Passivation mechanism of aluminates on the hydration of tricalcium silicate

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PASSIVATION MECHANISM OF ALUMINATES ON
THE HYDRATION OF TRICALCIUM SILICATE

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Abstract

To reduce contributing to the global warming greenhouse gas emissions, the new generation of cements will be increasingly blended with alumina-rich supplementary cementitious materials (SCMs). However, due to a lower reactivity of these compounds, the greatest limitation to use such cements is their reduced early compressive strength. Although there are several possible ways to activate the reaction of SCMs, this alone does not provide the desired improvement because of other effects that arise as a result of blended cements being highly coupled systems. In particular, accelerating the hydration of SCMs means that a high amount of aluminates is released into solution, which based on recent research may negatively impact the hydration kinetics of the original cement, more specifically its tricalcium silicate (C₃S) phase. Thus, to design the cements of tomorrow, fundamental knowledge is needed concerning the delicate interactions between silicates and aluminates and, in particular, their coupled hydration chemistry.

The mechanism of delaying silicates hydration by aluminates was studied to some extent in the past and remained debated around several hypotheses. This together with the fact that there are still many controversies also about the rate limiting steps in the hydration of the neat silicate system, means that further research is needed on this subject.

This work was aimed to provide a critical part of the scientific understanding needed to produce blended cements with high clinker replacements and reduced environmental footprints, but without decreasing cement quality. In this light, a fundamental study of
C₃S hydration with and without the presence of aluminates was carried out. The work contributes to the understanding of the complex hydration behavior of C₃S, determines the factors influencing the aluminate-silicate interactions and identifies the rate controlling mechanism.

For this to be possible, novel approaches to study the silicates hydration were developed. This largely relied on ²⁹Si-enriched C₃S to provide substantially enhance resolution by NMR. In this way, by using real time (or in situ) solid-state MAS NMR invaluable quantitative monitoring of the hydration progress was obtained. This provided crucial information on the mechanism of silicates dissolution, condensation and structuration of calcium silicate hydrates during the hardening of the paste.

The early hydration of C₃S in presence of aluminate ions was observed to be significantly retarded. Experiments with annealed samples as well as delayed additions of aluminate solutions provided strong evidence for the inhibitory effect to arise from the hindering of dissolution in active areas as etch pits and kink sites. It was, however, shown that this effect is complex and depends strongly on the initial concentration of aluminate ions in the system, as well as on the pH. Furthermore, results also point to a strong effect of particle size distribution that seems to result from coarser particles having a lower surface density of defects than fine particles. This mechanistic insight highlights the importance of reducing the aluminate concentration in solution, for example by forming ettringite, a well-known phenomenon for which additional mechanistic insight is also provided in this thesis.
Zusammenfassung


Der Mechanismus der Verzögerung der Silikathydratation durch Aluminate wurde in der Vergangenheit nicht abschliessend untersucht und die Erklärungen unterliegen etlichen Hypothesen. Zusammen mit dem Umstand, dass auch die limitierenden Mechanismen bei der Hydratationsgeschwindigkeit von reinen Silikaten weiterhin umstritten sind, bedeutet dies, dass weitere Untersuchungen zu diesem Thema nötig sind.

Diese Arbeit soll einen wesentlichen Teil des wissenschaftlichen Verständnisses liefern, das benötigt wird zur Herstellung von Mischzementen mit hohem Klinkerersatz
und tiefener Umweltbelastung ohne die Verringerung der Zementqualität. Dazu wurde
die Hydratation von Tricalciumsilikat (C₃S) ohne und mit Aluminaten untersucht. Die
Arbeit trägt zum Verständnis des komplexen Hydratationsverhaltens bei, ermittelt die
beeinflussenden Faktoren der Aluminat-Silikat Interaktion und schlägt die
zugrundeliegenden Mechanismen vor.

Zum Fortschritt bei diesem Thema war die Entwicklung von neuen Methoden zur
Untersuchung der Silikathydratation nötig. Echtzeit oder in situ Festkörper MAS NMR
mit vollständig charakterisiertem ²⁹Si-angereichertem C₃S hat die quantitative
Aufzeichnung des Hydratationsprozesses ermöglicht. Die Resultate bieten wichtige
Informationen zum Mechanismus der Silikatauflösung, der Kondensation und der
Strukturierung von Calcium Silikat Hydraten während der Erhärtung.

Es wurde beobachtet, dass die frühe Hydratation von C₃S in der Gegenwart von
Aluminat Ionen deutlich verzögert ist. Es wurde auch gezeigt, dass der erzeugte Effekt
komplex ist und von der anfänglichen Konzentration von Aluminat Ionen und vom pH
abhängt. Die Korngrößeverteilung und vor allem der Oberflächenzustand spielen eine
grosse Rolle bei dem beobachteten Verhalten, was den Mechanismus der
Dissolutionskontrolle nahelegt.
Papers of the dissertation and contribution

A summary of the contributions from the author of this thesis is given below. A more complete description is given at the beginning of each corresponding chapter.

Paper I:

E. Pustovgar, J.-B. d’Espinose de Lacaillerie, M. Palacios, A. Andreev, R. Sangodkar, B. Chmelka, R.J. Flatt, Revealing the steps of tricalcium silicate hydration, 14th International Congress on the Chemistry of Cement (ICCC 2015), Beijing.

Ms Pustovgar was responsible for the experimental part. The paper was entirely written by Ms Pustovgar under the guidance of Prof. Flatt, Prof. d’Espinose de Lacaillerie and Dr. Palacios.

Paper II:


Ms Pustovgar was the main investigator. She developed the synthesis of the Ca$_3$SiO$_5$ samples, designed and carried out the characterization and calorimetry studies. Ms Pustovgar together with A. S. Andreev, R. P. Sangodkar and Prof. d’Espinose de Lacaillerie performed the NMR experiments. She contributed to the analyses of the results and the writing of the manuscript.
**Paper III:**

E. Pustovgar, J.-B. d’Espinose de Lacaillerie, M. Palacios, A. Andreev, R. Mishra, R.J. Flatt, **Impact of aluminates on silicates hydration**, II International Conference on Concrete Sustainability (ICCS 2016), Madrid, 1260 - 1271.

Ms Pustovgar performed all experimental part and entirely wrote the paper under the guidance of Prof. Flatt, Prof. d’Espinose de Lacaillerie and Dr. Palacios.

**Paper IV:**


Ms Pustovgar performed all experiments and was responsible for writing the paper. The work was done under the guidance of Prof. Flatt, Prof. d’Espinose de Lacaillerie and Dr. Palacios.

**Paper V:**

E. Pustovgar, M. Palacios, J.-B. d’Espinose de Lacaillerie, T. Matschei, N. Ruffray, R. Verel, R.J. Flatt, **Retarding effect of aluminate ions on the C₃S hydration and possible solutions to mitigate it**, Cement and Concrete Research, in preparation for submission.

Ms Pustovgar performed most of the experimental work and was responsible for writing the paper. The work was done under the guidance of Prof. Flatt, Prof. d’Espinose de Lacaillerie and Dr. Palacios.
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1. Introduction

1.1 General introduction

Portland cement, a material known all over the world, consists of four main phases that are tricalcium silicate (in cement notation C₃S or alite¹), dicalcium silicate (C₂S or belite), tricalcium aluminate (C₃A) and tetracalcium aluminoferrite (C₄AF) to which small amounts of calcium sulfate are added. It is used in very large amounts and its demand continues to increase every year. Nevertheless, to provide sustainable construction material required by the growing needs, the technology of cement production has to develop continuously [1].

Nowadays, the cement industry faces one of its main challenges: The reduction of carbon dioxide emissions during clinker production. Researchers from many countries are looking for new opportunities to minimize energy consumption and CO₂ emissions during the decomposition of limestone used to produce cement. The most efficient way to reduce the significant effect that this process has on global warming is the partial substitution of the cement clinker by supplementary cementitious materials (SCMs) such as fly ash, blast furnace slag, calcined clays, limestone, etc [2]. These materials are the most industrially relevant because of their high availability, low cost and good long term reactivity. Additionally, besides its environmental benefits, clinker replacement by SCMs is economically driven because a lower amount of clinker not only means a lower production cost for the final blended cement, but also a lower CO₂ tax paid by cement producing companies.

At present, a large part of the research is focused on the development of the new combinations of the SCMs and Portland cement that would possess good mechanical properties and be

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¹ Alite is not a pure tricalcium silicate phase, but rather a solid solution with ~ 1 wt.% of Al and Mg.
environmental friendly [3]. Nevertheless, significant technological barriers must still be overcome before highly blended cements can be widely adopted. In particular, a major challenge is to increase amounts of clinker replacement without substantially reducing early compressive strength. The origin of the reduced strength certainly includes a lower reactivity of the SCMs [4], but possibly also a negative impact of the SCMs on the cement reaction [5,6]. Finding solutions to produce effective blended cements requires to understand how to further activate cement hydration at an early age in addition to preventing its passivation. Therefore, a thorough insight and understanding the mechanisms involved is required.

Hydration of plain cement systems appears to be already very complex due to different reaction rates of the components and variable composition of the formed products, explaining that this subject still remains debated [7]. Blending with SCMs, that are normally rich in silica and alumina, brings an additional level of complexity to the investigated system. Some studies have been done in order to understand the mechanism of their negative effect on the early hydration of cement, but so far no conclusive results can be found.
1.2 Scope and objectives

The main objective of this thesis is to develop the knowledge needed to increase the amount of alumina-rich SCMs in cement without compromising its present engineering properties. This would provide the needed keys to substantially reduce the environmental footprint of cement production.

For this, it is necessary to understand the passivation mechanism that SCMs can provide on the hydration of cement, in particular, to study the aluminate-silicate interplay. For this we simplify the investigated system as much as possible, but still keep it representative in terms of commercial Portland cement. As a model we use pure triclinic C₃S with additions of NaAlO₂.

The work is divided into two main parts. The first one is dedicated to the fundamental investigation of the C₃S hydration itself. It is an important and essential step before complicating the system with foreign ions, especially because, as mentioned before, the reaction is still not fully understood. The second part of the PhD is concerned with the systematic study of the effect of aluminates produced on the hydration of C₃S. The processes taking place are investigated at the atomistic level and compared with the observations at the macro scale. For this, we examine and further develop an approach suggested in the nineties to study hydration by real time solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) measurements. This is followed by considerations on factors affecting the reactivity in presence of aluminates.
1.3 Chapters overview

This is a cumulative dissertation, that includes 4 papers (chapters 3 – 6) and an additional one being finalized for submission (chapter 7). Although each one has its own introduction into the topic, in chapter 2 a general literature review, relevant to the materials and techniques used through the study, is also provided. It addresses three main questions that are explicitly discussed in this work:

(a) How does hydration of C₃S proceed?
(b) What is the effect of aluminate ions on the hydration of silicates?
(c) How can solid-state MAS NMR be applied to gain new insights into the hydration of cementitious materials?

In chapters 3 (reviewed conference paper: Revealing the steps of tricalcium silicate hydration) and 4 (research paper published in Nature Communications: Understanding silicate hydration from quantitative analyses of hydrating tricalcium silicates) unique information concerning C₃S hydration is presented. In chapters 5 (paper published in review conference proceedings: Impact of aluminates on silicates hydration) and 6 (research paper submitted to ISI-listed, peer-reviewed, international journal: Influence of aluminates on the hydration kinetics of tricalcium silicate) passivation mechanism induced by aluminate ions on hydration of C₃S is investigated and discussed. Chapter 7 contains additional findings concerning the aluminate-silicate interplay that are collected in a paper draft being in preparation for submission after the defense. Conclusions of this PhD work as well as further possible experiments are summarized in Chapter 8 (Conclusions and outlook). Finally, Chapter 9 (Annex) includes unpublished data and results relevant to the current study.
1.4 References


2. Literature review

2.1 Hydration of tricalcium silicate (C₃S)

C₃S constitutes the main phase of anhydrous cement clinker and is mainly responsible for the early and ultimate strength of the material as well as its durability. When mixed with water, it reacts exothermically according to equation 2.1:

\[
\text{Ca}_3\text{SiO}_5 + (3-x+y)\text{H}_2\text{O} \rightarrow x\text{CaO} \cdot \text{SiO}_2 \cdot y\text{H}_2\text{O} + (3-x)\text{Ca(OH)}_2
\]  

(2.1)

In a real cement paste, the stoichiometry of the calcium silicate hydrate is not fixed. In particular, the calcium/silicon ratio varies between 1.2 to 2.1 [1] while in C₃S pastes it is between 1.7 to 1.8 [2,3]. For this reason, calcium silicate hydrate is generically noted as C-S-H in the literature, being this product the main responsible for the binding properties of cement.

Experimentally, the advancement of the hydration reaction is most often followed by isothermal calorimetry and the same sequence of events is observed. In particular, according to the curves obtained by this technique, four main stages can be distinguished in the reaction of C₃S with water (Figure 2.1). The first one is pre-induction period (I), that corresponds to a brief initial, highly exothermic hydration peak. After this stage the reaction slows down and continues at a low reaction rate during the induction period (II). During the acceleration period (III), the reaction accelerates again and a large nucleation and growth of C-S-H and Ca(OH)₂ occurs. During this time the material sets and hardens. Finally, C₃S hydration is followed by a deceleration period (IV) defining the main hydration peak.
Figure 2.1. Isothermal calorimetry curve of C₃S hydration. Four regions are typically identified based on the heat flow profile with increasing hydration time, including pre-induction (I), induction (II), acceleration (III), and deceleration (IV) stages.

2.1.1 Pre-induction period

It is known that composition of the solution as well as the surface state of the solid phase determines the dissolution kinetics of the minerals [4,5]. Depending on the undersaturation of the solution with respect to the dissolving phase different dissolution mechanisms can be favored. For instance, in very dilute systems, the formation of vacancy islands on perfect surfaces or etch pits at dislocations take place, whereas at low level of undersaturation dissolution is mainly proceeds through step retreat at pre-existing roughness. Based on this, at far from equilibrium conditions, the pre-induction period (I) is normally attributed to a rapid hydrolysis of the C₃S surface releasing Ca²⁺, OH⁻ and H₂SiO₄²⁻ ions into solution [6]. At this
stage pitting of the surface can be observed [7]. This stage lasts only a few minutes and after that the initially high rate of hydration decreases leading to the induction period.

2.1.2 Induction period

The induction period plays an important role in terms of the time before which cementitious materials develop their load early strength. In particular, blended cements with a low environmental impact can critically suffer from undesired extensions of this period since their early strength is generally lower. In other words, understanding the physical and chemical factors responsible for the induction period and its duration represents an important scientific and industrial objective.

Already in the nineties Taylor summarized four main existed hypothesis explaining the origin of the induction period:

(a) formation of protective layer on the C$_3$S particles, that in the end of induction period becomes more permeable or is simply destroyed due to phase transformations [8,9]

(b) formation of semipermeable membrane, that can be destroyed with time due to osmotic bursting [10]

(c) limited nucleation and growth of the C-S-H particles [11,12]

(d) perturbation the growth of Ca(OH)$_2$ by SiO$_2$ that takes place until supersaturation is reached [13,14]

Based on the results available at that time [8,9,12,15,16], a combination of hypothesis (a) and (d) was favored to explain the origin of the induction period. In particular, hydroxylated C$_3$S [17] was thought to be dissolving with the formation of non-uniform protective layer at the surface of unreacted silicates, which isolates solid material from water. Later on with the growth of C-S-H destruction of the layer occurs, allowing water to access C$_3$S again.
Nowadays, there are two main competing explanations for the existence of an induction period [18–20]. The first explanation still relies on the formation of a diffusion barrier on the C₃S grains made of a metastable, semi-permeable, surface layer [21,22]. This layer is later destabilized, chemically or physically, and the hydration rate accelerates thus closing the induction period when the increase of calcium concentration in solution favors the conversion of this phase into C-S-H.

The second explanation, that appears to be more supportive not only experimentally [7] but also from modelling point of view [23,24], is based on the dissolution theory. It says that the induction period is determined by the rate of C₃S dissolution which is controlled by the degree of the undersaturation of the solution [7,25]. This slow dissolution is either due to the hydroxylation of the C₃S surface, which reduces its apparent solubility, or to the difficulty to activate etch pit opening, although they are found to be visible at this stage [20,26]. As a result, during the induction period, the hydration rate is considerably reduced until a critical concentration is reached allowing nucleation and growth of a rate controlling stable form of C-S-H. In addition, another hypothesis attributes the end of induction period to the precipitation of Ca(OH)₂ [27,28], although its necessity for the more rapid C-S-H growth is questionable [29].

2.1.3 Acceleration period

The acceleration stage is associated with an increase in the rate of C-S-H formation that can be effected by several parameters such as the amount of surface area available for nucleation and growth, possible transformation in the C-S-H structure and orientation of its growth [19,30-32].
2.1.4 Deceleration period

While the origin of the induction and acceleration period is still a matter of debate, substantial progress in the formulation of hypothesis has been made. This contrasts with the deceleration period for which more fundamental interrogations remain. At the moment the following explanations for the decrease of C$_3$S reaction rate are proposed and intensely debated:

(a) hindrance of C$_3$S through the coverage of the unreacted particles by hydration products [23,33]

(b) limited C$_3$S dissolution rate due to coalescence of pits [34]

(c) densification of the loosely packed C-S-H due to space restrictions or disturbance of hydrates growth by other growth [24,35,36]

(d) change in the way of C-S-H growth towards formation of a separate dense inner product [31,37]

Except (a) and (b), all the mechanisms listed above, are based on the fact C-S-H growth becomes limited rather than the supply of ions for it. Also, none of the postulated hypothesis fundamentally explain how C-S-H grows and what exactly eventually limits its formation.

Postulated mechanisms include the extension of sheets [22], a situation where the next sheet nucleates in localized nanocrystalline region of the previous one, or, alternatively, the aggregation of nano-platelets [38], but in general the process remains unclear.
2.2 Effect of aluminates on silicates hydration

It is known from geochemistry or marine chemistry areas that the presence of dissolved aluminium delays the reaction of silicates [39–43]. For example, Koning et al. [39] investigated by alkaline leaching the effect of aluminium on the yearly alteration of a particular silica-based material, namely the frustule of diatoms. The concentration of dissolved aluminium used in this work was only 100 nM. This is lower than the possible amount of aluminate ions found in the cement pore solution [44–46], but still the decrease of the silicates dissolution was quite evident. It was shown that 0.37 – 37 mM concentrations of dissolved aluminium can even stop the further dissolution of silica from diatom walls [40]. The main explanations proposed for the inhibiting effect were incorporation of Al into tetrahedral silica as well as the formation of surface complexes due to Al(OH)$_4$ adsorption on silanol sites.

In the field of concrete, the impact of aluminium on the dissolution of amorphous silica aggregates has been recently studied [46]. Chappex [46] concluded that 3 - 4 mM concentrations of dissolved aluminium reduce the dissolution of silica aggregates. It was confirmed by XPS analysis that indeed the aluminium species get incorporated into the silica framework of amorphous silica and do not just adsorb onto the surface.

More generally in cementitious materials, the retardation produced by dissolved aluminium on the reaction of calcium silicates was observed as well. It has been shown by calorimetry and conductivity measurements that in diluted suspensions [47] as well as in C$_3$S pastes [48-51] the aluminate ions dissolved from the alite or tricalcium aluminate inhibit the hydration process of the silicates. These observations raised several hypothesis concerning the origin of the retarding effect [49], although the mechanism remained undefined:

(a) early formation of aluminate hydrates on the space common for nucleation and growth
of C-S-H

(b) presence of aluminate ions in the pore solution

c) incorporation of Al into the C-S-H phase

Begarin et al. [51] proposed the formation of C-S-H containing Al (C-A-S-H) at early age of alite hydration due to the presence of aluminate ions in the pore solution. This would explain the delayed hydration since C-A-S-H represents a poor nucleation site and thus does not promote the C-S-H growth [50,51] (Figure 2.2).

![Figure 2.2. The role of C-S-H and C-A-S-H seeding in the hydration of alite investigated by electrical conductivity measurements [51].](image)

The effect of aluminates on the processes taking place at the water-C₃S interface has been studied as well [52,53]. Based on the combination of several experimental techniques and quantum chemical modelling [52], aluminate ions were proposed to be covalently bound to siliceous surface and therefore to inhibit the C₃S dissolution [52]. In addition, the observed behavior was strongly dependent on the pH and concentration of Ca ions in solution. In particular, Si-O-Al bond was proposed to be formed at mildly alkaline pH values and stabilized
by the presence of Ca$^{2+}$ [52]. Using micro-reactor approach Suraneni et al. confirmed the pronounced effect of aluminates on the C$_3$S dissolution [53]. In this work, dissolution behavior was monitored on the micron-sized gaps prepared in C$_3$S or alite grains by focused ion beam (FIB) [54] (Figure 2.3). It was observed that at pH 8 – 12 the presence of aluminates in the solution significantly reduces the extent of dissolution of silicates even when added in the delayed way after the reaction has already started. On the contrary, at pH higher than 13 there was no effect of aluminates. The inhibiting effect produced by aluminate ions was discussed to be relevant mainly to the dissolution and not to the nucleation of the C-S-H since small particles of the C-S-H were still observed on the surface. Moreover, complementary to this observation, the growth of the C-S-H has been reported despite the presence of Al in it [55].
To conclude, the mechanisms controlling the C₃S hydration in presence of aluminate ions remains unclear and the two main point of view are:

(a) aluminate ions effect nucleation and growth of C-S-H [50,51]

(b) presence of aluminates inhibit initial dissolution of silicates [52,53]
2.3 Solid-state nuclear magnetic resonance (NMR) applied to cementitious materials

Most of the models and proposed hypothesis concerning the C₃S hydration and effect of aluminates on it were constructed mainly through chemical composition of the pore solution [11], calorimetric [7,29] analysis as well as microstructural characterization (scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM)) [7,31,56] of concentrated or diluted C₃S suspensions. A few studies are also known applying X-ray photoelectron spectroscopy (XPS) [52], quasi-elastic neutron scattering (QENS) [57], and small-angle neutron scattering (SANS) [58]. However, these methods do not provide information about the silicon speciation with the spatial and temporal resolution necessary to validate or invalidate the proposed mechanisms. NMR technique is, in principle, able to answer these questions since it reveals the nature of the products through the speciation of the corresponding atoms [59]. The most relevant information, necessary to better understand silicates hydration in general and contribution of aluminates in particular, can be obtained by ²⁹Si, ²⁷Al and ¹H NMR.

2.3.1 Basics of the solid-state NMR

2.3.1.1 General description

First of all, to investigate the sample by NMR, it has to be placed in a static magnetic field (\(B_0\), the direction of this external static magnetic field is generally taken as Z axis in the rotating frame of considered Bloch magnetization model of NMR), where nuclear spins will align along this field (Figure 2.4). To move the nuclear spins from their thermodynamically stable position (from \(M_0\) along Z axis, e. g., to XY plane in the rotation frame), a radio frequency (RF) pulse is applied. Once moved, nuclear spins will precess around the \(B_0\) direction with the angular velocity (\(\omega_0\)), called the Larmor precession frequency. It is determined by the ratio of the magnetic dipole moment to the angular momentum of the nucleus, called gyromagnetic ratio
of the nucleus ($\gamma$) and $B_0$(equation 2.2).

$$\omega_0 = \gamma * B_0$$  \hspace{1cm} (2.2)

The spins of the nuclei in the sample are excited with a RF pulse, modulated close to $\omega_0$ to match the resonance conditions. The excitation occurs by means of simple LC RF contour (L stands for inductivity and C for capacitance, the exciting magnetic field is created in the coil), and the signal reception is done by the same coil to acquire the free induction decay (FID) signal (a function of intensity evolution in time) “emitted” by the sample. In general, the quadrature detection is implemented for signal acquisition, which permits recorder of phase sensitive NMR signal. Finally, the spectrum is achieved by subsequent Fourier transformation into the frequency domain.

Figure 2.4. Basic vector (Bloch) model of solid-state NMR experiment, where net magnetization vector (M) is the sum of all nuclear spins in the sample (adapted from [60]).
2.3.1.2 Relaxation times

In the NMR process two different relaxation times are determined. The spin-lattice (or longitudinal) relaxation time $T_1$ is related to recovery of the longitudinal component $M_z$ of the nuclear spin magnetization $M$ to its thermodynamic equilibrium. If a $-$ excitation pulse is applied, meaning $M_z(0) = 0$, then $T_1$ can be calculated from equation 2.3:

$$\frac{M_z(t)}{M_z(0)} = 1 - e^{-t/T_1} \quad (2.3)$$

In the NMR experiment, $T_1$ values are responsible for the repetition rate at which the spectrum can be acquired.

The second spin-spin (or transverse) relaxation time $T_2$ describes the decay of the $M_{xy}$, a component of nuclear spin magnetization perpendicular to $B_0$ and can be calculated from equation 2.4:

$$\frac{M_{xy}(t)}{M_{xy}(0)} = e^{-t/T_2} \quad (2.4)$$

This phenomenon is explained by dephasing of net magnetization. It occurs because slightly different local magnetic fields yield each spin to rotate at its own varied Larmor frequency. This causes exponential character of FID, thus contributing to linewidth in the frequency spectrum. The absence of $T_2$ relaxation time would mean the infinitely narrow lines in spectra (delta-functions).

2.3.1.3 Single-pulse experiment

To excite the nuclei, different pulse sequences can be applied depending on the desired information that needs to be extracted from NMR spectrum. The most general one is the so-called single- (or one-) pulse experiment (Figure 2.5a). After pulse delay is provided, that is necessary to allow magnetic equilibration known as the relaxation time, RF pulse is applied and the magnetization vector ($M$) is moved by an angle proportional to the strength and length
of the RF pulse. In order to maximize the signal, for $-\mathrm{nuclei\ spins}$, a $-\mathrm{excitation\ pulse}$ is normally used to move $M$ by $-\mathrm{to\ XY-plane}$ (Figure 2.4). In the case of quadrupolar nuclei (spin $> 1/2$) a $-\mathrm{pulse}$ is generally implemented where I is nuclear spin. The role of a short pulse for quadropolar nuclei is explained further.

2.3.1.4 Cross-polarization (CP) experiment

One-pulse experiments can often suffer from low sensitivity and long delays between pulse sequences due to rather long $T_1$ values for spin $1/2$ nuclei (e.g. $^{29}\mathrm{Si}$). To solve this problem CP NMR technique can be applied (e.g. $^{29}\mathrm{Si}^{}\{^1\mathrm{H}\} \mathrm{CP}$) [61]. This technique allows not only to shorten the pulse decay to the $T_1$ value of abundant spin but also to “filter” the signal to only the dilute nuclei X with a nucleus I in the nearest surroundings. The shortening of repetition delays is caused by the effect of long RF pulse (contact pulse) during which the nuclear spins relax much faster with so-called rotation frame relaxation time $T_{1p}$, being responsible for faster accumulation rate in CP experiment.

In CP NMR experiment, the magnetization is transferred from an abundant (i.e., high gyromagnetic ratio $\gamma$) nucleus I (e.g. $^1\mathrm{H}$) to a dilute nucleus X (e.g. $^{29}\mathrm{Si}$) to enhance the signal. At first, I spins are exited with $-\mathrm{excitation\ pulse}$ to ensure maximal transfer of polarization (Figure 2.5b). Next, during the contact time, the magnetization is transferred from I to dipolar coupled X spins, that is later detected. Importantly, the ratio between RF amplitudes of I and X should be equal to the invert ratio of gyromagnetic ratios to meet Hartmann-Hahn condition and, thus, provide the maximal signal enhancement [62].
2.3.1.5 Chemical shift and integrated intensity

A set of characteristic positions in the spectrum is called resonance frequencies, which in a given static magnetic field $B_0$ depend on the nature of the spins through their gyromagnetic ratio ($\gamma_{1H}$, $\gamma_{29Si}$, $\gamma_{27Al}$ and etc.). Moreover, the electrons surrounding a nucleus are not impassive in the magnetic field used in the NMR experiment, but they react to produce a secondary field. This secondary field contributes to the total field felt at the nucleus, and therefore has the potential to change the resonance frequency of the nucleus (shielding interaction). The frequency shift caused by this interaction in an NMR spectrum is called the chemical shift ($\delta$) [63]. However, the main disadvantage of chemical shielding nomenclature is that it is measured in absolute values for all nuclei. A more convenient approach consists in using a reference compound whose resonance frequency will serve to define a relative frequency scale for each nuclei. Then, the difference between the sample frequency ($\nu$) and that of the reference substance ($\nu_{\text{ref}}$) divided by the operating frequency of the spectrometer ($\nu_{\text{sp}}$) determines the measure of chemical shift ($\delta$) expressed in part per million (ppm) (equation 2.5).

Picture 2.5. Basic scheme of a) one-pulse and b) CP NMR experiment. pl and pw are used to characterize the excitation pulse and correspond to power level and width, respectively.
The observed RF signal, which is a function of the magnetic field, concentration of the investigated nuclei and its gyromagnetic ratio, yields qualitative information regarding the local atomic environment. The integrated intensity of a signal is a measure of a relative abundance of atoms in this configuration and is determined by integrating the area under the signal peak. For spin $\frac{1}{2}$ nuclei such as $^{29}\text{Si}$, the integral is directly proportional to the relative number of nuclei contributing to a signal at a particular frequency and hence will provide quantitative information regarding chemical structure. For quadrupolar nuclei such as $^{27}\text{Al}$, this is not generally true except if a particular excitation scheme is followed [64].

2.3.1.6 Quadrupolar nuclei

Quadrupolar nuclei have a non-spherical distribution of charge. Therefore, the interaction of nuclear spin and the external magnetic field is more complicated. The occurrence of an electrical quadrupole moment gives a substantial contribution to the spectra. Quadrupolar interactions are normally characterized by quadrupolar parameters such as the quadrupole coupling constant ($C_Q$), a measure of the strength of the coupling, and the asymmetry parameter ($\eta_Q$) which characterizes the deviation from axial symmetry. In the case when quadrupolar coupling is much larger than the strength of the RF pulse, selective excitation of the central transition occurs [64]. To provide the maximum signal intensity short excitation pulse (——) should be used.

2.3.1.7 Magic angle spinning (MAS)

In addition, in solid-state NMR, in order to overcome the line broadening of the observed resonances during the NMR measurements, MAS on the sample is applied. The linewidth has multiple origin, but the main contributions in diamagnetic non-conductive oxide are direct
(dipole – dipole) nuclear interactions as well as anisotropy of the chemical shift and electrical field gradient. MAS averages the frequency anisotropy in powdered solids by spinning the sample at a fixed angle during the experiment thus mimicking rapid time-averaged molecular motion that occurs in liquids. This angle corresponds to the zero of the second spherical harmonic \(3\cos^2\theta - 1\). To minimize the contribution of the dipolar and chemical shift anisotropy to the linewidth, this harmonic should ideally vanish, therefore the angle is set to 54.7° with respect to the external magnetic field [65].

2.3.2 \(^{29}\text{Si}\) MAS NMR

By NMR it is possible to detect structure development during hydration process, in particular, to estimate degree of reaction, since the amounts of anhydrous silicates and their hydrates can be measured [66]. This is possible by comparing the relative integrated \(^{29}\text{Si}\) NMR signal intensities, of which the isotropic chemical shift depends on the connectivity \((Q^n)\) of the tetrahedral silicon oxide via bridging oxygen to \(0 \leq n \leq 4\) to other silicon atoms [67]. In the particular case of the C\(_3\)S systems, Si connectivity changes from isolated in the anhydrous C\(_3\)S \((Q^0)\) [68] to chained tetrahedra \((Q^1\) and \(Q^2\)) in the final hydration product C-S-H [69,70]. Globally, the advancement of the C\(_3\)S hydration reaction can thus be followed by tracking the change of chemical shift of the \(^{29}\text{Si}\) resonances from \(Q^0\) (between -66.5 and -73.5 ppm range) to \(Q^1\) (at ca. -79 ppm) and \(Q^2\) (-85 ppm) (Figure 2.6).
In addition, a resonance at -83.2 ppm has been reported to correspond to the bridging tetrahedra \( (Q^{2\text{L}}) \) in a C-S-H [71]. It is supposed to be developed by joining two dimers for the formation of longer chains. The location of guest ions, such as \( \text{Al}^{3+} \) for example, in the C-S-H gel can be also monitored by \(^{29}\text{Si} \) MAS NMR [72]. They were found to be in the substituting position of the bridging silicon tetrahedral, leading to a shift of the adjacent \( Q^2 \) sites to values very close to the chemical shift of the \( Q^{2\text{L}} \) site, thus implying uncertainties in the resolving of such species [69].

