basis for examining the nature of equations (5.4) and (5.7). Additionally, as related elsewhere, the adsorption of PCEs on cementitious materials often shows a linear increase almost up to the plateau. For consistency with equation (5.4), in what follows, we express the polymer concentration in terms of total number of repeat units. In the linear regime, the amount of adsorbed repeat units \( y_i \), expressed per unitary surface area, more specifically per number of surface charges is:
where $K_i$ is the equilibrium constant of the polymer with respect to phase $i$ and $C_{RU}$ is the concentration of repeat units in solution.

The mass balance over the repeat units gives:

$$C_{RU} V + \sum_i S_i y_i = n_{RU}^{\text{tot}}$$  \hspace{1cm} (5.9)$$

where $n_{RU}^{\text{tot}}$ is the number of repeat units introduced in the system, $V$ is the solution volume and $S_i$ is the number of surface charges of phase $i$.

Substitution of equation (5.8) into equation (5.9) and rearranging gives:

$$C_{RU} = \frac{n_{RU}^{\text{tot}}}{V + \sum_i K_i S_i}$$  \hspace{1cm} (5.10)$$

The surface coverage of phase $B$ is then obtained by substitution into equation (5.8):

$$y_B = \frac{n_{RU}^{\text{tot}}}{\frac{V}{K_B} + \sum_i K_i S_i}$$  \hspace{1cm} (5.11)$$

If adsorption leads to only a low concentration of polymer remaining in solution, or at least a low amount from the adsorbing part of the molecular structure distribution, then we have:

$$y_B = \frac{n_{RU}^{\text{tot}}}{\sum_i \frac{K_i}{K_B} S_i}$$  \hspace{1cm} (5.12)$$

Moreover, for the competition between two surfaces $A$ and $B$, whereby most polymers are adsorbed we get:
\[ y_B \propto \frac{n_{\text{tot}}^{\text{RU}}}{K_A S_A + S_B} \]  \hspace{1cm} (5.13)

where \( S_A \) and \( S_B \) are the total number of surface charges on \( A \) and \( B \), while \( K_A \) and \( K_B \) are the affinity constants of the polymer for \( A \) and \( B \). They have been described in relation to PCE structure by the following scaling law, using the structural parameters in Figure 1b:

\[ K_i \propto k_i \frac{(C/E)^2}{nP^5(C/E + 1)^5} \]  \hspace{1cm} (5.14)

where \( k_i \) is a numerical constant that depends on the nature of the surface \( i \) but not on the polymer structure. This equation relies on first principle considerations as the charge per surface occupied by an adsorbed molecule, as well as an entropic contribution by each side chain. These scaling relations are not expected to change depending on whether surface \( A \) or \( B \) are considered, so that \( K_A/K_B = k_A/k_B \), which is independent of polymer structure.

Moreover, according to our previous arguments, we consider that delaying hydration involves the blocking of specific areas. These would correspond to surface \( B \) and would also account for a small fraction of the total surface area, making \( S_B \) negligible in equation (5.13). This leads to a direct proportionality between \( y_B \) and \( n_{\text{tot}}^{\text{RU}} \), explaining the experimentally observed proportionality between \( \Delta t \) and \( n_{\text{tot}}^{\text{RU}} \) or \( (n_{\text{tot}}^{\text{RU}} - n_{\text{ett}}^{\text{RU}}) \) respectively in equations (5.4) and (5.7).

Concerning the second part of those equations, they introduce a dependence on molecular structure in the form of \( \left( \frac{C/E}{C/E + 1} \right)^{3/2} \), which would express the dissolution blocking capacity of each repeat unit. A priori, this may depend on a local charge density of functional groups at the surface of the silicate phases.

More specifically, we consider the electric field, \( \Sigma \), produced by the polymer backbone on the surface where it is adsorbed. For a long cylinder (i.e. the backbone),
this is inversely proportional to the distance from the backbone and proportional to the linear charge density expressed as:

\[ \rho_L \propto \frac{C/E}{C/E + 1} \]  

(5.15)

Because of the limited range of the electrostatic interactions due to the high ionic strength, we only consider the points of shortest distance to the backbone and estimate an average value thereof. This is done by considering the local charge concentration close to the surface, in the zones where the polymer is adsorbed (in red, Figure 5.27). This is dominated by the polymer functional groups rather than the bulk ionic strength. Therefore, we define a second length scale for the local screening of the surface charge in those areas. By analogy to Debye length, this should be inversely proportional to the square root of the charge density:

\[ h \propto \left(\frac{C/E + 1}{C/E}\right)^{1/2} \]  

(5.16)

This leads to the following expression for the electric field \( \Sigma \):

\[ \Sigma \propto \frac{\rho_L}{h} \propto \left(\frac{C/E}{C/E + 1}\right)^{3/2} \]  

(5.17)

Finally, equations (5.4) and (5.7) can be thought of as a product between the number of added repeat units and a blocking capacity of each repeat unit, which depends on the electric field induced by the polymer on the surface.
Figure 5.27. Schematic representation of molecular and sub-molecular scale characteristics of an adsorbed comb-copolymer. The bottom figure shows the blob model describing the polymer as 2D self excluding chain of half spheres\textsuperscript{114}. The occupied surface is given by equation (5.5). The sub-molecular scale defines the local interaction of the functional groups with the surface. The middle figure schematically highlights the expectation that the backbone is not fully lying down on the surface. The graded red area below it defines the electrical field felt on the surface, which is maximum directly below the backbone, (explaining the dark color in its center). For visual representation, the comb-copolymer is segmented in boxes each containing a backbone monomer. The upper figure illustrates a single repeat unit of which the length is proportional to $C/E + 1$. The average distance of the backbone to the surface (here represented by the box height) is proportional to the inverse square of the linear charge density in the polymer backbone. The box width, $\lambda$, is taken arbitrarily for the purpose of the illustration.
5.5 Conclusion

By using a specially designed model cement, it has been possible to illustrate various processes, sometimes competitive, that arise in a multicomponent reactive system in presence of organic additives. The main outcome has been to quantify, through basic principles, the hydration delay of tricalcium silicate caused by comb-copolymers in relation to their dosage and molecular structure. The mechanism by which this takes place appears to involve the adsorption of polymers that block reactive areas controlling the dissolution rate of the tricalcium silicate. Strong and direct experimental evidence for this is provided.

A fundamental outcome is that retardation develops from a combination of molecular and sub-molecular scale phenomena (Figure 5.27). The first, that concerns polymer surface occupancy, typically comes from polymer physics and can be described by scaling laws. This phenomenon was described by the direct addition case, where the polymer is present during ettringite nucleation. The second phenomenon deals with interactions of chemical nature that we rationalize in terms of an electrical field from the charged backbone felt at the surface.

Quantitatively establishing that our system is controlled by a combination of molecular and sub-molecular scale properties has broad reaching implications. Starting with real cements and direct addition, we can better understand the broad variety of results found in the literature. Indeed, different processes are at stake and their relative importance should change depending on the chemical and mineralogical compositions of cement, which are known to be quite variable. Here, thanks to our model system and the separation of both addition modes, it has been possible to propose the first quantitative rationalization of these effects.
Chapter 6
Impact of PCEs on Pure C₃S Hydration

The content of this chapter is presently not included in any publication or draft publication. However, in combination with Chapter 4, it is planned to write at least one ISI journal paper.

6.1 Introduction

This chapter focuses on the hydration of pure tricalcium silicate in presence of comb-shaped polycarboxylates from two addition modes as studied with the model cement in the previous chapter. With respect to the strong similarities observed between the model clinker and ordinary Portland cement, two important questions are raised: How is the direct interaction between the PCEs and the pure silicate phase in absence of the aluminates? and can it be directly linked to the retardation process occurring during cement hydration?

The first part of the chapter deals with the influence of the addition mode of one PCE dosage on the evolution of the phase assemblage following the quantification method validated in Chapter 4. This is followed by the effect of increasing dosages of different PCE structures on the heat release. Finally, the retardation of silicate hydration observed in the calorimetric measurements is discussed in relations to the dosages and structures of the PCEs used.
6.2 Effect of the PCEs on the phases assemblage evolution

Figure 6.1 shows the phase assemblage associated to the heat release during hydration of pure C₃S with direct and delayed addition of 0.1% (w/w) 3PMA1000. In both cases, a faster consumption of C₃S is clearly visible at the beginning of the acceleration period. In particular, we observe that this corresponds perfectly with the accelerated formation of portlandite. This also correlates with the evolution of “Others”, which mainly represents the evolution of C-S-H formed as explained in Chapter 4. However, as a reminder, other amorphous phases and fitting errors from Rietveld refinement are counted in the absolute mass fraction reported as “Others”.

Figure 6.1. Effect of the direct (top) and delayed (bottom) addition of 0.1 % (w/w) 3PMA1000 on the heat flow and evolution of the phase assemblage measured by XRD during the first hours of pure C₃S hydration. The dashed line between the three last points is only an eye guideline and do not represent the real evolution of the phases.
6.2.1 General features of the heat release

Figure 6.2 to Figure 6.5 show for each phase the different evolutions between the reference paste and the systems with the polymer. Before analysing further the phases evolution, it is necessary to compare briefly the heat release of each system and introduce their main features (Figure 6.2). For more information about the influence of increasing dosages of different PCEs on the heat release of pure C₃S, a detailed analysis is reported later in section 6.3.

First, for the same dosage, the direct addition induces higher retardation. The opposite is generally observed with ordinary Portland cement due to the fast reaction of the aluminates that consume part of the PCEs present in the water. This has already been explained in section 2.4 of Chapter 2 and illustrated for our model cement in Chapter 5.