To follow the hydration of silicate phases, apart from direct excitation of \(^{29}\text{Si} \) nucleus, \(^{29}\text{Si} \{^1\text{H}\} \) CP/MAS NMR measurements are widely spread [21,73]. By this technique, \(^{29}\text{Si} \) nuclei is excited indirectly through the protons, which means that only \(^{29}\text{Si} \) nuclei in very close proximity to protons can be detected. Thus by a combination of CP and non-CP NMR it is possible to distinguish between hydrated and anhydrous silicate species.

However, solid-state NMR suffers from several drawbacks that have limited its interest for the study of the first hydration products of C\(_3\)S and of its interaction with solvated ions. It is
essentially a bulk method, thus efficient to reveal and quantify massively present cement hydration products [74], but which failed so far to reveal the minor surface species controlling the surface reactivity. Nevertheless, this limitation can be overcome by improving the sensitivity of the technique through $^{29}\text{Si}$ isotopic enrichment. It is necessary because $^{29}\text{Si}$ is the only NMR silicon isotope with a non-zero spin but its natural abundance is below 5%, a value which is definitely not enough to obtain a sufficient signal to noise ratio in less than a few hours.

Indeed, it has been already shown that enrichment increases the time resolution of solid-state NMR [73] and enables in situ time-resolved study of the silicon speciation throughout the reaction [75,76]. Thus, it was established that, initially, isolated monomeric silicon tetrahedral becomes hydroxylated (Q$^0(h)$) and later on the hydration proceeds with the formation of silicate dimers and its closure is characterized by an increase in the population of pentamers.

Two-dimensional (2D) NMR technique has been shown to be useful tool to establish molecular proximities and to refine the structure of the C-S-H [77]. In comparison to one-dimensional MAS NMR, the signals of 2D experiments are spread into a 2D frequency map and thus can increase the resolution of the obtained spectra. Various pulse sequences are applied depending on the correlation type between nuclei. To gain information regarding local connectivities in the silicate chains of C-S-H phase, the double quantum homonuclear $^{29}\text{Si}\{^{29}\text{Si}\}$ correlation is known be successfully applied. For instance, the structural evolution with a change in Ca/Si ratio can be captured [77]. In its turn, heteronuclear $^{29}\text{Si}\{^{1}\text{H}\}$ correlation (HETCOR) is helpful to study the proton environment of the silicates [74]. In particular, it is possible to distinguish protons which contribute to the C-S-H structure from those in water.

Nowadays, in general the structure of the C-S-H can be described as calcium oxide layer in between of linear silicate chains, that have ‘dreierkette’ repeating unit (two paring and one
bridging silicon tetrahedral) [78]. Such sheets are separated by interlayer space that can be occupied by water, hydroxyl or calcium ions.

2.3.3 $^{27}$Al MAS NMR

Solid-state $^{27}$Al MAS NMR is a powerful analytical tool for analysis of cement hydration. Besides the characterization of aluminate phases and their hydrates, over the last years the main interest was also focused around incorporation of Al into the C-S-H phase [79]. The natural abundance of $^{27}$Al is about 100% thus no enrichment of the material is required. Despite this fact, observed resonances are often found to be broader and less resolved than in the case of $^{29}$Si MAS NMR measurements due to the higher spin state of aluminum, i.e. $^{27}$Al is a quadrupolar nucleus. In particular, for $^{27}$Al the quantum spin number is – and this nucleus has six spin energy levels when interacting with the external field. In this case, in addition to chemical shift position, quadrupolar parameters discussed in section 2.3.1 ($C_Q$ and $\eta_0$) can provide valuable information for successful identification and characterization of different Al sites [80,81].

It was illustrated in the literature that by $^{27}$Al MAS NMR different coordination of Al can be distinguished in Al-O systems: tetrahedral Al appears between 50 and 90 ppm, pentahedral between 20 and 50 ppm and octahedral Al belongs to the range between -5 and 20 ppm. Despite these general rules, the Al site coordination needs to be proved for each sample series since specific phases can cause incorrect assignment. In the range of 4-fold Al, the presence of Al guest-ion in alite and belite can be identified. This provides a broadened lineshape between ca. 90 and 30 ppm [82].

When hydrated, it is known that Al enters the structure of C-S-H as 4- and 5-fold coordinated [71,83–85]. In the area of tetrahedral coordination, the $^{27}$Al MAS NMR spectrum
can include several resonances between 58 - 74 ppm, depending on the Ca/Si ratio in the C-S-H (Figure 2.7). It was confirmed experimentally, that the assigned Al is mainly incorporated in the bridging sites of the silicates chains [72,83,86], although when polymerization degree of silicate chains decreases, Al can also be found in the pairing position [86]. Penta-coordinated Al appears at about 38 ppm and it is ascribed to aluminium substituted Ca\(^{2+}\) in the interlayer of the C-S-H structure (Figure 2.7). In addition, it has been shown that when samples become carbonated the observed resonances shift towards lower frequency values. In particular, a new resonance at 55 ppm was observed, that was assigned to Al incorporated into the silica phase, formed due to C-A-S-H and C-S-H decomposition [87].

A variety of calcium aluminate phases and their hydration products were characterized by \(^{27}\)Al NMR including their quadrupole coupling parameters [80]. During the reaction of aluminate phases the coordination of Al changes from tetrahedral in nonhydrated powder to octahedral found in AFm or hydroxy AFm phases between 9 - 12 ppm. AFm phases are called calcium aluminate hydrates that belong to the layered double hydroxide family, structurally related to hydrocalumite. The most common ions for cementitious systems that can be situated in the interlayers are hydroxyl, sulfate and carbonate. Hydroxy AFm phase can be represented as Ca\(_4\)[Al(OH)\(_6\)]\(_2\)(OH)\(_2\)\(\cdot\)xH\(_2\)O, where x can vary between 4 and 12. When sulphates are added to the system \(^{27}\)Al MAS NMR measurements have shown that formation of ettringite (Ca\(_6\)Al\(_2\)(SO\(_4\))\(_3\)(OH)\(_{12}\)\(\cdot\)26H\(_2\)O) and its conversion to monosulphate (Ca\(_4\)Al\(_2\)(SO\(_4\))(OH)\(_{12}\)\(\cdot\)6H\(_2\)O) can be also quite well distinguished [84]. In alumina-rich cement \(^{27}\)Al NMR measurements have shown that the presence of strätlingite (Ca\(_4\)Al\(_2\)(OH)\(_{12}\)[AlSi(OH)\(_8\)]\(_2\)\(\cdot\)2H\(_2\)O) with alternating tetrahedral and octahedral layers structure results in the resonances observed at 61 ppm and 9.9 ppm [88]. This type of AFm phase shows resonance of slightly higher intensity in the area of 6-fold Al when compared to the one in the 4-fold area accompanied by a small shoulder at 68 ppm.
So-called third aluminate hydrate (TAH) assigned to aluminate surface species on the C-S-H phase [84] appears at 5 ppm (Figure 2.7). Investigations performed by NMR in combination with other characterization techniques suggest that TAH is an amorphous or disordered species that contains hydrogen atoms in its nearest coordination sphere.

Figure 2.7. $^{27}$Al MAS NMR of a series of synthetic C-S-H with variable Ca/Si and fixed initial Al/Si = 0.05 (adapted from [71]). AFm phase at 10 ppm presents in all spectra (◇) on the left side from TAH.
2.4 References


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3. Paper I: Revealing the steps of tricalcium silicate hydration

This chapter consists of the reviewed conference paper “Revealing the steps of tricalcium silicate hydration”. It was presented at the 14th International Congress on the Chemistry of Cement (ICCC 2015), which was held in Beijing, China. (E. Pustovgar, J.-B. d’Espinose de Lacaillerie, M. Palacios, A. Andreev, R. Sangodkar, B. Chmelka, R.J. Flatt, Revealing the steps of tricalcium silicate hydration, 14th International Congress on the Chemistry of Cement (ICCC 2015), Beijing)

This paper is the result of the preliminary work, which was necessary to do before exploring more in detail specific aspects of the C₃S hydration, that are presented in chapter 4.

The idea to study cement hydration by in situ NMR using ²⁹Si-enriched C₃S was given to Ms Pustovgar at the beginning of her PhD thesis, without any preliminary studies done in the group. Ms Pustovgar developed the entire experimental approach, that included the synthesis and recycling of ²⁹Si-enriched C₃S, protocol for in situ NMR measurements. 1D NMR measurements were performed by Ms Pustovgar together with Dr. Andreev and Prof. d’Espinose de Lacaillerie. 2D NMR measurements were done by R. Sangodkar, Ms Pustovgar and Prof. Chmelka. This paper was entirely written by Ms Pustovgar under the guidance of Prof. Flatt, Prof. d’Espinose de Lacaillerie and Dr. Palacios.
Abstract

The excellent binding properties of Portland cement rely on the reaction of its main mineral phase, tricalcium silicate (C₃S), with water to produce calcium silicate hydrates (C-S-H) and calcium hydroxide (CH). Hydration of C₃S exhibits complex kinetics that is not yet fully understood. Solid-state ²⁹Si nuclear magnetic resonance (NMR) has proven to be successful in studying hydration kinetics and in elucidating the poorly crystalline structure of silicate hydrates. However, due to the low natural abundance of ²⁹Si, this method has mostly been applied to samples of which the hydration has been stopped and mainly at high degrees of hydration. In this work, ²⁹Si-enriched C₃S has been carefully synthesized and the evolution of C-S-H has been followed in situ by NMR. In this way, unique information concerning hydration mechanisms has been obtained with a time resolution of 30 minutes and up to 28 days. The role of the specific surface area on cement hydration has been also evaluated.

Our results reveal that the surface and sub-surface of the C₃S is hydroxylated to a large extent for the material with higher specific surface area (SSA). During the induction period of the isothermal calorimetry, no significant amount of hydrates were formed. During the acceleration period, C-S-H grows forming new silicate dimers while polymerization of C-S-H increases during the deceleration period.

Finally, ²⁹Si enrichment allowed the realization of solid-state two-dimensional (2D) dipolar-mediated ²⁹Si{²⁹Si} correlation NMR experiment that probe dipole-dipole ²⁸Si-²⁸Si interactions. This provided information on the proximities between different ²⁹Si species in C-S-H chains.
3.1 Introduction

C₃S is the main mineralogical phase of cement and it controls the hardening of concrete, the most widely used manufacture construction material. The hydration rate of C₃S varies with time as a first period of apparent inactivity, the induction period, is followed by a sudden but short-lived hydration peak. This apparent variability of the hydration rate is influenced by the surface area of the cement and is not yet fully understood although different mechanisms have been proposed based on kinetics controlled by diffusion, solubility or crystal growth [1,2]. These models differ but all rely on the successive formation of different metastable hydrates, surface states or nuclei.

Experimentally, the advancement of the hydration is normally followed by isothermal calorimetry. But it has been shown before that solid-state NMR is also a very useful and powerful tool for studying C₃S reaction [3] and for elucidating the structure of silicate hydrates, especially when the reaction is stopped or completed. It should be taken into account that ²⁹Si NMR has a very low sensitivity, which is a limitation to study the first hydration products and their interaction with solvated ions. The only known way to overcome this limitation is using ²⁹Si isotopic enrichment. ²⁹Si is the only NMR responsive silicon isotope and its natural abundance is low, 4.7% that is why only a few studies have been done on the dynamics of silicate hydrates formation in situ [4].

In the present work we developed a synthesis of ²⁹Si-enriched C₃S together with its recycling procedure after the hydration experiments. In addition, the objective of this work was to evaluate an optimum protocol for in situ NMR measurements. This paper shows that solid-state magic angle spinning (MAS) NMR can be used successfully not only to follow qualitatively the hydration of C₃S but also quantitatively. For these reasons, the aim of this
The study was to get an insight into the kinetics of the \( \text{C}_3\text{S} \) hydration and the role of its specific surface area.

### 3.2 Experimental

#### 3.2.1 Raw Materials

Pure triclinic \( \text{C}_3\text{S} \) was synthesized by the solid-state reaction method. Precursors \( \text{CaCO}_3 \) (\( \geq 99\% \), Sigma Aldrich) and \( \text{SiO}_2 \) (99.9% enriched in \( ^{29}\text{Si} \), Cortecnet or non-enriched, Sigma Aldrich) were dry homogenized during 24 h in stoichiometry quantity. The final powder was pressed and small pellets were fired afterwards in a platinum crucible at 1600 °C for 8 h. Pellets were quickly quenched in the compressed air flow atmosphere. To reach the full transformation of the starting materials into the synthesized phase, the whole procedure had to be repeated 4 times for the synthesis of the \( ^{29}\text{Si} \)-enriched \( \text{C}_3\text{S} \), until no reflections due to free lime could be observed by X-ray diffraction. At the same time, for pure triclinic nonenriched \( \text{C}_3\text{S} \) one cycle of firing was enough. Finally, the material was ground with absolute ethanol in a micronizing mill (McCrone). SSA of the final \( \text{C}_3\text{S} \) powders were measured by nitrogen adsorption (Micromeritics Gemini 2375 Nitrogen Adsorber) applying BET model for the data interpretation after degassing the sample at 200 °C during 1 h. The measured BET surface areas were 4.4, 3.6, 1.4 and 0.8 m\(^2\)/g. In addition, part of the \( ^{29}\text{Si} \)-enriched \( \text{C}_3\text{S} \) was also sieved below 20 μm and used without the definite BET surface area determination due to limited amount of the material. In this case the specific surface was estimated based on the particle size distribution (PSD), using the relation between PSD and specific surface of the other powders. This resulted in a value of 0.5 m\(^2\)/g. Results of PSD for all used samples determined by laser diffraction scattering technique are shown in Figure 3.1.
3.2.2 Experimental Process

Taking into account the costs of the $^{29}$Si isotope, the procedure of the C-S-H recycling into initial $^{29}$Si-enriched C$_3$S was developed. It included the intermediate firing at 1000 °C for about 2 h to decarbonate the hydrated paste and further sintering of the desired material according to the procedure described before. Figure 3.2 shows that the recycled C$_3$S was identical to the one used before.

**Figure 3.1.** PSD of the used synthesized C$_3$S.

**Figure 3.2.** Recycling of C-S-H followed by XRD.
NMR experiments were performed with 4 mm ZrO$_2$ rotors at spinning frequencies of 7 kHz using a Bruker Avance-500 spectrometer (magnetic field is 11.7 T). Chemical shifts were referenced to tetrakis(trimethylsilyl)silane (TMS) with the accuracy of ±0.1 ppm. The single-pulse $^{29}$Si MAS NMR spectra were acquired with a $\pi/2$ pulse length of 6 s, a recycle delay of 1000 s for the enriched anhydrous C$_3$S sample and 100 s for the hydrated ones. Cross-polarization (CP/MAS) spectra were acquired with a $^1$H rf power of 93 kHz, a contact times of 5 ms and recycle delays of 10 s. A typical numbers of scans were 184 for hydrated $^{29}$Si-enriched C$_3$S samples and 5840 for non-enriched one. Hartmann-Hahn matching was ensured by a ramp on the $^{29}$Si rf field. 2D $^{29}$Si{$^{29}$Si} dipolar-mediated correlations NMR spectra were acquired at 11.7 T, 25 °C and 4.6 kHz MAS. 2D $^{29}$Si{$^{29}$Si} spectra were acquired by using CP to generate $^{29}$Si magnetization, with a 7 ms recoupling time to reintroduce homonuclear $^{29}$Si dipolar interactions, and was recorded in 25 h.

Pastes for in situ NMR measurements were prepared by mixing 0.3 g of $^{29}$Si-enriched C$_3$S and 0.24 g of ultrapure water in a cylindrical 2 ml plastic vial during 3 min using vortex mixer (Analog, VWR) at 2500 rpm. With the help of an appropriate syringe and a needle this paste was introduced as such in the zirconia rotor thus enabling the acquisition of the NMR spectra during the reaction in real time.

For a set of samples hydration was stopped by stirring them in isopropanol with the ration of 1 : 25 during 5 min. Afterwards, the powdered samples were filtered and dried in desiccator over silica gel until a constant mass.

The kinetic of $^{29}$Si-enriched C$_3$S hydration was measured by isothermal calorimetry using a TAM Air microcalorimeter at 23 °C. 1 g of $^{29}$Si-enriched C$_3$S was mixed with 0.8 g of ultrapure water in the same conditions as for NMR measurements. The degree of reaction of $^{29}$Si-
enriched C₃S was calculated by dividing the cumulative heat released at a certain time by the enthalpy of reaction of C₃S, -520 J/g C₃S [5,6].

The thermal analysis (TGA) was recorded from 40 to 1000 °C at a heating rate 10 °C/min in N₂ atmosphere.

3.3 Results and Discussion

Thanks to enrichment we could monitor by *in situ* ²⁹Si[¹H] CP NMR experiments how hydration proceeds with a time resolution of 30 min during first 6 hours (Figure 3.3a,b). It was established that independently on the SSA of the investigated C₃S, first dimers (Q¹ species at -79 ppm) start to form only after 1.5 h of hydration and the growth of the Q² species was observed after 5 h, what corresponds the signal around -85.5 ppm. At the same time the presence of hydroxylated (Q⁰(h)) species identified prior to hydration (Figure 3.4) was detected through the whole set of experiments.

![Figure 3.3. Hydration species formation at early stage of reaction followed by ²⁹Si[¹H] CP NMR for ²⁹Si-enriched C₃S of a). 4.4 m²/g b). 1.4 m²/g BET specific surface area.](image)

The evidence of this Q⁰(h) during the hydration process of C₃S has been reported by some authors [3,7]. However, in comparison to the previous work by Rodger *et al.* [3], we
synthesized 100% $^{29}$Si-enriched C₃S, which allowed us to establish the presence of Q⁰(h) in the samples even before the actual hydration takes place. It means that these species are formed in the sample without direct water addition simply interacting with water vapors from the atmosphere. In addition, in the present work we added the sophistication of a very careful control of the structure and granulometry of the C₃S grains, thus our results clearly show, that the process of Q⁰(h) formation is controlled by the surface area of the C₃S (Figure 3.4). It means that the amount of the Q⁰(h) in the sample is a function of the available surface area of the powder.

\[ \text{Figure 3.4. Influence of surface area on the Q}^0(\text{h}) \text{ formation.} \]

By the use of in situ hydration, we were able to detect the first hydrates formation (Q¹ and Q²) that takes place after the induction period, during main hydration peak when compared with isothermal calorimetry measurements. To study hydration at later ages additional NMR experiments on the hydrated C₃S with a SSA of 1.4 m²/g were carried out. In this case, hydration was stopped after 1, 3, 7 and 28 days. The spectra obtained using one-pulse technique confirm the growth of Q¹ and Q² species over time and the consumption of non-hydrated C₃S with the reaction, but they do not provide information concerning Q⁰(h) species due to
overlapping of the resonances in the $Q^0$ range (Figure 3.5a). Based on the obtained one-pulse $^{29}$Si NMR spectra, the amount of the hydration products was quantified by comparison of the integrated signal intensities. The degree of reaction was estimated based on the calculated results. These data were compared with the isothermal calorimetry measurements of the same sample and they were found to be in a good agreement (Figure 3.5b). The advancement of hydration at 3 days was also confirmed by TGA and resulted in 55% as well.

**Figure 3.5. a). Hydration species formation between 1 and 28 days followed by $^{29}$Si one-pulse NMR, b). Comparison of NMR and calorimetry data.**

It is well known, that PSD together with the SSA of C$_3$S play an important role in C$_3$S hydration [8]. By decreasing the SSA of the C$_3$S phase, we observe the decrease in reactivity rate by comparing the length of the induction period and the slope of the acceleration stage (Figure 3.6a). It was found that there is a linear correlation between the SSA of the material and its maximum heat rate. In addition, the maximum of this peak appears at times that vary linearly with the SSA (Figure 3.6b). Finally, with decrease in the available reactive surface there is a decrease in the cumulative heat released during first week of hydration. Cumulative heat obtained by 1 day of C$_3$S hydration also shows linear dependency with respect to SSA of the investigated samples (Figure 3.6c). This allows us to predict the degree of hydration of different samples just by knowing their SSA and without any further experimental
determination, although a calibration curve for a desired water/cement ration has to be performed first.

![Graph a](image1)
![Graph b](image2)
![Graph c](image3)

**Figure 3.6.** a). Heat rate of C₃S with different surface areas, b). Correlation of main hydration peak position and C₃S surface area, c) Correlation of cumulative heat at 1 day of reaction and C₃S surface area.

Selected ²⁹Si MAS NMR spectra obtained during *in situ* hydration of ²⁹Si-enriched C₃S with 0.5, 1.4 and 4.4 m²/g SSA are shown in Figure 3.7a-c. Results of the quantitative analyses performed on these samples are collected in Figures 3.7d,e. Depending on the SSA of the used C₃S, different amounts of the formed hydration products were detected at the same hydration time. This is particularly true for the formation of Q¹ dimers. At early stages of hydration this amount gradually increases with increasing SSA (Figure 3.7d). At 1 day (Figure 3.7e) it shows a linear effect on SSA. Additionally, there is a linear decrease in the amount of the non-
hydrated C₃S. This is consistent with the previous results obtained by isothermal calorimetry presented in Figure 3.6c. Moreover, the SSA of the C₃S does not seem to affect (as) much on the Q² formation, although overall their amount is still too low at the investigated hydration times.

Figure 3.7. A selection of a sequence of ²⁹Si MAS NMR spectra obtained from an anhydrous and hydrated in situ samples with BET SSA of a) 0.5 m²/g b) 1.4 m²/g c) 4.4 m²/g. Quantitative analyses of the Q⁰ (C₃S), Q¹ and Q² species present after hydration during d) 10 h and e) 1 day.

To detect and identify ²⁹Si site proximities between different ²⁹Si species in C-S-H present in ²⁹Si-enriched C₃S hydrated at room temperature for about a month 2D ²⁹Si{²⁹Si} dipolar-mediated correlation NMR was used (Figure 3.8b,c). The insert in Figure 3.8a shows a schematic diagram of ²⁹Si moieties in hydrated C₃S, with arrows showing molecular-level dipole-dipole interactions between various ²⁹Si species, as established by the intensity correlations in the 2D spectra. The ²⁹Si signals and corresponding intensity correlations are
assigned based on previous theoretical predictions [9] and experimental NMR studies [10] of the $^{29}$Si isotropic chemical shifts of silicon species in C-S-H. Several correlated signals are observed in the 2D spectrum shown in Figure 3.8c,d, specifically those labeled (i) – (v) which are discussed below:

(i) Correlated 2D intensity is resolved between signals at -82.6 and -84.4 ppm arising from $Q^2L$ and $Q^2$ $^{29}$Si species, respectively, in a pentameric (five-membered linear chain) or longer C-S-H chain. A $Q^2L$ silicate tetrahedron is charge-balanced primarily by protons (from silanol moieties), compared to $Q^2$ silicate tetrahedron that is charge-balanced by Ca$^{2+}$ cations present in the main plane, as indicated in the schematic diagram in Figure 3.8a.

(ii) Strong intensity correlations between signals at -79 and -85 ppm arise from $Q^1$ and $Q^2$ $^{29}$Si species present in C-S-H.

(iii) Partially resolved correlated intensity is observed between signals at -79 and -83 ppm that are associated with $Q^1$ and $Q^2L$ $^{29}$Si species.

(iv) Correlated intensity is observed between the signals at -77 and -84 ppm from another type of $Q^1$ and $Q^2$. These species are chemically distinct due to their different molecular proximities to Ca$^{2+}$ cations and/or hydroxyl moieties. Such differences in the local atomic $^{29}$Si environments have been previously proposed [9] and are supported by theoretical predictions of the $^{29}$Si isotropic chemical shifts of silicon species in C-S-H.

(v) Correlated intensity between $Q^0(h)$ and $Q^1$ was difficult to observe since the sample is almost fully hydrated and only a few $Q^0(h)$ left.
Figure 3.8. Solid-state a). 1D single-pulse $^{29}$Si MAS b), c). 2D $^{29}$Si{$^{29}$Si} dipolar-mediated correlations NMR spectra of $^{29}$Si-enriched CsS hydrated for 1 month.
3.4 Conclusions

In this paper we show that \textit{in situ} time-resolved study of the silicon speciation of $^{29}$Si enrichment is a relevant approach to understand the hydration of the main phase of cement. Firstly, an optimum protocol for the synthesis and recycling of the used $^{29}$Si-enriched $C_3S$ was established and an effective way to study hydration \textit{in situ} without perturbing the C-S-H structure was found. NMR and isothermal calorimetry results confirm the importance of the surface area of the starting material showing that the degree of hydration decreases when courser $C_3S$ is used. Furthermore, linear correlation between the parameters of the main hydration peak and SSA of the used $C_3S$ was found. In addition, 2D NMR shows detailed information on the proximities between various $^{29}$Si species in C-S-H structure. To be able to see the definite covalent connectivities formed between various species in the same sample similar work with $J$-mediated correlation would be done.
3.5 References


4. Paper II: Understanding silicate hydration from quantitative analyses of hydrating tricalcium silicates

This chapter consists of the paper “Understanding silicate hydration from quantitative analyses of hydrating tricalcium silicates”. It was published in Nature Communications. (E. Pustovgar, R P. Sangodkar, A. S. Andreev, M. Palacios, B.F. Chmelka, R.J. Flatt, J.-B. d'Espinose de Lacaillerie, Understanding silicate hydration from quantitative analyses of hydrating tricalcium silicates, Nature Communications 7 (2016), 10952)

This paper presents the main results of the work dedicated to the hydration of C₃S. With the help of the preliminary work done in the previous chapter, it shed new light on the rate limiting steps of the silicates hydration.

Ms Pustovgar was the main investigator. She developed the synthesis of the ²⁹Si-enriched C₃S samples, designed and carried out the characterization and calorimetry studies. Prof. d’Espinose, Prof. Flatt and Dr. Palacios designed the project. Prof. Chmelka proposed the 2D J-mediated and relaxation NMR experiments. Ms Pustovgar, Dr. Andreev, Prof. d’Espinose and R. Sangodkar performed the NMR experiments. R. Sangodkar calculated the relative populations of ²⁹Si silicate species associated with C-S-H units of different chain lengths. All authors contribute to the analyses of the results and the writing of the manuscript.
Abstract
Silicate hydration is prevalent in natural and technological processes, such as, mineral weathering, glass alteration, zeolite syntheses and cement hydration. Tricalcium silicate (C$_3$S), the main constituent of Portland cement, is amongst the most reactive silicates in water. Despite its widespread industrial use, the reaction of C$_3$S with water to form calcium silicate hydrates (C-S-H) still hosts many open questions. Here, we show that solid-state nuclear magnetic resonance (NMR) measurements of $^{29}$Si-enriched triclinic C$_3$S enable the quantitative monitoring of the hydration process in terms of transient local molecular composition, extent of silicate hydration and polymerization. This provides insights on the relative influence of surface hydroxylation and hydrate precipitation on the hydration rate. When the rate drops, the amount of hydroxylated C$_3$S decreases, thus demonstrating the partial passivation of the surface during the deceleration stage. Moreover, the relative quantities of monomers, dimers, pentamers and octamers in the C-S-H structure are measured.
4.1 Introduction

Since Le Chatelier [1], it is well understood that Portland cement hydration is initiated by the dissolution of calcium silicate monomers in water, followed by the precipitation of less soluble layered calcium silicate hydrates (C-S-H), in which silicate ions condense to form short chains. However, despite two centuries of widespread applications and a century of detailed study, the molecular mechanisms behind the kinetic stages of hydration (that is, induction, acceleration and deceleration) are still debated. Similar kinetic stages are observed in various heterogeneous hydration processes occurring during mineral weathering [2,3], glass alteration [4,5] and hydrothermal syntheses. For example, although hydrothermal zeolite syntheses under alkaline aqueous conditions proceeds over different timescales [6], the effective reaction rates in cementitious and zeolite systems exhibit similar distinct stages (induction, acceleration and deceleration), and are governed by several coupled parameters varying in space and time near the liquid–solid interface. This situation is thus extremely complex to describe accurately. An added difficulty is that for porous materials such as cement or zeolites, interfacial energy contributes to the stabilization of nanoscale intermediates, which are typically challenging to characterize. For Portland cement in particular, the lack of quantitative experimental data obtained with sufficient time resolution has precluded the validation of existing models aimed at explaining the complex kinetics of cement hydration.

Similar to the homogeneous versus heterogeneous pathways dichotomy in zeolite crystallization mechanisms [7], two landmark competing theories have been proposed to explain the early-age time dependence of the rate of C$_3$S hydration, the principal component in commercial Portland cements responsible for the development of mechanical strength [8–10]. The first theory proposes that early-age hydration products form a diffusion barrier on the surfaces of C$_3$S particles, thus affecting subsequent reactions of the underlying non-hydrated
core [11]. The second theory [12–14] suggests that the early-age time-dependence of the rate of hydration is determined by the rate of C₃S dissolution and by a change in the associated rate limiting step from etch pit formation to step retreat, which is a mechanism also often invoked in the geochemical literature on natural weathering [15,16]. The relevance of these theories to silicate hydration can be examined by understanding the molecular compositions and structures of species at the solid–liquid interfaces during the early stages of hydration. Similar questions are raised in heterogeneous catalysis and geochemistry; however, Portland cement hydration faces the additional complexity that the main product, C-S-H, is not only poorly crystalline but also nanostructured with variable stoichiometry and silicate coordinations [17,18]. These challenges have been previously addressed partially through numerical modelling of hydration reactions at C₃S surfaces [19,20] and of the local structure and disorder of the resulting hydration products [21]. Nevertheless, these models suffer from a lack of experimental support at the molecular level.