Second, in both systems with PCE, the heat release during the induction period is lower but does not go down to zero. This demonstrates that hydration reactions still occur but at a lower rate.

Apart from this, both systems containing the PCE show a similar feature that is not identifiable in the reference paste. It is the presence of a small peak in the induction period, one that is usually attributed to portlandite precipitation before the onset of rapid formation of C-S-H. Additionally, for the systems with PCE, the induction period is followed by a less sharp transition to the acceleration period. Both these features render the determination of the onset of the acceleration period more difficult and somewhat arbitrary.
6.2.2 Evolution of C₃S content

Figure 6.2 also shows the comparison of the evolution of C₃S during the first hours of hydration between the reference and both systems with PCEs. As observed earlier, in all cases, the consumption of C₃S clearly accelerates after the onset of the acceleration period and the time at which this occurs increases in presence of the PCE. Interestingly, when the hydration rate reaches its maximum, the remaining amount of C₃S (shown by the dashed lines) is only slightly lower than the reference for the delayed addition, but significantly lower for the direct addition. We can see three reasons for this.
First, the non-zero heat flow observed in the induction period implies that hydration reactions, i.e. C₃S dissolution, still occur. This means that already at the onset of the acceleration period, slightly more C₃S may have dissolved in the direct addition system than in the reference paste, simply because this onset occurs later in time. This hypothesis would require C₃S dissolution not to be strongly affected by the PCE. However, as mentionned in Chapter 5 (Figure 5.25), this is not the case.

An alternative explanation could be that, in pure C₃S without aluminate phases to uptake and regulate the adsorption of the polymer, PCEs might also affect the nuclei formed in the very first seconds after the contact with the water. This would concern the situation of direct addition and could involve a process of templating, whereby more nuclei would be formed. While this alone would rather accelerate hydration kinetics, including an increase of the slope in the acceleration period, an additional and detrimental impact of PCEs on growth or dissolution rate could account for the overall retardation.

Finally, a last explanation could come from the presence of the PCE in the pore solution and their binding ability with Ca-ions. In a system with only pure C₃S, at the very beginning of hydration, the pH and Ca-ion concentration are relatively low, which limits PCEs adsorption. Their presence in pore solution in a large number in addition to their calcium binding ability could artificially keep a high undersaturation degree longer. This would influence the anhydrous surface by creating more reactive sites and therefore favour the dissolution until the PCEs can effectively adsorb on the silicate phase. This might explain why in the direct addition, more C₃S dissolved than in the reference. In a system with aluminates, this would not occur or to a lesser extent as the PCE adsorb faster.

From this point of view, we can only state that PCEs disturb a series of coupled chemical reactions, which overall lead to more C₃S having reacted at the peak of hydration in direct addition.
6.2.3 Evolution of hydrates content and composition

The fact that more C₃S has reacted in presence of PCE at the hydration peak (specially in the direct addition case) seems to be coherent with the higher content of “other” phases (Figure 6.3).

![Graph showing evolution of hydrates content and composition](image)

Figure 6.3. Comparison of the evolution of the “other” phases, that mostly include C-S-H, during hydration of the reference paste (no PCE) and the pastes with direct and delayed addition of 0.1 % (w/w) of 3PMA1000. The vertical discontinuous lines locate the points of maximum heat flow. The horizontal ones shows the weight fraction of C-S-H estimatate to have at the corresponding times, highlighting the higher amount of C-S-H formed in presence of PCEs at the hydration peak. This effect is more marked in direct rather than in delayed addition.

However, this contrasts with the evolution of portlandite that does not seem to follow C₃S from a stoichiometric point of view (Figure 6.4). Indeed, its content at the maximum of the peak is similar for the direct addition system but slightly lower for the delayed addition, which is the opposite of what is expected when considering the C₃S evolution. Moreover, the portlandite contents just before the onset of the acceleration period are very similar for all systems (Figure A.3.1).
A parameter that can help to understand this difference is the ratio in mass between the amount of reacted C₃S and the amount of portlandite formed, ΔC₃S/ΔCH (Figure 6.5). In contrast to the reference paste, where this ratio monotonically increases towards the value of 2.32, in stoichiometric accordance with equation (4.1), both systems with PCEs display a peak value of this ratio at a time that coincides with the maximum of the main peak. This maximum of the ΔC₃S/ΔCH ratio is around 3.2 for direct addition and 2.9 for delayed addition, thus in excess of the value expected from the stoichiometry of equation (4.1). After these maxima, the ΔC₃S/ΔCH ratios decrease and in both cases tend towards the expected value of 2.32 at longer times. This means that in both addition modes, there is a period during which not enough portlandite is forming with respect to the amount of C₃S dissolved, at least according to equation (4.1). It means that either the PCE inhibits the formation of portlandite
and/or the Ca/Si ratio in C-S-H is higher than expected as suggested by the determination of the ratio from the mass balance of the calcium between the amounts of C₃S dissolved and portlandite precipitated considering that all the Si-ions were in the C-S-H (Figure A.3.2 in the Appendix). As shown in Chapter 4, it is possible to estimate the content of water of the C-S-H with respect to the calculated Ca/Si ratio using the solid solution models for C-S-H by Kulik.₂²⁰ This in turn gives the mass of the corresponding C-S-H in each sample. We had already reported that this works very well for a system without PCE (Figure 4.3). Here, we can add that the values are also very similar to the content of "Others" in samples with PCEs (Figure A.3.3 in the Appendix).

![Figure 6.5. Comparison of the evolution of the mass ratio, ΔC₃S/ΔCH, during hydration of the reference paste (no PCE) and the pastes with direct and delayed addition of 0.1 % (w/w) of 3PMA1000. The vertical discontinuous lines locate the points of maximum heat flow. The horizontal ones show the ΔC₃S/ΔCH at the corresponding times, highlighting the peak that appears at the hydration peak in presence of PCEs. This effect is more marked in direct rather than in delayed addition.](image)

Having identified that the PCE affects the ΔC₃S/ΔCH ratio is very important for our method development of phase quantification by XRD. Indeed, cement pastes dispersed with PCEs typically bleed if prepared at a water to solid ratio that also
makes it possible to prepare (mix) a reference paste without PCE (issue of dispersion). This bleeding, even if minor, leads to the preferential presence of portlandite at the sample surface and is why researchers attempting to exploit the continuous measurement capacity of XRD instruments have to introduce a correction factor for portlandite enrichment at the surface of their samples. The way in which this is done requires the knowledge of $\Delta C_3S/\Delta CH$. Typically, it is taken to be a constant, which our results demonstrate not to be true. Additionally, the clear impact of the polymer on this ratio means that it is not possible to determine a reference calibration curve for this ratio since it varies from case to case. In other words, the results presented in this section provide a very strong support for our decision to use multiple samples of which the hydration is stopped to quantify the phases, rather than attempting to use continuous XRD measurements for this. Despite some drawbacks, including more experimental work, it is a much better option for studying the impact of PCEs on hydration whether of $C_3S$ or of our model cement.

### 6.2.4 Calculation of the heat release from XRD on pure $C_3S$ with PCEs

As demonstrated in the case of pure $C_3S$ without admixtures (section 4.3), the heat release can be calculated from the amount of $C_3S$ reacted over time according to equation (4.1) with the enthalpies given in Table 4.1. As previously explained, this procedure works despite variations in the stoichiometry of equation (4.1) because most of the heat comes from dissolution. Using this procedure, we calculated the cumulative heat and heat flow of the systems with the direct and delayed addition of 3PMA1000 (Figure 6.6 and Figure 6.7).

In the case of direct addition, up to 10 hours (and also later at 30 hours), the calculated heat flow matches the calorimetry curve. Quite remarkably, it also perfectly follows the small peak between 2 and 5 hours usually attributed to nucleation of portlandite and/or to the onset of the acceleration period. However, after 10 hours, the calculation does not fit the direct measurement so well and seems to show a slightly earlier maximum heat flow. This is also visible in the
cumulative heat where the points between 10 and 15 hours are higher than the directly measured ones, although the evolution still remains very similar.

Figure 6.6. Comparison between measured and calculated cumulative heat (left) and heat flow (right) of pure C₃S hydration with 0.1% (w/w) 3PMA1000 added in a direct mode (at 23°C for a water to C₃S ratio of 0.35).

The calculation of the heat release for the delayed addition (Figure 6.7, empty square markers) shows more discrepancy with calorimetry. It leads to an overestimation of the heat release, visible by a higher slope during the acceleration period in the cumulative heat (Figure 6.7 left) and by a higher maximum of the main peak on the heat flow (Figure 6.7 right).
Several reasons linked to the thermodynamic properties of C-S-H and its Ca/Si ratio might explain this discrepancy and different corrections may be considered to account for this. The first comes from the estimation of the enthalpy of dissolution of C-S-H. In Kulik,\textsuperscript{220} the enthalpy is estimated from the reaction free energy using a reaction entropy of 70 J K\(^{-1}\) mol\(^{-1}\) for the formation of a jennite-type C-S-H with a Ca/Si of 1.67. This value of entropy comes from Lothenbach et al. who fitted temperature solubility data to another free energy solid-solution model for C-S-H.\textsuperscript{226} However, the same data can also be considered as independent of temperature (Lothenbach, personal communication). Moreover, as observed for well-balanced isocoulombic reactions where the one-term method for extrapolating equilibrium constants for aqueous reactions is used,\textsuperscript{246,247} the difference of entropy can most often be assumed equal to 0. For the formation of C-S-H considered this represents a “just as reasonable choice” as taking the value of 70 reported by Lothenbach et al. (personal communication with Kulik and Lothenbach).

This difference in the entropy for C-S-H introduces a range of C\(_3\)S hydration enthalpy \(\Delta_{\text{hyd}}H\) between 103 and 124 kJ mol\(^{-1}\) that includes the value of 118 kJ mol\(^{-1}\) used for the simple calculation of heat release in Figure 6.7 (empty squares “calculated \(\Delta_{\text{hyd,C3S}}H\)”). Furthermore, in the delayed addition case, we calculate the range of enthalpy of C\(_3\)S hydration from the measured cumulative heat and the amount of C\(_3\)S.
reacted determined by XRD. This gives us a variation from 96 to 122 kJ mol\(^{-1}\), which matches the range given above (due to the different possible assumptions concerning the reaction entropy). This means that most probably, there is a difference of entropy coming from a change of C-S-H structure induced by the presence of the PCE. The PCE may modify the assemblage of C-S-H crystallites without being incorporated in the final structure as reported for other systems.\(^{180-182,248}\) Figure 6.7 shows the calculation of the heat release using a \(\Delta H_{\text{hyd,C\text{3S}}}\) 103 kJ mol\(^{-1}\) that corresponds to an entropy equal to 0 for a jennite-type C-S-H (filled squares "correction entropy"). This seems to lead to a better estimation of the heat release.

The range of hydration enthalpy used for the first correction is calculated for a C-S-H with a Ca/Si ratio of 1.67. However, as shown in Figure 6.5 and Figure A.3.2, the stoichiometry of equation (4.1) is not respected, which might lead to differences in the calculated heat if the amount of portlandite and C-S-H as well as its Ca/Si ratio are properly taken into account. To examine this possibility, we use the measured amounts of reacted C\(_3\)S and precipitated CH and C-S-H, redefining the hydration reaction with a time dependent stoichiometry. With this in hand, we estimate the corresponding heat released using the respective dissolution enthalpies of portlandite and C\(_3\)S (Table 6.1) using the enthalpies of formation reported in Table 4.1.

**Table 6.1. Enthalpy of dissolution of C\(_3\)S and portlandite.**

<table>
<thead>
<tr>
<th>Phase/species</th>
<th>(\Delta_{\text{diss}}H) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_3)S</td>
<td>-142</td>
</tr>
<tr>
<td>Portlandite</td>
<td>-18</td>
</tr>
</tbody>
</table>

With the same approach used to determine the water content of our C-S-H, its enthalpy of dissolution was calculated for each Ca/Si ratios that are in the range of the model of Kulik using a reaction entropy of zero.\(^{220}\) The resulting enthalpies vary from 33.3 kJ mol\(^{-1}\) to 34.8 kJ mol\(^{-1}\). As shown in Figure 6.7 with the data labelled as
“correction C-S-H”, this leads to a much better match of the calculated and measured heat flow, apart for the point at the longest measuring time.

If applied to the direct addition system, this same procedure leads to an overcorrection of the heat release during the acceleration period. These variations must find their origin in differences of influence of PCEs on C-S-H formation whether the polymer is added directly in the water or later in the paste. Determining the exact composition and structure of C-S-H and solid solution thermodynamic models for C-S-H could in principle account for this.

However, in the context of this chapter, the most important point is that these results once again show that overlooking the impact of stoichiometry changes of equation (4.1) is not always an acceptable solution. Once again, it highlights the fact that assuming a constant value of $\Delta C_3S/\Delta CH$ to correct for portlandite enrichment during continuous XRD measurements is not an acceptable solution for studying the impact of PCEs on hydration. It further confirms that our QXRD methodology is reliable and leads to a good quantitative agreement with calorimetry data, considering the range of changes that this stoichiometry factor can entail.

6.3 Effect of PCEs dosage and structure on the measured heat release

6.3.1 General impact on heat release

Calorimetric measurements were used to observe the effect of different dosages of the PCEs added either directly in the water or later in the paste of pure $C_3S$ (Figure 6.8 and Figure 6.12). As observed earlier, for the same dosage and for all the PCEs, the direct addition induces higher retardation, which is the opposite of what is generally observed for ordinary Portland cement.
Furthermore, as mentioned in section 2.4.2.1 of Chapter 2, for the same dosage in mass, the comb copolymers with the highest charge densities (2.26 mmol of COOH per gram of 3PMA1000 and 3.61 mmol/g for 6PMA1000) induce the highest retardation compared to the other ones (Figure 6.8 and Figure 6.9 respectively). Another observation for these highly charged PCEs concerns the heat release during the induction period. In the case of very high dosages, the heat release during this period is basically inexistent until the onset of the acceleration period, when there is a sharp increase of the slope to its maximum.

However, in the case of 3PMA3000 (Figure 6.10), 6PMA3000 (Figure 6.11) and 1PMA1000 (Figure 6.12), that have the lowest charge densities, as well as for low dosages of 3PMA1000 and 6PMA1000, the heat flow does not drop to zero, showing that reactions still occur during the induction period. These differences strongly suggest that the changes in reaction are linked to the content of carboxylates in the system, which is why we use the carboxylate content rather than the polymer mass as an expression of dosage later in this chapter.
Figure 6.8. Effect of the direct (a) and delayed (b) addition of different dosages of 3PMA1000 on the heat release of pure C₃S.

Figure 6.9. Effect of the direct (a) and delayed (b) addition of different dosages of 6PMA1000 on the heat release of pure C₃S.

Figure 6.10. Effect of the direct (a) and delayed (b) addition of different dosages of 3PMA3000 on the heat release of pure C₃S.
In the cases where the heat flow does not drop to zero during the induction period, it remains constant or slightly increases, with a more gradual transition from the induction to the acceleration period. As explained earlier, this makes the determination of the onset of the acceleration period more delicate and its comparison with other systems more complicated than for our model cement. For studying retardation, it implies that the delay observed at the onset of the acceleration period does not always represent the delay observed at the inflexion point during the acceleration or the delay at the maximum of the main peak. In the face of this problem, we decided to use the time of occurrence of the maximum peak for further comparison, rather than the time of onset, because it is much easier to
define. However, this choice could potentially lead to overlooking some important events such as the precipitation of portlandite, which is further discussed in the next subsection.

An unusual observation seen for the case of 3PMA1000 (Figure 6.8) and 6PMA1000 (Figure 6.9), is that for both addition modes, the highest dosages of PCE affect the shape of the main peak leading to two distinct maxima. This could come from a hydration differenciation between the dispersed particles due to the bimodal particle size distribution of the pure C₃S. However, to the best of our knowledge, such an effect has never been reported, probably because the considered dosages are quite high and lead to very strong retardation (up to 4 days in the worst case).

### 6.3.2 Apparent impact on dissolution, nucleation and growth

The small peak in the induction period that is usually attributed to portlandite precipitation⁴⁴⁻⁴⁵ seems to be influenced by the addition mode, the dosage and the structure of the PCEs. This peak is not visible in the reference system, as the acceleration period occurs after a very short time. In direct addition, this peak appears clearly for all the dosages of the low charged PCEs (3PMA3000, 6PMA3000 and 1PMA1000), and the low dosages of the highly charged PCEs (3PMA1000 and 6PMA1000). For the low charged PCEs, it seems to be reduced, and slightly delayed compared to the main peak.

However, this peak is much more attenuated or does not appear at all in the delayed addition of all the polymers, except for low dosages of 6PMA1000. This suggests that in delayed addition there is a higher amount of polymer available to impact portlandite formation. It is compatible with our previous statement that an excess of polymers may be consumed in direct addition owing to the templating of C-S-H. It is also in line with recent studies showing that organic admixtures, such as sugars, can strongly interfere with the precipitation of portlandite⁴⁹ and that portlandite can effectively adsorb PCEs (Lex Reiter, personal communication).
With this in mind, the complete or partial ‘switch off’ of the hydration reactions may involve an impact on the nucleation and growth of hydrates. This would come in addition to the impact on dissolution for which direct evidences were given in Figure 5.25 in Chapter 5.\(^1\) However, considering the case of portlandite discussed above, we would expect these effects to be most important at high dosages and for more strongly adsorbing PCEs. In other words, the impact on hydrates might occur only if enough polymers are added to saturate the initially available surfaces. In the next section, we attempt to go beyond these speculations and assess the role of molecular structure and dosage on retardation.

### 6.4 Effect of PCEs dosage and charge density on retardation of C\(_3\)S hydration

The delay of C\(_3\)S hydration is discussed here in terms of the time of occurrence of the maximum heat flow. Values obtained with different PCEs are reported with respect to carboxylate dosages as shown in Figure 6.13. A first observation, as mentioned earlier, is that for all PCEs, direct addition induces stronger retardation than the delayed one. The second observation is that all the polymers show a similar ranking of their retardation capacity in both addition modes.
Interestingly we observe two regimes of retardation as a function of carboxylate dosage. In the first regime, up to a critical dosage of carboxylates denoted $\Delta c_0$, the polymer has no or only little influence on the hydration of $C_3S$ (Figure 6.14). Above this critical dosage, retardation then increases roughly linearly with the number of carboxylates introduced in the system. For direct addition, the first regime is much narrower and not as easy to define as for delayed addition (Figure 6.14, right). Concerning the second regime, direct addition leads to higher slopes than delayed addition. This means that an incremental dosage of carboxylate groups has a more dramatic impact on retardation in direct addition.