Here, solid-state NMR measurements of triclinic ²⁹Si-enriched C₃S hydration are used to determine the transient molecular level compositions at silicate surfaces and the interactions between silicate species, hydroxyl groups and water molecules, which influence the rates of hydration reactions. The isotopic ²⁹Si enrichment provides significantly enhanced NMR signal sensitivity that can be used to monitor the structures of the hydrates in situ during the hydration process, as a function of hydration time. In addition, ²⁹Si enrichment enabled two-dimensional (2D) through-bond (J-mediated) NMR measurements that are sensitive to ²⁹Si-O-²⁹Si covalent bonding. They are used to crucially provide detailed information on the local atomic-level compositions, structures and site connectivities in hydrated silicate species, here C-S-H. These analyses shed new insights on the origin of rate limiting steps and the kinetics of silicate polymerization at the solid–liquid interface during C₃S hydration.
4.2 Methods

4.2.1 NMR spectroscopy

The $^1$H and $^{29}$Si NMR isotropic chemical shifts were referenced to tetramethysilane using tetrakis(trimethylsilyl)silane (TMS) [((CH$_3$)$_3$Si)$_4$Si] as a secondary standard [22]. All measurements were performed using zirconia rotors and at room temperature. Solid-state one-dimensional (1D) $^{29}$Si NMR experiments were carried out using a Bruker Avance-III 500 spectrometer (magnetic field 11.7 T). Magic angle spinning (MAS) spectra were measured using a Bruker MAS NMR probe with 4 mm rotors, at spinning frequencies of 7 kHz, and without decoupling. The single-pulse $^{29}$Si MAS NMR spectra were acquired with a $\pi/2$ pulse length of 6 $\mu$s, a recycle delay of 1000 or 100 s, and 64 or 16 scans for the $^{29}$Si-enriched non-hydrated and hydrated C$_3$S samples, respectively. $^{29}$Si-$^1$H} CP/MAS NMR spectra were recorded using a $^1$H rf power of 93 kHz, a contact time of 5 ms, and recycle delay of 10 s. The number of scans was 184 for hydrated C$_3$S samples and 2000 for nonhydrated sample. Hartmann-Hahn matching was ensured by a ramp on the $^{29}$Si rf field intensity. 2D $^{29}$Si-$^1$H} heteronuclear dipolar correlation (HETCOR) experiments were conducted on a Bruker Avance-700 (16.4 T) spectrometer at ambient temperature, under 4 kHz MAS conditions, with a 7 ms CP contact time, recycle delay of 10 s and 66 $t_1$ increments of 50 $\mu$s each. Solid-state 2D $^J$-mediated $^{29}$Si-$^{29}$Si} DQ correlation NMR experiments were conducted using the refocused- INADEQUATE technique [23] and a 18.8 T Bruker AVANCE-III NMR spectrometer. The experiments were conducted under conditions of 12.5 kHz MAS using a Bruker 3.2 mm H-X double resonance probehead. The 2D $^{29}$Si-$^{29}$Si} spectrum was acquired using a 2.5 $\mu$s $^1$H $\pi/2$ pulse, 3.5 ms contact time for $^{29}$Si-$^1$H} CP, 6.0 $\mu$s $^{29}$Si $\pi/2$ pulses, SPINAL-64 $^1$H decoupling [24], 152 $t_1$ increments, an incremental step size of 80 $\mu$s, a recycle delay of 2 s and 3072 scans for each $t_1$ increment, which corresponds to an experimental time of 260 h (≈ 11 days).
4.2.2 Hydration experiments

Paste for in situ NMR measurements was prepared by mixing 0.3 g of non-hydrated $^{29}$Si-enriched C$_3$S and 0.24 g of ultrapure water in a cylindrical 2 ml plastic vial for 3 min using a vortex mixer (Analog, VWR) at 2500 r.p.m. With the help of a syringe and needle, part this paste was introduced as such in the zirconia MAS rotor thus enabling the acquisition of the NMR spectra during the reaction and avoiding any possible microstructural changes caused by the commonly used drying techniques [25]. After 6 h of hydration, the paste was removed from the ZrO$_2$ rotor to prevent its hardening inside the rotor, and the NMR measurements were continued on the part of the sample previously set aside and stored in the closed vial at room temperature. The kinetics of $^{29}$Si-enriched C$_3$S hydration were measured by isothermal calorimetry using a TAM Air microcalorimeter at 23 °C. One gram of $^{29}$Si-enriched C$_3$S was mixed with 0.8 g of ultrapure water under identical conditions as for samples prepared for NMR measurements. The paste was immediately sealed in a glass ampoule and placed in the isothermal calorimeter. The degree of reaction of $^{29}$Si-enriched C$_3$S was calculated by dividing the cumulative heat released at a certain time by the enthalpy of the hydration reaction of C$_3$S (-520 J/g C$_3$S) [26,27]. Additional details of synthesis, C$_3$S characterization and NMR quantitative analysis are reported in the Supplementary information, sections 4.6.1 - 4.6.3.

4.3 Results and Discussion

4.3.1 Experimental approach.

To the seminal approach of $^{29}$Si enrichment by Brough et al. [28], we added for the first time the sophistication of carefully controlled structure and granulometry of the C$_3$S particles (see Supplementary information, sections 4.6.1, 4.6.2) and hydration reaction conditions (see Supplementary information, section 4.6.4). Indeed, the surface structure and area of the C$_3$S particles strongly affect their reactivity, which must be carefully controlled to ensure meaningful results [29]. For example, the high surface area of the synthesized $^{29}$Si-enriched
C₃S (4.4 m²/g, see Supplementary information) allowed ~ 90% of the silicate hydration process to be monitored in 24 h of NMR spectrometer time, without external acceleration. In this way, subtle and unique quantitative information pertinent to hydration mechanisms can be obtained non-invasively and with a time resolution of 30 min (measurement time for the NMR spectra). Consequently, the progress of the hydration reaction could be accurately and quantitatively correlated to the corresponding ²⁹Si speciation. In addition, ²⁹Si enrichment allows NMR measurements to be performed on samples without the need for conventional water removal schemes for quenching the hydration process [25], which otherwise often disrupt the fragile microstructure of the C-S-H or may detrimentally alter chemical composition. Representative one-pulse ²⁹Si and ²⁹Si{¹H} cross-polarization (CP/MAS) NMR spectra are presented in Figure 4.1a,b, respectively, for non-hydrated and hydrated C₃S. In anhydrous triclinic C₃S which exhibits long-range crystalline order and well-defined local atomic ²⁹Si environments, eight distinct and narrow (< 0.5 ppm full-width at half maximum (FWHM)) ²⁹Si signals are resolved between -68 and -75 ppm corresponding to anhydrous Q⁰ species (Supplementary information, Figure 4.7). In contrast, in hydration products, the ²⁹Si resonances are broad (3-4 ppm FWHM) with signals centred at -72, -79 and -85 ppm from silanol Q⁰(h), hydrated Q¹ and hydrated Q² silicate species, respectively (Figure 4.1). The last two species are associated with the C-S-H structure (Qⁿ refers to silicon atoms that are covalently bonded via bridging oxygen atoms to 0 ≤ n ≤ 4 other silicon atoms [30]). These molecular-level insights of the local silicate structures in C₃S hydration products (C-S-H) are consistent with previous ²⁹Si NMR [31,31], ¹⁷O NMR [33], X-ray and neutron scattering results [18] for C-S-H.
Figure 4.1. Dynamics of silicate hydrates formation studied in situ by $^{29}$Si NMR. a) $^{29}$Si MAS NMR and b) $^{29}$Si(^1H) CP/MAS NMR spectra of $^{29}$Si-enriched triclinic C$_3$S sample in its initial non-hydrated state (in black) and after hydration for 11 h or 12 h (in red) and 28 days (in blue). $^{29}$Si resonances from isolated silicate (Q$^0$) species in non-hydrated C$_3$S, hydroxylated surface Q$^0$ (Q$^0$(h)) species and polymerized calcium silicate hydrates (Q$^1$ and Q$^2$) are clearly resolved and can be quantified as a function of time.
The degree of silicate hydration is determined by quantitative in situ $^{29}$Si NMR analyses and forms the crux of our results, which are summarized in Figure 4.2. These results are in close agreement with the degree of silicate hydration as established by independent isothermal calorimetric measurements, which reveal the successive stages of initial dissolution, induction, acceleration and deceleration (Figure 4.2b) during the silicate hydration process. This comparison crucially establishes the accuracy of the quantitative $^{29}$Si NMR results acquired during C$_3$S hydration, and indicates that the hydration process is negligibly altered by factors such as the MAS conditions of the NMR experiment (see Supplementary information, sections 4.6.3 and 4.6.4). This detailed time-resolved, in situ, quantitative NMR analysis answers three central questions about C$_3$S hydration: the molecular origin of the reduced apparent solubility of C$_3$S during the induction period, the possible ‘switch’ from one type of hydration products to another between the acceleration and deceleration period, and the relative proportions of silica oligomers in the final C-S-H structure.
Figure 4.2. Quantitative monitoring of silicate speciation during the hydration of $^{29}$Si-enriched triclinic C$_3$S. a) The quantities of different $^{29}$Si silicate species as established by $^{29}$Si MAS and $^{29}$Si{H} CP/MAS NMR measurements for hydration times up to 28 days (see Supplementary information, section 4.6.3). The quantities, normalized to the initial amount of C$_3$S, of anhydrous Q$^0$ (in black), hydroxylated Q$^0$(h) (in pink), hydrated Q$^1$ (in green), hydrated Q$^2$ (in blue), and total silicate species (in red) resulting
from this analysis are as shown. b) Comparison of the quantities of different $^{29}$Si silicate species and the reaction heat flow rate determined by isothermal calorimetry (cyan line) for C$_3$S up to 24 h of hydration. Based on the heat released in the calorimetry measurements, four stages in the hydration process can be identified: first a brief exothermic peak during the first few minutes (<15 min) corresponding to initial dissolution of C$_3$S, then a short (15 min – 2 h) induction period during which no significant heat is released, followed by a peak corresponding to the acceleration period (2 – 10 h), and finally the deceleration period (> 10 h) associated with decreasing rate of heat release. c) Comparison of the degree of silicate hydration determined independently by $^{29}$Si MAS and $^{29}$Si{$^1$H} CP/MAS NMR quantitative analyses (squares) and isothermal calorimetry results (black line), which are in close agreement. The fact that the total amount of Si atoms remains constant, within the uncertainties of the measurements, over the entire hydration period (28 days) establishes the accuracy of the associated quantitative NMR methods and analyses. Details of these analyses are included in the Supplementary information, section 4.6.3.

4.3.2 Induction period

The apparent solubility of C$_3$S during the induction period of hydration has been reported to be lower compared with pristine anhydrous C$_3$S [11-13]. This reduced apparent solubility has been proposed to arise from the deposition of a layer of hydration products (the metastable barrier hypothesis) [11] or from surface hydroxylation [12,13]. The molecular compositions at the C$_3$S surface during this induction period (as determined by the NMR analyses presented here) points towards the latter scenario. The $^{29}$Si{$^1$H} CP/MAS NMR measurements of the initial sample (that is, non-hydrated) (Figure 4.1b) establish the presence of Q$^0$ silicate species in proximity to protons (henceforth labelled Q$^0$(h)) on C$_3$S particle surfaces, even before contact with bulk water. Although previous studies have reported the presence of similar Q$^0$(h) silicate species at the surfaces of ‘anhydrous’ C$_3$S particles [28,31], it has not been largely publicized nor quantitatively analysed. The 2D $^{29}$Si{$^1$H} heteronuclear correlation (HETCOR) NMR spectrum of the same sample of non-hydrated C$_3$S (Figure 4.3) exhibits correlated intensities between the $^{29}$Si signal at -72 ppm from Q$^0$(h) species and unresolved $^1$H signals around 1.3 and 0.9 ppm from -SiOH and -CaOH moieties, thereby establishing the close
molecular-level proximities of surface Q⁰(h) species to at least one type of such ¹H moieties. In addition, the absence of resonances characteristic of polymerized hydration products (that is, Q¹ and Q² species), establishes that the reaction of surface silicate species in non-hydrated C₃S with atmospheric moisture results solely in the formation of hydroxylated Q⁰(h) species at particle surfaces, within the sensitivity limits of the measurement. In other words, no separate hydrate phase forms at this stage, it is solely the C₃S particle near-surface which is hydroxylated.

![Diagram](image)

**Figure 4.3.** Proton to silicon signal intensity correlations on the initial non-hydrated ²⁹Si-enriched triclinic C₃S. a) The 2D ²⁹Si{¹H} HETCOR NMR spectrum shows intensity correlations between ²⁹Si and ¹H signals that result from molecular proximity between ²⁹Si and ¹H nuclei. ²⁹Si CP/MAS and ¹H MAS 1D spectra are shown along the horizontal and vertical axis of the 2D spectrum. The chemical shift of ²⁹Si is detected (horizontal dimension), while chemical shift of ¹H is recorded in the indirect (vertical) dimension. b) The right inset schematizes the protonated moieties detected on the C₃S surfaces.

From a crystal chemistry perspective, the C₃S particle surface is unlikely to be inert when exposed to atmospheric water vapor. Specifically, C₃S is an ionic crystal of Ca²⁺ cations with
oxide and monomeric silicate anions (3Ca$^{2+}$·O$^{2-}$·SiO$_4^{4-}$) [19,34]. There is a strong ionization of the atoms (+1.5 on Ca$^{2+}$ and -1.5 on O$^{2-}$) [19] and consequently C$_3$S acts as a basic oxide that readily yields hydroxide ions when reacting with water,

$$O^2- + H_2O \rightarrow 2 OH^-$$  \hspace{1cm} (4.1) \\

Therefore, one expects OH$^-$ to replace oxide ions on the particle surfaces. However, replacement of one O$^{2-}$ by two OH$^-$ would yield a heterogeneous distribution of local atomic environments at the C$_3$S surface, due to the different sizes and formal charges of these anions. Indeed, the Q$^0$(h) $^{29}$Si NMR resonance of the initial sample is very broad (Figure 4.1b), reflecting a wide distribution of local $^{29}$Si environments. In summary, the $^{29}$Si NMR analyses reveal that near-surface $^{29}$Si species on C$_3$S particles are predominantly hydroxylated and that negligible quantities of polymerized silicate hydration products form (within the sensitive detection limits of the measurements), a result consistent with previous force-field atomistic simulations [19]. Overall, hydroxylated Q$^0$(h) species are predominant at particle surfaces during the induction period and expected to result in the reduced apparent solubility of C$_3$S, compared with pristine anhydrous C$_3$S whose level of hydroxylation is lower.

4.3.3 Acceleration stage

With the progress of C$_3$S hydration, the monomeric Q$^0$ silicate species polymerize to form oligomeric units of C-S-H. As shown in Figure 4.2, while the population of hydroxylated Q$^0$(h) species remains constant, the populations of Q$^1$ species increase significantly during the acceleration stage (~2 – 10 h). Compared with the induction stage (< 2 h), the $^{29}$Si polymerization during the acceleration stage results predominantly in the formation of Q$^1$ species (dimers) at early times, and a combination of Q$^1$ and Q$^2$ species (for example, pentamers and octamers) at later time (10 - 20 h). In particular, the population of Q$^1$ species increases approximately linearly with the progress of hydration (Figure 4.2b) across the entire
acceleration stage, consistent with the formation of predominantly dimeric C-S-H units. No significant change nor in the silicon second coordination sphere of the hydration products nor in their rate of formation could be detected at this stage.

4.3.4 Deceleration stage

The data in Figure 4.2 indicate that at the end of the acceleration stage (after ~ 10 h in the present case) greater quantities of long (> 2 silicate tetrahedra) C-S-H chains containing Q^2 species are formed compared with dimeric C-S-H units (without Q^2). Although the amounts of Q^2 species increase progressively after the hydration peak (~ 20 h), the population of Q^1 species remains approximately constant, which indicates the formation of longer silicate chains besides the dimers. By comparison, the amount of Q^0(h) species remains constant for several hours (~ 10 h) during the induction and acceleration stages, it subsequently decreases just when, according to isothermal calorimetry, the C_3S hydration slows down, that is during the so-called deceleration stage. This observation provides important insights regarding the debate on the origin of the deceleration period. While some previous studies suggest that the deceleration period results from coverage of C_3S particles by hydration products [35], others claim that hydration initially results in products forming a low-density structure, the subsequent densification of which corresponds to the beginning of the deceleration stage [36,37]. Our analyses suggest that compared with the acceleration period that is associated with the formation of predominantly dimeric C-S-H units, the deceleration period corresponds to the formation of greater relative fractions of C-S-H units with longer chain lengths. Such increasing extents of silicate polymerization might possibly be accompanied by an increased density of the C-S-H that consequently would present a diffusion barrier for mass transport and, thus, slow the rate of hydration reaction, consistent with the deceleration stage. This alone is not conclusive as it could either support the view according to which the deceleration would
be based indeed on the filling of an ultra-low-density gel [38] or the one based on an inhibition of hydration by hydrates themselves [39], impinging on each other’s growth [40,41]. Nevertheless, the decrease of the amount of near-surface $Q^0(h)$ species population at the onset of the deceleration period reflects a proportional decrease of the average surface area available to drive hydration by silicate dissolution. The decrease of the particles surface area as revealed here by NMR supports strongly the conclusions of recent modelling studies [42], namely that the deceleration stage results from the reduction of the average particle surface area available for reaction due to increasing surface coverage of the C$_3$S particles by hydration products. This conclusion is also supported by the fact that at 7 days 5% of the C$_3$S has not yet hydrated, bringing support to a coverage and passivation of its surface by deposited hydrates. Moreover, the long period during which $Q^0(h)$ remains constant suggests that during dissolution, the surface decrease due to the reduction in particle size is compensated by roughening (opening of etch pits and step retreat) [43]. In other words dissolution does not simply proceed by shrinking of the core of the particles, but also by etching.

### 4.3.5 Final C-S-H structure

The atomic site interconnectivities of different silicate species can be used to elucidate the molecular structures and lengths of silicate chains in the C-S-H. Such detailed insights can be obtained by using solid-state 2D $J$-mediated $^{29}$Si-$^{29}$Si correlation NMR techniques [23] that probe $J$-coupled $^{29}$Si-O-$^{29}$Si spin pairs and have been previously applied to establish silicate framework connectivities in a variety of heterogeneous materials [44–47]. Previously, Brunet et al. [48] have conducted 2D dipolar-mediated $^{29}$Si-$^{29}$Si NMR measurements that rely on through-space $^{29}$Si-$^{29}$Si dipolar couplings and which yield information on the molecular-level proximities of different $^{29}$Si moieties in synthetic C-S-H. However, such measurements cannot be used to directly establish the covalent connectivity among different $^{29}$Si moieties in the C-S-H structure. In contrast, by relying on through-bond $J$-interactions associated with
$^{29}$Si-O-$^{29}$Si moieties ($J$-interactions between $^{29}$Si spin pairs separated by more than two covalent bonds are negligibly small and consequently expected to be below the detection limits of the 2D $J$-mediated $^{29}$Si-$^{29}$Si NMR measurement) 2D $J$-mediated $^{29}$Si-$^{29}$Si double-quantum (DQ) correlation NMR measurements provide detailed insights regarding the tetrahedral site connectivity in the C-S-H chains. Notably, the 2D $J$-mediated $^{29}$Si-$^{29}$Si NMR spectrum of hydrated $^{29}$Si-enriched C$_3$S shown in Figure 4.4b provides significantly enhanced $^{29}$Si resolution, compared with the single-pulse $^{29}$Si MAS spectrum (Figure 4.4a), and unambiguously establishes distinct $^{29}$Si-O-$^{29}$Si covalent connectivities in the silicate chains.

The 2D $J$-mediated $^{29}$Si-$^{29}$Si NMR spectrum (Figure 4.4b) exhibits three well separated regions of correlated intensities in the Q$^1$ (approximately -79 ppm) and Q$^2$ (approximately -85 ppm) chemical shift ranges along the single-quantum (SQ)-DQ $y = 2x$ line, and two pairs of cross-correlated peaks between the Q$^1$ and Q$^2$ chemical shifts ranges. The broad continuous distribution of correlated chemical shifts in the 2D $^{29}$Si-$^{29}$Si spectrum between signals at -82 and -87 ppm in the $^{29}$Si SQ dimension are attributed to different $^{29}$Si-O-$^{29}$Si Q$^2$ moieties, consistent with the structural disorder of C-S-H. Interestingly, the spectrum reveals narrow (0.6 ppm FWHM) ridges of intensity correlations that are parallel to the SQ-DQ line. Such features typically arise from structural disorder on length scales (> 1 nm) that are larger than the distances between the $^{29}$Si-$^{29}$Si spin pairs (or also due to anisotropy in the magnetic susceptibility) [49]. The presence of such poor long-range structural order is consistent with the broad distributions of local $^{29}$Si environments that are associated with the heterogeneous nature of the C-S-H. Nevertheless, careful analysis of the 2D spectrum distinguishes discrete correlated signal intensities that are resolved to greater than a tenth of a ppm. Specifically, a strong correlated intensity (labelled $i$) between the $^{29}$Si signals centred at -84.8 and -85.4 ppm in the SQ dimension and at -170.2 ppm in the DQ dimension (Supplementary information, Figure 4.15) unambiguously establishes the presence of two
chemically distinct $Q^2$ $^{29}$Si species that are covalently bonded through a shared bridging oxygen atom. The different isotropic $^{29}$Si chemical shifts of these distinct $Q^2$ species likely reflect differences in the number and types of species in the C-S-H interlayer (calcium ions or proton moieties such OH groups or water molecules) that are in close ($<1$ nm) molecularlevel proximity to the non-bridging oxygen atoms of the four-coordinate silicate units. Indeed, the different electronegativities of Ca$^{2+}$ and H$^+$ result in different $^{29}$Si nuclear shielding, as shown by recent density functional theory calculations [50]. These molecular-level differences in the $Q^2$ species are shown in the schematic diagram (Figure 4.4a, inset) of a postulated structure of C-S-H that is consistent with the observed 2D NMR correlations (as well as previous experimental [33,18] and modelling analyses [17,51]). Although the $Q^{2L}$ resonances (the four-coordinate $Q^2$ silicate units that are positioned away from the interlayer space between two C-S-H chains, as shown in the inset in Figure 4.4) are not resolved in the spectrum, the external ridges of the $Q^2$ correlation spot correspond to correlated intensity between the $^{29}$Si SQ signals of the two $Q^2$ silicate species at -85.4 and -84.8 ppm with the $^{29}$Si SQ signals from the $Q^{2L}$ species to which they are, respectively, bound. Within this hypothesis and with the constraint that the DQ frequency must be the sum of the SQ frequencies, two additional correlations can be identified for the $Q^2$ species at SQ signals -85.4 and -84.8 ppm at DQ signals approximately -168.9 ppm (ii) and -168.1 ppm (iii), respectively, thus establishing the presence of two distinct $Q^{2L}$ species with SQ signals at -83.5 and -83.1 ppm. Furthermore, the same $^{29}$Si SQ signals at -85.4 and -84.8 ppm from the two $Q^2$ silicate species are also separately correlated with $^{29}$Si signals centred around -79 ppm (iv, v) (DQ = -164 ppm) from $Q^1$ species, further corroborating that these $Q^2$ species are indeed chemically distinct. Therefore, analyses of the 2D $J$-mediated $^{29}$Si-$^{29}$Si spectrum establish the occurrence of oligomeric silicate units with two distinct $Q^2$ and two distinct $Q^{2L}$ species in the C-S-H structure.
The partially resolved pair correlated intensities \((ix-xii)\) in the range of -77 to -80 ppm reveal the presence of different types of \(Q^1\) silicate species associated with at least four distinct dimeric C-S-H units. These results are further corroborated by differences in the spin–spin \((T_2)\) relaxation-time behaviours of the associated \(^{29}\text{Si} Q^1\) species, which were exploited to provide improved \(^{29}\text{Si}\) resolution by using 1D \(T_2\)-filtered \(^{29}\text{Si}\) MAS measurements (Supplementary information, Figure 4.16). In combination, the different pair correlated intensities establish the presence of dimeric units \((ix-xii)\) and C-S-H chains that consist of two distinct \(Q^1-Q^2 (iv, v)\) and \(Q^2-Q^{2L} (ii, iii)\) connectivities and at least one \(Q^2-Q^2 (i)\) connectivity. To accommodate this diversity of atomic connectivity revealed by the 2D \(^{29}\text{Si}\{^{29}\text{Si}\} \) NMR measurements, the C-S-H structure must contain a linear chain of at least eight four-coordinated silicate units (that is, an octamer). A similar analysis of pair correlated intensities \(vi-viii\) indicate the presence of pentameric C-S-H units, as discussed in the Supplementary information, section 4.6.6. This result is supported by recent studies using density functional theory that have evaluated the relative stabilities of linear C-S-H units of different chain lengths and proposed the presence of stable octameric units [52], for which no direct experimental evidence has previously been available.
Figure 4.4. Molecular structures and silicate site connectivities in partially polymerized calcium silicate hydrates. a), b) Solid-state a) 1D single-pulse $^{29}$Si MAS and b) 2D $J$-mediated $^{29}$Si-$^{29}$Si correlation NMR spectra of hydrated (1.5 month, 25 °C) $^{29}$Si-enriched triclinic C$_3$S. The lowest contour lines in the 2D spectrum are 9% of the maximum signal intensity. The ‘double-quantum’ filter used to acquire the spectrum in (b) enables selective detection of pairs of signals ($i, j$) from distinct $^{29}$Si nuclei that are covalently bonded. Consequently, the 2D spectrum exhibits intensity correlations between $^{29}$Si signals at distinct frequencies ($\omega_i, \omega_j$) from $^{29}$Si-O-$^{29}$Si spin pairs ($i, j$) in the horizontal SQ dimension (isotropic $^{29}$Si chemical shifts) and at the sum of these frequencies ($\omega_i + \omega_j$) in the vertical DQ dimension. Therefore, correlated intensities at these specific positions in the 2D spectrum unambiguously establish the presence of covalently bonded $^{29}$Si silicate species corresponding to the distinct isotropic $^{29}$Si chemical shifts. The inset in (a) shows a schematic diagram of the different silicate moieties present in the C-S-H with double-headed arrows indicating the $J$-interactions.
in $^{29}\text{Si}$-$\text{O}$-$^{29}\text{Si}$ species that are established by the intensity correlations in the 2D spectrum, specifically from dimeric (green), pentameric (blue), or octameric (red) units. For sake of clarity, the calcium layers are not represented.

The relative populations of $^{29}\text{Si}$ silicate species associated with C-S-H units of different chain lengths (for example, dimers and octamers) are determined based on the enhanced $^{29}\text{Si}$ resolution afforded by the 2D $^{29}\text{Si}$($^{29}\text{Si}$) NMR spectrum. Specifically, the single-pulse $^{29}\text{Si}$ MAS spectrum shown in Figure 4.5a can be simulated by using the peak positions of $^{29}\text{Si}$ signals as established by the 2D $^{29}\text{Si}$($^{29}\text{Si}$) NMR spectrum and the relative fractions of Q$^1$, Q$^2$ and Q$^{2L}$ species associated with C-S-H units of different chain lengths (for example, Q$^2$/Q$^1 = 2$, Q$^2$/Q$^{2L} = 2$ for octamer as shown in Figure 4.5b). Such an analysis yields estimates of 44, 7 and 42% ($\pm$ 4%) for the relative populations of $^{29}\text{Si}$ silicate engaged in octameric, pentameric and dimeric units, respectively. These values correspond to 20 mole% octamers, 5 mole% pentamers and 75 mole% dimers in the C-S-H. The salient result is, thus, that despite the fact that the average chain length is 5, pentamers are actually a minority feature. Such distributions of chain lengths are consistent with previous studies that have reported mean chain lengths for C-S-H, which suggest the presence of pentamers and octamers, in addition to dimers [22,53–55]. It must be understood that the high amount of octamers was obtained here in a relatively short hydration times (1.5 month) compared with what would be required in a usual cement paste. Specifically, the use of pure C$_3$S, the high surface area (4.4 m$^2$/g) of the non-hydrated sample and the water-to-solids ratio (0.8) used in this study are expected to result in relatively fast hydration kinetics and a faster precipitation of C-S-H. The end result is a higher extent of hydration and silicate cross-linking. Interestingly, the analysis also indicates that small quantities of monomeric $^{29}\text{Si}$ silicate species, such as hydroxylated Q$^0$(h) (5 ± 1%) and anhydrous Q$^0$ (2 ± 1%), are present even after hydration of C$_3$S for 1.5 months at 25 °C. These monomers likely arise from remnants of surface hydroxylation of C$_3$S particles or are
components of the C-S-H structure, which is consistent with recent numerical modelling results [51].

Figure 4.5. Relative populations of $^{29}$Si silicate species in hydrated triclinic C$_3$S. 
a) Solid-state 1D single-pulse $^{29}$Si MAS spectrum (black) of hydrated (1.5 month, 25 °C) $^{29}$Si-enriched C$_3$S and corresponding simulated fit (red) to the spectrum based on the signal decompositions shown in (b). b) Signal decompositions and relative populations of the different $^{29}$Si moieties that comprise anhydrous Q$^0$, Q$^0$(h), and octameric, pentameric and dimeric C-S-H units, which contribute to the simulated fit (red) in (a). Insets in (b) show schematic diagrams of the possible types of C-S-H units and the associated silicate moieties.
4.4 Conclusions

The carefully synthesized $^{29}$Si-enriched sample enables, for the first time, 2D $J$-mediated (through $^{29}$Si-O-$^{29}$Si bonds) $^{29}$Si{$^{29}$Si} NMR measurements that provide detailed insights regarding the different silicate species, their respective site connectivities, and relative populations, especially for previously unidentified discrete silicate moieties in the C-S-H. Consequently, the lengths of C-S-H chains and the relative populations of associated silicate species are determined, which can be used to evaluate the validity of molecular models for Portland cement hydration that have been previously proposed in the literature [17,21,51]. This opens new perspective for understanding the complex molecular-level mechanical properties of C-S-H.

Solid-state $^{29}$Si NMR measurements of $^{29}$Si-enriched triclinic C$_3$S also enable the transient silicate speciation and polymerization in the developing C-S-H structure to be monitored and quantified as a function of hydration time, especially during the crucial induction, acceleration and deceleration stages. Importantly, hydroxylated monomeric (Q$^0$(h)) silicate species can be detected and quantified by using $^{29}$Si{$^1$H} CP/MAS NMR measurements to monitor changes in surface composition with the progress of hydration. The NMR results presented here establish that nonhydrated C$_3$S particle surfaces predominantly consist of Q$^0$(h) silicate species with negligible quantities of Q$^1$ and Q$^2$ hydration products, including for the pre-induction and induction stages of the hydration process. Such detailed insights of silicate-water mixtures have heretofore been challenging and often infeasible to determine by other characterization techniques due to the low absolute quantities, complicated structures and poor longrange order of the hydroxylated surface species. Compared with the induction period, the onset of silicate polymerization (that is, Q$^1$ and/or Q$^2$ species) during hydration corresponds to the formation of dimeric units in C-S-H during the acceleration stage, consistent with previous cement
literature. Interestingly, during the deceleration stage the hydration rate reduces (at a hydration level of 50%) before any significant reduction of the $Q^0(h)$ populations are observed at the C$_3$S surface. This corresponds to a relatively fast decrease in the reaction rate compared with the rate of reduction of the hydroxylated species available for reaction at the surface, which indicates that part of the surface is likely covered by C-S-H products. These results are consistent with previous studies that suggest that the rate of hydration is controlled by the surface coverage of C-S-H species during the deceleration stage [42]. Calculations based on a shrinking core model (hydration reaction slows down due to consumption of the particles) indicate that for monodispersed spherical particles, a decrease in volume by a factor of 0.5 would be accompanied by a decrease in surface area by a factor 0.63 ($2^{-2/3}$). C$_3$S particles are neither spherical nor monodisperse but the present NMR results are definitely not compatible with a shrinking core model. Consequently, the surface area available for reaction is clearly modified by the surface roughness produced by dissolution driven etching of the surface [43].

The relations directly observed here for the first time between surface passivation and etching phenomena on the one hand and the succession of the induction, acceleration and deceleration stages of hydration of C$_3$S on the other hand, provide new understanding for the occurrence of this complex kinetic behaviour actually observed in a variety of silicate systems. C$_3$S, because of its high reactivity, constitutes an interesting model for understanding long term silicate hydration processes occurring during geochemical weathering or hydrothermal synthesis [29].
4.5 References


4.6 Supplementary information

4.6.1 Synthesis of $^{29}$Si-enriched C$_3$S

Pure C$_3$S with $^{29}$Si isotopic enrichment was synthesized by the solid-state reaction method:

$$3 \text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_3\text{SiO}_5 + \text{CO}_2 \uparrow$$  \hspace{1cm} (4.2)

Precursors CaCO$_3$ (≥ 99%, Sigma Aldrich) and SiO$_2$ (99.9% enriched in $^{29}$Si, Cortecnet) in a 2.94 : 1 mass ratio were dry homogenized in a turbula for 24 h. Batches of approximately half a gram of the resulting powder were pressed into 1 cm pellets under a 25 kN load and fired afterwards in a platinum crucible at 1600 °C for 8 h. Since the triclinic C$_3$S is a metastable phase, which tends to dissociate into CaO and Ca$_2$SiO$_4$ [1], pellets were quenched by fast cooling under an air gun. To reach the full transformation of the starting materials into the desired triclinic phase, the whole procedure was repeated 4 times, until no reflections due to free lime (CaO) were observed by X-ray diffraction.

Loss of SiO$_2$ during the homogenization process was unavoidable due to the strong electrostatic attraction of SiO$_2$ particles to the walls of the plastic container. Consequently, deviation from the stoichiometric ratio was necessary to prevent CaO from remaining in the final material.

The final material was ground using an agate mortar and then with absolute ethanol in a micronizing mill (McCrone) with agate grinding elements for 10 min. Absolute ethanol was used to ensure a better dispersion of the particles and to prevent heating that may otherwise result in undesirable structural modifications of the C$_3$S.
4.6.2 Characterization of $^{29}\text{Si}$-enriched $\text{C}_3\text{S}$

$^{29}\text{Si}$-enriched $\text{C}_3\text{S}$ was characterized by X-ray diffraction (Figure 4.6) using a Bruker AXS D8 diffractometer ($\text{Co K}_\alpha$, $\lambda = 1.7903$ Å). $2\theta$ was scanned between 4 and 90º by steps of 0.02º. The X-ray tube was operated at 40 kV and 30 mA. Rietveld analyses were performed using the AutoQuan software and confirmed the triclinic crystal structure of the final material establishing the absence of any significant amounts of impurities with long-range structural order (refinement factor “weighted pattern” $R_{wp} = 8.7\%$).