This two-steps regime reminds us of the phenomenon observed with the direct addition in the model cement (Figure 5.21). In that case the retardation also starts after a critical dosage that was found to correspond to the point when the ettringite surface (modified by the PCEs) was fully covered by the PCEs. The transition to the second regime was attributed to polymers becoming available to delay silicate hydration. Moreover, provided this amount was properly estimated, the impact of PCE molecular structure was found to be the same as in delayed addition.

Therefore, for a better comparison of the retarding effect of different PCEs on pure $C_3S$, we also introduce here two parameters, one for each regime. The first
parameter is the minimum dosage, $\Delta c_0$, needed to initiate the retardation. We determined it by extrapolating the linear regime to the dosage corresponding to zero retardation (Figure 6.14, left). The second parameter is the slope of the second regime where retardation increases linearly with the number of carboxylates: $m_{dir}$ and $m_{del}$ for direct and delayed addition respectively (Figure 6.14, right). Due to missing points at low dosages of 3PMA1000 this PCE was excluded from the following analysis.

![Diagram](image_url)

**Figure 6.14.** Example of determination of the minimum dosage for retardation (left) and the slopes $m_{dir}$ and $m_{del}$ (right) on data of C$_3$S retardation induced by 3PMA3000.

To examine the role of addition mode, we first consider the ratio of these parameters $\Delta c_0^{dir}/\Delta c_0^{del}$ and $m_{dir}/m_{del}$. Also, guided by the expectation that the influence of the PCEs on the heat release seems to be driven by their charge density (section 6.3) we report these data as a function of their surface charge density, $q/S_{PCE}$ (Figure 6.15), where $q$ is the number of charges for one molecule and is given by $n*C/E$ and $S_{PCE}$ is the surface occupied by one molecule according to equation (2.16) (see Table 3.4).
Figure 6.15. Ratios between the direct and delayed minimum dosages and slopes with respect to the surface charge density of each polymer, $q/S_{PCE}$. $q$ is the number of charges for one molecule and is given by $n^C/E$. $S_{PCE}$ is the surface occupied by one molecule according to equation (2.16).

Two opposite behaviours are observed in Figure 6.15. For the critical dosages, the ratios are all lower than 1, meaning that the minimum dosage for the direct addition is always lower than the one for delayed addition. In contrast, all the ratios between the slopes are larger than 1, so the slope in direct addition is always larger than the one in delayed addition. These observations are separately discussed in the next section.

6.4.1 Critical dosage for pure C₃S hydration retardation

A higher minimum dosage in the delayed addition is not surprising and might be explained by the fact that during the first minutes of hydration, prior to PCEs addition, reactions occur as usual, opening etch pits, but also forming nuclei and precipitating the first hydrates, that all increase the surface available for PCE
adsorption. Therefore it would be expected that more polymer molecules would be needed in delayed addition before a retarding influence is detected. This is fully consistent with recent work by Suraneni et al. obtained using micro-reactors carved into C₃S grains by a focused ion beam. Indeed, in their experiments, these authors found that hydration of C₃S could be effectively stopped in direct addition but not in delayed addition.

This means that \( \Delta c_0 \) might provide an estimation of the surface that the polymer affects or occupies before inducing retardation. Therefore, to quantitatively analyse the meaning of the values of \( \Delta c_0 \), we transform these data into the corresponding surface that they would be expected to occupy according to equation (2.16) (Table 6.2 and Figure 6.16).

<table>
<thead>
<tr>
<th>PCEs</th>
<th>( \Delta c_0^{\text{direct}} ) (( \mu \text{mol/g of C}_3\text{S} ))</th>
<th>( \Delta c_0^{\text{delayed}} ) (( \mu \text{mol/g of C}_3\text{S} ))</th>
<th>( S^{\text{direct}} ) (m²/g of C₃S)</th>
<th>( S^{\text{delayed}} ) (m²/g of C₃S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1PMA1000</td>
<td>0.41</td>
<td>0.72</td>
<td>0.83</td>
<td>1.46</td>
</tr>
<tr>
<td>6PMA1000</td>
<td>1.40</td>
<td>1.84</td>
<td>0.83</td>
<td>1.08</td>
</tr>
<tr>
<td>3PMA3000</td>
<td>0.37</td>
<td>1.01</td>
<td>0.93</td>
<td>2.51</td>
</tr>
<tr>
<td>6PMA3000</td>
<td>0.56</td>
<td>1.01</td>
<td>0.87</td>
<td>1.50</td>
</tr>
</tbody>
</table>
Figure 6.16. Covered surface corresponding to $\Delta c_0$ for each system and polymer in function of the surface charge density of each polymer, $q/S_{\text{PCE}}$. $q$ is the number of charges for one molecule and is given by $n^*C/E$. $S_{\text{PCE}}$ is the surface occupied by one molecule according to equation (2.16).

Very interestingly, in the case of direct addition, the corresponding surfaces are very similar for all the polymers, indicating that retardation only starts once a fixed surface of about 0.87 m$^2$/g of hydrating C$_3$S is covered. Mathematically, the fact that this surface is constant means that there should be a direct proportionality between $\Delta c_0^{\text{dir}}$ and the surface charge density, $q/S_{\text{PCE}}$. This is confirmed in Figure 6.17 where $\Delta c_0^{\text{dir}}$ increases linearly with an ordinate at the origin of zero.
Figure 6.17. Minimum dosage $\Delta c_0$ function of the surface charge density of all the PCEs, $q/S_{PCE}$. $q$ is the number of charges for one molecule and is given by $n^*C/E$. $S_{PCE}$ is the surface occupied by one molecule according to equation (2.16). The ordinate at the origin of the linear fit for the direct addition was fixed to zero. The linear fit for the delayed addition was optimised to have a parallel slope to the direct addition fit.

Somewhat counter-intuitively, this indicates that the relation of carboxylates content to surface charge density is not expressing a real affinity, but rather the fact that a given surface must be covered before retardation begins in direct addition. Provided this conclusion is correct, the case of delayed addition should be considered with similar arguments. In particular, the linear increase observed in Figure 6.17, with a slope parallel to the direct addition, suggests that the same surface has to be covered. In this case however, there is a non-zero ordinate at the origin. This implies that regardless of the polymer structure, a given amount of carboxylic groups must be provided additionally before retardation begins. The use or location of this additional amount of carboxylates is however still unknown.
6.4.2 Relative change of slope of C₃S retardation

In contrast of the model clinker and cement, in the case of pure C₃S we have not been able to relate the slope of retardation versus carboxylate dosage to the structure of the PCEs. The reason for this is unclear but it shows that while C₃S may show common behaviours with cement hydration, it is different enough not to be useable to quantify effects of molecular structure of PCE on cement. This is why we do not further discuss this question, but rather focus on how the retardation slopes vary between both addition modes.

For this we highlight in Figure 6.15, a linear correlation between $\frac{m_{\text{dir}}}{m_{\text{del}}}$ and $q/S_{\text{PCE}}$, which additionally shows an ordinate at the origine of 1. Therefore, we define the relative change of slope $\Delta m_{\text{rel}}$ of a given polymer:

$$\Delta m_{\text{rel}} = \frac{m_{\text{dir}}}{m_{\text{del}}} - 1 = \frac{m_{\text{dir}} - m_{\text{del}}}{m_{\text{del}}}$$

(6.1)

Based on Figure 6.15, this relative change of slopes should be proportional with the surface charge density. Here because $\Delta m_{\text{rel}}$ is unitless, we rather expect that the correlation really reflects an impact of the surface charge density and thereby of the molecular structure. If this is correct, it means that the impact of polymer structure is not the same in direct as in delayed addition. This contrasts with our findings for the case of model clinker from which we would not have expected such a dependence. However, also in relation to the results on model clinker, it would be necessary to carry out measurements of the specific surface area of all these samples. Only with such data would it be possible to conclude whether indeed the polymer structure effects differ between both addition modes. While this would have been interesting to examine, it would have taken the work of this chapter beyond its main scope, but it is foreseen that this question will be picked up in future research projects.
Figure 6.18. Proportionality between the relative change of slope between the direct and delayed addition and the surface charge density of all the polymers, $q/S_{PCE}$. $q$ is the number of charges for one molecule and is given by $n^*C/E$. $S_{PCE}$ is the surface occupied by one molecule according to equation (2.16).

6.5 Conclusion

The first part of this chapter focused on one type of PCE and reported the evolution of the phases during hydration of pure C₃S measured by XRD together with the resulting calculation of the heat release. The differences between the calorimetric curves and these calculations showed that in presence of PCEs there is a variation of the calcium to silicon ratio in C-S-H of which the impact on heat flow calculations cannot be neglected. This demonstrates that proper phase quantification cannot be obtained by continious XRD measurements in presence of PCEs, since these lead to surface enrichment of portlandite that cannot be accurately corrected for. Rather it was essential in our case to use multiple samples, thermostated and of which the hydration is stopped prior to XRD measurements.
The second part focused on the influence of the PCE dosage and structure on retardation. We first observed that systems are more delayed in direct than in delayed addition, which is opposite to what is generally found in cement but which is consistent with another recent study using a different methodology.250

Furthermore, it was observed that the retardation is induced only above a critical carboxylate dosage. For direct addition, the minimum dosage corresponds to a fixed surface, suggesting that some phase monopolizes the polymer before letting it initiate retardation by hindering enough the dissolution process to induce retardation. In the case of delayed addition, the same phenomenon appears to take place, but in this case an additional amount of carboxylates is required, independently of the PCE molecular structure.

We also found that the relative difference in reactivity between direct and delayed addition is polymer dependent and varies with the surface charge density of those polymers in their adsorbed state. This can be understood on the basis of a change in the dissolution, but a more detailed analysis of this observation would still be needed. In particular, systematic measurements of the surface area in both addition modes, for several polymers and dosages should be carried out to determine if the molecular structure differently affects the linear regimes in direct and delayed addition.

Overall, this chapter presents a new step in understanding the effect of PCEs on C₃S hydration. However, the impact of PCEs does not follow the same molecular structure dependence as on cement, even if qualitatively some similar trends can be pin-pointed. This is why this chapter does not further investigate the molecular structure dependence of retardation highlighted in the last subsection and why this thesis rather focussed its efforts on the model clinker presented in the previous chapter, since it is more representative of cement and « paradoxically » easier to rationalize, understand and quantify.
Chapter 7
Conclusion and Outlook

The content of this chapter is presently not included in any publication or draft publication. However, the Outlook section and Appendix A.4, which define the approach to molecular design are being considered for an ISI journal paper. This will however involve additional and more systematic experimental measurements of the type reported in the Appendix A.4.

7.1 Main outcome

The main outcome of this thesis has been the quantification of the impact of polycarboxylate ether superplasticizers on the reactivity of a model system representing cement hydration. By synthesizing a clinker composed of tricalcium silicate and tricalcium aluminate mixed with hemihydrate as sulfate carrier, we elucidated how competitive processes between simultaneously reacting mineral phases can be disturbed by the presence of comb copolymers.

In particular, by using structurally well-defined PCE superplasticizers, the hydration delay that comb copolymers cause on the silicate phase was defined with respect to their addition mode, dosage and molecular structure through their charge density. This is well illustrated by the delayed addition case where the retardation can be reliably predicted by a product between the number of repeat unit introduced in the system and the charge density of the interaction volume that the backbone has with the mineral surface. This submolecular scale effect implies the blocking of reactive
sites controlling the dissolution of the anhydrous silicate by the adsorbed polymers, involving their local charge densities and interaction with the ionic environment.

The case of direct addition revealed the importance of the ettringite and the affinity of the PCEs for the aluminate phases. It was already demonstrated in other studies that PCEs favour ettringite nucleation. What is new in this thesis is the quantified correlation between the surface created by such a favoured nucleation and the portion of polymer adsorbing on it. By uptaking the polymers and therefore preventing their adsorption on the silicate phase, the ettringite surface plays the role of "buffer" for silicate hydration. It was observed that the delay of hydration could only take place if the total surface occupancy of the polymers was larger than ettringite surface. The quantified relation between the specific surface created and the surface occupied by the polymer was only possible because of known structural parameters and previously established molecular conformation of the polymers. This means that a similar analysis could be applied to other types of admixtures as long as their molecular structure, i.e. charges disposition and density, and conformation in their adsorption state are either known or predictable, for example, by molecular modelling.

In industrial cement under conditions of direct addition both molecular and submolecular scale effects will be at play. Here, the prediction of the behaviour critically depends on knowing to what extent PCEs will modify the surface of ettringite, something that this thesis has not dealt with. As subsequently mentioned, this represents an important challenge for future research. Importantly, it should be recognised that the surface creation will vary among different cements. This explains why most findings, up to now, are not generalizable. Only thanks to our model system and systematic approach, essential elements of this puzzle could be quantitatively determined and specific questions for future steps in research be accurately defined.
7.2 Importance of the model system

Although the aluminates content of the model cement is higher than what is generally found in cements, the same dependence on the dosage and molecular structure was observed for the ordinary Portland cement tested. However, this was not the case for pure tricalcium silicate where a similar analysis did not lead to the same dependence. This is most probably due the different ionic concentrations in the pore solution and, particularly, the presence of aluminium ions. This also demonstrates the importance of using a reliable system that reproduces the main hydration reactions of cement, while reducing the complexity and facilitating its quantitative analysis. An ideal balance between the reactivity of the silicate and aluminate phases is indeed important to deconvolute effects related to one or the other. Establishing the exact relation between the polymer architecture and their effect on the reaction of the different cement phases was also only possible thanks to the development of a reliable quantification of phase assemblage during hydration.

To achieve these results, not only a reproducible system in accordance with cement as well as a precise protocol for phase quantification were necessary, but also systematic variations of the molecular structure of reliably characterised PCEs. This involved the selection of adequate materials such as the methacrylic acid monomers for the backbone. Such monomers provide ether bonds to the PEG side chains stable at the high pH values found in cementitious systems. Also very important was the decision to use prepolymerized backbones onto which the side chains were grafted. Only thanks to this, we could access to reliable information on all the structural parameters. Moreover, the polymethacrylate comb copolymers represent the most used compound in worldwide practice. This and the structural variations of these polymers selected in this thesis offer a perfect model system to unravel the phenomena controlling the effect of organic compounds on hydration reactions.
7.3 Future work

7.3.1 Effect of PCEs on silicates

The phase quantification performed on pure C$_3$S revealed that PCEs not only induce the delay by slowing down dissolution, but also have an influence on the stoichiometry of C$_3$S hydration. This was inferred from the evolution of the ratio between the amount of C$_3$S reacted and the precipitated portlandite, which was significantly higher in presence of the PCE. From this observation, it was assumed that the PCE inhibits the formation of portlandite and/or the Ca/Si ratio of C-S-H is higher than expected. It is also proposed that the PCE disturbs the structuring of C-S-H, changing its entropy. NMR measurements on $^{29}$Si-enriched C$_3$S and labelled organic compounds in addition to advanced microscopy techniques, such as STEM (scanning transmission electron microscopy) tomography, and molecular modelling would probably be needed to understand the influence of PCEs on the formation of C-S-H.

7.3.2 Effect of PCEs on aluminates

Although the favoured nucleation of ettringite is a well-known aspect of cement hydration in presence of organic admixtures, it has never been rigorously studied from a quantitative point of view and therefore remains insufficiently understood. Two specific questions have to be addressed. First, how does a PCE enhance nucleation? And second, what is the influence of the molecular structure on this nucleation and on the subsequent growth and development of the surface of ettringite? Pore solution analysis and BET specific surface area measurements, as used in this thesis, could be further exploited to systematically address these questions. Recent advances were made in the development of protocols for pore solution analysis dedicated to superplasticized samples. In particular, the analysis of low concentration elements, such as aluminium, has been shown to be a key point in understanding the influence of the PCEs on nucleation. Critical aspects as
complexation but also polymer aggregation probably induced by aluminium and magnesium ions have been identified and probably represent essential elements to understand for elucidating the level of molecular impact of PCEs on the nucleation of ettringite in cement.

### 7.4 Outlook

One of the main outcomes of this thesis is the possibility to master cement hydration retardation induced by the PCEs using knowledge-based modifications of their molecular structure. This is shown in Chapter 5 by the master curve obtained for the cement with delayed addition of the PCEs. In a broader sense, this paves the way to the molecular design of organic admixtures to quantitatively control the reactivity of cement.

However, for PCEs it only makes sense to do this while simultaneously considering their dispersive effect. Indeed, the main purpose of using PCEs is the improvement of the rheological properties of concrete and the increase of durability and strength by reducing the water content. This can also be controlled by modifying PCEs architecture as shown in 14,110,135,251. Therefore, a next step in mastering PCEs properties would be to the optimisation of their structure to keep a high dispersive ability but to reduce the undesired side effect of retardation.

In this section, we outline here what such an approach might look like. For this we use a simple rheological analysis described in Appendix A.4 and that leads to a set of empirical equations that well account for the rheological impact of PCEs in relation to their structure and dosage. It is out of our scope to examine how broadly these relations hold or their possible underlying physical meanings, but rather to use them as an example to illustrate what a process of molecular design of PCEs may look like.

The relation we use here considers that two polymers are dosed in such amounts that they induce the same yield stress. Under these conditions, the ratio of silicate retardation induced by these two polymers can be written as:
\[ \frac{\Delta t_1}{\Delta t_2} = \left( \frac{N_1 P_2}{P_1 N_2} \right)^{\gamma_2} \cdot \left( \frac{N_2 + P_2}{N_1 + P_1} \right) \cdot \left( \frac{(N_1 - 1)N_2}{(N_2 - 1)N_1} \right)^{3/2} \]  

(7.1)

where \( N_1, N_2, P_1 \) and \( P_2 \) are the structural parameters of polymers 1 and 2, respectively. \( \gamma_2 \) is a fitted parameter that contributes to quantifying the response of the flow spread test to adsorption (an indirect measure of yield stress). This parameter is independent of the polymer, but is expected to vary depending on the type of cement and w/c selected. As indicated above, determining those dependencies is beyond the scope of this section, since our present focus is simply the use of equation (7.1) to illustrate the principle of molecular design.

Indeed, with this equation we can build an abacus-type plot that shows the evolution of the retardation as a function of changes of structural parameters with respect to a reference polymer dosed to achieve the same fluidity (Figure 7.1). The reference is polymer 1 with \( N_1 = 4 \) and \( P_1 = 23 \), which represents well commonly used commercial PCEs. The circle shows the case where polymer 2 has the same structural parameters as polymer 1. This plot is constructed with \( N_1/N_2 \) as x-axis since the side chain spacing is an easily adjustable parameter. The curved lines determine the ratio of retardation \( \Delta t_1/\Delta t_2 \) for different side chain lengths. These are chosen to represent lengths typically available on a large scale and reported in the corresponding literature.

Considering Figure 7.1, we see that if we keep the same length of side chains (\( P_1 = P_2 \), green line) and we multiply the distance between side chains by two (number of monomers in a backbone unit; i.e. \( N_2 = 2*N_1 \rightarrow N_1/N_2 = 1/2 \)), then the ratio of retardation \( \Delta t_1/\Delta t_2 \) decreases to 0.8 (filled square). This means that the retardation caused by polymer 2 is slightly higher. In the opposite direction, dividing \( N_1 \) by two (i.e. \( N_1/N_2 = 2 \)), increases the retardation ratio substantially (empty square). More specifically, the delay caused by polymer 2 is more or less divided by two.