The $^{29}\text{Si}$-enriched $\text{C}_3\text{S}$ was also characterized by solid-state NMR using $^{29}\text{Si}$, $^1\text{H}$ one-pulse and $^{29}\text{Si}\{^1\text{H}\}$ CP experiments. The $^{29}\text{Si}$ one-pulse NMR spectrum (Figure 4.7) shows 8 $^{29}\text{Si}$ resonances corresponding to the 9 distinct crystallographically inequivalent Si-sites in triclinic $\text{C}_3\text{S}$ (two overlapping $^{29}\text{Si}$ resonances are observed at -73.2 ppm) [2]. With the help of $^1\text{H}$ one-pulse and $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR, it was possible to retrieve information concerning the initial state of the sample. It was found out that the material adsorbed water either during storage or milling since peaks at 0.9 ppm (-Ca-O-H), 1.3 ppm (-Si-O-H) and 5.0 ppm (H$_2$O) were observed in the $^1\text{H}$ NMR spectrum (Figure 4.8). The $^{29}\text{Si}\{^1\text{H}\}$ CP NMR spectrum exhibited a signal centered at -72 ppm, which confirmed the presence of $\text{Q}_0^\text{h}$ species, even before mixing with water (Figure 4.9).

The specific particle size distribution (PSD) (Figure 4.10) was measured by laser diffraction (Mastersizer, Malvern Instruments) after dispersion of the $^{29}\text{Si}$-enriched $\text{C}_3\text{S}$ in isopropanol. The surface area of the final $\text{C}_3\text{S}$ powder was $4.38 \pm 0.02$ m$^2$/g. It was measured using a BET multi-point physisorption apparatus (Micromeritics Tristar II 3020). The sample was degassed in an external degassing station (VacPrep 061 from Micromeritics) at 200 ºC for 1 h.
Figure 4.6. XRD pattern of as-synthesized pure triclinic $^{29}$Si-enriched C$_3$S.

Figure 4.7. Solid-state $^{29}$Si MAS NMR spectrum of as-synthesized $^{29}$Si-enriched C$_3$S.
Figure 4.8. Solid-state $^1$H MAS NMR spectrum of as-synthesized (before hydration experiments) $^{29}$Si-enriched C₃S.

Figure 4.9. Solid-state $^{29}$Si{$^1$}H CP/MAS NMR spectrum of as-synthesized (before hydration experiment) $^{29}$Si-enriched C₃S.
Figure 4.10. PSD of as-synthesized $^{29}\text{Si}$-enriched $\text{C}_3\text{S}$.

4.6.3 Note 1. Quantitative comparison between isothermal calorimetry and NMR

4.6.3.1 Quantitative analysis of the NMR spectra

The originality of the NMR results presented here lies mainly in their quantitative analysis. This is not trivial as CP experiments are known to provide signal intensities that depend on several parameters, namely the Hartman-Hahn matching, the relaxation rates, the dipolar coupling, molecular mobility, and the extent of the proton bath. It is thus important to provide in detail the procedure followed that allowed seamless quantification based on the CP and one-pulse experiments.

All one-pulse NMR experiments were performed with identical acquisition conditions. The same is true for the CP experiments (see section 4.2.1).

From the NMR spectra in the frequency domain, the integrated intensity corresponding to each chemical environment $Q_n$, was determined by decomposition of the $^{29}\text{Si}$ one-pulse and $^{29}\text{Si}\{^1\text{H}\}$
CP/MAS spectra using the program DMFit 2011 [3]. To fit the signals a mixture of Gaussian (G) and Lorentzian (L) functions was applied as a model, which was kept constant together with the position and width for each specific resonance throughout the analyses of the NMR spectra (Table 4.1).

Table 4.1. Fit parameters for each type of $^{29}$Si environments in hydrated C$_3$S.

<table>
<thead>
<tr>
<th>chemical environment</th>
<th>One-pulse spectra</th>
<th>2$^{9}$Si $^{1}$H} cross-polarization spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>chemical shift (ppm)</td>
<td>Q$^0$</td>
</tr>
<tr>
<td></td>
<td>width (ppm) xG/(1-x)L</td>
<td>-68.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td></td>
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<td>0</td>
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</table>

After all integrated intensities were obtained, they were normalized to the number of scans, receiver gain and mass of C$_3$S used for the measurements. The normalized intensities obtained by one-pulse and cross-polarization at a given time $t$ are noted $I_{op}^n(t)$ and $I_{cp}^n(t)$ respectively.

Because a fully relaxed one-pulse NMR signal is directly proportional to the number of exited spins (here $^{29}$Si) and because the number of $^{29}$Si atoms introduced in the rotor is constant for a given hydration experiment, $I_{op}^n(t)$ can be expressed directly in arbitrary units of atoms of Si per mass of C$_3$S.

In contrast, the cross-polarization NMR spectra are affected by the spins relaxation and polarization transfer dynamics [4]. In samples with natural abundance $^{29}$Si, the heat capacity
of the silicon spin systems can be neglected compared to the one of the protons. Considering further that the relaxation of the silicon nuclei is much slower than the one of the protons, the cross-polarization dynamics between the $^{29}\text{Si}$ and the $^{1}\text{H}$ can be modelled as the superimposition of two first-order kinetics, namely the one of the $^{1}\text{H}$ relaxation in the rotating frame and the one of the polarization transfers between each $^{29}\text{Si}$ species and a unique $^{1}\text{H}$ bath [5]. In $^{29}\text{Si}$-enriched samples however, the assumption that the $^{29}\text{Si}$ spin heat capacities can be neglected versus the one of the $^{1}\text{H}$ falls. Consequently, there is no analytical solution to the set of differential equations describing the polarization intensity as a function of the contact time and the only option is to assess the relative heat capacities of each silicon spin bath by numerical modelling, as discussed by I. Klur in his doctoral thesis [6]. To avoid this lengthy procedure, it was preferable to calibrate the cross-polarization response at a given contact time with respect to the quantitative one-pulse response. The following procedure was followed.

At a given contact time (5 ms), $I_{\text{cp}}^n(t)$ is measured (note that $t$ is the hydration time, not the contact time of the CP experiment) (Figure 4.11). $I_{\text{cp}}^n(t)$ is proportional to the number of $^{29}\text{Si}$ spins but the proportionality constant $(k^n)$ between the quantitative one-pulse and the CP intensities for the chemical environment $Q^n$,

$$k^n = \frac{I_{\text{op}}^n(t)}{I_{\text{cp}}^n(t)}, \quad (4.3)$$

is an unknown function of the experimental conditions (Hartman-Hahn mismatch, rotation speed, contact time). It strongly depends on the acquisition conditions of the cross-polarization spectra but will be a constant for a given chemical environment if these conditions are not varied as is the case in the present study. $k^n$ is thus obtained by comparison of the CP intensities, $I_{\text{cp}}^n(t)$, with the quantitative one-pulse ones, $I_{\text{op}}^n(t)$, at hydration times when both experiments provide a satisfactory signal to noise ratio.
Figure 4.11. Polarization growth curve on C₃S hydrated for 90 days. The bar marks the 5 ms contact time used to measure \( I(t) \) and from which the quantitative intensities \( (\cdot) \)' are derived. The continuous curves are fits to equation 4.8.

In practice, \( k^n(t) \) is evaluated for hydration time \( t \) 21 h, 72 h, 168 h and 672 h, and the average \( \overline{k}^n \) is calculated. The values are reported in the Table 4.2.

At shorter time when only the CP spectra can be obtained, this allowed to estimate a quantitative cross-polarization “one-pulse-like” intensity, \( I^\circ_{cp}(t)' \), by inverting equation 4.3

\[
I^\circ_{cp}(t)' = \overline{k}^n \times I^\circ_{cp}(t)
\]

(4.4)

Table 4.2. Average measured values.

<table>
<thead>
<tr>
<th>( \overline{k}^1 )</th>
<th>( \overline{k}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.06 ± 0.02</td>
<td>0.94 ± 0.25</td>
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Since the $Q^0(h)$ species is a minor occurrence not revealed with sufficient resolution by one-pulse NMR, $I_{cp}^{0(h)}$ is not measurable in that manner. It was thus assumed that the true proportion of the $Q^0(h)$ resonance in the CP spectra was close to the one in the one-pulse spectra (which is equivalent to make the approximation of a common $k^*$ value for all silicon species)

$$\frac{I_{cp}^{0(h)}(t)'}{I_{cp}^1(t)'+I_{cp}^2(t)'} = \frac{I_{cp}^{0(h)}(t)}{I_{cp}^1(t)+I_{cp}^2(t)}$$

(4.5)

and thus that $I_{cp}^{0(h)}(t)'$ can be estimated from the one-pulse and CP spectra decomposition through

$$I_{cp}^{0(h)}(t)' = \left[\frac{1}{k^*}I_{cp}^1(t) + \frac{1}{k^*}I_{cp}^2(t)\right] \frac{I_{cp}^{0(h)}(t)}{I_{cp}^1(t)+I_{cp}^2(t)}$$

(4.6)

When the $Q^1$ and $Q^2$ resonances where not observable in the CP spectra ($t < 1h$), $I_{cp}^0(t < 1h)'$ was obtained simply by comparing with the intensity at later time:

$$I_{cp}^{0(h)}(t \leq 1h)' = I_{cp}^{0(h)}(t > 1h) \frac{I_{cp}^{0(h)}(t \leq 1h)}{I_{cp}^{0(h)}(t > 1h)}$$

(4.7)

This simplified procedure is an approximation as in principle, the polarization transfer efficiency, and thus the conversion coefficient $k$ is expected to differ for each $Q^p$ resonance. This approximation was validated in the following manner. On a selected sample (hydration time 90 days), the quantitative intensity was extracted from a full polarization signal build-up curve (Figure 4.11), neglecting the heat capacity of the silicon spin bath using the usual polarization growth relation and adjusting the polarization transfer and relaxation parameters $T_{cp}$ and $T_{1p}^H$

$$I_{cp}^n(t) = \frac{1}{1-T_{cp}/T_{1p}^H} \left[ \exp\left(-t_{cp}/T_{1p}^H\right) - \exp\left(-t_{cp}/T_{cp}\right) \right]$$

(4.8)
where the Hartman-Hahn mismatch $\alpha$ only acts as a constant scaling factor.

The resulting relative intensities were found to be within 5% of the ones obtained by our simplified procedure.

Finally, $Q^n(t)$, the proportion of silicon atoms in each $Q^n$ environment in arbitrary units at hydration time $t$ is obtained from the CP spectra through

$$Q^n(t) = I_{cp}^n(t) = k^n \times I_{cp}^n(t)$$

for hydration times up to 10 h, \(4.9\)

and from the one-pulse spectra directly through

$$Q^n(t) = I_{op}^n(t)$$

for longer hydration times. \(4.10\)

4.6.3.2 Validation of the NMR quantitative analysis by comparison with isothermal calorimetry

The degree of reaction ($\alpha$) was calculated based on NMR quantitative analyses and compared with the value obtained by calorimetric measurement (Figure 4.12). The values based on NMR data were calculated according to the following equations:

$$\alpha = 1 - \frac{Q^0(t)}{Q^0(t=0)}$$ \(4.11\)

and

$$\alpha = \frac{Q^{0(h)}(t) + Q^1(t) + Q^2(t)}{Q^0(t=0)}$$ \(4.12\)

The NMR data matched the calorimetry results thus establishing the validity of the NMR quantitative analysis.
Figure 4.12. Comparison of the degree of reaction calculated from quantitative NMR results (in red) and isothermal calorimetry (in blue).

4.6.4 Note 2. Isothermal calorimetry

Since the sample temperature in the in situ NMR measurements may deviate from "room temperature" as a result of frictional heating during MAS experiments, calorimetric measurements were performed to assess potential frictional heating artefacts (Figure 4.13). Indeed, this effect has been evaluated to account for a 4 °C increase under our experimental conditions using the lead nitrate procedure [7,8]. Following our protocol for the NMR measurements, after 6 h of hydration the paste was removed from the ZrO\textsubscript{2} rotor to prevent its hardening inside the rotor and the subsequent loss of the rotor. The NMR measurements were continued on the part of the sample previously set aside in the closed vial and stored at room temperature.

The maximum possible consequences of a 4 °C temperature variation are illustrated with the isothermal calorimetry measurements represented in Figures 4.13 and 4.14. These were run with C\textsubscript{3}S paste at 27 and 23 °C. The first three hours are identical, with a difference emerging
only between 3 and 6 hours. In fact, this explains the slight observed difference at that time in the comparison between NMR and calorimetry data of Figure 4.2c. The cumulative effect of this temperature variation was appreciated by measuring the heat release of the paste at 23 °C for the first 7 h and then moving the sample to another calorimeter set at 27 °C for the remaining experimental time. The heat flow (and thus the advancement of hydration) obtained during this measurement is very close to the one observed at 23 °C. It can thus be concluded that the effect of the frictional heating during MAS is negligible under our experimental conditions.

![Figure 4.13](image.png)

**Figure 4.13. Hydration of C₃S at 23 and 27 °C studied by isothermal calorimetry.**
Figure 4.14. Heat release rate during hydration of C₃S studied by isothermal calorimetry at 23 °C (cyan), 27 °C (red) and under a combined cycle of 7 h at 23 °C followed by an increase to 27 °C (black). The gap corresponds the time needed to switch the sample between the calorimeters and to stabilize the equipment.
Figure 4.15. Site connectivity in C-S-H. a), b) 1D $^{29}$Si spectra that are slices at different DQ $^{29}$Si chemical shifts from the 2D $J$-mediated $^{29}$Si-$^{29}$Si correlation NMR spectrum (Figure 4.4b). Different pairs of intensity correlations (labelled by roman numerals in the 2D spectrum) between $^{29}$Si signals at distinct frequencies ($\omega_i$, $\omega_j$) in the SQ dimension (isotropic $^{29}$Si chemical shifts) and at the sum of these frequencies ($\omega_i + \omega_j$) in the DQ dimension (indicated for each slice) unambiguously establish that the associated distinct $^{29}$Si species ($i$, $j$) are covalently bonded through a shared bridging oxygen atom. The spectra in (b) are identical to those in (a), but shown over a narrower SQ $^{29}$Si chemical shift range (-75 to -90 ppm). The DQ $^{29}$Si chemical shifts and signal-to-noise ratios (S/N) are indicated for each slice.
Figure 4.16. Different extents of silicate polymerization in C-S-H. a)-c) Solid-state 1D a) single-pulse $^{29}$Si, b) $^{29}$Si{$^1$H} CP, and c) $T_2$-filtered $^{29}$Si{$^1$H} CP/MAS spectra of hydrated (1.5 month, 25 °C) $^{29}$Si-enriched triclinic C$_3$S. The spectra were acquired at a) 18.8 T, 12.5 kHz MAS, 25 °C or b), c) 11.7 T, 4.6 kHz MAS, 25 °C. In (c), a nuclear spin-spin ($T_2$) relaxation-time filter ($t_{T2}$) of 20 ms and a $^{29}$Si 180° pulse were applied before signal detection, to detect selectively $^{29}$Si species with long (> 20 ms) $T_2$ relaxation times. The inset in (c) shows a magnified version of the spectrum over the chemical shift range of -75 to -80 ppm.

The quantitative single-pulse $^{29}$Si MAS spectrum (Figure 4.16a) reveals signals from all anhydrous and hydrated $^{29}$Si species, including Q$^0$, Q$^1$, and Q$^2$ moieties, as previously discussed in the main text of the manuscript. In contrast, the $^{29}$Si{$^1$H} CP/MAS experiment selectively detects $^{29}$Si nuclei that are dipole-dipole-coupled to $^1$H nuclei and thus are in close (< 1 nm) molecular-level proximity. Correspondingly, the $^{29}$Si{$^1$H} CP/MAS spectrum exhibits $^{29}$Si signals centred at -73 ppm (from Q$^0$(h) species), -79 ppm (from hydrated Q$^1$ species), and -85 ppm (from hydrated Q$^2$ species) that arise from $^{29}$Si species in silicate hydration products. The relative intensities of the $^{29}$Si signals in the $^{29}$Si{$^1$H} CP/MAS
spectrum depend on the strengths of the heteronuclear $^{29}\text{Si}^{-1}\text{H}$ dipole-dipole couplings, which are determined by the molecular proximities and mobility of the associated chemical species. Nevertheless, signals with similar isotropic $^{29}\text{Si}$ chemical shifts, but with different relative intensities, are observed in the spectra in Figure 4.16a,b.

By comparison, improved spectral resolution can be achieved by exploiting differences in the nuclear spin-spin ($T_2$) relaxation times of different hydrated silicate species to resolve their otherwise overlapping $^{29}\text{Si}$ signals. The $T_2$ relaxation times are sensitive to molecular structures and proximities of $^{29}\text{Si}$ species to dipole-dipole-coupled species, including $^1\text{H}$ moieties, and consequently can be used to distinguish their associated $^{29}\text{Si}$ NMR signals. This is accomplished by applying a $T_2$-filter ($t_{T2}$), during which signals from fast-relaxing $^{29}\text{Si}$ species ($T_2 < t_{T2}$) decay away, followed by a $^{29}\text{Si}$ 180° pulse (Hahn-echo-like technique) prior to the $^{29}\text{Si}$ NMR signal detection. The resulting signal consists of contributions exclusively from slow relaxing ($T_2 > t_{T2}$) $^{29}\text{Si}$ species in the calcium silicate hydrates. The calcium silicate hydrates exhibit strong through-space dipole-dipole-couplings between $^{29}\text{Si}$ and $^1\text{H}$ nuclei due to the abundance of $^1\text{H}$ species, including from hydroxyl moieties and water molecules, which are present in close ($<1$ nm) molecular proximity of the silicate species. The magnitude of the $T_2$ relaxation time is attenuated by the increased strengths of the dipolar couplings, which consequently depend on molecular proximities and mobility. In $^{29}\text{Si}$-enriched solids, as in the present case, the $^{29}\text{Si}^{-1}\text{H}$ dipole-dipole-couplings are further strengthened due to the significantly greater fractions of $^{29}\text{Si}$ nuclei compared to natural abundance conditions (4.7%), which correspondingly reduce the $^{29}\text{Si}$ $T_2$ relaxation times. These molecular-level structural differences are manifest in Figure 4.16c as resolved $^{29}\text{Si}$ signals from the distinct silicate species, which were previously indistinguishable (Figure 4.16a,b). For example, the $T_2$-filtered $^{29}\text{Si}^{-1}\text{H}$ CP/MAS spectrum exhibits partially resolved $^{29}\text{Si}$ signals at -77.7 and -78.9 ppm from chemically distinct $Q^1$ species that are associated with long $T_2$ relaxation times ($>20$ ms). Such
structural differences in the $^{29}$Si environments of Q$^1$ species that result in long $T_2$ relaxation times arise from their different proximities to water molecules and hydroxyl moieties, which influence the strengths of the heteronuclear $^{29}$Si-1H dipolar couplings. The $^{29}$Si signal at -77.7 ppm (from Q$^1$ species) is consistent with the presence of dimeric C-S-H units that exhibit similar isotropic chemical shifts, as established based on the 2D $J$-mediated $^{29}$Si{$^{29}$Si} spectrum (Figure 4.5b). Additional $^{29}$Si signal intensity is resolved at ca. -82 ppm and is attributed to Q$^{2L}$ species. These results corroborate and complement the analyses of the 2D $^{29}$Si{$^{29}$Si} spectrum, thereby increasing the confidence associated with the signal assignments and analysis of the silicate site connectivity.

4.6.6 Note 4. Commentary on 2D $J$-mediated $^{29}$Si{$^{29}$Si} NMR spectrum in Figure 4.4b

Analyses of the pair correlated intensities in 2D $^{29}$Si{$^{29}$Si} NMR spectrum of hydrated (1.5 month, 25 °C) $^{29}$Si-enriched C$_3$S shown in Figure 4.4b indicates the presence of pentameric C-S-H units, in addition to the octameric and dimeric units discussed in the main text of the manuscript.

A pentameric C-S-H unit consists of covalently bonded species with the sequence Q$^1$-Q$^2$-Q$^{2L}$-Q$^2$-Q$^1$ and thus does not present -Q$^2$-Q$^2$- connectivity. The latter can be observed only in an octamer Q$^1$-Q$^2$-Q$^{2L}$-Q$^2$-Q$^2$-Q$^{2L}$-Q$^2$-Q$^1$ or in longer chains. (Q$^{2L}$, the so-called bridging tetrahedral, are four-coordinate Q$^2$ silicate moieties that are positioned away from the interlayer space between C-S-H chains and link dimers, as shown in the inset in Figure 4.4.) A series of connectivities including Q$^1$-Q$^2$, Q$^2$-Q$^{2L}$ but no Q$^2$-Q$^2$ connectivities is thus a signature of pentamers. The 2D $J$-mediated $^{29}$Si{$^{29}$Si} NMR spectrum in Figure 4.4b reveals correlated intensities between the $^{29}$Si SQ signal at -84.4 ppm from Q$^2$ species and -82.2 ppm (DQ = -166.6 ppm, vi), -79.7 ppm (DQ = -164.1 ppm, vii), and -78.2 ppm (DQ = -162.5 ppm, viii) that are associated with Q$^{2L}$ species and two distinct Q$^1$ species, respectively. Therefore,
the pairs of correlated intensities labelled \( vi, vii, \) and \( viii \) in the 2D spectrum (Figure 4.4b) establish the presence of one \( Q^2\)-\( Q^{2L} \) and two distinct \( Q^2\)-\( Q^1 \) connectivity, respectively, in the associated C-S-H unit. Furthermore, there is no detectable correlated intensity, within the sensitivity limits of the measurement, between this \( Q^2 \) species with a \(^{29}\)Si SQ signal at -84.4 ppm and any other resonance in the \( Q^2 \) range (only with \( Q^{2L} \) and \( Q^1 \) as stated above). This indicates that the associated C-S-H unit exhibits no direct \( Q^2\)-\( Q^2 \) connectivity, and thus, must be attributed to pentamers, as shown in the inset of Figure 4.5b. This is in agreement with the previously proposed relative stabilities of C-S-H units of different chain lengths [9,10].
4.6.7 Supplementary references


5. Paper III: Impact of aluminates on silicates hydration

This chapter consists of the reviewed conference paper “Impact of aluminates on silicates hydration”. It was published in the proceedings of the Second International Conference on Concrete Sustainability (ICCS 2016), which was held in Madrid, Spain. (E. Pustovgar, J.-B. d’Espinose de Lacaillerie, M. Palacios, A. Andreev, R. Mishra, R.J. Flatt, Impact of aluminates on silicates hydration, II International Conference on Concrete Sustainability (ICCS 2016), Madrid, 1260 - 1271)

This paper is the preliminary study concerning the effect of aluminates produced on the hydration of silicates. It is the first step towards understanding of the reaction mechanism.

Ms Pustovgar performed all experimental part, analyzed the data and entirely wrote the paper under the guidance of Prof. Flatt, Prof. d’Espinose de Lacaillerie and Dr. Palacios. Dr. Andreev and Prof. d’Espinose de Lacaillerie helped with the NMR investigations. All authors participated in the discussion of the results.
Abstract

Replacement of clinker by supplementary cementitious materials (SCMs) is one of the most promising routes to decrease the carbon footprint and embodied energy of Portland cement. However, increasing amounts of alumina-rich SCMs leads to a delay of cement hydration and a decrease of early mechanical strength.

In this study, the passivation induced by aluminates on silicates hydration was investigated at the molecular level using nuclear magnetic resonance (NMR). In situ $^{27}$Al magic angle spinning (MAS) NMR experiments allowed quantifying tricalcium silicate (C$_3$S) hydration in presence of different concentration of aluminates. Since the natural abundance of $^{27}$Al is practically 100%, the NMR sensitivity is sufficient to realize this characterization in situ with the necessary time-resolution. The advantage of this approach is that the sample is not dried thus insuring that the calcium silicate hydrates (C-S-H) structure is not perturbed. This study was complemented with isothermal calorimetry tests. The effect of specific surface area (SSA) of C$_3$S on its hydration kinetics was also evaluated.

Results have shown that the delay of silicates hydration increases with the increase of aluminates concentration and the most pronounced effect is observed when coarser C$_3$S is used. Furthermore, the presence of aluminates in solution promotes the formation of AFm phases that are converted into another aluminate phase at later time of hydration.
5.1 Introduction

Portland cement is the most widely used manufactured material and its production contributes to 5 – 8% of the worldwide CO$_2$ emissions thus playing a significant role in the climate change [1]. There are several strategies to minimize this effect, and clinker substitution is currently the most effective one. The use of alumina-rich SCMs such as slag, fly ashes as clinker replacement reduces the embodied emissions in cement; however, blended cements react slower than Portland cement compromising the early mechanical strength of cement and concrete [2]. To create the binder of tomorrow, fundamental knowledge has to be obtained with respect to the possible interactions between the main mineral components of blended cements. In particular, the possible delay of silicates hydration induced by the aluminates [3].

The passivating effect of dissolved aluminium on the dissolution rate of silicates has already been investigated to some extent in geochemistry [4-8] and the following possible mechanisms were proposed:

(a) formation of an insoluble silicates layer on the surface of silica due to the presence of dissolved aluminium [5]

(b) incorporation of aluminum into the silica framework [6,8] and

(c) adsorption of aluminate ions on silanol sites [7].

In the case of cementitious systems, the effect of aluminate ions has been also investigated [9-11]. Nicoleau et al. [9] concluded that under particular pH and Ca$^{2+}$ concentration C$_3$S hydration is inhibited due to covalent bond formation between the aluminate ions and the silicate surface. In addition, Suraneni and Flatt [10] suggested that aluminate ions may act inhibiting step retreat rather than the opening of etch pits. Quennoz and Scrivener [11] discussed poisoning effect produced by aluminates acting mainly during nucleation and growth of C-S-H. Moreover, incorporation of Al into the C-S-H has been researched by NMR [12-19],
that proved the formation of species containing pentahedral and octahedral aluminium. However, the passivation mechanism induced by aluminate ions still remains unclear.

The main objective of this work is to understand the effect of aluminates on the hydration of the main cement phase – $\text{C}_3\text{S}$. For this reason, $\text{C}_3\text{S}$ hydration in presence of aluminates has been followed by isothermal calorimetry as well as by $^{29}\text{Si}$ and $^{27}\text{Al}$ solid-state NMR techniques.

5.2 Experimental

5.2.1 Materials

Pure triclinic $\text{C}_3\text{S}$ was synthesized from stoichiometric quantities of $\text{CaCO}_3$ and $\text{SiO}_2$ (> 99% pure, Sigma Aldrich). 10 g pellets pressed under a 350 bar load were fired in a platinum crucible at 1600 °C for 8 h and immediately quenched under a flow of compressed air to stabilize $\text{C}_3\text{S}$ [20]. The final material was ground in a micronizing mill (McCrone) with agate grinding elements in order to achieve 3.6, 1.4 or 0.8 m$^2$/g BET SSA, measured after degassing the powder at 200 °C during 1 h. The synthesized $\text{C}_3\text{S}$ was characterized by X-ray diffraction (XRD) and NMR. While the XRD and $^{29}\text{Si}$ MAS NMR results were in line with what is expected for pure triclinic $\text{C}_3\text{S}$, $^{27}\text{Al}$ one-pulse MAS NMR revealed the presence of approximately 0.1 wt.% of Al coming from the $\text{SiO}_2$ used as a precursor for the synthesis.

$\text{NaAlO}_2$ solutions of different concentrations, 3, 30 and 60 mmol/l (pH 10.8, 11.8 and 12.1, respectively) were prepared dissolving defined quantities of solid $\text{NaAlO}_2$ (> 95% pure, VWR) in ultrapure water (Milli – Q, Millipore). To adjust pH solid NaOH (> 99% pure, Merck KGaA) was used.
5.2.2 Experimental methods

Pastes for isothermal calorimetry measurements were prepared by mixing 1 g of C₃S and 0.8 g of prepared solution in a plastic container during 3 min using a vortex mixer (Analog, VWR) at 2500 rpm. Experiments were performed at 23 °C using TAM Air microcalorimeter. The degree of hydration was estimated by dividing the cumulated heat released at a certain time by the enthalpy of total C₃S reaction determined as -520 J/g C₃S [21,22]. The time corresponding to the end of induction period was defined estimating the point after which deviation from the minimum heat flow takes place with subsequent increase in the heat flow.

Reproducibility of the data obtained during calorimetric experiments was proved by repeating randomly selected experiments for different C₃S and NaAlO₂ concentrations. Obtained data were found to be in a good agreement.

Hydration of C₃S samples with a SSA of 1.4 m²/g and 3.6 m²/g was first studied by NMR after stopping reaction at different times. C₃S with SSA of 1.4 m²/g was mixed 3 mM NaAlO₂ solution and the hydration was stopped at 1 h, 8 h, 1 day, 3 days and 7 days of curing by mixing during 5 min the pastes with isopropanol (IPA) in 1 : 25 (C₃S : IPA) ratio. Afterwards, the powdered samples were filtered using a nylon 0.45 µm membrane filter and dried in a desiccator over silica gel until constant weight.

For in situ NMR measurements (without stopping hydration), C₃S with SSA of 3.6 m²/g was mixed with 3 or 30 mM NaAlO₂ solution. The paste was then introduced into the NMR zirconia rotor using a syringe and a needle.

²⁷Al and ²⁹Si MAS NMR experiments were performed with 4 mm ZrO₂ rotors at spinning frequencies of 15 kHz and 7 kHz, respectively using a Bruker Avance-500 spectrometer.
(magnetic field of 11.7 T). Chemical shifts were referenced to 1 M aqueous solution of Al(NO₃)₃ for ²⁷Al or to tetrakis(trimethylsilyl)silane (TMS) for ²⁹Si with the accuracy of ± 0.1 ppm. The single-pulse ²⁷Al MAS NMR spectra were acquired with a π/6 pulse length of 2 µs, a recycle delay of 1 s and typically 3200 scans for in situ and 8000 scans for the measurements when hydration was stopped. The single-pulse ²⁹Si MAS NMR spectra were acquired with π/2 pulses of 5.9 µs, a recycle delay of 100 s and 560 number of scans. ²⁹Si{¹H} cross-polarization (CP/MAS) spectra were acquired at 7 kHz spinning speed with a contact times of 5 ms and recycle delays of 10 s. A typical numbers of scans were 5016. Hartmann-Hahn matching was ensured by a ramp on the ²⁹Si rf field.

Based on the obtained one-pulse ²⁷Al NMR spectra, the amount of the products was estimated comparing the integrated signal intensities. Quantities of different species containing Al were calculated using the program DMFit 2011 [23]. To fit the signals, Gaussian and Czjzek functions were used with fixed parameters varying only amplitudes through the whole set of experiments. In addition, a constant artifact signal of the probe was taken into account by introducing an extra broad peak with fixed parameters [16].

5.3 Results

5.3.1 Effect of Al studied by calorimetry

Figures 5.1 and 5.2 show the heat flow and cumulative heat curves of C₃S hydration in presence of different concentrations of NaAlO₂ solutions.

Figure 5.1 shows that the length of the induction period increases, and that the appearance of the main hydration peak is retarded, with the increase in the concentration of NaAlO₂. Furthermore, while the increase of the induction period is about the same regardless the SSA of the used C₃S (Figure 5.3a), the delay induced by the aluminates on the time of appearance
of the main hydration peak is more pronounced as the surface area of the C3S decreases (Figure 5.3c), mainly when 60 mM NaAlO2 is used. In addition, there is a linear trend between the time corresponding to the delay of the main hydration peak and the concentration of NaAlO2 solution when added to C3S with SSA of 1.4 m²/g but no clear one when mixed with finer or coarser powders (Figure 5.3c).