If we keep the same number of charges in the backbone (i.e. \( N_1 = N_2 \), vertical orange line) and divide the length of the side chain by two (i.e. \( P_2 = 11 \)), then the retardation increases by a factor close to 2 (empty triangle). However, multiplying \( P_1 \) by two (\( P_2 \))...
(\phi = 45) or three \((P_2 = 68)\) increases the ratio of retardation to 2 and 3.25 respectively (filled triangles). This shows that the retardation is drastically reduced to more than three times in the most extreme case.

Figure 7.1. Abacus of retardation ratios \(\Delta t_1/\Delta t_2\) function of \(N_1/N_2\) ratio. This plot shows the evolution of the retardation as a function of changes of structural parameters with respect to a reference polymer dosed to achieve the same dispersion ability. The reference is polymer 1 with \(N_1 = 4\) and \(P_1 = 23\). The circle shows the case where polymer 2 has the same structural parameters as polymer 1. The curved lines determine the ratio of retardation \(\Delta t_1/\Delta t_2\) for different side chain lengths. The vertical dotted line represents the case where \(N_1 = N_2\). The green line shows the evolution of the retardation ratio for the case where \(N\) is changed but not \(P\). The orange one is the opposite case where \(P\) is changed but not \(N\). The red dashed lines show how to modify both structural parameters to reduce retardation by a factor three. The stars show the retardation ratio obtained for each side chain length in optimising \(N_1/N_2\) to have an adsorption equilibrium constant of 70.

The aim of this abacus is to show how to change the structural parameters of a PCE to minimise the retardation without compromising the effect on rheology. As an example, to reduce retardation by a factor three (i.e. \(\Delta t_1/\Delta t_2 = 3\), dashed red line), there are two possible combinations, for the side chain lengths considered in Figure
7.1. These require to use respectively $N = 4.8$ and $N = 2.5$ for the side chains of $P = 68$ and $P = 45$. Whether this works or not depends on whether these polymers follow the general adsorption trend described in Figure A.4.3 (Appendix) with an adsorption of 79% of the dosage. For this, the adsorption equilibrium constant should be of at least 70. Using this as an additional condition, we can calculate that the number of side chains on these polymers should be at the most 4 and 2. This would mean that the backbone molar mass would be respectively 1700 and 400 g/mol instead of 5000 g/mol, which has been used in most of this thesis. A decrease from 5000 to 1700 g/mol is important but would probably give a polymer that works well as long as the length of the side chains do not disturb much the adsorption efficiency. This is confirmed to some extent in Figure 5.20 where a polymer having a backbone molar mass of around 2100 g/mol ($n = 6$) was shown to induce the same retardation as a polymer with similar $P$ and $N$ but a longer backbone. However, in the second case, a backbone decrease to 400 g/mol might be too substantial for the polymer to keep the same adsorptive behaviour. Additionally, as explained in Appendix A.4, changing the backbone length might introduce effects of polydispersity that do not cancel out any more in equation (7.1).

We may also look at the question of polymer optimisation from another point of view. We can choose to impose the use of the same reference backbone (around 5000 g/mol) and determine, for the different side chains available, which retardation should be obtained for an equilibrium constant of 70 that allows a reasonable adsorption behaviour (the corresponding points are marked with a star in Figure 7.1). For a $P_2 = 68$, we predict a retardation ratio of 2.50 using $N_2 = 7.1$. For $P_2 = 45$, the retardation ratio is of 1.80 using $N_2 = 5.5$. These two polymers present “reasonable” structural parameters. The last case with $P_1 = P_2$ would only lead to very small changes in retardation ratio of 1.06. This is an interesting result, since it emphasises that with respect to the reference polymer, it is not possible to substantially reduce the retardation by decreasing the grafting density because of limitations on adsorption.

The above results demonstrate that increasing the side chain length is an effective measure to decrease the retardation without changing fluidity. However, this
decreases the adsorption equilibrium constants, leading to lower polymer affinity for the surface, which represents a limiting factor. This may be partially addressed by increasing $N$, but in many cases does not offer a sufficient impact on $K$ with respect to the decrease of retardation that it brings along.

The challenge is to find the right compromises to simultaneously obtain an adequate adsorption and dispersion, while not enhancing too much the undesired retardation. One solution would be to change the nature of the monomers in the backbone to have stronger anchoring group, such as maleic or phosphoric monomers. The retardation would of course increase as well as the affinity for the surface. The question would then be to know the relative importance of these increases. If the adsorption equilibrium constant (i.e. affinity) increases more than retardation, changing the anchor group would be beneficial. However, although these considerations open the door to much broader ranges of structural variations, they would come along with polymers that cannot be as reliably characterised, so that experimental confirmation of these predictions would be tedious at best.

This abacus, presented in Figure 7.1, is certainly not a true one as it depends on a reference polymer and it still has to be confirmed experimentally. For example, assumptions are made on similar efficiency of PCEs adsorption, while this can differ with the type of cement, aluminates and alkalis content as well as the presence of other organic admixtures. More importantly, we only consider the case of delayed addition, which attenuates such effects, makes things easier to predict, but also differs more from what is done in practice where direct addition is most commonly used. Furthermore, additional dimensions would have to be added to this polymer optimisation, as for example the time over which fluidity can be retained. For commercial applications, cost would also be an issue, but this will in first order scale with the mass needed to achieve a given fluidity. Our equations in fact allow us to determine this factor. For the two cases mentioned above, using the reference backbone and giving retardation ratios of 2.5 and 1.8, the needed dosages of Polymer 2 would represent 90% and 93% of the dosage of Polymer 1. Considering a price of 0.80 € per kilogram of ethylene oxide monomers and 1.50 €/kg of methacrylate acid monomers (average prices provided by Sika Technology AG), the
use of the alternate Polymers 2 would lead to a saving of around 14 % in both cases. Therefore, the substantial reductions of retardation (factors of 2.5 and 1.8) should come along with a 14% cost saving of raw materials.

Although this abacus still needs to be experimentally proven, it represents a first step to define new options in polymer development and offers a very promising tool for the design of molecular structure through the optimization of three macro-scale performance characteristics of PCEs: fluidity, retardation and (even) cost.
References


64. Quennoz, A. Hydration of C3A with Calcium Sulfate Alone and in the Presence of Calcium Silicate. (2011).


86. Zajac, M. Etude des relations entre vitesse d’hydratation, texturation des hydrates et résistance mécanique finale des pâtes et micro-mortiers de ciment Portland. (Dijon, 2007).


146. Flatt, R. J. *et al.* Interaction of superplasticizers with model powders in a highly alkaline medium. in *Proc. 5th CANMET/ACI Intern. Conf. on Superplasticizers and other Chemical Admixtures in Concrete* 743–762 (American Concrete Institute, Farmington Hills, Mi, USA, 1997).


195. Robeyst, N. & De Belie, N. Effect of superplasticizers on hydration and setting behaviour of cements. in 9th ACI international conference on Superplasticizers and other chemical admixtures in Concrete 61–73 (American Concrete Institute (ACI), 2009).


239. Sowoidnich, T. A study of retarding effects on cement and tricalcium silicate hydration induced by superplasticizers. (Bauhaus-Universität, 2015).


Appendix

A.1. Chapter 3 – Materials and Methods

Figure A.1.1. Angular range of the XRD patterns of pure C₃S (black) and model clinker (red). The peak at 33.4° corresponds to the cubic tricalcium aluminate present in a high amount, 18.4% (w/w), in the model clinker.
**A.2. Chapter 5 – Impact of PCEs on Model Cement Hydration**

![Graph](image-url)

Figure A.2.1. Quantification of phase evolution during hydration of model clinker with 5% (w/w) of hemihydrate without PCE. The heat release shows that we are in presence of a metastable system where the sulfate depletion point, also called aluminate peak, occurs right after the maximum of the silicate peak, which is shown by the second vertical dashed line. The vertical dashed lines indicate the assumed beginning of the acceleration period and its end at the maximum of the silicate peak. The exact time of occurrence of the onset of the acceleration period is not precisely known as the peak attributed to the formation of gypsum occurs at the same time after 2 hours of hydration.
Figure A.2.2. Influence of the addition mode of 3PMA3000 on the hydration of the model cement initially in the metastable state (with 5% (w/w) hemihydrate). a) direct addition and b) delayed addition.

Figure A.2.3. Influence of the addition mode of 6PMA1000 on the hydration of the model cement initially in the metastable state (with 5% (w/w) hemihydrate). a) direct addition and b) delayed addition.

Figure A.2.4. Influence of the addition mode of 6PMA3000 on the hydration of the model cement initially in the metastable state (with 5% (w/w) hemihydrate). a) direct addition and b) delayed addition.
Figure A.2.5. Influence of the addition mode of 1PMA1000 on the hydration of the model cement initially in the metastable state (with 5% (w/w) hemihydrate). a) direct addition and b) delayed addition.

Table A.2.1. Ions concentration in pore solution of the model cement without PCE and with 0.1 % (w/w) of 3PMA1000 added in direct and delayed addition. The pore solution was extracted before and after the peak attributed to gypsum precipitation.