The addition of NaAlO2 decreases the cumulative heat during the first 10 – 11 h of hydration (see Figure 5.2). This depends on the concentration of NaAlO2, but not on the surface area of starting C3S. After approximately 11 h there is an increase in the amount of heat released in the presence of NaAlO2. Figures 5.2 and 5.3d-e show that this depends on the concentration of NaAlO2 added and on SSA of the used C3S. For instance, for C3S with SSA equal 3.6 m²/g cumulated heat is equally enhanced by 30 and 60 mM NaAlO2 solution, whereas for C3S with SSA 0.8 m²/g this increase is only produced by 60 mM. Despite this dramatic increase in the cumulated heat after 15 h of reaction in the presence of NaAlO2, by 7 days of hydration this difference is minimized, and even almost disappears, in the case of hydration of finer C3S (Figure 5.2, Figure 5.3e).

It is important to mention that the NaAlO2 solutions used in the described experiments have different pH values. To distinguish if the observed effects on the calorimetry curves were induced by the presence of aluminate ions and not by the initial pH difference of the starting solutions, a set of additional experiments was performed. During those experiments the pH of the starting solutions containing 0 and 3 mM NaAlO2 was adjusted with NaOH to 11.8, value corresponding to the pH of the 30 mM NaAlO2 solution. Figure 5.4 confirms that this increase of pH has no detectable influence on C3S hydration in absence and presence of NaAlO2.
Figure 5.1. Heat rate during hydration of C₃S with different NaAlO₂ concentrations. SSA of C₃S: 0.8 m²/g (left), 1.4 m²/g (middle) and 3.6 m²/g (right).

Figure 5.2. Cumulated heat released during hydration of C₃S with different NaAlO₂ concentrations. SSA of C₃S: 0.8 m²/g (left), 1.4 m²/g (middle) and 3.6 m²/g (right).
Figure 5.3. Summary of the calorimetric data pointing out a). Increase in induction period, b). Heat rate of the main hydration peak c). Increase in time corresponding to the end of acceleration period d). Increase in cumulated heat at 1 day e). Increase in cumulated heat at 7 days due to NaAlO$_2$ addition for C$_3$S with different surface areas as a function of NaAlO$_2$ concentration.

Figure 5.4. Effect of pH of the starting solution on the hydration rate of C$_3$S.
5.3.2 Effect of Al studied by NMR

The nature of the products that are formed during hydration of C₃S with NaAlO₂ solution was followed by ²⁷Al MAS NMR. Since the natural abundance of this element is almost 100% no additional enrichment was necessary. Figure 5.5 shows NMR measurements obtained on the samples hydrated with 3 mM solution up to 7 days, and where hydration was previously stopped. The spectra obtained on the non-hydrated C₃S shows a resonance in the area of 4-fold Al with the center of gravity at 82.2 ppm corresponding to the presence of Al in the initial C₃S and a broad resonance in the area of 6-fold Al coming from the used probe. During the first 8 h of hydration a small resonance with the center of gravity at 9.8 ppm is visible. As the hydration proceeds, the intensity of the peak at 82.2 ppm decreases and 5 additional signals appear, one in the area of 4-fold Al (69.8 ppm), two for 5-fold Al (35.8 and 20 ppm) and two for 6-fold Al (9.8 and 5 ppm). After 1 day of hydration no signal at 9.8 ppm is observed.

Figure 5.5. ²⁷Al one-pulse NMR data of the C₃S hydrated with NaAlO₂ (c = 3 mM) between 1 h and 7 d. Hydration was stopped.

²⁹Si one-pulse and ²⁹Si₋¹ H CP NMR show progress of C₃S hydration with 3 mM NaAlO₂ up
to 7 days (Figure 5.6). The spectra obtained confirm the formation of silicate dimers Q\(^1\), longer chains containing Q\(^2\) species and the consumption of non-hydrated C\(_3\)S (Q\(^0\)) over time. In addition, by \(^{29}\text{Si}\{^1\text{H}\}\) CP NMR the presence of hydroxylated (Q\(^0\)(h)) species was established. Surprisingly no clear resonances attributed to Al in C-S-H (Q\(^2\)(1Al)) can be distinguished in either experiment. This resonance has been observed in the literature before between –80 and –82 ppm \([13,15,17]\) but in our case the Al concentrations are most likely too low to see pronounced effect in the silicon spectra.

![Figure 5.6. \(^{29}\text{Si}\) one-pulse (left) and \(^{29}\text{Si}\{^1\text{H}\}\) CP (right) NMR data of the C\(_3\)S hydrated with NaAlO\(_2\) (c = 3 mM) between 8 h and 7 d. Hydration was stopped. Q\(^n\) refers to silicon atoms that are covalently bonded via bridging oxygen atoms to 0 ≤ n ≤ 2 other silicon atoms \([24]\).](image)

*In situ* NMR measurements, where hydration was not stopped with isopropanol, were also performed (Figure 5.7). C\(_3\)S of 3.6 m\(^2\)/g SSA was hydrated with 3 and 30 mM NaAlO\(_2\) solution during 6 h. The reaction was followed by \(^{27}\text{Al}\) MAS NMR. Comparing the data obtained in *in situ* experiments with the data from the samples when hydration was stopped, both showed the same resonances for 4, 5 and 6-fold Al. Quantitative analyses of the obtained spectra confirms that as hydration takes place the amount of Al in C\(_3\)S decreased. In addition, the resonance at
9.8 ppm was clearly observed during hydration in the 30 mM NaAlO$_2$ solution already after 1 h 30 min of reaction but it disappeared as the 5 ppm and 69.8 ppm resonances started to grow. The quantitative analysis summarized in Figure 5.7 shows that the rate of formation of the phase at 5 ppm was higher when a 30 mM NaAlO$_2$ solution is added than in the case of a 3 mM one. Concerning the 5-fold Al species as they are formed in negligibly small amounts regardless of the NaAlO$_2$ concentration that was used, they were not included in the quantitative analyses.

Figure 5.7. Real time measurements by $^{27}$Al one-pulse NMR using C$_3$S hydrated in a) 3 mM, b) 30 mM NaAlO$_2$ solution and quantitative analyses of the hydration products.
5.4 Discussion

By comparison to previous studies, in this paper we systematically studied the impact of NaAlO$_2$ on the C$_3$S hydration by varying the concentration of added aluminate ions and SSA of the used C$_3$S. In the presence of aluminates, C$_3$S hydration is retarded, being higher the delay with the increase concentration of aluminate ions in solution. Figure 5.4 proved that the increase of the initial pH when adding NaAlO$_2$ (up to pH = 12) does not have any impact on the hydration kinetics of C$_3$S. Furthermore, the SSA of the silicates does not seem to play a role on the extension of the induction period induced by the aluminates but clearly influences the position of the main hydration peak. The role of the SSA on the delaying effect of NaAlO$_2$ is in particular clear at concentrations of 60 mM NaAlO$_2$, where the retardation increases with the decrease of the SSA. This could suggest and support the hypothesis that aluminate ions probably act through a surface mechanism [9,10], by adsorption or forming covalent bonds on active kink sites, decreasing their reactivity.

Isothermal calorimetry curves (Figure 5.2) confirms that after the initial retardation of C$_3$S hydration, the presence of the aluminates increases the heat released and consequently the degree of reaction after 11 h of hydration. This increase was additionally proved by $^{29}$Si MAS NMR (Figure 5.8) on C$_3$S hydrated for 1 day with NaAlO$_2$ 60 mM. In particular, $^{29}$Si MAS NMR confirms higher reactivity of C$_3$S and consequently higher amount of C-S-H formed in the presence of NaAlO$_2$ compared to the sample that was just prepared with water.
Figure 5.8. Right: Degree of C₃S hydration with and without NaAlO₂ (c = 60 mM) addition studied by isothermal calorimetry (lines) and ²⁹Si one-pulse NMR (squares) Left: ²⁹Si one-pulse NMR spectra used to calculate degree of hydration.

Based on the first results discussed in this study, NMR measurements performed in situ seem to be especially interesting as they prevent the use of any drying technique normally used to stop hydration. Based on previous research it is expected that during these experiments an acceleration of the C₃S hydration takes place, possible due to the increase of the temperature induced by frictional heating during spinning in the in situ measurements [25]. Nevertheless, if results are compared with those obtained on the samples when hydration was stopped it can be seen that this type of experiments provide similar information on the nature of the products that are formed but continuously as hydration proceeds thus additionally minimizing experimental time.

Based on what has been previously reported in the literature most likely the resonance that are observed by ²⁷Al MAS NMR during C₃S hydration with NaAlO₂ are the following: at 69.8 ppm - Al in C-S-H, at around 35 ppm - Al³⁺ substituting Ca²⁺ in the interlayer of C-S-H, 9.8 ppm – AFm (described in section 2.3.3 of this work) and 5 ppm – third aluminate hydrate (TAH) [12-19]. Nevertheless, additional techniques have to be used to confirm the formation of the
mentioned phases. This is not an easy task as its concentration might be very low thus below the detection limit of many techniques. For example, this could explain the absence of resonance around -81.5 ppm in the $^{29}$Si one-pulse NMR spectra (Figure 5.6 and 5.8) attributed to Al in C-S-H ($Q^2(1Al)$).

5.5 Conclusions

The presence of aluminates increases the induction period regardless of the SSA of the used C$_3$S. Furthermore, it also retards the main hydration peak; this delay is more pronounced with the decrease of the SSA.

After 11 h of C$_3$S hydration, the addition of NaAlO$_2$ promotes the increase of the degree of hydration of the silicates.

$^{27}$Al one-pulse NMR experiments performed in situ and on the samples after hydration was stopped revealing similar products formed due to addition of NaAlO$_2$. Increased amount of NaAlO$_2$ promotes formation of phase appearing at 9.8 ppm that is most likely represent AFm but has to be confirmed by other techniques. At later time of reaction another aluminate phase at 5 ppm starts to grow and dominate in the system.
5.6 References


6. Paper IV: Influence of aluminates on the hydration kinetics of tricalcium silicate

This chapter consists of the journal paper “Influence of aluminates on the hydration kinetics of tricalcium silicate”. It has been submitted to Cement and Concrete Research. (E. Pustovgar, R.K. Mishra, M. Palacios, J.-B. d’Espinose de Lacaillerie, T. Matschei, A. Andreev, H. Heinz, R. Verel, R.J. Flatt, Influence of aluminates on the hydration kinetics of tricalcium silicate, Cement and Concrete Research, submitted)

This paper is focused on the effect of aluminates produced on the hydration of silicates. It presents the main findings obtained during the second half of the PhD study.

E. Pustovgar designed and carried out all experimental work. Dr. A. Andreev, Dr. R. Verel and Prof. J.-B. d’Espinose de Lacaillerie helped her to perform the NMR measurements. Dr. R. K. Mishra ran molecular dynamic simulations. Dr. T. Matschei did the thermodynamic modelling. All authors contributed to the analyses of the results and the writing of the manuscript. The work was done under the guidance of Prof. Flatt, Prof. J.-B. d’Espinose de Lacaillerie and Dr. M. Palacios.
Abstract

We used a combination of experimental and modelling techniques to study the effect of NaAlO₂ on tricalcium silicate (C₃S) hydration. pH sensitive inhibition of C₃S hydration occurred at an early age of reaction, but was followed by an increased amount of hydrates formed at later stages. Most results can be interpreted assuming that aluminates hinder C₃S dissolution. It is hypothesized that this takes place in active dissolution areas, present with a higher density on finer particles. Annealing reduces their number and increases retardation for a given dosage of aluminates. The view that aluminates act by hindering dissolution is supported by molecular dynamics simulations. They establish that aluminates can adsorb on the hydroxylated C₃S mainly through strong ionic interactions between aluminate and calcium ions on the surface. Upon progress of hydration and at higher pH values, the binding strength of aluminates to the hydroxylated C₃S decreases so that its passivating effect, and retardation, are reduced.
6.1 Introduction

Hydration of silicates, and in particular, C₃S, the main clinker phase of commercial Portland cement, has been and continues to be studied extensively [1,2]. Nowadays, clinker replacement by supplementary cementitious materials (SCMs) is one of the most effective approaches to reduce carbon footprint and embodied energy of Portland cement production [3]. However, these materials are less reactive, in particular at early ages, so that various chemical routes are explored to enhance their reactivity [4,5]. In non-sulfate optimized systems, many of these routes also lead to a larger release of aluminate ions since many SCMs are alumina-rich, and this, can delay cement hydration [6–11], thus counteracting efforts to increase the early reactivity of blended cements. An under-sulfated behavior can also be triggered by chemical admixtures [12], something that has been shown to result from increased ettringite formation at early ages [13]. More generally, this phenomenon may develop in the course of hydration even without chemical activators or chemical admixtures, compromising in these cases more the late than the early strength of cementitious materials. To overcome current challenges in producing highly blended cements, it therefore becomes necessary to better understand the molecular interactions between aluminate ions and calcium silicate surfaces with variable surface chemistry.

Several mechanisms have been suggested to explain the inhibition of silicate reaction in presence of dissolved aluminium [6–9,14–16]. The first one is an action of aluminates on the dissolution of silicates. In this case, a surface poisoning is proposed to take place through the adsorption of aluminate ions on pre-existing etch pits or through covalent bonding between aluminate ions and the surface of silicates [7,14]. Another mechanism that has been proposed, is a negative effect on the nucleation and growth of silicates hydrates. For instance, Begarin et al. [6] concluded that the calcium aluminate silicate hydrates (C-A-S-H) formed during alite
hydration (containing 0.1% of aluminium) do not act as a nuclei for calcium silicate hydrates (C-S-H) and consequently extend the induction period. Finally, a mechanism proposed by Quennoz and Scrivener [8] involves a poisoning of alite by aluminium ions, but according to the same authors the presence of aluminate hydrates in the space available for the nucleation and growth of C-S-H may be also responsible for the passivation of the silicates hydration. The existence of these different interpretations, highlights the fact that the passivation mechanism of C₃S hydration by aluminates remains poorly defined.

It is well known that silicates dissolution as well as Al chemistry varies depending on the pH. Experimentally, the influence of pH on the effect of Al on cement and C₃S was thus investigated by various authors [7,14]. Nicoleau et al. [14] concluded that the inhibition of C₃S dissolution is caused by a covalent bond formation between aluminate ion and silicate surface and is only possible under particular pH and calcium concentration. Suraneni et al. [7] found out that indeed above pH 13 the dissolution inhibition caused by Al is strongly decreased.

Clearly the question at stakes requires molecular level insight into the reactions occurring at solid-liquid interfaces. The lack of knowledge at an atomistic level presently represents a barrier to better understanding the interactions between aluminate and silicate ions in alkaline media. One possible way to take on this challenge is to use quantum-mechanical techniques such as density functional theory (DFT). Indeed, it has been shown that such computational methods can be applied to gain insight into the chemical kinetics as well as thermodynamics of cement hydration at the scale of chemical bonds [14,17]. For example, in a recent study on aluminate interactions with silicates, a combination of DFT simulations and solvent models was used in an attempt to identify which types of chemical bonds may form and under which conditions [14]. Probably due to the present limitations of such techniques, this led to a combination of results both compatible and incompatible with experiments. However, when
focusing on the most meaningful results, the authors of that study could better rationalize the nature of aluminate-silicate interactions [14]. Having said this, it should be further mentioned that the simulation of aqueous interfaces, selective adsorption of inorganic moieties and assembly of nano-objects by the specific DFT methods used in the study discussed before is associated with large uncertainties. This is due to the modest sizes of simulation systems [18], something that we address differently in this paper using molecular dynamic (MD) simulations with accurate atomistic force field parameterization. DFT methods are also known to produce variable outcomes depending on density functional and incur a shortage in accessible length and time scales by a factor of ten million compared to force field methods.

Considering all proposed hypotheses and experimental facts, it is very important to develop the knowledge needed to increase the amount of SCMs in blended cements without compromising their engineering properties. That is why we investigate the effect of aluminates on the C₃S hydration by a combination of various techniques that provide information at different scales. Calorimetry provides the macroscopic kinetics of hydration. This method is robust and well established in the literature. At the molecular level, this information can be correlated to the evolution of aluminium speciation during hydration as followed by ²⁷Al solid-state magic angle spinning nuclear magnetic resonance (MAS NMR). As the natural abundance of ²⁷Al is practically 100%, this characterization can be realized in situ and with a fast time-resolution without resorting to the use of any drying technique. The mechanism by which aluminates can passivate C₃S hydration can be elucidated by MD simulations. This approach builds upon previous work in which MD simulations were found helpful to understand the binding mechanisms between cement clinker surfaces and organic additives using well validated force field models [19–21]. More specifically, in this paper we introduce an extended force field for hydroxylated C₃S that was tested to reproduce the structural, vibrational, mechanical and interfacial properties of C₃S and silica [19,22]. We apply this model to study
the full range of variable surface chemistry expected to be found on C₃S surfaces as a function of pH and determine the interactions between these surfaces and aluminate ions.

Thus, the main objective of this study is to correlate the hydration kinetics of C₃S with the speciation of aluminium ions during the reaction. Consequently, the organization of this paper is as follows. We use isothermal calorimetry to study the influence of the aluminates on the kinetics of C₃S hydration and MAS NMR to establish quantitatively the evolution of the species formed during the reaction (section 6.2). Details of surface structures as a function of pH, force field for the hydroxylated C₃S and solid-liquid interfacial energies are presented (section 6.3). Section 6.4 describes the experimental and modeling results. The discussion of experimental and modeling results follows in section 6.5. Conclusions are presented in section 6.6.

6.2 Experimental

6.2.1 Synthesis of C₃S

Triclinic C₃S was synthesized by solid-state reaction using a dry homogenized powder that contained the stoichiometric quantities of reagent-grade (> 99% pure) CaCO₃ and SiO₂ from Sigma Aldrich. This powder was pressed into approximately 10 g pellets under 350 bar load and fired afterwards in a platinum crucible at 1600 °C for 8 h. Since the triclinic C₃S is a metastable phase, which tends to dissociate into CaO and Ca₂SiO₄ [23], pellets were quenched fast in a compressed air flow atmosphere. Sintering was repeated until no reflections assigned to free lime were observed by X-ray diffraction (XRD). The final material was ground in a micronizing mill (McCrone) with agate grinding elements during 8 min achieving powder with a BET specific surface area (SSA) of 1.4 m²/g (Micromeritics Tristar II 3020), measured after degassing the powder at 200 °C during 1 h. The particle size distribution (PSD) of the obtained powder determined by laser diffraction technique (MALVERN MASTERSIZER S) is presented in Figure 6.1.
Figure 6.1. PSD of the synthesized C₃S.

The initially synthesized C₃S was also characterized by ²⁷Al MAS NMR. It was unexpectedly found out that the obtained C₃S contains tetrahedral Al in its composition, as revealed by a resonance at 82 ppm (Figure 6.2). Further investigations revealed that this contamination came from the SiO₂ used as a precursor for the synthesis. Rough estimations suggest that the amount of Al element present in C₃S is about 0.1 wt.%, a value below the detection limit of most usual analytical techniques.

Figure 6.2. ²⁷Al one-pulse MAS NMR spectrum of the initial C₃S. The main resonance in the 4-fold chemical shift range demonstrates the occurrence of Al in the C₃S sample.
used in this study. The broad resonance corresponds to the probe-rotor background. Spinning side bands are marked with ※.

6.2.2 Preparation of pastes

For all experiments, C\textsubscript{3}S pastes were prepared with a liquid/solid (l/s) weight ratio of 0.8. C\textsubscript{3}S was mixed with the different solutions during 3 min using a vortex mixer (Analog, VWR) at 2500 rpm. Ultrapure Millipore water with resistivity > 18 MΩ cm at 25° C (Milli - Q) was used in the preparation of the different solutions.

6.2.2.1 Impact of aluminium on C\textsubscript{3}S hydration

C\textsubscript{3}S was mixed with NaAlO\textsubscript{2} (> 95% pure, VWR) solutions of different concentrations: 0, 3, 30, 60 and 230 mmol/l. As shown in Table 6.1, the pH of the solutions increases with the NaAlO\textsubscript{2} concentration. The purity and concentration stability of these solutions were examined by inductively coupled plasma optical emission spectrometry (ICP-OES) using the method defined by Caruso \textit{et al.} [24] and did not result in the detection of any other foreign ions. \textsuperscript{27}Al one-pulse liquid state NMR of the NaAlO\textsubscript{2} solution showed a sharp signal at 80.4 ppm, which corresponds to the tetrahedral aluminate ions Al(OH)\textsubscript{4}\textsuperscript{−} (Figure 6.3).
Figure 6.3. $^{27}$Al one-pulse NMR spectrum of the initial 30 mM NaAlO$_2$ solution. The narrow resonance at 80.4 ppm corresponds to the Al(OH)$_4^-$ ions in solution.

Table 6.1. pH of different NaAlO$_2$ solutions.

<table>
<thead>
<tr>
<th>Concentration of NaAlO$_2$ (mM)</th>
<th>3</th>
<th>30</th>
<th>60</th>
<th>230</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.8</td>
<td>11.8</td>
<td>12.1</td>
<td>12.4</td>
</tr>
</tbody>
</table>

6.2.2.2 Impact of pH

C$_3$S was mixed with two NaOH (> 99% pure, Merck KGaA) solutions of pH = 12.8 and pH = 13.1 and with a 60 mM solution of NaAlO$_2$. Delayed addition of NaOH was also investigated in C$_3$S pastes containing 60 mM NaAlO$_2$. In this case, C$_3$S was initially mixed with 60 mM NaAlO$_2$ solution (pH = 12.1) during 1 min and afterwards pH was increased above 13.1 by means of a 1 M NaOH solution. The paste was then mixed for 2 additional minutes.
6.2.3 Characterization methods

Hydration of the prepared pastes was studied by in situ $^{27}$Al MAS NMR experiments and isothermal calorimetry. Reproducibility of the data obtained was also checked.

6.2.3.1 Isothermal calorimetry

The hydration kinetics were studied by isothermal calorimetry at 23 °C after external mixing. For this, a TAM air calorimeter (TA instruments) was used.

6.2.3.2 Nuclear magnetic resonance (NMR)

$^{27}$Al one-pulse NMR

NMR experiments were carried out using a Bruker Avance III 500 spectrometer (magnetic field 11.7 T) at the resonance frequencies of 130.31 MHz for $^{27}$Al. MAS spectra were measured using a Bruker MAS NMR probe with 4 mm (outer diameter) ZrO$_2$ rotor at spinning frequency of 15 kHz. For the single-pulse $^{27}$Al MAS NMR spectra $\pi/6$ pulses of 2 µs with a recycle delay of 1 s were implemented to insure $^{27}$Al central transition selective excitation thus providing quantitatively reliable $^{27}$Al NMR signal intensities. A spectrum of the 30 mM NaAlO$_2$ aqueous solution was also acquired under the same conditions but without spinning. In that case, 16 scans were sufficient to acquire the spectrum. The spectra were referenced to 0.1 M aqueous solution of Al(NO$_3$)$_3$; the accuracy of the chemical shift was ±0.1 ppm. $^{27}$Al MAS NMR spectra of hydrated samples were collected with typically 3200 scans.

Most of the NMR measurements were done in situ. This means that hydration was not stopped with the help of any drying technique but the paste was introduced into the rotor as such thus preserving the original structure of the hydrates. Considering the applied spinning rate, the g-forces are around 900.000. Therefore, centrifugation could overcome capillary pressure and
remove water from pores larger than about 15 nm. To prevent centrifugation in the paste during the NMR measurements, in situ experiments began after 2 h of C₃S hydration thus allowing the initial setting of the material. The initial C₃S paste was divided in 2 fractions. The first fraction was analyzed in situ up to 7 h of hydration. Afterwards, the paste was removed from the ZrO₂ rotor to prevent its hardening inside and the NMR measurements were continued on the second portion of C₃S paste sample stored at room temperature. That second sample was already hard enough to be ground and introduced as a powder into the rotor.

The amounts of the different species containing Al were determined based on the integrated intensities of the ²⁷Al MAS NMR spectra normalized with respect to the weight of the sample. Peak decomposition of ²⁷Al one-pulse spectra was done using the program DMFit 2011 [25] (Supporting information Figure 6.20). To fit the signals Gaussian and Czjzek [26] functions were applied as models with parameters (chemical shift, width and a quadrupolar product (C_Q)) that were kept constant for each specific resonance throughout the whole set of spectra (Table 6.2). Since for ²⁷Al NMR, the chemical shift is affected by second order quadrupolar effect, its value differs from the peak maximum in Czjzek model. Complete fitting of resonance 3 shown in Table 6.2, was only possible with the help of an additional narrow line (Resonance 3_b) introduced at 5 ppm. A small broad NMR probe signal occurred in the aluminium frequency range between -50 and + 50 ppm [27]. This signal was modelled from the ²⁷Al one-pulse NMR spectra of an empty rotor and was taken into account in the final evaluation of the measured spectra by introducing an ad hoc extra broad peak of fixed shape and amplitude.
Table 6.2. Fit parameters for different type of $^{27}$Al environments.

<table>
<thead>
<tr>
<th></th>
<th>Resonance 1</th>
<th>Resonance 2</th>
<th>Resonance 3_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>peak maximum (ppm)</td>
<td>82.2</td>
<td>9.8</td>
<td>5</td>
</tr>
<tr>
<td>chemical shift (ppm)</td>
<td>82.4</td>
<td>10.3</td>
<td>6.4</td>
</tr>
<tr>
<td>$\langle \cdot \rangle$ (KHz)</td>
<td>1420</td>
<td>1250</td>
<td>3330</td>
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</table>

Gaussian function

<table>
<thead>
<tr>
<th></th>
<th>Resonance 4</th>
<th>Resonance 5</th>
<th>Resonance 3_b</th>
</tr>
</thead>
<tbody>
<tr>
<td>chemical shift (ppm)</td>
<td>69.8</td>
<td>35.7</td>
<td>5</td>
</tr>
<tr>
<td>width (ppm)</td>
<td>12</td>
<td>11</td>
<td>2</td>
</tr>
</tbody>
</table>

$^{29}$Si/$^{27}$Al CP NMR

CP/MAS NMR involving quadrupolar nuclei has been scantily applied in the literature [28–31] and to the knowledge of the authors this is the first time that this technique has been attempted to study cement hydration. The use of $^{29}$Si-enriched C$_3$S, synthesized according to [2], made possible the $^{29}$Si/$^{27}$Al CP/MAS NMR. $^{29}$Si-enriched C$_3$S was mixed with a 60 mM NaAlO$_2$ solution and hydration was stopped after 2 h. For this, the pastes were mixed for 5 min with isopropanol using a solvent/solid ratio of 25. The suspension was filtered and the powder was stored afterwards in a dessicator until constant mass.

The experiment was set up based on the procedure applied to albite (NaAlSi$_3$O$_8$) reported by De Paul et al. [32]. The spectra were acquired with a Bruker Ultrashield Avance AMX 400 spectrometer (magnetic field 9.4 T) using 4 mm rotors at spinning speed of 10 kHz. The $^{27}$Al and the $^{29}$Si frequencies were 104.26 MHz and 79.5 MHz, respectively.
1D $^{29}$Si/$^{27}$Al CP/MAS NMR spectra were recorded by selective excitation of the central transition of $^{27}$Al using a $\pi/6$ pulse of 1.5 µs. During the cross-polarization (CP) NMR experiments, contact times of 50 ms were employed at recycle delays of 1 s. A typical number of scans was 14720. The Hartmann-Hahn conditions were set-up on albite by looking for the $^{29}$Si power amplitude leading to maximum signal intensity. On the cement paste, to increase stability, this amplitude of the silicon contact pulse was ramped. No proton decoupling was used during acquisition.

6.3 Atomistic modelling approach

6.3.1 Molecular models and validated force field parameters

6.3.1.1 Monoclinic and triclinic C$_3$S

Earlier we developed and validated the force field model of monoclinic C$_3$S [19] that is part of the INTERFACE force field [21]. For the purpose of the present study, it is important to also validate the model of triclinic crystal system since it is the triclinic polymorph of C$_3$S that is used experimentally. We have used the X-ray crystal data from Golovastikov et al. [33] to create a unit cell structure of triclinic C$_3$S. The space group is $P\bar{1}$ and the triclinic unit cell with lattice parameter, $a=1.167$ nm, $b=1.424$ nm, $c=1.372$ nm. Lattice parameters reproduction of triclinic structure (Table 6.3) was done using the polymer consistent force field (PCFF) energy expressions (equation 6.1) with the help of MD simulations keeping constant number of particles (N), pressure (P) and temperature (T) throughout the simulation (constant NPT). Molecular models of C$_3$S were also validated with Chemistry at HARvard Macromolecular Mechanics (CHARMM), Consistent Valence Force Field (CVFF), and the AMBER force field which uses 12–6 Lennard-Jones potential for van der Waals interactions (equation 6.2) [19]. The force field parameters used in this study are presented in Table 6.4 and are the same as previously published including one change in the Si-O equilibrium bond.
parameter $r_0$ from 168 to 172 pm for the triclinic mineral.

6.3.1.2 Hydroxylated C$_3$S

We extended the dry C$_3$S model to hydroxylated C$_3$S which includes the formation of free silanol groups in silicate ions and hydroxide ions on the surface (Figure 6.4). In Figure 6.4, the changes in the protonation state are related to pK values of the silicic acid (H$_4$SiO$_4$, pK$_{a1}$ = 9.84, pK$_{a2}$ = 13.2 at 25 °C) [34]. According to the pK values, the turning point should be pH 13.2 rather than pH 13 (pK$_{a2}$ = 13.2) in Figure 6.5c. But it is known that the concentration of many charged groups at an interface, compared to individual free silicic acid anions in solution, is less favorable and may shift the effective pK values by 0.1 to 0.5 unit lower in comparison to free silicic acid. We introduce an extended force field for hydroxylated tricalcium silicate that was verified to reproduce the structural, vibrational, mechanical and interfacial properties of C$_3$S and silica (Table 6.4) [19,21,22]. Force field parameters described in Table 6.4 include van der Waals parameters for 9-6 and 12-6 Lennard-Jones potential used in the Consistent Force Field (CFF), PCFF, COMPASS (equation 6.1) and Chemistry at HARvard Macromolecular Mechanics (CHARMM), Consistent Valence Force Field (CVFF), AMBER (equation 6.2), respectively. To understand the initial steps of surface hydration mechanisms of the C$_3$S, we propose to consider several hydration steps of a dry C$_3$S surface, as shown in Figure 6.4. Scheme 6.1 shows an example of possible step of partial dissolution of C$_3$S which also describes the changes in the partial atomic charges of oxygen and hydrogen in the silanol group. The hydroxylation reaction decreases the polarity of the C$_3$S surface (Figure 6.4 and Scheme 6.1). Atomic charges of oxygen and hydrogen in the silanol group are consistent with the force field of silica [22]. A minor change was done on the atomic charge of oxygen (-0.65e) in the silanol group with respect to the partial charge of oxygen (-0.675e) in silica to make it appropriate for hydroxylated C$_3$S. We used the Material Studio graphical interface and
Discover program [35] to model hydroxylated C₃S surfaces.