<table>
<thead>
<tr>
<th>Hydrating system</th>
<th>Extraction time</th>
<th>[S] mM</th>
<th>[Ca] mM</th>
<th>[Si] mM</th>
<th>PCE adsorbed %</th>
</tr>
</thead>
<tbody>
<tr>
<td>No PCE</td>
<td>27 min (before gypsum)</td>
<td>51.2</td>
<td>89.4</td>
<td>41.1</td>
<td>-</td>
</tr>
<tr>
<td>No PCE</td>
<td>2 h (after gypsum)</td>
<td>19.8</td>
<td>51.9</td>
<td>52.9</td>
<td>-</td>
</tr>
<tr>
<td>Direct</td>
<td>30 min (before gypsum)</td>
<td>41.8</td>
<td>75.8</td>
<td>47.9</td>
<td>86.5</td>
</tr>
<tr>
<td>Direct</td>
<td>2 h (after gypsum)</td>
<td>17.0</td>
<td>53.9</td>
<td>71.4</td>
<td>86.6</td>
</tr>
<tr>
<td>Delayed</td>
<td>37 min (before gypsum)</td>
<td>38.4</td>
<td>76.8</td>
<td>43.2</td>
<td>76.7</td>
</tr>
<tr>
<td>Delayed</td>
<td>3 h (after gypsum)</td>
<td>19.6</td>
<td>50.9</td>
<td>97.9</td>
<td>82.8</td>
</tr>
</tbody>
</table>
Figure A.2.6. Master curve of retardation of the maximum of the silicate peak as a function of PCE structure and dosage obtained for an ordinary Portland cement (cem2).
A.3. Chapter 6 – Impact of PCEs on Pure C₃S Hydration

![Comparison of the evolution of portlandite during hydration of the reference paste (no PCE) and the pastes with direct and delayed addition of 0.1 % (w/w) of 3PMA1000. The orange rectangle focuses on the similar contents of portlandite for all the systems before their respective onset of acceleration.](image)

Figure A.3.1. Comparison of the evolution of portlandite during hydration of the reference paste (no PCE) and the pastes with direct and delayed addition of 0.1 % (w/w) of 3PMA1000. The orange rectangle focuses on the similar contents of portlandite for all the systems before their respective onset of acceleration.
Figure A.3.2. Heat flow and evolution of the estimated Ca/Si ratio of the C-S-H formed. The Ca/Si ratio of C-S-H was only determined from the mass balance of the calcium between the amounts of C₃S dissolved and portlandite precipitated considering that all the Si ions were in the C-S-H. The dashed lines only indicate the value of the ratio at the maximum of the main peak.
Figure A.3.3. Heat flow and evolution of the C-S-H content determined by two different ways. The first estimation (filled markers) comes from the subtraction of the portlandite and C₃S mass from the total mass of the sample. The second estimation (empty markers) is determined from the Ca/Si ratio (Figure A.3.2) using C-S-H models described by Kulik²² for determining the water content associated to each Ca/Si ratio.
A.4. Chapter 7 – Conclusion and Outlook

Introduction

In this appendix we examine the impact of PCEs on yield stress by using spread flow tests. These were performed with different dosages of PCEs added in a delayed mode on an ordinary Portland cement (cem2). We decided to work in delayed addition to eliminate the problem of modifying ettringite nucleation and because this leads to the same dependence on the molecular structure as found with our model cement (Figure A.2.6).

The challenge consists in relating the yield stress to molecular structure. Moreover, any such relation must involve a prediction about adsorption in early stages. In fact, from the literature it is known that in direct addition flow spread measurements vary linearly with the adsorbed amount of polymer and are independent of the polymer structure.\textsuperscript{14,110} While this result is not fully understood it is useful, since provided adsorption can be predicted, flow spread and yield stress can be calculated directly.

However, this linear relation between flow spread and adsorption has never been tested in delayed addition. We have done this for the first time and, as shown in Figure A.4.1, find that the relation between flow spread and adsorption remains linear but is dependent of the molecular structure. This complicates the prediction of fluidity only based on the structure. In what follows we propose a systematic examination of these data to extract some empirical relations that can apply to the polymers tested. The objective here is not to understand the underlying processes but to provide equations that can be used in the Outlook chapter to illustrate a process of molecular design in which different properties are simultaneously optimised by changing molecular structure.
Appendix

Figure A.4.1. Flow spread diameter function of the amount of adsorbed PCE. The relation between the spread and adsorption is linear and dependent on the molecular structure. For each polymer, the linear fit has been done with the reliable spread diameters (filled markers). The extreme values of spread (empty markers) were excluded as they are out of the range of reliability of the spread flow test.

Analysis of the flow spread data

In addition to showing linear relations between flow spread diameters and adsorption, the data series in Figure A.4.1 have the particularity of sharing the same ordinate at the origin. This is not surprising since the ordinate at the origin should reflect the yield stress in absence of polymers and therefore be common to all polymers. The fact that its value is negative means that the yield stress of the reference paste cannot be measured by the spread test measurement at the w/c value used.

Various relations have been proposed to calculate yield stress from flow spread measurements. Here we use the one proposed by Flatt et al. because it involves an exponential relation between the spread diameter and the yield stress.
and therefore offers a possible extrapolation to negative values of flow spread. While we understand the limitations of such extrapolations, we have found this to provide useful information in the context of our present objective. The relation is:

$$\tau_0 = \exp(b - aD)$$ \hspace{1cm} (A.4.1)

where $D$ represents the diameter of the spread.

When $D$ is very high, $\tau_0$ tends to 0 and when $D$ is lower than 0, $\tau_0$ becomes very large, but remains “real”. In this case, a negative value of spread simply means that the yield stress is higher than the range of yield stress measurable by the mould used for the spread flow test. Therefore we fit all the data series in Figure A.4.1 with a common ordinate at the origin that is simply the average of their individual ordinate:

$$D = D_0 + \alpha_{PCE} \cdot c_{ads}$$ \hspace{1cm} (A.4.2)

where $D_0$ is the spread for a system without polymer and $c_{ads}$ is the concentration of adsorbed PCEs. The slope $\alpha_{PCE}$ therefore becomes a parameter that reflects the role of molecular structure on yield stress. Empirically, we have found it to be well fitted by a power law of the ration between side chain length ($P$) and spacing of side chains ($N$) (Figure A.4.2):

$$\alpha_{PCE} = \gamma_1 \cdot \left(\frac{P}{N}\right)^{\gamma_2}$$ \hspace{1cm} (A.4.3)

where $\gamma_1$ and $\gamma_2$ are constants that do not depend on the molecular structure, but possibly on the cement (something beyond the scope of this thesis).

The above equation indicates that when $P$ increases and/or $N$ decreases, the slope increases, so that higher fluidity should result. This dependence on the ratio $P/N$ is consistent with changes in adsorbed layer thickness described in equation (2.15), although the power law dependence is different.
Figure A.4.2. Slope of the spread diameter vs PCE adsorption (Figure A.4.1) function of the ratio of the structural parameters $P/N$.

Analysis of the adsorption data

We have just defined a relation between flow spread and adsorption. Here we examine how to express adsorption as a function of PCEs structure and dosage. Figure A.4.3 reports adsorption versus the dosage and a striking observation is that three out of the four polymers show an almost linear behaviour with a common slope of 79% over a large dosage range. This indicates that up to relatively high dosages (represented by empty markers that most probably correspond to the plateau of adsorption) about 79% (w/w) of the polymer dosed, $c_{PCE}$ (here in mg/g of cement), is adsorbed:

$$c_{ads} = 0.79 \cdot c_{PCE} \quad \text{(A.4.4)}$$

Any polymer with a similar behaviour should therefore have a flow spread that can be predicted assuming that 79% (w/w) of the dosed polymer is adsorbed. More
specifically, this flow spread would be determined using equation (A.4.2) with an ordinate at the origin of -70 and a slope given by equation (A.4.3) in relation to its molecular structure.

Figure A.4.3. Adsorbed PCE function of the initial dosage. 3PMA1000, 6PMA1000 and 6PMA3000 show an almost linear behaviour with a common slope of 79 (dashed line). This indicates that up to relatively high dosages (represented by empty markers that most probably correspond to the plateau of adsorption) about 79 % (w/w) of the initial polymer dosed is adsorbed.

However, as shown in Figure A.4.3, not all the PCEs follow the same adsorption behaviour with respect to dosages. In our case, 3PMA3000, which has the lowest adsorption equilibrium constant $K$, shows lowest extent of adsorbed PCE. This might be due to its higher sensitivity to adsorption competition with sulfates in cement paste. All other polymers have a relatively high $K$-value and should consequently be less sensitive to this. In principle adapting the side chain length, and therefore $n$, would allow to modify $K$, without changing the dispersion response that seems conditioned by $P/N$, which is consistent with adsorption conformation. In the case of
3PMA300, we would therefore expect that decreasing $n$ from 13.9 to 3.5 ($K = 68$) would lead it to have a similar adsorption behaviour as the other polymers. For the other PCEs, the fact that a constant fraction of the dosed polymer adsorbs is probably due to polydispersity, as mentioned in section 2.3 of Chapter 2. This fraction may therefore change if the backbone length is changed. However, for the time being, we overlook this issue and treat adsorption as 79% of the dosage. This hypothesis should be acceptable up to dosages of about 1.3 mg/g, where the adsorption plateau generally seems to be reached.