Figure 6.4. Schematic models of surface chemistry of tricalcium silicate upon initial surface hydration and protonation as a function of pH ( ). a) Initially dry C₃S surface before reaction with water. b) Protonation of surface oxide ions to hydroxylated C₃S above pH 18. c) Protonation of silicate ions on the surface at pH ~ 15. d) Second protonation of silicate ions on the surface at pH ~ 13.5. e) Further protonation trihydrogen silicate at pH ~ 11.5. f) Dissolution of Ca(OH)₂ at pH < 10, which does not occur during cement hydration due to pH values above 10. After long hydration times, the surfaces at pH 12 to 13 undergo further oligomerization of individual silicate species and deposit C=S=H gels. pH values lower than 10 would lead to formation of silicic acid and condensation into solid silica over time. The surface models are derived from known pK values of silicic acid and experimental data on the surface chemistry of silicates [22], [34], [66].
For our MD simulations, the total potential energy ($E_{pot}$) (equation 6.1 and equation 6.2) of the system is the sum of the energy contributions for quadratic bond stretching ($E_{bonds}$), quadratic angle bending ($E_{angles}$), as well as electrostatic ($E_{Coulomb}$) and van-der-Waals interactions ($E_{vdW}$) between atoms and as such depends only on the Cartesian coordinates of the atoms along the directions of the three coordinate axes. The latter two terms, the electrostatic interactions and the van-der-Waals interactions, represent nonbond interactions. Parameters $r_0$, $\theta_0$, $K_r$, $K_\theta$, $\varepsilon$, and $\sigma$ represent equilibrium bond lengths, equilibrium bond angles, vibrational constants for bond stretching, vibrational constants for angle bending, equilibrium nonbond energy and equilibrium nonbond distance between two atoms of the same type, respectively. In mixtures with other elements or compounds, the parameters $\varepsilon_{ij}$ and $\sigma_{ij}$ for nonbond interactions between different atom types $i$ and $j$ can be obtained by combination rules. Further details on the above mentioned parameters as well as combination rules used in the equation 6.1 and 6.2 can be found in the INTERFACE force field paper [21].

\[
E_{pot} = \sum_{ij \text{ bonded}} K_{r,ij} (r_{ij} - r_{0,ij})^2 + \sum_{ijk \text{ bonded}} K_{\theta,ijk} (\theta_{ijk} - \theta_{0,ijk})^2 + \frac{1}{4\pi\varepsilon_0} \sum_{ij \text{ nonbonded} \ (1,3 \text{ excl})} \frac{q_i q_j}{r_{ij}} + \sum_{ij \text{ nonbonded} \ (1,3 \text{ excl})} \varepsilon_{ij} \left[ 2 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^9 - 3 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} \right] \tag{6.1}
\]

\[
E_{pot} = E_{bonds} + E_{angles} + E_{Coulomb} + \sum_{ij \text{ nonbonded} \ (1,3 \text{ excl})} \varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 - 2 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \tag{6.2}
\]
Table 6.3. Cell parameters of tricalcium silicate (triclinic as well as monoclinic crystal) according to X-ray data [33,36] and molecular dynamics simulation in the NPT ensemble using the PCFF-INTERFACE force field (PCFF-IFF) under standard temperature and pressure.

<table>
<thead>
<tr>
<th>Method</th>
<th>Cell (Crystal cell)</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>V (nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt [33] (Triclinic)</td>
<td>2×1×1</td>
<td>2.3340</td>
<td>1.3720</td>
<td>1.4240</td>
<td>105.5</td>
<td>90</td>
<td>94.3</td>
<td>4.3808</td>
</tr>
<tr>
<td>PCFF-IFF</td>
<td>2×1×1</td>
<td>2.3448</td>
<td>1.3695</td>
<td>1.4158</td>
<td>104.9</td>
<td>90</td>
<td>94.4</td>
<td>4.3791</td>
</tr>
<tr>
<td>Expt [36] (Monoclinic)</td>
<td>2×3×2</td>
<td>2.447</td>
<td>2.121</td>
<td>1.8596</td>
<td>90</td>
<td>116.31</td>
<td>90</td>
<td>8.6554</td>
</tr>
<tr>
<td>PCFF-IFF</td>
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<td>2.443</td>
<td>2.113</td>
<td>1.8685</td>
<td>90</td>
<td>116.18</td>
<td>90</td>
<td>8.6557</td>
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</table>

Table 6.4. Force field parameters for tricalcium silicate and superficially hydrated tricalcium silicate for use with various force fields containing 9-6 and 12-6 Lennard-Jones potentials for nonbond interactions, bonded parameters, and partial charges for Coulomb energy.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge (e)</th>
<th>9-6 LJ PCFF</th>
<th>12-6 LJ CVFF</th>
<th>CHARMM</th>
<th>COMPASS</th>
<th>AMBER</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>σ₀,ii (pm)</td>
<td>ε₀,ii</td>
<td>σ₀,ii (pm)</td>
<td>ε₀,ii</td>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
<td>O[silicate]</td>
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<td>340</td>
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<td>0.08</td>
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<td>347</td>
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<td>0.12</td>
<td>347</td>
<td>0.12</td>
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<td>0.013</td>
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<table>
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<tr>
<th>Bonds</th>
<th>r₀ (pm)</th>
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<td>Si–O (in SiOₓ)</td>
<td>168ᵃ, 172ᵇ</td>
<td>250</td>
</tr>
<tr>
<td>O–H (in OH⁻)</td>
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<td>495</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>III. Angle</th>
<th>θ₀ (deg)</th>
<th>K₀ (kcal/(mol⋅rad²))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–Si–O (in SiO₄⁻)</td>
<td>109.5</td>
<td>160</td>
</tr>
</tbody>
</table>

134
Si–O–H (in SiO(OH)₃)

| Bond length for monoclinic crystal structure | 115 |
| Bond length for triclinic crystal structure | 50 |

\[ 3\text{Ca}^{15+}(s) + 0^{1-}(s) + 2\text{H₂O}(l) + \left[ \begin{array}{c}
\text{O}^-
\text{Si}
\text{O}^-
\end{array} \right]^{3.0-} \rightarrow 3\text{Ca}^{15+}(aq) + 3\text{C}^{1.05+}\text{H}^{3.30+}(aq) + \left[ \begin{array}{c}
\text{O}^-
\text{Si}
\text{O}^-
\end{array} \right]^{2.25-} \]

Scheme 6.1. One of the possible steps during dissolution of the C₃S surface. The balance of partial atomic charges in the chemical reaction is shown as represented by the force field types in Table 6.4.

6.3.1.3 Sodium tetrahydroxyaluminate

We use a molecular model of NaAl(OH)₄ to understand the molecular interactions of aluminate ions with the hydroxylated C₃S surface. We apply the force field model of NaAl(OH)₄ (scheme 6.2, Table 6.5) to understand the binding mechanisms of aluminate ions on hydroxylated C₃S surface using MD simulations. The force field parameters used for NaAl(OH)₄ are consistent with those that have been previously validated for tricalcium aluminate (Table 6.5) [20]. The dissolution of solid NaAlO₂ into Na⁺ and Al(OH)₄⁻ ions could be analyzed in a series of MD calculations or ab-initio MD calculations, however, direct modelling of the chemical reaction poses challenges on kinetics, computation time, and was not the focus in this study [37] [38].

To understand the effect of pH on C₃S hydration in the presence of aluminate ions, we apply MD simulations to calculate the binding energy of NaAl(OH)₄ at specific pH values using the NPT ensemble. We increased the pH from 11.5 to 13.4 by adding extra NaOH (0.26 M) in the aqueous solution of the simulation box. Aluminate ions were relaxed at the aqueous solution -
hydroxylated C₃S interface using the NPT ensemble.

Scheme 6.2. Structure of sodium tetrahydroxyaluminate, NaAl(OH)₄ with partial charge. Force field parameters are shown in Table 6.5 for MD simulations.

Table 6.5. Force field parameters of sodium tetrahydroxyaluminate, NaAl(OH)₄ for the PCFF-INTERFACE energy expression.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge (e)</th>
<th>(\sigma_{0,j}) (pm)</th>
<th>(\varepsilon_{0,i}) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>+1.00</td>
<td>330</td>
<td>0.08</td>
</tr>
<tr>
<td>Al</td>
<td>+1.20</td>
<td>420</td>
<td>0.50</td>
</tr>
<tr>
<td>O</td>
<td>−0.90</td>
<td>352</td>
<td>0.06</td>
</tr>
<tr>
<td>H</td>
<td>+0.35</td>
<td>109.8</td>
<td>0.013</td>
</tr>
</tbody>
</table>

6.3.2 Model validation of hydroxylated C₃S surface

Further validation of hydroxylated C₃S surface model would best be done by computing the interfacial energy with water using accurate all-atom force field [21] and comparing to experimental data. Unfortunately, quantitative experimental data on C₃S-water interfacial energies are not available. However, since the hydration reaction of C₃S with water is exothermic [2], the interfacial energy of C₃S-water should decrease with increasing hydroxylation of the surface (Table 6.6). We can therefore check whether our MD simulation qualitatively capture this trend (Figure 6.5). Next, we also calculate the hydration energy using computed values of cleavage energy and interfacial energy [19]. Hydration energy data are provided in Table 6.6 using the relation: “hydration energy = interfacial energy – cleavage energy”.
It should be noted that in our MD simulations, it is not possible to simulate chemical reactions such as hydration as a whole. However, we can examine intermediate steps of these reactions, which can be defined from chemical insight into the way such reactions must proceed. Specifically, for C$_3$S hydration these steps are illustrated in Figure 6.4 and we have computed interfacial energy of each C$_3$S surface with water.

![Figure 6.5. Solid-liquid interface of the tricalcium silicate (010) surface under ambient condition for pH ~ 13.5 and pH ~ 11.5.](image)

The thickness of the Ca(OH)$_2$ interfacial layer increases toward lower pH value. Hydroxide ions are shown using a stick representation at the C$_3$S-aqueous interface. c) Schematic of the pH dependent surface chemistry of C$_3$S.
Table 6.6. Interfacial energy of different types of hydroxylated (Hyd.) C₃S surfaces (described in Figure 6.4) with water using MD simulations in NVT/NPT ensemble.

<table>
<thead>
<tr>
<th>Types of C₃S surface</th>
<th>Interfacial Energy (mJ/m²)</th>
<th>Cleavage Energy (mJ/m²)</th>
<th>Hydration Energy (mJ/m²)</th>
<th>pH</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry C₃S (a)</td>
<td>450 ± 35</td>
<td>1300 ± 50</td>
<td>-850 ± 43</td>
<td>&gt;15</td>
<td>298</td>
</tr>
<tr>
<td>Hyd. C₃S (b)</td>
<td>-267 ± 28</td>
<td>600 ± 50a</td>
<td>-867 ± 39</td>
<td>&gt;15</td>
<td>298</td>
</tr>
<tr>
<td>Hyd. C₃S (c)</td>
<td>-386 ± 30</td>
<td>490 ± 50a</td>
<td>-876 ± 40</td>
<td>~15</td>
<td>298</td>
</tr>
<tr>
<td>Hyd. C₃S (d)</td>
<td>-516 ± 35</td>
<td>400 ± 50a</td>
<td>-916 ± 42</td>
<td>~13.5</td>
<td>298</td>
</tr>
<tr>
<td>Hyd. C₃S (e)</td>
<td>-830 ± 40</td>
<td>340 ± 50a</td>
<td>-1170 ± 45</td>
<td>~11.5</td>
<td>298</td>
</tr>
</tbody>
</table>

Cleavage energies did not change further upon changes in pH within the margin of uncertainty, mainly due to the presence of superficial calcium hydroxide (known to have a cleavage energy of ~ 1180 ± 100 mJ/m² for the perfect crystal [39]).

6.3.3 MD simulation protocols

For the geometry of the crystal super cell reproduction of triclinic C₃S using MD, we run our simulations under isothermal-isobaric (NPT) ensemble under ambient pressure (0.0001 GPa) and temperature (298.15 K) with a time step of 0.5 fs with a spherical cutoff of van der Waals interactions at 1.2 nm, and Ewald summation of Coulomb interactions with an accuracy of 10⁻⁵ kcal/mol.

To compute the interfacial energies of dry and hydroxylated C₃S surfaces with water, we used
different setups to simulate individual surface types (e.g. pure C₃S and modified C₃S surface due to hydroxylation) shown in Figures 6.21 and 6.22 (Supplementary information). In both cases, we use the PCFF-INTERFACE energy expression (equation 6.1) to calculate solid-liquid interfacial energy. The size of simulation boxes for the C₃S slab, the bulk water and the C₃S slab-water are 2.5×2.8×2.5 nm³, 2.5×4.0×2.5 nm³, and 2.5×6.8×2.5 nm³, respectively. The rectangular cell of C₃S is of the same translational symmetry as well as density with respect to the original unit cell [16]. For the hydroxylated C₃S system, the simulation box is slightly larger than for dry C₃S slab as the density of the hydroxylated slab is slightly lower than the density of the pure C₃S that is 3.154 g cm⁻³. Further hydroxylation steps can also be simulated in a similar manner.

For the computation of adsorption energy (shown in Supplementary information, Figure 6.23), the simulation box containing the C₃S mineral surface, water and the adsorbate has a size of 2.5×11×2.5 nm³ when the adsorption is calculated on the (010) plane. We used two approaches (two boxes as well as four boxes as explained in the Supplementary information, Figure 6.22) to compute the adsorption energy of aluminate ions on the hydroxylated surface. We get the same order of adsorption energies from both methods, but only present the values using the two box methods, which is preferred in strongly ionic systems where ions explore the entire box size.¹ In the simulation box, the thickness of the water layer is 9 nm to avoid any (010) surface-surface interactions as well as adsorbate interactions with the upper surface due to periodic boundary conditions. We employed MD simulation under constant number of particles (N), volume (V) and temperature (T) (NVT), as well as in the NPT ensemble. The temperature

¹ Order of adsorption energy is the same from both methods, but the four box method gives slightly higher values of adsorption energies than the two box method. Also two box method is more universal than four box method. We checked both methods due to the presence of counter ions in our simulation systems.
was 298.15 K, the time step 1 fs, the summation of van der Waals interactions was carried out using a spherical cutoff at 1.2 nm, and the summation of Coulomb interactions was carried out using Ewald summation with an accuracy of $10^{-4}$ kcal/mol.

6.4 Results

6.4.1 Effect of Al on C₃S hydration

6.4.1.1 Isothermal calorimetry studies

Figures 6.6 and 6.7 illustrate the effect of NaAlO₂ concentration on the C₃S hydration. In agreement with what was reported in the literature [16], as the concentration of NaAlO₂ increases up to 60 mM, the duration of the induction period, the time of appearance of the inflection point during the acceleration stage and the time of the main peak also increase (Figure 6.6). An unusual feature in these data is a particularly pronounced upwards inflection point, which for the reference paste hydrated with pure water occurs at about 3 h. This seems to separate two roughly linear zones, which we will argue to represent the reaction of the two particle size populations found in our sample (Figure 6.1).

Figure 6.6. Calorimetry measurements on C₃S pastes hydrated with aqueous solutions of different NaAlO₂ concentrations. a) Heat release rate, b) Cumulated heat release.
Interestingly, we see that at higher dosages of added NaAlO₂, such as 230 mM, the previously-mentioned inflection point disappears and one notices the appearance of an additional resolved peak right after the end of the induction period (Figure 6.7).

Despite the initial delay of the C₃S hydration in the presence of aluminates, the maximum heat release rate (intensity of the main peak) and the total cumulated heat released after 10 h of reaction increases with the NaAlO₂ concentration (Figure 6.6, 6.7), involving a higher degree of hydration of the C₃S. This was confirmed by ²⁹Si solid-state MAS NMR revealing a difference of approximately 10% in the degree of C₃S reaction at 24 h between the pastes without and with 60mM NaAlO₂ addition [40].

![Figure 6.7. Calorimetry measurements on C₃S pastes hydrated with a 230 mM NaAlO₂ aqueous solution. a) Heat release rate, b) Cumulated heat release.](image)

Preliminary annealing of synthesized C₃S at 650 °C during 6 h with subsequent slow cooling changes the hydration kinetics (Figure 6.8). It results in an extension of the induction period and the disappearance of the additional inflection point during the acceleration period. In regard to what was previously stated concerning the role of particle size, this suggests that after annealing, both classes of particle size react with similar rates as discussed later in this paper.
Figure 6.8. Effect of annealing on heat release rate during C₃S hydration.

6.4.1.2 ²⁷Al MAS NMR studies

**Effect of the spinning on C₃S hydration**

Figure 6.9 shows the NMR spectra of the paste prepared with 30 mM NaAlO₂ and hydrated for 3 h 15 min. To evidence the effect of spinning on hydration, the experiment was repeated with the same total hydration time but with different spinning times prior to measurement. In both spectra, the same resonances at 82.2 ppm and 69.8 ppm (4-fold Al), 35.7 ppm (5-fold Al), 9.8 ppm and 5 ppm (6-fold Al) can be identified, however, their intensities are clearly different. According to the literature, [41] and references therein, the signal at 69.8 ppm corresponds to the 4-fold Al incorporated in C-S-H phase, the 5-fold Al is possibly assigned to Al³⁺ substituting for Ca²⁺ in the interlayers of the C-S-H and the 6-fold signals at 9.8 and 5 ppm correspond to the calcium aluminate hydrate phases called AFm [42,43] and third aluminate hydrate known as TAH [44], respectively. Compared to the spectrum of the sample spun after 2 h 20 min of hydration, when the sample is spun after only 20 min of hydration, that is when the spinning time is longer, the intensity of the 6-fold resonance assigned to TAH is higher, while the one assigned to AFm is lower. The higher amount of TAH, a species intimately associated with C-S-H [44] suggests an acceleration of the C₃S hydration reaction, while the
decrease of the relative AFm contribution implies a premature conversion between aluminates during the spinning time. This could be due to an increase of the temperature induced by the high spinning during the in situ measurements. According to the literature and our own calibration, this increase is of about 20 K [45] (considering the speed of 15 kHz at which the rotor was spun for $^{27}$Al MAS NMR measurements). For this reason, no correlation of the NMR with the calorimetry data has been attempted, as it would be incorrect. Nevertheless, all NMR experiments being performed consistently, they provide the correct relative effect of the different solutions on the nature and sequence of aluminate phases forming. Indeed, similar NMR spectra were obtained in in situ experiments and on quenched samples, suggesting that centrifugal forces in the rotor are not playing a main role on the nature of the hydrates in real-time measurements (supporting information Figure 6.24 and Table 6.8).

Figure 6.9. Effect of spinning at 15 KHz during continuous one-pulse $^{27}$Al MAS NMR experiments on C$_3$S hydrated with a 30 mM NaAlO$_2$ aqueous solution. Hydration time is 3 h 15 min in both cases a) MAS starts after 2 h 20 min and lasts until the end of the measurements which was at 4 h 10 min (total spinning time 1 h 50 min) b) idem but MAS starts after 20 min of hydration (total spinning time 3 h 50 min).
**In situ NMR measurements**

Figure 6.10 shows the $^{27}$Al MAS NMR selected spectra of the C₃S pastes hydrated *in situ* for 10 and 18 h with 3, 30 and 60 mM NaAlO₂ solutions. These pastes were introduced in the NMR device and spun after 2 h 20 min of hydration. The analysis of all the NMR spectra obtained during *in situ* measurements of both fractions of the C₃S paste is shown in Figure 6.11. A slight discontinuity of the measurements on the first and on the second fraction of the paste is visible in these figures on both sides of the vertical discontinuous lines. Although this roughly lies within experimental errors, it confirms that the spinning has an influence on the hydration kinetics. However, as the nature of the phases is the same and their evolution is consistent between both samples, we conclude that the chemical nature of the formed hydrates is not altered by the fast spinning.

The first observation in the *in situ* spectra is that the signal from aluminates in solution is not visible. This means that all aluminates reacted or adsorbed before the first NMR analysis (2 h 20 min). Indeed, adsorbed species might remain undetected because of the strong quadrupolar broadening due to the electrical field gradient induced by the surface. This point is supported by the fact that the total amount of NMR-visible aluminium increases with time (Figure 6.11, straight lines). This results from the fact that the *NMR invisible*, or poorly quantified tetrahedral aluminate species (adsorbed ions but also to a certain extent Al in C₃S), convert to octahedral coordinated aluminium species (Figure 6.11, filled triangles) that are fully detectable by NMR.
Figure 6.10. $^{27}$Al one-pulse MAS NMR spectra. Effect of the NaAlO$_2$ concentration ($c = 3, 30$ and $60$ mM) on C$_3$S hydration at a) 18 h and b) 10 h.
Figure 6.11. Quantitative analyses as a function of time of the $^{27}$Al one-pulse MAS NMR data obtained for C$_3$S hydration in presence of 3, 30 and 60 mM of NaAlO$_2$ aqueous solutions. AFm (◯), TAH (▲), Al in C-S-H (■) and Al in C$_3$S (◇). The total amount of NMR-visible Al is figured as a straight line. The time reported is the average hydration time during NMR measurement. The vertical discontinuous lines indicate the time at which the switch between the first and second sample was made (see experimental section for details).

Quantitative analysis of these spectra confirms that the amount of the AFm species formed right in the beginning of the C$_3$S hydration is roughly proportional to the concentration of the NaAlO$_2$ added (Figure 6.12) within the range considered. Note that the consumption of calcium released from C$_3$S dissolution in the formation of AFm phase is almost negligible considering the low amount of aluminium initially introduced in the system. With the hydration time, the intensity of the peak at 10 ppm decreases at the same time as the one at 5 ppm increases, suggesting the transformation of AFm phase into TAH. In addition, with the increase of either hydration time or NaAlO$_2$ concentration, more Al incorporates into C-S-H (around 70 ppm). In the particular case of adding 3 mM NaAlO$_2$, we observe almost no formation of AFm phases and the intensities of the peaks assigned to TAH and Al in C-S-H are significantly lower with respect to the samples with 30 and 60 mM NaAlO$_2$ addition.
Figure 6.12. Relative amount of formed AFm phases presented in arbitrary units (a.u.) as a function of NaAlO$_2$ concentration. The relative amount of Al in the AFm phase is obtained by integration of the corresponding $^{27}$Al one-pulse MAS NMR resonance.

6.4.1.3 $^{29}$Si-$^{27}$Al CP NMR

$^{29}$Si-$^{27}$Al CP NMR experiments were performed to provide information about the positional relationship between the silicon and aluminium species. As shown in Figure 6.13, no resonances were observed at 2 h of hydration. This meant that aluminium was not close to silicon (within a few angstrom) or that the two nuclei were too mobile with respect to each other to allow for polarization transfer by dipolar coupling. From this, it could be concluded that the aluminates are precipitated from solution or are only physically bound to the silicate surface. That is, no Si-O-Al covalent bound were evidenced by NMR. The incorporation of Al in the C-S-H, as seen from the 65 ppm resonance in the $^{27}$Al one-pulse NMR spectra, was probably too small to allow a detectable $^{29}$Si-$^{27}$Al CP signal.
6.4.2 Effect of pH on C₃S hydration

As shown in Table 6.1, the pH value of NaAlO₂ solutions increases with the aluminates concentration. For this reason, the effect of pH on C₃S hydration was also investigated separately.

Figure 6.14 shows the $^{27}$Al MAS NMR spectra of the C₃S paste mixed with water and with 60 mM NaOH (pH = 12.8) at 8, 11, 13 and 24 h of hydration. As expected, without any additional sources of Al, the coordination of the Al, coming from the impurities in the C₃S, changes from tetrahedral (around 80 ppm) to octahedral (5 ppm) as hydration proceeds. As seen by NMR, this transformation is not affected by the presence of 60 mM NaOH (pH = 12.8). Isothermal calorimetry measurements (Figure 6.15) confirm that the replacement of mixing water by a solution with pH raised to 12.8 by NaOH does not impact the hydration kinetics since neither the heat release rate nor the cumulative heat curves changed. On the contrary, when the pH of the hydrating solution is higher than 13, in particular pH = 13.1, a slight acceleration of the C₃S hydration is observed (Figure 6.15).
Figure 6.14. $^{27}$Al one-pulse MAS NMR spectra. Effect of NaOH on the hydration of C₃S studied between 8 and 24 h.
Blue line: C₃S hydrated in water,
Black line: C₃S hydrated with NaOH addition.

Figure 6.15. Isothermal calorimetry curves of C₃S pastes with and without NaOH.
In contrast, when the mixing liquid is 60 mM NaAlO$_2$ solution, the pH of the solution has a significant influence on C$_3$S hydration. The results shown in Figure 6.16a confirm that in presence of 60 mM NaAlO$_2$ solution at an initial pH of 12.1, a delay of 3 h of the maximum of the main peak is observed with respect to the reference paste. However, when the C$_3$S hydrates with a 60 mM NaAlO$_2$ solution adjusted with NaOH to pH $= 13.1$, the retarding effect produced by Al is totally cancelled and the additional inflection point in acceleration period disappears. In addition, an increase of the heat release is observed (Figure 6.16b). This is accompanied by the enhancement of the amounts of the C-S-H and Ca(OH)$_2$ (CH) phases as was additionally established by thermogravimetric analysis (TGA) (Supplementary information, Figure 6.25). If the NaOH needed to bring the pH from 12.1 to 13.1 is added after 1 min as a concentrated solution, rather than including it in the mixing water, then the accelerating effect is practically lost (Figure 6.16a). This confirms the importance of the interplay between the role of the initial pH of the mixing solution and the presence of aluminate ions. Additionally, we observe that in pastes prepared with a delayed increase of the pH, the heat released after 12 h decreases with respect to those prepared with direct addition of NaAlO$_2$ 60 mM with pH 12.1 and 13.1.

![Figure 6.16. Effect of NaAlO$_2$ at different pH studied by isothermal calorimetry during C$_3$S hydration.](image)

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6.4.3 Molecular level investigations

6.4.3.1 Binding mechanism by molecular simulation

As a possible reason for the impact of Al on C₃S hydration, we try to understand the interaction of aluminate ions with C₃S surfaces. For this, we computed the adsorption energies of NaAl(OH)₄ on the hydroxylated C₃S surface using molecular dynamics simulations (Table 6.7). The first two rows in Table 6.7 show adsorption energies of NaAl(OH)₄ at pH 11.5 and 12.5 on two types of hydroxylated C₃S surfaces, corresponding to initial and advanced amount of surface hydration. The two cases were modelled assuming the hydration reaction proceeds from one molecular layer to two molecular layers of protonated silicate, respectively. The increase in hydration depth in the pH range of 11-13 reflects the rise in the amount of hydration product with time, not the change in the degree of hydroxylation (SiO₂(OH)₂⁻, SiO(OH)₃⁻ etc). A high amount of hydroxylation (double layer) leads to a further increase in pH value due to formation of a larger amount of calcium and hydroxide ions at the interface. More specifically, we consider that upon contact of the dry C₃S surface with water, all silicate and oxide ions protonate and that the degree of this hydration process changes over time and further depends upon the pH of the system, which can be represented by the steps in Figure 6.4. These steps occur before oligomerization of individual silicate species and formation of C–S–H. Therefore, the initial and advanced amount of hydration considered in Table 6.7 aim at representing successive steps of the initial hydration reaction and more specifically of the C₃S dissolution.

Negative values of the adsorption energy indicate that adsorption of NaAl(OH)₄ is thermodynamically favored (Table 6.7, row 1 and 2). The adsorption energies also show that an increase in the hydration depth of the C₃S surface decreases the thermodynamic driving force toward aluminate adsorption.
Table 6.7. Adsorption energy of NaAl(OH)$_4$ on the hydroxylated C$_3$S surface under ambient conditions for different hydration depth and added NaOH.

<table>
<thead>
<tr>
<th>Type of C$_3$S surface</th>
<th>Adsorption energy (kcal/mol/molecule)</th>
<th>pH</th>
<th>Amount of hydration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyd. C$_3$S (SiO(OH)$_3$)$^{1-}$</td>
<td>$-24 \pm 6$</td>
<td>11.5</td>
<td>Single-molecular-layer</td>
</tr>
<tr>
<td>Hyd. C$_3$S (SiO(OH)$_3$)$^{1-}$</td>
<td>$-6 \pm 3$</td>
<td>12.5</td>
<td>Double-molecular-layer</td>
</tr>
<tr>
<td>Hyd. C$_3$S (SiO(OH)$_3$)$^{1-}$ + NaOH</td>
<td>0</td>
<td>13.4</td>
<td>Single-molecular-layer</td>
</tr>
</tbody>
</table>

For initial hydration (one molecular layer), aluminate was observed in direct contact (at distance $\leq 3\ \text{Å}$) with the hydroxylated C$_3$S surface along with a strongly negative adsorption energy of $-24\ \text{kcal/mol}$ at pH 11.5 (Figure 6.17a). In this case, adsorption appears to be dominated by strong ionic interactions of aluminate with calcium ions on the surface of C$_3$S. Additional hydrogen bonds between aluminate and silicate surface ions are formed and were identified by the occurrence of characteristic H···O lengths between 1.6 and 2.5 Å and H···O–H angles between 155° and 170°. However, the contribution of these hydrogen bonds to the reported adsorption energy is expected to be small as similar hydrogen are already present in water and therefore only be reformed when water is desorbed, with an energy balance expected to be small with respect to the -24 kcal/mol reported above.
Figure 6.17. Interactions of aluminate ions with the hydroxylated C₃S surface according to molecular dynamics simulations. a) Interactions of aluminate ions with the initially hydrated C₃S surface (one molecular layer) at pH ~ 11.5 involve strong bonding to calcium ions on the surface as well as interfacial hydrogen bonds (Al-OH···O-Si and Al-OH···OH-Si). b) Interactions of aluminate ions with the C₃S surface after double-layer hydration at pH ~ 12.5 are weaker. Dissolution of silicate ions and formation of ionic complexes between aluminate and calcium ions, aluminate ions and silicate ions (circular highlight), as well as overall surface reconstruction can be seen.

For increased hydration depth (two molecular layers), a higher surface density of dissolved calcium and hydroxide ions is predicted at the interface and aluminate ions exhibit less direct contact with the silicate surface (Figure 6.17b). Dissolved portlandite in the aqueous media provides stabilizing ionic interactions between Ca²⁺ ions and Al(OH)₄⁻ ions, reducing direct aluminate contact with the surface sites. Protonated silicates also begin to dissociate from the surface and form complexes with aluminates, driven by ionic interactions via shared cations (Na⁺, Ca²⁺) as well as hydrogen bonds between silanol and aluminol groups. Presence of more dissolved Ca²⁺ and OH⁻ and surface reorganization render aluminate adsorption less favourable with an adsorption energy of only ~6 kcal/mol (Table 6.7). The dominance of ionic interactions in the reconstructed surface also reduces hydrogen bonding between aluminate ions and silicates at the interface, in accordance with general values of ionic bond strengths.
(20-70 kcal/mol) [19] and H bond strengths (4-6 kcal/mol) [46,47].

Overall, the simulation results suggest that the driving force for adsorption of sodium aluminate at pH values of 11.5 to 13 is the formation of hydrated calcium aluminate complexes and/or amorphous Ca(OH)$_2$ surface layer, that would hinder dissolution. In reality we may assume this to take place at reactive sites, so that these simulations carried out on well-cleaved crystal planes are only an indication of what may really happen. Despite this, we can tentatively express the formation of the hydrated calcium aluminate complex by the following reaction with a dissolved calcium and hydroxide ions on the surface of hydroxylated C$_3$S, accompanied by the formation of sodium hydroxide, which slowly diffuses outward into solution:

$$
2 \text{Na}^+ \text{(aq)} + 2 \text{Al(OH)}_4^- \text{(aq)} + \text{Ca}^{2+} \cdots [\text{OH}^-]_2 \text{(s)} \rightleftharpoons \text{Ca}^{2+} \cdots [\text{Al(OH)}_4^-]_2 \text{(s)} + 2 \text{Na}^+ \text{(aq)} + 2 \text{OH}^- \text{(aq)} \quad (6.3)
$$

Thereby, the aluminate is attracted to the initially hydrated C$_3$S surface, covered by dissolved calcium and hydroxide ions, allowing strong adsorption and passivating the C$_3$S surface from water attack. Upon deeper surface hydration, however, the amount of dissolved portlandite increases and the aluminate no longer covers the immediate surface. As a result, adsorption energies of aluminate move from negative closer to zero, the surface-protection effect diminishes, and retardation effects subside.

In summary, we find that adsorption of aluminate ions to the hydroxylated C$_3$S surface during initial hydration is due to ionic interactions with Ca$^{2+}$ ions, forming a hydrated calcium aluminate complex, as well as to the formation of hydrogen bonds with silicate surface groups (Al-OH···O-Si and Al-OH···OH-Si) at the interface / surface sites. Adsorption strength and direct surface contact weakens as hydration progresses into further subsurface layers, accompanied by silicate dissolution and aluminate coordination with dissolved calcium ions.
further above the C₃S surface.

6.4.3.2 Effect of increased pH

Initial hydration (single molecular layer) at a higher pH value of 13.4 taken upon addition of 0.26 M of NaOH in the simulation box leads to little direct contact of aluminate with silicate surface ions (Figure 6.18). However, at pH = 13.4, the formation of complexes between silicate anions and tetrahedrally coordinated aluminate ions was still observed away from the surface (Figure 6.17b and 6.18b).

When the pH is increased by addition of NaOH, the equilibrium in equation 6.3 shifts to the left, thus decreasing, due to proximity of sodium ions, direct binding of aluminate to Ca²⁺ ions on the hydroxylated C₃S surface, or to the superficial portlandite layer, respectively. Binding energies are then near zero or positive (Table 6.7, row 3), and no passivation of dissolution can be expected, which is consistent with the experimental data (Figures 6.15 and 6.16).