**Putting things together to predict flow spread**

With the substitution of equations (A.4.3) and (A.4.4) in equation (A.4.2), the dosage of PCEs inducing a flow spread of diameter $D$ can be expressed as a function of the structural parameters $P$ and $N$ as follows:

$$c_{PCE} = \frac{D - D_0}{0.79 \cdot y_1} \cdot \left(\frac{N}{P}\right)^{\gamma_2} = \beta_D \cdot \left(\frac{N}{P}\right)^{\gamma_2}$$  \hspace{1cm} (A.4.5)

This expression can be used to calculate which dosage of a given polymer is needed to obtain a given spread (for the w/c and cement selected). In an optic of molecular design, we are interested in reducing retardation without compromising flow properties. For this we can use the above equation to define the dosage used in equation (5.4) to predict the retardation of silicate hydration $\Delta t$. This leads to:

$$\Delta t = \beta_D \cdot \left(\frac{N}{P}\right)^{\gamma_2} \cdot \frac{1}{M_{RU}} \cdot \left(\frac{N - 1}{N}\right)^{3/2}$$  \hspace{1cm} (A.4.6)

where $M_{RU}$ is the mass of the repeat unit given by $P \cdot M_{SC} + N \cdot M_{BB}$ with $M_{SC}$ and $M_{BB}$ respectively the molar masses of side chain and backbone monomers.

Using equation (A.4.6), let us now consider two polymers (1 and 2) that would be dosed in such a way as to achieve the same spread $D$. The ratio between the
retardation that they induce is a function of their structural parameters $N_1, N_2, P_1$ and $P_2$:

$$\frac{\Delta t_1}{\Delta t_2} = \left(\frac{N_1 P_2}{P_1 N_2}\right)^{\gamma_2} \cdot \left(\frac{N_2 + P_2}{N_1 + P_1}\right) \cdot \left(\frac{(N_1 - 1)N_2}{(N_2 - 1)N_1}\right)^{3/2} \quad \text{(A.4.7)}$$

This ratio very elegantly eliminates the role of $D, D_0$ and $\gamma_1$ and provides a more general relation, with $\gamma_2$ being the only remaining fitted parameter. Interestingly also, the role of polydispersity is canceled out (provide its effect is the same on both polymers).

With this relation we can build an abacus with the ratio of retardation function of the number of monomers on the backbone $N_1/N_2$ (Figure 7.1). It is this figure that is used in the Outlook section to discuss the perspective of molecular design by the optimization of different PCEs properties.
Curriculum Vitae

Delphine MARCHON

delphine_marchon@yahoo.com

Date of birth : 31.01.1985
Nationality : Switzerland
Languages: French (native), English (fluent), German (C1)

Research interests

- Chemistry of cement hydration
- Comb copolymer superplasticizers (PCEs)
- Retardation of cement hydration due PCEs
- Rheology of cement paste and concrete
- Incompatibility between PCEs and alkali activated cementitious systems

Education

10.2011 – 04.2016 ETH Zurich, Swiss Federal Institute of Technology, Zurich (CH)
PhD of Sciences of ETH Zurich for the work "Controlling cement hydration through the molecular structure of comb copolymer superplasticizers"

Master in Materials Science and Engineering
Orientation: structural materials for use in transport, energy and infrastructure

Bachelor in Materials Science and Engineering

09.2000 – 06.2004 Maturité fédérale (Swiss high school graduation), Collège du Sud, Bulle / FR (CH)
Specific option: application of mathematics and physics
Complementary option: chemistry

Research projects


2010 - 2012 “Cardboard cement composite” (Physical Chemistry of Building Materials PCBM, ETH Zurich), patent pending.
Development of a patented ultrafluid and high strength cementitious coating for cardboard elements. (Results of this study led to the creation of a post-doc position and an internship of one year)
Curriculum Vitae

2009 - 2011
“Comb polymers as dispersants for alkaline-activated binders” (Sika Technology AG / Powder technology laboratory LTP, EPFL / Physical Chemistry of Building Materials PCBM, ETH Zurich), patented, supervised by Prof. Robert J. Flatt and Prof. Paul Bowen.

09.2009 – 03.2010
“Chemical admixtures for environmentally friendly concrete”, Master thesis (Sika Technology AG / Powder technology laboratory LTP, EPFL), supervised by Prof. Robert J. Flatt and Prof. Paul Bowen.

Spring 2009
“Mechanisms of external sulfate attack under field and laboratory conditions: Effects of wetting and drying cycles on damage and phase assemblage”. (Laboratory of Construction Materials LMC, EPFL), supervised by Dr Aude Chabrelie and Prof. Karen Scrivener.

Fall 2008
"Study on the implementation and the performances of micro-tubular solid oxide fuel cells (SOFC)”. (Powder Technology Laboratory LTP, EPFL), supervised by Samuel Vionnet and Prof. Véronique Michaud.

Spring 2008
“Modeling of a laminated sail fabric”. (Laboratory of Polymer and Composite Technology LTC, EPFL), supervised by Dr Nicolas Barbi and Prof. Andreas Mortensen.

Fall 2007
“Study on the toughness of a TiAl intermetallic”. (Laboratory of Mechanical Metallurgy LMM, EPFL), supervised by Dr Aude Chabrelie.

Work experiences

01.2010 - present ETH Zurich:
- Teaching assistant, Materials I (bachelor level course for civil engineers)
- Teaching assistant, Materials III (bachelor level lab courses for civil engineers: concrete, metal, corrosion lab)
- Supervision of bachelor thesis (3 students) and master project (1 student)
- Supervision of internships (8 students)

09.2009 – 07.2010 Sika Technology AG, Zurich (CH), research on rheology of cement paste with superplasticizers

02.2009 – 06.2009 EPFL, LMM, Lausanne (CH), teaching assistant for metal lab (1 semester)

08.2007 ETML, Lausanne (CH), machining training

2005 - 2007 Cycle d’Orientation de la Gruyère, Bulle / FR (CH), substitute teacher

Since 2002 Support courses in mathematics, physics and chemistry

Advanced training courses attended

- 4th Gibbs Energy Minimization Software (GEMS) workshop, on thermodynamic modeling of cementitious systems organized by EMPA, Dübendorf (Switzerland), 2014.
- XRD and Topas course, organized by Bruker AXS GmbH, Karlsruhe (Germany), 2014.
- Introduction to GEMS, organized by PSI, Villigen (Switzerland), 2013.
- Thematic school on Physics, chemistry and mechanics of cementitious materials, organized by CNRS and ATHIL, La Grande Motte (France), 2011.
Curriculum Vitae

- Summer School and Workshop in Calorimetry, organized by University of Lyon and CNRS, Lyon (France), 2011.

<table>
<thead>
<tr>
<th>Awards</th>
</tr>
</thead>
<tbody>
<tr>
<td>01.2017</td>
</tr>
<tr>
<td>10.2016</td>
</tr>
<tr>
<td>10.2015</td>
</tr>
<tr>
<td>06.2004</td>
</tr>
</tbody>
</table>

Oral presentations

**Invited talks**

- Controlling cement hydration through the molecular structure of comb copolymer superplasticizers, 2nd International Conference on the Chemistry of Construction Materials (ICCCM), Munich, Germany, October 2016.
- Impact of PCE superplasticizers on polyphasel cement hydration, Cemnet (network of Swiss academic groups active in cement research), Berne, Switzerland, September 2014.
- Polycarboxylate ether (PCE) superplasticizers and cement hydration, Nanocem Cement Hydration Workshop, Villars, Switzerland, June 2014.

**Talks delivered at international conferences**

- Tailored control of tricalcium silicate reactivity through molecular design of comb copolymers, Junior Euromat 2016, Lausanne, Switzerland, July 2016.
- Controlling cement hydration through the molecular structure of comb copolymer superplasticizers, 11th Annual International Concrete Sustainability Conference, Washington DC, USA, May 2016.
- Effect of molecular structure of polycarboxylate superplasticizers on polyclinker hydration, 14th International Congress on the Chemistry of Cement, Beijing, China, October 2015.
- Impact of polycarboxylate superplasticizers on polyphased clinker hydration, 6th Advances in cement-based materials, Manhattan, USA, July 2015.
Impact of polycarboxylate superplasticizers on polyphased dinker hydration, *11th International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, Ottawa, Canada, July 2015.


**Publications**

**Chapters in books**


**Papers in peer-reviewed international journals**

- Marchon, D., Juilland, P., Gallucci, E., Frunz, L. and Flatt, R.J., Molecular and sub-molecular scale effects of comb-copolymers on tricalcium silicate reactivity: Towards molecular design, *Journal of the American Ceramic Society*, accepted as feature article.


**Papers in peer-reviewed proceedings of international conferences**


- Palacios, M., Reiter, L., Sanz-Pont, D., Marchon, D. and Flatt, R.J., Heating cement to slow down hydration, *14th International Conference on Cement Chemistry*, Beijing, China, 2015.
Papers in conference (others)

- Marchon, D., Juilland, P., Gallucci, E., Frunz, L. and Flatt, R.J., Tailored control of tricalcium silicate reactivity through molecular design of comb copolymers, 2nd International Conference on the Chemistry of Construction Materials (ICCCM), Munich, Germany, 2016 (extended abstract).
- Marchon, D., Juilland, P., Frunz, L., Palacios M. and Flatt, R.J., Impact of polycarboxylate superplasticizers on polyphased clinker hydration, 11th International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Ottawa, Canada, 2015.

Patents


Review activities in international journals

- Cement and Concrete Research
- Materials and Structures
- Journal of Sustainable Cement-based Materials

Other experiences

09.2015 Diving, PADI Advanced Open Water
07.2005 Substitute airfield manager, Aérodrome de la Gruyère (Switzerland)
07.2003 Course FVS I.
1992 - 2005 Saxophone player (Music academy, member of 3 harmony orchestras)

Technical skills

Operating systems : Windows, Mac OS X
Programming languages : C
Software : MS Office, Mathematica, VCCTL, GEMS