For deeper hydration (two molecular layers) adsorption may be more strongly defavoured, as shown above for the systems without NaOH.

The simulations also suggest that higher surface charge (at higher pH) shifts the competition for adsorption towards electrostatic contributions. Then, binding of small highly charged ions such as Ca²⁺ and OH⁻ to the C₃S surface is preferred over Na⁺ ions of lower charge and Al(OH)₄⁻ ions with spatially more widely delocalized charge. A decrease in surface charge (lower pH) changes the adsorption mechanism to less electrostatically driven adsorption, allowing ions such as aluminate to directly approach the surface, and increases the contribution of hydrogen bonds to adsorption. These trends are consistent with prior findings of adsorption of charged molecules on hydroxyapatite, silica, and other ionic minerals [37,48] and reflected in equation 6.3. Finally, we note that the observed silicate-aluminate complexes at pH 12.5 and
13.4 may evolve to covalent bonds, but this is something that classical molecular dynamics simulations cannot capture without further extensions.

Figure 6.18. Assembly of aluminate ions on the hydroxylated C₃S surface with added NaOH at pH 13.4 as seen in molecular dynamics simulations. a) Initial position of aluminate ions and NaOH on the hydroxylated C₃S (SiO(OH)₃⁻) surface (after 10 ps). b) Equilibrium positions of aluminate ions and NaOH on the hydroxylated C₃S (SiO(OH)₃⁻) surface (after 10 ns). Surface reconstruction and complex formation between aluminate and silicate ions can be seen (circular highlight). NaOH weakens the interactions between aluminate ions with Ca²⁺ and silicate ions of the hydrated C₃S surface, shifting the equilibrium towards aluminate desorption.

6.5 Discussion

In this section we segmented the discussion of our main results in five main sections. The final section wraps up our conclusions concerning the mechanistic impact of aluminates on C₃S hydration, which is that dissolution is inhibited. In the sections leading up to that final statement, various results are discussed taking this into account. When necessary explicit mention of this is made, but the detailed argumentation is kept for the last section to avoid too many repetitions.

6.5.1 Kinetic effect of Al on C₃S hydration

Many studies have addressed the influence of aluminium on the composition and structure of
C-S-H [49–52]. In contrast, the focus of this paper is to provide a broader picture of the effect of aluminates on the hydration of C₃S, in particular in terms of kinetics.

In this work, the hydration of C₃S has been confirmed to be clearly inhibited by aluminium and increasingly so with higher concentrations of aluminates in solution (see Figure 6.6) [16]. This is consistent with equation 6.3. During the acceleration stage two periods of different reactivity can be identified, which can be reasonably attributed to the bimodal particle size distribution of our C₃S powder. Interestingly, the addition of NaAlO₂ shifts the onset of both hydration periods to later times (identified by extrapolating both linear regimes to zero heat flow). The presence of two peaks becomes particularly obvious with the highest concentration of aluminates (Figure 6.7).

To examine more carefully the impact of Al on the reactivity of the different size fractions (Supplementary information, Figure 6.26 and Table 6.9), it is convenient to analyze the induction time of each peak (t) with respect to the value in the absence of Al (t₀). More specifically we look at the normalized retardation given by \((t - t₀) / t₀\). When doing this, it can be observed that both fractions of the C₃S particles are affected by aluminates roughly to the same extent (Figure 6.19). This implies that the relative effect produced by aluminates is not influenced by the particles size, although the absolute retardation is affected by it. It suggests that the same physico-chemical process is affecting the reaction of both classes of particle size.
Figure 6.19. Effect of NaAlO$_2$ concentration relative to the system void of NaAlO$_2$ on the onset of hydration of finer (○) and coarser (●) particles of C$_3$S fitted with power law. The onset of hydration is obtained as described in the Supplementary information (Figure 6.26).

Another important insight into the mechanism of action of aluminates comes from the annealing experiment. There we observe that the annealed sample only shows one period of reactivity, as if after annealing both classes of particle size had the same reactivity (Figure 6.8). This may be rationalized in terms of a number of defects on C$_3$S particles. Indeed, in the non-annealed samples, the finer particles can be expected to have a higher density of defects than the coarser ones, something Nicoleau had already commented upon [53]. When the material is annealed, the defect density of the particles decreases [54] and this should lead both classes of particle size to reach a similar surface state or defect density, explaining the disappearance of the additional inflection point during the acceleration period.

In addition, when NaAlO$_2$ solution is used with the annealed C$_3$S, the induction period is massively extended (Figure 6.8). In the context of the impact of aluminium on hydration, this would mean that reactive sites as kinks would be more effectively blocked, leading to a lower
reactivity. This would involve, but not be limited to, fewer etch pits opening.

We have also observed that the addition of aluminates enhances the intensity of the main hydration peak and increases the total heat released after 10 h (Figure 6.6). This means that although in the beginning Al slow down C\textsubscript{3}S hydration, it nevertheless increases the degree of hydration at later times [40]. A possible explanation for this may lie in the seeding effect linked to our bimodal particle size distribution. Indeed, our experiments suggest that in presence of aluminates, C-S-H first forms from the smaller C\textsubscript{3}S particles (below 1 μm), which could be viewed as an in situ seeding process taking place before most of the coarser particles start to react [55]. Therefore by the time the coarser particles really react, they will do so in presence of already hydrated fine particles, a system very similar to one to which C-S-H seeds would have been added [55].

6.5.2 Nature of Al containing reaction products

The analysis of the reaction products based on the in situ \textsuperscript{27}Al one-pulse MAS NMR spectra confirms the formation of three main Al containing hydration products: Al in C-S-H at 69.8 ppm, AFm at 9.8 ppm and TAH at 5 ppm, of which the amounts increase with the initial concentration of NaAlO\textsubscript{2} (Figure 6.10, 6.11). Several attempts were made in order to better characterize and understand their composition. Unfortunately, XRD measurements failed due to detection limit of this technique thus distinguishing only CH and triclinic C\textsubscript{3}S in the investigated system (Supplementary information, Figure 6.27). On the contrary, additional \textsuperscript{27}Al one-pulse NMR experiments shed the light on the composition of the formed AFm when compared with the synthesized [Ca\textsubscript{4}Al\textsubscript{2}(OH)\textsubscript{14}]\textsuperscript{x}\textsubscript{H\textsubscript{2}O}\textsubscript{y} (C\textsubscript{4}AH\textsubscript{x}) compound (Supplementary information, Figure 6.28). It can be seen that the shape and position of the obtained resonances look similar thus suggesting that the 10 ppm resonance in our system can be attributed to the calcium aluminate hydrate phase of the following composition: C\textsubscript{4}AH\textsubscript{x} (h-AFm). Based on a
thermodynamic assessment (Supplementary information, Table 6.11) assuming close to equilibrium conditions for C-S-H and portlandite the formation of $C_4AH_{19}$ is favored.

It was also found that during hydration of $C_3S$ more products containing 6-fold rather than 4-fold Al are formed. This is also in good agreement with what had been reported previously in the studies on synthetic C-S-H with high Ca/Si ratio [43,49,56]. Moreover, as shown in Figure 6.11, at early times mainly AFm species are formed, while at later hydration times the amount of Al in C-S-H and TAH dominate. Similar to the reaction of white Portland cement [57], direct TAH formation was observed when $C_3S$ reacts with water (Figure 6.13), but with the use of NaAlO$_2$ solution initial AFm precipitation perturbs the formation of TAH, most likely due to the low Ca/Si ratio available in solution for its formation [44]. Based on our results we propose the transformation from AFm into the TAH and C-S-H phases, although the presence of Al in initial $C_3S$ impedes a definitive conclusion from being drawn. $C_4AH_x$ can be destabilized with time in the presence of the formed C-S-H [58] resulting in the appearance of TAH and favoring some amount of Al to be taken into the C-S-H (Figure 6.11). It was reported before that at high Ca/Si ratio of the C-S-H this uptake becomes limited [59], which correlates well with our quantitative findings presented in Figure 6.11.

In previous studies the inhibition of $C_3S$ hydration was explained by the formation of covalent bonds Si-O-Al. According to Nicoleau et al. [14], this silicoaluminate species would be identified at around 55 ppm in $^{27}$Al MAS NMR spectra. However, the NMR spectra shown in Figures 6.10 do not provide any clear signal at this chemical shift. Therefore, if such bonds are present, they are below the detection level of our measurements. Furthermore, bidimensional NMR measurements (see Figure 6.13) have not identified $^{27}$Al-$^{29}$Si correlations, suggesting the absence of Si-O-Al covalent bonds. To further scrutinize the eventuality of the presence of such bonds, further experiments could be considered with substantially longer acquisition times.
and possibly also in different concentration ranges.

6.5.3 Effect of pH on passivation of C₃S hydration by aluminates

A higher initial pH seems to cancel the inhibiting effect of aluminates (Figure 6.16), in agreement with previous studies [7,14,60]. This is consistent with our MD results, showing direct contact of aluminate ions with surface ions below pH 13 and no such contacts above it. It is also in qualitative agreement with the pH dependence of the proposed adsorption mechanism tentatively described by equation 6.3. It is interesting to observe that the sodium ions are found to play a crucial role in this process. Indeed, they are in close proximity to the aluminate ions as well as to surface sites [22], thus inhibiting the interaction between aluminate ions and surface ions.

Nicoleau et al. [14] explained the pH dependent inhibition through the formation of Si-O-Al covalent bonds that are unstable at higher pH. Our MD simulations, show that pH dependent changes in adsorption energy alone can explain the pH effect. However, Nicoleau et al. [14] also make the interesting comment that the covalent Si-O-Al bond once formed cannot be simply destroyed by an increase of pH at later hydration time. As mentioned before, we could not resolve the resonance attributed to Si-O-Al covalent bond in our NMR experiments. However, our findings based on isothermal calorimetry (Figure 6.16) show that indeed, a delayed increase of the pH does not cancel the inhibitory effect of Al. While this observation could suggest the formation of Si-O-Al bonds, we propose to also consider the following alternative interpretation. When the pH is raised in a delayed way, the pore solution already contains some dissolved C₃S. It is therefore no more the same situation as if the pH is raised from the start. Consequently, even if aluminates desorbed, the undersaturation of the solution with respect to C₃S may not be high enough to effectively open etch pits, so that the cement hydration is not “re-activated”.

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In order to understand if the nature of hydration products (AFm, TAH etc) is different above pH 13, additional $^{27}$Al one-pulse NMR experiments were performed. This was done on the C$_3$S samples hydrated in 60 mM NaAlO$_2$ solution of pH = 12.1 or pH = 13.1 and for which hydration was stopped before measurements (Supplementary information, Figure 6.29). Results show that $^{27}$Al NMR resonances are very similar, indicating that the increase in pH does not affect the nature of the Al containing phases formed.

6.5.4 Molecular dynamic simulations

6.5.4.1 Model validations

We found that we could use the same force field parameters for both crystal structures of C$_3$S (monoclinic as well as triclinic) except the bond length parameter between Si and O atoms in silicate ions (Table 6.4). This makes sense due to higher bond length of Si–O in the triclinic system (1.634 Å) with respect to the monoclinic crystal (1.597 Å). Additionally, the corresponding density of the triclinic crystal structure of C$_3$S (3.120 g/cc) is lower than for the monoclinic (3.153 g/cc) [33,36]. Furthermore, the force field model of hydrated C$_3$S is consistent with parameters for C$_3$S and silica with minor adjustments [19,22].

6.5.4.2 C$_3$S - water interfaces

From MD simulations, we see that the diffusion of calcium and hydroxide ions into the aqueous solution increases as the degree of surface hydration increases (Figure 6.5), which is clearly expected. There is also no penetration of water molecules into the C$_3$S surface. Rather we observe a process of surface reorganization due to an increase in the amount of hydration products as well as a change in pH. This happens due to enthalpic changes which involve the displacement of cationic and anionic groups on the surface [61]. The negative value of solid-liquid interfacial energy reflects the spontaneous nature of the process of hydration for hydroxylated C$_3$S. We also note that the hydration energies (shown in Table 6.6) are negative
since all mentioned C₃S surfaces are water-soluble and solvation occurs with a release of energy in the form of heat. Logically also, the hydration energy increases with the increasing degree of hydroxylation imposed on the C₃S surfaces in our calculations.

6.5.4.3 Interactions of aluminates with hyd. C₃S

The computed adsorption energies of sodium tetrahydroxyaluminate show consistent trends with respect to the degree of hydroxylation (pH) as well as the depth of the hydration layers. We thus obtain what appears to be reasonable ranges for aluminate binding to the hydroxylated C₃S surface through ionic interactions and hydrogen bonds (Figure 6.17). Nevertheless, while these simulations are encouraging, one must not forget their intrinsic limitations. In particular, it is necessary to properly define not only the force field, but also the intermediate stages of the chemical reaction. In our case, the later issue concerns the degree of hydroxylation of the C₃S surface. While this can be done with chemical insight, it nevertheless remains an a priori limitation of this approach, just as other approaches have other limitations. However, within this frame we have the possibility to explicitly model surfaces at an atomic scale, something that is essential for the problem considered in this paper. DFT calculations have difficulties predicting chemical shifts and electronic shielding for aluminate ions adsorption on the hydroxylated C₃S due to large system size and complexity of the simulated system [62]. Earlier DFT findings were focused on the Al substitution in the lattice structure instead of aluminate adsorption on the surface sites [14,63].

6.5.5 Mechanistic origin of the retardation

Our interpretations of the aluminate impact remains anchored in the view that aluminates most probably have an impact on C₃S dissolution, in accordance with previous statements about this [7,14]. From an experimental point of view, calorimetric experiments appear to support this interpretation. In particular, for each class of particle size, the corresponding part of the
acceleration period is shifted to later time with little change in slope. This strongly suggest a delay on the activation of the C₃S dissolution without a change in the number of nuclei formed.

In addition, we find that annealing leads to hydration curves only showing one characteristic behavior. This suggests that the small and large particles react at a similar rate after annealing, which we attribute to both classes of particles having similar surface density of defects after this heat treatment. Viewing the effect of aluminium as a direct impact on dissolution contradicts Begarin et al. [6], who claimed that Al poisons the nucleation and growth of C-S-H through the formation of C-A-S-H, a mechanism that would not account for the impact of annealing.

Another mechanism found in the literature is that the formation of AFm could explain the hydration delay of C₃S [64]. It is true that our experiments clearly show that AFm formation dominates the consumption of aluminates (a small amount of C-A-S-H is however also measured by NMR and discussed below). The experimentally observed AFm formation is consistent with our thermodynamic calculations. Due to a competition between C-A-S-H and AFm for calcium, AFm formation may slightly impact C₃S hydration kinetics. Nevertheless, the consumption of calcium released from C₃S to form this AFm is negligible due to the comparatively low amount of total alumina in the system. In regard to the possibility of AFm accounting for retardation, our NMR results and thermodynamic calculations do not show a change in the aluminate phases as a function of pH. In other words, AFm formation cannot explain the pH dependence on retardation (existing below pH 13 and disappearing above it).

We note that the formation of AFm requires C₃S to supply calcium by dissolving. From our NMR measurements, it appears that the fate of the silicon associated to this partial dissolution ends up in C-A-S-H (as shown in the supplementary information in Figure 6.30 and Table
6.10. From a microstructural point of view, the difference between the case with and without aluminium is shown in Figure 6.31. Clearly, in absence of aluminium, C-S-H is visible on the surface of C₃S grain and not otherwise. This implies either that the C-A-S-H identified by NMR is deposited elsewhere, or that it forms a very homogenous layer. Using a simple mass balance, the thickness of this hypothetical layer can be estimated to be between 5 and 10 nm. Implications on hydration kinetics are however not trivial and would appear very speculative to explain the kinetic effects reported in this paper.

Let us now come back to the view that C₃S dissolution is affected by aluminate ions and that this may explain its pH dependence. The later had previously been attributed by Nicoleau et al. [14] to the formation of Si-O-Al covalent bonds at the outermost surface of C₃S, indicating that although these species are stable in solution at high pH they may not be stable on the surface under those conditions. Our MD simulations suggest that below pH 13, strong ionic interactions between calcium ions and tetrahydroxoaluminate ions as well as interfacial hydrogen bonds (Al–OH···O—Si and Al–OH···OH–Si) are formed on the hydroxylated C₃S surface. We therefore infer that it is these adsorbed complexes that inhibit C₃S hydration. Importantly, the same MD simulations show that above pH 13, calcium aluminate complexes form in solution but not on the C₃S surface, which offers a fully consistent picture of retardation by aluminates and its pH dependence. At this point, it is worth noting that the calcium aluminate complexes could be considered as precursors or building blocks of an amorphous AFm having a stoichiometry defined in equation 6.3. However, the ensemble of these complexes does not constitute a true phase from a thermodynamic point of view. Additionally, the desorption of these complexes is characteristic of each of these species taken individually rather than a phase transition.

Finally, we note that these molecular modelling results also specifically identify the formation
of ion pairs and hydrogen bonds between aluminate and silicates, providing molecular insight into the blocking of C₃S dissolution. These results are consistent with the view that aluminates passivate the dissolution by blocking the kink sites, a high density of which are found in etch pits that were shown to constitute highly reactive areas for mineral dissolution [65]. A similar conclusion, developed at further length, was recently reached for the impact of polycarboxylate polymers on cement hydration [13]. Having said this, and in regard to the simulations presented in this paper, we must not forget that these are performed on well cleaved surfaces and do not capture the different energetics of reactive defect sites as kink.

6.6 Conclusions

In this paper we systematically studied the effect of NaAlO₂ concentrations on the hydration of C₃S by isothermal calorimetry and ²⁷Al one-pulse MAS NMR. The addition of NaAlO₂ solutions changes the hydration kinetics mainly during induction stage. Concerning the longer term impact of aluminates, we show that this depends mainly on aluminate concentration and pH of the solution during first seconds of hydration. It has been established by ²⁷Al one-pulse MAS NMR that the increase in the NaAlO₂ dosage promotes the formation of AFm phases, enhances Al incorporation in C-S-H and increases the amount of TAH at later times.

By MD simulations, using a hydroxylated C₃S model with a validated force field, we found that, below but not above pH 13, aluminates adsorb directly to the C₃S surface covered by dissolved calcium and hydroxide ions. The adsorption occurs through ionic interactions and the formation of hydrogen bonds. The equilibrium shifts to desorption at higher surface charge (higher pH) when more highly charged ions including calcium, sodium, and hydroxide interact with the silicate surface directly. The formed silicate-aluminate complexes may evolve to covalent bonding, but this is something that classical MD can clearly not capture. However, we did not detect such bonds by NMR in our experiments.
The ensemble of our results appears to support the view that C₃S hydration in presence of NaAlO₂ can be explained based on the dissolution controlled theory. In particular, we infer that the adsorption of aluminates on the reactive sites of silicate surfaces inhibits further reaction. We saw that the induction period depends on particle size, probably because of differences in defect density. However, the relative efficiency of aluminates to retard the hydration of particles of different size is constant, since retardations normalized by the induction period of a given particle size class, show a roughly common dependence on aluminate dosage. This indicates that the same physico-chemical process is at stake. Moreover, the fact that annealed powders show a single behavior with more massive retardation further supports the view that aluminates inhibit C₃S hydration at active dissolution areas.

Finally, we note, our MD simulations cannot account for the fact that a delayed pH increase does not reactivate hydration. Possibly this is due to the formation of covalent bonds in too low number to be detected by our NMR measurements and not accountable by our simulations. However, a change in the understaturation of the system may also be advocated to explain this. Further investigation would seem worthwhile to elucidate this question and complete the vision proposed in this paper on how aluminates can hinder C₃S hydration.
6.7 References


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[59] E. L’Hôpital, Aluminium and alkali uptake in calcium silicate hydrates (C-S-H), Thesis of the EPFL (Lausanne), Switzerland, 2014.


6.8 Supplementary information

6.8.1 Supplementary figures

Figure 6.20. Example of peak decomposition of a $^{27}$Al one-pulse MAS NMR spectrum. As discussed in the main text Resonance 1 correspond to Al in C$_3$S, Resonance 2 – AFm, Resonance 3a and 3b – TAH, Resonance 4 – Al in C-S-H, Resonance 5 – Al$^{3+}$ substituting for Ca$^{2+}$ in the interlayers of the C-S-H.

Figure 6.21. Schematic illustration for the calculation of the dry mineral surface–water interfacial energy. Three simulation boxes with a) dry mineral, b) pure water, and c) mineral–water interface were employed.
Figure 6.22. Schematic illustration for the calculation of the hydroxylated mineral surface–water interfacial energy. Three simulation boxes with a) hydroxylated mineral, b) pure water, and c) mineral–water interface were employed.

\[ \gamma_{MW} = \frac{(E_{MW} - E_W - E_M)}{2A} \]

Figure 6.23. Schematic illustration for the calculation of adsorption energy of adsorbate. a), b) A two box approach or a), c), d), e) a four box approach can be employed. a) The hydroxylated mineral–water–adsorbate system with the adsorbate close to the mineral surface. b) Hydroxylated mineral–water–adsorbate system with the adsorbate detached from the mineral surface. c) Mineral–water interface. d) Water with adsorbate molecule and e) Pure water.
Figure 6.24. $^{27}$Al one-pulse MAS NMR measurements of C₃S hydrated during 4 h in 60 mM NaAlO₂ solution. Measurements were done in situ and on the samples after hydration was stopped by solvent exchange with isopropanol.
Table 6.8. Fit parameters for different type of $^{27}$Al environments for C₃S hydrated with 60 mM NaAlO₂ during 4 h. Comparison of measurements performed *in-situ* and quenched samples.

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<th>Resonance 3_a</th>
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<td>Al in C₃S</td>
<td>AFm</td>
<td>TAH</td>
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<td>3330</td>
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<tr>
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Figure 6.25. Thermal analyses (TGA) of the C₃S hydrated in 60 mM NaAlO₂ solution of pH = 12.1 (solid) and pH = 13.1 (dashed) during 8 h. Hydration was stopped with isopropanol. Measurements were performed from 40 to 1000 °C at a heating rate 10 °C/min in N₂ atmosphere.

Figure 6.26. Heat rate during hydration of C₃S with different concentration of NaAlO₂. Parallel red lines correspond to the slope in the second part of the acceleration period,
that we attribute mainly to hydration of coarser particles with the onset $t(L)$ determined as an intercept with the extended induction period. The onset of finer particles reaction $t(S)$ was determined at the point of initial deviation from the minimal heat rate.

Table 6.9. Linear fit equations used in Figure 6.26.

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<td>60</td>
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Figure 6.27. XRD patterns of the non-hydrated C$_3$S (black) and C$_3$S hydrated 8 h with a 60 mM NaAlO$_2$ aqueous solution (red line). Measurements were done using Co K$_\alpha$, ($\lambda = 1.7903$ Å) anode.
Figure 6.28. $^{27}$Al one-pulse MAS NMR measurements of C$_3$S hydrated in 60 mM NaAlO$_2$ solution during 4 h (black) compared to the resonance of C$_4$AH$_5$ (red).

Figure 6.29. $^{27}$Al one-pulse MAS NMR measurements of C$_3$S hydrated during 8 h in 60 mM NaAlO$_2$ solution with (red) and without pH adjustment (blue line).
Figure 6.30. $^{29}\text{Si}$ one-pulse MAS NMR measurements of C$_3$S hydrated during 5, 8 and 18 h in 60 mM NaAlO$_2$ solution.

Table 6.10. Fit parameters for different type of $^{29}\text{Si}$ environments of C$_3$S hydrated with 60 mM NaAlO$_2$ during 5, 8 and 18 h.

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<td>xG/(1-x)L</td>
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<td>20 0.98 2.37</td>
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<tr>
<td>8 h, %</td>
<td>11.4 6.06 5.96 11.3 7.43 6.38 5.52</td>
<td>39.34 2 4.62</td>
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<td>18 h, %</td>
<td>9.8 5.5 5 9.77 6.35 5.2 4.6</td>
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Figure 6.31. C₃S with water (left column) and with 60 mM NaAlO₂ solution (right column) after 1 h 15 min of hydration. The samples without aluminates are rapidly covered by C-S-H. In contrast the surface of the samples prepared with aluminates shows a smooth surface and the presence of an additional phase, probably AFm.

6.8.2 Notes on thermodynamic modelling

Supplementary thermodynamic calculations were done with Phreeqc v. 3.1.7 [1]. Phreeqc is a geochemical software enabling calculation of equilibrium chemistry in heterogeneous systems. Meaningful calculations require a self-consistent thermodynamic database. For cement hydrates a database, cemdata07, was developed [2,3] following careful analysis of published solubility data complemented by fresh data acquisition where necessary (see https://www.empa.ch/web/s308/cemdata). Originally this database contained standard state properties of cement hydrates and was implemented in the code GEM-Selector [4]. Diederick 2010 has converted the cemdata07 database into the Phreeqc format and performed a benchmark test of the calculation output of GEMS vs. Phreeqc for verification. The applied dissolution constants and reactions for relevant minerals at 25 °C are given in [5]
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<th>Si</th>
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184
Comments

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- undersaturated with respect to portlandite

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- close to saturation of OH hydrogarnet,
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Comments

- Strongly supersaturated with respect to portlandite

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- undersaturated to OH AFm,
- supersaturated with respect to C-S-H and Si hydrogarnet

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<th>6.85</th>
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<th>0.25</th>
<th>61.88</th>
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1) equilibria involving hydroxylated C3S were modelled assuming the following dissolution reaction: $\text{Ca}_3\text{SiO}_5 + 3\text{H}_2\text{O} = 3\text{Ca}^{2+} + 4\text{OH}^- + \text{SiO}_2(\text{OH})_2^{2-}$ $\log_k = 17$ [6]

2) equilibria involving C-S-H were based on an ideal solid solution model between Jennite and Tobermorite as described by Kulik and Kersten [7]
References


7. Paper V: Retarding effect of aluminate ions on the C₃S hydration and possible solutions to mitigate it

This chapter consists of the draft for the journal paper “Influence of aluminates on the hydration kinetics of tricalcium silicate”. It is planned to be submitted to Cement and Concrete Research. 

(E. Pustovgar, M. Palacios, J.-B. d’Espinose de Lacaillerie, T. Matschei, N. Ruffray, R. Verel, R.J. Flatt, Retarding effect of aluminate ions on the C₃S hydration and possible solutions to mitigate it, Cement and Concrete Research, in preparation)

This paper draft extends the previous work further exploring the effect of aluminates produced on the hydration of silicates. It is intended to be submitted after the PhD thesis is defended. The comments from all the Jury members will be included in the final version of the paper.

E. Pustovgar planned and carried out most of the experimental work. N. Ruffray performed the microscopy measurements. Dr. R. Verel and Prof. J.-B. d’Espinose de Lacaillerie helped Ms Pustovgar to perform the NMR measurements and they developed $^{29}\text{Si}^{[27}\text{Al}]$ CP/MAS NMR measurements. All authors contributed to the analyses of the results and the writing of the manuscript. The work was done under the guidance of Prof. Flatt, Prof. J.-B. d’Espinose de Lacaillerie and Dr. M. Palacios.
Abstract

It was recently proposed that the inhibiting effect of aluminates on the hydration of tricalcium silicate (C₃S) can be explained considering dissolution as rate limiting factor. The findings of this work strengthen this hypothesis. We investigate the influence of aluminate ions on the kinetics of C₃S hydration as well as the changes in the surface state of the silicates. In this work special attention is also paid to the influence of the aluminates addition time on the different stages of C₃S hydration. It was revealed that, depending on the initial and total dosage of aluminate ions in the hydrating system, the length of the induction period and the time of the main peak position vary differently, but in the ways that are consistent with dissolution being rate limiting. In addition, different mineral additions were examined in order to be able to cancel the inhibitory effect produced by aluminates.
7.1 Introduction

$C_3S$ is one of the main phases of Portland cement that determines its reactivity and major mechanical properties. Representing on average 60% of cement clinker, $C_3S$ is frequently used to model hydration of cement [1–4]. It is now agreed that the hydration proceeds by a dissolution – precipitation process causing the disappearance of non-hydrated $C_3S$ and the formation of calcium silicate hydrates (C-S-H) and portlandite. It has been previously observed that in presence of aluminates, reaction of silicates is delayed [5-8].

In Portland cement several situations are known that favored the presence of Al ions in the system. First of all, Al comes from the raw materials, specifically clays, thus favoring the situation of Al being incorporated into the silicates structure during the cement production. In particular, it was established that the presence of 0.1 - 1% of aluminium in the monoclinic structure of the $C_3S$, known as alite, inhibits its hydration [9,10]. Comparing to pure triclinic $C_3S$, alite exhibits lower early hydration rate and the time of occurrence of the main peak is retarded. The dissolution of tricalcium aluminate ($C_3A$), another important mineral phase in cement, enriches the pore solution in aluminate ions. An increased concentration of aluminates in solution was shown to be responsible for the decrease in early age reactivity of the $C_3S$, but the mechanism remained undefined [9,11]. Such a difference in reactivity of silicates in presence of aluminates can be the consequence of the affected dissolution of silicates [5,6,8] or nucleation of the C-S-H [10].

Nowadays, the widely spread blending of Portland cement with alumina-rich supplementary cementitious materials (SCMs) further enhances Al content in the system. In this case, aluminate ions being released into the solution as well as those present in the solid phases retard the early hydration of silicates and, consequently lead to slower strength development and/or to lower ultimate strengths.
In the standard Portland cement systems, the negative effect produced by aluminates can be handled by gypsum addition, since the formation of ettringite decreases the aluminates concentrations in the pore solution. Furthermore, the main negative effect of aluminates, reflected by a decrease in early strength, is something that has recently been stated to be effectively counteracted by the addition of CaCO$_3$. This is particularly interesting since, due to high availability of limestone, ternary blends consisting of Portland cement, aluminosilicates (metakaoline, fly ash, blast furnace slag etc.) and limestone are in any case of great interest. Therefore, these blends may also offer the possibility to suppress delay of C$_3$S hydration by the consumption of aluminate ions to form calcium carboaluminates [12,13]. Nevertheless, to the best of our knowledge there are no systematic studies done on pure model systems to better validate this hypothesis.

For the present paper, we used a combination of several analytical techniques such as isothermal calorimetry, nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) to get deeper understanding of the processes occurring in the bulk as well as at the surface of the C$_3$S after the contact with aluminate solutions. The aim is to explain the negative impact of aluminate ions present in the pore solution on the hydration of C$_3$S. Moreover, it is important to examine possible solutions to minimize this negative effect, in particular, through addition of sulfates or CaCO$_3$.

7.2 Materials and Methods

7.2.1 Materials

C$_3$S was synthesized following the procedure described in our previous study [5]. $^{29}$Si-enriched C$_3$S and non-enriched C$_3$S containing about 0.1 wt.% of Al impurities were obtained using 99.9% enriched in $^{29}$Si SiO$_2$ (Cortecnet) and SiO$_2$ (> 99% purity, Sigma Aldrich), respectively. C$_3$S was synthesized without addition of Al$_2$O$_3$. The presence of Al impurities in C$_3$S was
ensured due to the use of contaminated with Al SiO₂ precursors, as established by ²⁷Al magic angle spinning (MAS) NMR (Figure 7.1). The amount of such Al impurities is lower than 0.1 wt.%, which is below the detection limit of X-ray diffraction (XRD). Although the synthetic procedure was similar in both cases, different numbers of firing and quenching cycles were required to ensure the full transformation of the stating materials into the C₃S. In particular, to successfully synthesize ²⁹Si-enriched C₃S 4 cycles were necessary, when for non-enriched C₃S, 2 cycles were enough. All synthesized C₃S were milled in a micromill with agate beads and 20 ml absolute ethanol during 8 min. Particle size distribution (PSD) of non-enriched C₃S was measured by laser diffraction (MALVERN MASTERSIZER S) and results are presented in Figure 7.2, where bimodal distribution is evident. The BET specific surface area measured using Micromeritics Tristar II 3020 after degassing the sample at 200 °C for 1 h resulted in about 1.3 ± 0.05 m²/g for both synthesized powders.

NaAlO₂ (> 95% pure, VWR) was dissolved in ultrapure water (resistivity > 18 MΩ cm at 25 °C). Thus solutions of different concentrations between 3 and 60 mM were prepared and used as a source of aluminate ions. As mineral admixtures CaCO₃ (> 99.95% dry basis, Sigma Aldrich), CaSO₄ * 2 H₂O (gypsum, 98% pure, Acros Organics) and Na₂SO₄ (anhydrous for analysis, Merck) were added.
Figure 7.1. $^{27}$Al MAS NMR spectra of SiO$_2$ (> 99% purity, Sigma Aldrich, blue line) and $^{29}$Si-enriched SiO$_2$ (Cortecnet, red line).

<table>
<thead>
<tr>
<th></th>
<th>C$_3$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{10}$, µm</td>
<td>2.8</td>
</tr>
<tr>
<td>$d_{50}$, µm</td>
<td>14.7</td>
</tr>
<tr>
<td>$d_{90}$, µm</td>
<td>28.1</td>
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</tbody>
</table>

Figure 7.2. PSD of C$_3$S containing Al impurities.
7.2.2 Experimental Methods

7.2.2.1 Mix design and paste preparation

All C₃S pastes were prepared with a liquid/solid (l/s) ratio of 0.8 mixing during 3 min with vortex mixer. Normally, all amount of NaAlO₂ was introduced directly into the mixing water before addition of C₃S (Mixtures called “M”). In the experiments with separate NaAlO₂ addition (Mixtures “MS”), C₃S was firstly mixed during 1 minute with a l/s ratio of 0.4 containing N1 µmol of NaAlO₂ / gram of C₃S. Afterwards, the second half of the solution with N2 µmol of NaAlO₂ was added and the paste was mixed for 2 min more. In this sense, the name of each mix in these experiments was chosen to be as following: MS(N1-(N1+N2)). Concentration of NaAlO₂ included in the mixing water from the start (M) as well as used for the separate addition experiments (MS) are summarized in Table 7.1. pH of the prepared NaAlO₂ solutions varied between 10.8 and 12.1. This increase of pH didn’t have an influence on the hydration as previous studies showed [5].

In order to better model the situation for which aluminate ions are released into the pore solution gradually, as would occur in hydrating blended cement, we also performed “titration experiments” (MT). The effect of the continuous addition (titration) of NaAlO₂ on C₃S hydration was therefore investigated in the following way. In this experiment, that we call MT(24-48), 1 g of C₃S-al was first mixed with 0.4 g of 60 mM concentrated NaAlO₂ solution during 1 minute. Afterwards, the rest of 60 mM NaAlO₂ solution in the amount of 0.4 g was added continuously drop by drop during 8 min, while the paste was being mixed using the vortex mixer. Thus, it was possible to add the equivalent amount of Al as in the case of direct addition of 60 mM NaAlO₂ solution but this time the addition was distributed over 9 min of reaction. During the delayed “titration” mode (MT(0-24)) the same protocol was applied. The
only difference was that the initial C₃S paste was initially mixed with water (l/s = 0.4) and 60 mM NaAlO₂ solution was continuously added afterwards during 15 min.

<table>
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<tr>
<th>Mix</th>
<th>N1 (µmol/g C₃S)</th>
<th>N2 (µmol/g C₃S)</th>
<th>T (µmol/g C₃S)</th>
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<tbody>
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<td>-</td>
<td>2.4</td>
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<td>MT(0-24)</td>
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CaCO₃ was blended with C₃S using 1 : 1 ratio keeping the same l / s ratio and mixing time. Sulfates, Na₂SO₄ and gypsum, were added in the dosage of 10 and 12 mg per g of C₃S, respectively. Based on our estimations this amount should be enough to consume all NaAlO₂ added through the formation of ettringite. During measurements by isothermal calorimetry Na₂SO₄ was added to the paste together with 48 µmol of NaAlO₂ / g of C₃S or after 15, 60 or 120 min of hydration. The effect of gypsum in presence of the same amount of NaAlO₂ was studied during simultaneous addition and delayed addition after 60 min.

Hydration in presence of CaCO₃ was followed during the first 24 h by in situ ²⁷Al one-pulse NMR measurements. Details on the measurements was described in our previous studies [4,5].
Hydration was stopped with isopropanol after 2 h for the samples used in $^{29}\text{Si}\{^{27}\text{Al}\}$ cross-polarization (CP) NMR and XPS, and after 15 min, 1 h, 4 h, 8 h and 24 h for SEM experiments. For these measurements, the prepared paste was stirred during 5 min with the organic solvent taken in the 1 : 25 mass ratio. The prepared suspension was filtered using a vacuum pump and the obtained powder was stored in the desiccator.

7.2.2.2 Isothermal Calorimetry

All measurements were done at 23 °C using TAM air calorimeter from TA instruments. Pastes were prepared outside the calorimeter and introduced into the equipment in the amount of 1.5 g for each experiment. This amount was enough to obtain reproducible data as was confirmed by separate tests.

7.2.2.3 Nuclear magnetic resonance

$^{27}\text{Al one-pulse NMR}$

$^{27}\text{Al}$ NMR experiments were carried out using a Bruker Avance-500 spectrometer (magnetic field is 11.7 T) at the resonance frequencies of 130.31 MHz. MAS spectra were measured using a Bruker MAS NMR probe with 4 mm (outer diameter) ZrO$_2$ rotor at the spinning frequency of 15 kHz, what led to the temperature increase estimated as 20 K [5,14]. To acquire single-pulse $^{27}\text{Al}$ MAS NMR spectra, $\pi/6$ pulses of 2 µs with a recycle delay of 1 s were implemented to insure $^{27}\text{Al}$ central transition excitation thus providing quantitatively reliable $^{27}\text{Al}$ NMR signal intensities. The spectra were referenced to 1 M aqueous solution of Al(NO$_3$)$_3$. The accuracy of the chemical shift was $\pm$ 0.1 ppm. $^{27}\text{Al}$ MAS NMR spectra of hydrated samples were collected with typically 3200.
$^{29}$Si($^{27}$Al) CP NMR

CP/MAS NMR involving quadrupolar nuclei is more complicated than $^{29}$Si($^1$H) CP, which is why it has only recently been applied [15–19].

The experiment was set up based on the procedure reported by De Paul et al. and tested using albite (NaAlSi$_3$O$_8$) as a model sample [20]. The spectra were recorded using Bruker Ultrashield Avance AMX 400 spectrometer (magnetic field 9.4 T) and 4 mm rotors at spinning speed of 10 kHz. The $^{27}$Al and the $^{29}$Si frequencies were 104.26 MHz and 79.5 MHz, respectively.

1D $^{29}$Si($^{27}$Al) CP/MAS NMR spectra were recorded by selective excitation of the central transition using 55.5 KHz $\pi/6$ pulse of 1.5 $\mu$s. During the CP experiments, contact times of 50 ms were employed at recycle delays 1 s with a typical number of scans equal to 14720. To have Hartmann-Hahn conditions a more stable ramp (ramp70.80) contact pulse on silicon was implemented. No proton decoupling was utilized during acquisition. The $^{29}$Si bandwidth was 8012.8 Hz.

7.2.2.4 XPS

One spot on a reference powder (pure $^{29}$Si-enriched C$_3$S) as well as two spots on a hydrated in NaAlO$_2$ solution powder sample were investigated by XPS. Acquisition included a survey spectrum and detailed spectra of Ca 2p, Si 2p, O 1s, C 1s, Al 2p, Na 1s. Elements present in the first 5–10 nm of the outmost part of the material were determined within the sensitivity of the instrument (ca. 0.5–1 at.%).

The device used for X-ray photoelectron spectroscopy was a Phi5000 VersaProbe spectrometer (ULVAC-PHI, INC). The samples were prepared on double sided adhesive carbon tape. Spectra were acquired at a base pressure of 5*10$^{-8}$ Pa using a focused scanning monochromatic Al-K source (1486.6 eV) with a spot size of 205 $\mu$m and 50 W scanning an area of
400*400 µm. The instrument was run in the FAT analyzer mode with electrons emitted at 45° to the surface normal. Pass energy used for survey scans was 117.4 eV and 46.95 eV for detail spectra. Obtained spectra were calibrated to C 1s electron binding energy at 285.0 eV.

Data were analyzed using the program CasaXPS (Version 2.3.16). The signals were integrated following Shirley background subtraction. Sensitivity factors were calculated using published ionization cross-sections [21] corrected for attenuation, transmission-function of the instrument and source to analyzer angle. As a results, the measured amounts are given as apparent normalized atomic concentration and the accuracy under the chosen condition is approximately ± 10%.

7.2.2.5 SEM

Scanning electron microscopy investigations were performed in high vacuum (approx. 2.5e-6 mbar) using Leo 1530 Gemini (Carl Zeiss AG, Oberkochen, Germany). Secondary electron images were acquired on the samples without any coating using a 1.0 kV accelerating voltage and a 4.0 ± 0.2 mm working distance.

7.3 Results

7.3.1 Effect of NaAlO₂ on hydration of C₃S

7.3.1.1 Titration experiments

Results obtained by NMR in our previous study [5] have shown that consumption of Al from the solution happens immediately with the formation of calcium aluminate hydrate phases (AFm) and no resonance from the NaAlO₂ solution can be observed. This means that the concentration of Al in solution decreases very rapidly in our system, a situation that contrasts with what is expected during cement hydration where the solution can be considered to be buffered by aluminate containing phases. For this reason, we decided to devise experiments
that allow us to get closer to the situation where the concentration of Al is kept constant due to SCMs dissolution. One possibility is to add only half of the NaAlO$_2$ solution to C$_3$S powder in the beginning and to subsequently “titrate” the paste with the rest of the solution. This involves a change of the l / s ratio over the first 9 min of reaction. However, separate experiments showed that such a dilution only minimally affects C$_3$S hydration as far as heat release can show (Supplementary information, Figure 7.2).

As in our previous study [5], we observe the presence of an additional inflection point during the acceleration stage. As indicated in that paper, we believe that this is due to the bimodal PSD of the used C$_3$S. More specifically, this inflection point separates the reaction of two different particle size fractions represented by roughly linear zones of different hydration rates (Figure 7.3a, 7.4a). These linear zones make it possible, by extrapolation to minimal heat flow rate, to estimate the induction time of each particle size fraction. This provides useful additional information for separating effects on the induction period from ones on the position of the main peak.

Concerning the titration experiments themselves, we first examine the case MT(24-48) for which NaAlO$_2$ 24 µmol/g are included in the initial mixing water and another 24 µmol/g are added in titration mode to the mix (Figure 7.3). The result is compared to the samples M(24) and M(48) for which respectively 24 and 48 µmol/g were included in the mixing water and nothing was added in the titration mode. Results in Figure 7.3 show very similar calorimetry curves for MT(24-48) and M(24). This suggests that the initial concentration has a greater impact on the long term hydration than the total aluminates dosage.

To further test this hypothesis, we performed an experiment in which the initial Al dosage was only 2.4 µmol of Al / g. Here, in addition to using this amount directly in the mixing water M
(2.4), we also titrated the system to deliver a much higher ultimate amount of 24 µmol/g in increments such that only 2.4 µmol would be obtained after the first addition (sample MT(0-24)). Figure 7.4 shows once again that the position of the main hydration peak as well as the cumulated heat at 24 h is similar for the sample having been exposed to the same initial Al concentration, independently of the ultimate dosage.

However, the situation is quite different, if we examine the end of overall induction period (Figure 7.5), most likely associated to the beginning of the acceleration period of the finer particle fraction. In this case both Figures 7.5a and 7.5b show that the initial hydration rate of the titrated samples (MT(24-48) and MT(0-24)) is higher than the corresponding samples with similar bulk additions (M(48) and M(24)). Additionally, the time at which this occurs seems to depend on the total amount of aluminum and not on the initial concentration.

On the contrary, for the induction time of coarser particles (t), the initial concentration of aluminates in the mixing water seems to be more important than the total one (Table 7.2). The onset of coarser particles hydration, in the paste MT(24-48) is much closer to M(24) than to M(48) and MT(0-24) is much closer to M(0) (pure H2O) than to M(24).

**Table 7.2. Normalized onset of hydration of coarser particles. t₀ – induction time of coarse particles in pure H2O.**

<table>
<thead>
<tr>
<th>Mix</th>
<th>(t − t₀) / t₀, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0</td>
</tr>
<tr>
<td>M(2.4)</td>
<td>0.16</td>
</tr>
<tr>
<td>M(24)</td>
<td>0.4</td>
</tr>
<tr>
<td>M(48)</td>
<td>0.84</td>
</tr>
<tr>
<td>MT(24-48)</td>
<td>0.32</td>
</tr>
<tr>
<td>MT(0-24)</td>
<td>-0.04</td>
</tr>
</tbody>
</table>

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Figure 7.3. Comparison of the a) heat release rate and b) cumulated heat obtained for C₃S hydrated for different addition modes of NaAlO₂. A reference case for 24 and 48 µmol/g included in the mixing water are shown, M(24) and M(48), respectively. The sample labelled MT(24-48) refers to an experiment in which NaAlO₂ (48 µmol/g) is added over a period of 9 min. The final reached w / c is 0.8.

Figure 7.4. Effect of delayed titration with NaAlO₂ (MT(0-24)) on C₃S hydration during first day. A reference case with direct NaAlO₂ addition in the amount of 2.4 µmol/g (M(2.4)) and 24 µmol/g (M(24)) is shown.
Figure 7.5. Induction period during addition of NaAlO$_2$, zoomed in Figure 7.3a and 7.4a.

7.3.1.2 Separate addition

To better understand the effects observed in the “titration” experiments, a set of measurements for which the addition of NaAlO$_2$ was separated into two parts was performed and results are summarized in Figure 7.6. A first observation is that the degree of hydration at 24 h increases with the aluminium dosage (Figure 7.6a), but non linearly since MS(3-3) and MS(3-24) are quite similar and substantially lower than MS(3-48). The initial concentration also plays a non-trivial role. As shown in Figure 7.6b, MS(24-48) and MS(48-48) are similar and higher than MS(3-48).

Additionally, as shown in Figure 7.6c, the position of the main hydration peak is determined by the initial amount of added NaAlO$_2$. It remains constant when C$_3$S is firstly hydrated in solution containing 3 µmol of NaAlO$_2$ / g of C$_3$S (MS(3-3), MS(3-24), MS(3-48)) regardless of the extra aluminates introduces to the paste after 1 min of hydration. In contrast, if the total dosage is kept constant by splitting the added amount in different proportions for both addition times, we see in Figure 7.6d, that the position of the main peak is shifted to later times when the initially dosed aluminium amount is higher (MS(3-48) versus MS(24-48)), etc. As for the end of the overall induction period, it again depends on the total dosage of NaAlO$_2$.
(Figure 7.6f) being the same for MS(3-48), MS(24-48) and MS(48-48). Nevertheless for the coarser fraction it seems to be mainly affected by the initial amount of aluminates in the system being longer for MS(48-48) than for MS(3-48).

Figure 7.6. a), b) Cumulated heat and c) - f) heat rate measured during delayed addition tests. e), f) show magnified induction period of c) and d), respectively.
7.3.1.3 Electron Microscopy

To establish differences in the microstructure of C₃S caused by the aluminates two set of samples were investigated on M(48) and a reference without aluminates. Surface state as well as advancements in hydration with and without NaAlO₂ addition were compared at several times between 15 min and 24 h after reaction was stopped by isopropanol. These times are indicated by the vertical bars in Figure 7.7.

![Heat rate and cumulative heat curves for C₃S hydration](image)

**Figure 7.7.** Time, marked with vertical line on the calorimetric curves, used to stop hydration for SEM investigations. In particular, 15 min, 1 h 15 min, 4 h, 8 h and 24 h.

The first two selected points in time, which are 15 min (Figure 7.8a) and 1 h 30 min (Figure 7.8b), correspond to the induction period on the calorimetric curve, the next two (Figure 7.8c and 7.9a) – to the acceleration or beginning of the deceleration stage and the last one (Figure 7.9b) to the long term hydration.

When no aluminates are added, small precipitates of C-S-H (Figure 7.8a, b) can be seen on the surface of the C₃S grains during induction period. After 4 h of reaction the growth of the C-S-H needles is observed (Figure 7.8c, Figure 7.9a) with subsequent densification of the structure around 24 h (Figure 7.9b).
Addition of NaAlO$_2$ to the mixing water dramatically changes the surface state of the investigated material. First of all, a precipitation of a phase with different microstructure is observed right in the beginning of hydration (Figure 7.8a$_{2}$, b$_{2}$). Elongated needles or possibly platelets that appear as needles due to the angle at which images were taken. The amount of such precipitates does not seem to grow over time (Figure 7.8a$_{2}$ - c$_{2}$). It is also possible to see etch pits on the surface of C$_3$S (Figure 7.8c$_{2}$) in the beginning of the acceleration period. These were most likely also present, but not visible during hydration of the reference sample due to extensive coverage of the surface by C-S-H from the first minutes of reaction.

In addition, it can be noticed that, in presence of NaAlO$_2$, C-S-H does not grow uniformly over the grains as in the plain system. Even after 8 h of reaction completely inhibited reactive areas on the surface of the C$_3$S can be identified (Figure 7.9a$_{2}$), whereas the reference sample completely covered by C-S-H needles (Figure 7.9a$_{1}$).
Figure 7.8. Early age hydration of C₃S in water (left column) and with 48 µmol/g of C₃S NaAlO₂ (right column), M(48). At early times the samples without aluminates are rapidly covered by C-S-H and while etch pits may be present, they are difficult to identify because of that. In contrast the surface of the samples prepared with aluminates shows a smooth surface for a long time. They also show the presence of an additional phase, probably AFm. The appearance of etch pits can be clearly seen in this case at 4 h.
Figure 7.9. Hydration of C₃S in water (left column) and with 48 µmol/g of C₃S NaAlO₂ (right column) at 8 and 24 h (M(48) samples).

In addition, to exaggerate the effect of aluminates ca. 4 times higher dosage of NaAlO₂ was also used (M(184)). At this dosage, the hydration of the fine and coarse fractions is decoupled [5]. The hydration was stopped at 5 h so that, as suggested by calorimetry data, the hydration should be extensively completed for the fine particles, and barely initiated for the coarser ones (Figure 7.10). This is confirmed by our micrographs that show the surface of the larger particles having remained very smooth with barely any etch pits to be visible (Figure 7.11b). Additionally, small lumps of hydrates can be seen that are reasonably attributed to the fine particles having hydrated. Therefore, under these conditions, the inhibition produced by aluminates is even more clearly identified.
Finally, we also note that some platellets found in the sample hydrated with NaAlO$_2$ remind the hexagonal shape (Figure 7.11b), thus could be intuitively prescribed to Portlandite, but they could also represent the pieces of initial C$_3$S, that particles shape was far from spherical due to milling (Figure 7.12).

![Graph](image-url)

Figure 7.10. Heat release rate measured on hydrated M(184) C$_3$S paste [5].

![Images](image-url)

Figure 7.11. C$_3$S hydrated in a) water and b) solution containing 184 µmol/g of C$_3$S NaAlO$_2$ for 5 h. Hydration was stopped right after reaction of finer particles was complete based on calorimetric measurements.
7.3.1.4 X-ray Photoelectron Spectroscopy (XPS)

In order to determine chemical composition of the $^{29}\text{Si}$-enriched C$_3$S surface after hydration for 2 h in presence of NaAlO$_2$ solution (48 µmol/g), XPS analyses were done. Results were compared with the surface state of the $^{29}\text{Si}$-enriched C$_3$S before hydration (Table 7.3 and 7.4). Concentrations of different elements identified during the measurements are reported in Table 7.4. Pure $^{29}\text{Si}$-enriched C$_3$S was chosen to avoid any misunderstanding of the spectra due to the presence of Al in the structure and to facilitate comparison with results from $^{29}\text{Si}\{^{27}\text{Al}\}$ CP NMR that are discussed later in this work.

For non-hydrated C$_3$S the measured Si 2p electron binding energy of 101.2 eV is in agreement with data reported in other studies [22,23]. The Si-2p binding energy spectrum changes by 0.7 eV and the FWHM by 0.3 eV after mixing with 48 µmol/g of C$_3$S NaAlO$_2$ (Table 7.3). This shift to higher binding energy corresponds to the polymerization of silicate and subsequent formation of the C-S-H. The Ca / Si ratio on the surface of the material is close to 3 in the reference sample and goes to 1.8 after 2 h of reaction.

Figure 7.12. SEM investigation of initial non-hydrated C$_3$S.
The presence of Na and Al in the 2 : 1 ratio was identified on the surface of the sample after 2 h exposure to NaAlO$_2$ solution. Although the concentrations of the ions are, probably, low for a precise analysis, the deficit of Al compared to the presence of Na suggests that at least half of the added Al did not stay on the surface. In addition, since no decrease in the binding energies of Si and O was observed, it is reasonable to suspect that there is no incorporation of Al into the silicate structure [24–26]. The detected Al is most likely adsorbed on the surface or part of the precipitated phase.

A significant amount of carbon was also detected most likely due to partial adsorption of isopropanol used to stop hydration and/or carbonation.

<table>
<thead>
<tr>
<th>Table 7.3. Binding energies and Full Width at Half Maximum (FWHM) of the measured transitions, calibrated to C 1s C=C at 285.0 eV.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reference C$_3$S</strong></td>
</tr>
<tr>
<td>Binding energy (eV)</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>Na 1s</td>
</tr>
<tr>
<td>Al 2p</td>
</tr>
<tr>
<td>Si 2p</td>
</tr>
<tr>
<td>O 1s</td>
</tr>
<tr>
<td>O 1s</td>
</tr>
<tr>
<td>Ca 2p$_{3/2}$</td>
</tr>
<tr>
<td>Ca 2p$_{1/2}$</td>
</tr>
</tbody>
</table>
To describe the positional relationship between the formed species \(^{29}\text{Si}\{^{27}\text{Al}\}\) CP/MAS NMR was carried out. During this NMR experiment we first subjected aluminium to radio-frequency irradiation and then the magnetization was transferred via dipolar couplings to the detecting nucleus, which is silicon in our case. Enrichment of the investigated material with \(^{29}\text{Si}\) isotope is essential for this experiment thus the measurements were done using pure \(^{29}\text{Si}\)-enriched C\(_3\)S and \(^{29}\text{Si}\)-enriched C\(_3\)S containing trace contaminations by Al (\(^{29}\text{Si}\)-enriched C\(_3\)S-al). This \(^{29}\text{Si}\)-enriched C\(_3\)S contamination by Al was not intentional and resulted from a slight impurity of one of the raw materials used in a specific batch.

Results obtained after hydration of \(^{29}\text{Si}\)-enriched C\(_3\)S-al with NaAlO\(_2\) solution during 2 h show several resonances in the range of the Q\(^0\) species (Figure 7.13). Since the position of the Al currier frequency did not have an influence on the intensity of the obtained spectra it was not possible to distinguish which Al containing phase contributes at the most (4-fold Al, Al in C\(_3\)S and Al in C-S-H, or 6-fold Al, which is AFm phase as shown in the insert of Figure 7.13a). Similar measurements were done on the pure \(^{29}\text{Si}\)-enriched C\(_3\)S, which did not result in any resonances thus indicating that all magnetization in the previous experiment was provided by Al in C\(_3\)S. Further study on the \(^{29}\text{Si}\)-enriched C\(_3\)S hydrated for 9 months also did not result in the observed \(^{27}\text{Al} – ^{29}\text{Si}\) correlations (Figure 7.14) thus suggesting aluminates are not close to silicates, at least not with a few angstroms.

| Table 7.4. Normalized elemental atomic concentration measured on the surface of the two powders. |
|----------------------------------------------------------|----------------|----------------|----------------|----------------|----------------|
| (At.-%) | Ca | Si | O | Al | C | Na |
| Reference C\(_3\)S | 19.4 | 6.6 | 43.8 | 0.0 | 28.0 | 0.0 |
| Hydrated C\(_3\)S | 17.2 | 9.6 | 46.7 | 0.8 | 23.7 | 1.6 |

7.3.1.5 \(^{29}\text{Si}\{^{27}\text{Al}\}\) CP NMR
Figure 7.13. $^{29}\text{Si}^{27}\text{Al}$ CP NMR spectra of the hydrated for 2 h $^{29}\text{Si}$-enriched C$_3$S in presence of NaAlO$_2$ added in the amount of 48 µmol/g of C$_3$S. Carrier frequency was set at 75 ppm in (a) and compared to the one set at 10 ppm in (b).

Figure 7.14. $^{29}\text{Si}^{27}\text{Al}$ CP NMR spectra of the $^{29}\text{Si}$-enriched C$_3$S hydrated for 9 months in presence of NaAlO$_2$ (48 µmol/g). Carrier frequency was set at 69 ppm or at 5 ppm. As discussed in [5], the phase at 69 ppm is attributed to Al in C-S-H and at 5 ppm to third aluminate hydrate (TAH).
7.3.2 Influence of sulfates addition

In the NaAlO$_2$ free system adding sulfates increases the rate of hydration during the acceleration period. The main hydration peak is higher, but occurs at a slightly later time than in the sulfate free system. The induction period of the fine C$_3$S particles during hydration is thus longer in the presence of sulfates (Figure 7.15, 7.16).

The situation is very different when sulfates are added to an aluminate containing system. In those cases, we observe that the addition of Na$_2$SO$_4$ cancels the retarding effect of the aluminates. At least, the position of the main hydration peak is moved to earlier time and the induction period is shortened (Figure 7.15a). Results show that this effect decreases with the delay in addition time of the Na$_2$SO$_4$ (Figure 7.15a). Additionally, when gypsum is used, it also reduces the negative impact of NaAlO$_2$, although not that strongly as Na$_2$SO$_4$ does. Figure 7.16 shows that in this case there is not much difference observed between direct and delayed addition mode.

$^{27}$Al MAS NMR on the C$_3$S sample hydrated during 8 h in the presence of Na$_2$SO$_4$ and NaAlO$_2$ (48 µmol/g of C$_3$S) revealed the formation of ettringite (Aft) [27], which corresponds to a new resonance around 14 ppm (Figure 7.17a) comparing to the reference sample (Figure 7.17b).
Figure 7.15. Effect of direct and delayed Na$_2$SO$_4$ addition on C$_3$S hydration with and without the presence of NaAlO$_2$ studied by isothermal calorimetry.

Figure 7.16. Effect of direct and delayed gypsum addition on C$_3$S hydration with and without the presence of NaAlO$_2$ studied by isothermal calorimetry.
Figure 7.17. Effect of Na$_2$SO$_4$ on C$_3$S hydrated with NaAlO$_2$ (48 µmol/g) during 8 h studied by $^{27}$Al MAS NMR (a) with 10 mg of Na$_2$SO$_4$ per g of C$_3$S (b) without Na$_2$SO$_4$. Hydration was stopped with isopropanol.

7.3.3 Influence of CaCO$_3$ addition

To model the composition of blended cement with a ternary composition of Portland cement, aluminosilicates and limestone, mixes of C$_3$S, NaAlO$_2$ and calcite were used respectively. To elucidate the effect of carbonates no addition of sulfates was considered. The impact of CaCO$_3$ used to substitute 50% of C$_3$S in the paste containing aluminates is presented in Figures 7.18–7.20. Hydration of the blended mixtures in presence of different concentration of NaAlO$_2$ was studied by isothermal calorimetry (Figures 7.18, 7.19) and $^{27}$Al NMR (Figures 7.20).
7.3.3.1 Isothermal calorimetry

Figure 7.18 shows that addition of CaCO$_3$ considerably increases the extent of hydration of C$_3$S. In particular, the paste enters acceleration period with higher rate (Figure 7.18a) and the cumulated heat released is much higher than for the reference sample when calculated per gram of C$_3$S, more than double at 24 h as shown in Figure 7.18b.

Nevertheless, addition of NaAlO$_2$ in the amount of 2.4 and 48 µmol/g of solid phase directly in the mixing water still retards the hydration process. The length of the induction period slightly increases after addition of CaCO$_3$ (Figure 7.19), but it ends with more rapid start into the acceleration stage. The position of the main peak is affected as well. The retardation of the peak produced by 2.4 µmol/g of solid is more evident in the blended system, while the impact of NaAlO$_2$ in the dosage of 48 µmol/g of solid phase is lower with respect to CaCO$_3$-free C$_3$S (Figure 7.18a). In addition, there is not such a dramatic increase in the cumulated heat produced by higher NaAlO$_2$ concentration after 10 h of reaction as in the reference system (Figure 7.18b).

![Figure 7.18. Isothermal calorimetry data obtained during hydration of C$_3$S with and without CaCO$_3$ addition. Heat rate and cumulative heat are calculated per gram of C$_3$S. Amount of NaAlO$_2$ is per gram of solid phase.](image-url)
Figure 7.19. Induction period during hydration of C₃S with and without CaCO₃ addition. Zoomed in Figure 7.18.

7.3.3.2 ²⁷Al MAS NMR

In situ ²⁷Al NMR experiments revealed similar phase assemblage as well as similar amounts of the formed AFm phases after 3 h of hydration in presence of NaAlO₂ (48 µmol/g of solid) with and without addition of CaCO₃ (Figure 7.20a). This indicates that even without CaCO₃ addition there is enough Ca²⁺ in the system in order to bring dissolved Al into the form of calcium aluminate hydrates (AFm). During in situ hydration of C₃S in the presence of CaCO₃ the conversion of AFm into TAH also takes place. Nevertheless, this process is slower in the system where CaCO₃ is added (Figure 7.20b). Thus, after 1 day of reaction in the paste with CaCO₃, the amount of AFm phases is roughly the same as the amount of TAH, although in the system without CaCO₃ addition most of the AFm phases are converted into TAH.
Figure 7.20. Effect of CaCO₃ on C₃S hydrated in situ with NaAlO₂ (48 µmol/g of solid phase) during a) 3 h, b) 1 day studied by $^{27}$Al MAS NMR.
7.4 Discussion

In our previous study we discussed the inhibitory effect produced by NaAlO\textsubscript{2} on the hydration of C\textsubscript{3}S [5]. Experimental results showed, in accordance with the literature, that addition of aluminates extends the induction period of silicates and retards the appearance of the main hydration peak. These observations were proposed to result from an inhibition of dissolution. This was, for example, supported by analogous effects that annealing had on hydration kinetics with respect to aluminate addition. Moreover, by molecular dynamics simulations we determined that adsorption of aluminate ions on the hydroxylated C\textsubscript{3}S can occur through formation of ionic bonds to the C\textsubscript{3}S surface as well as interfacial hydrogen bonds between aluminate and silicate ions covered by dissolved calcium and hydroxide ions. These bonds lead to the formation of hydrated calcium aluminate complexes on the surface of C\textsubscript{3}S and are proposed to reduce its dissolution rate.

In the present work, we further examined this proposed mechanism. Recognizing that in cementitious systems, aluminates are supplied to solution over time rather than in an initial burst, we devised a series of experiments involving both titration and separate addition of NaAlO\textsubscript{2}. This provides the first insight on the role of the initial concentration of aluminates versus their ultimate dosage. In this section, our observations will be discussed in relation to the different effects observed on: Medium to long term hydration (10 h – 24 h), position of the main peak and induction period. The effect of additions on the same will be discussed more concisely in a separate sub-section.

7.4.1 Effect of NaAlO\textsubscript{2} on C\textsubscript{3}S hydration at 10-24 hours

As in our previous study [5] we observe an increase in cumulated heat after 11 h of hydration in presence of aluminates. These differences correlate with the micrographs in Figure 7.9 that also show a higher degree of hydration in presence of aluminates.
This increase in cumulated heat depends on the initial concentration of aluminates added to the system as seen in Figures 7.3b, 7.4b and 7.6b and Table 7.5. In particular, in Figure 7.3b MT(24-48) is similar to M(24) but clearly lower than M(48), in Figure 7.4b MT(0-24) is similar to M(2.4) but lower than M(24) and in Figure 7.6b MS(24-48) is between samples MS(3-48) and MS(48-48). However, when the initial concentration is the same, for example, 3 µmol/g, as in Figure 7.6a, the cumulated heat increase happens due to the total amount of aluminates present, being higher for MS(3-48) than for MS(3-3).

<table>
<thead>
<tr>
<th>Mix</th>
<th>M(2.4)</th>
<th>M(24)</th>
<th>M(48)</th>
<th>MT(0-24)</th>
<th>MT(24-48)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumulative heat (J/g)</td>
<td>185</td>
<td>234</td>
<td>280</td>
<td>184</td>
<td>234</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mix</th>
<th>MS(3-3)</th>
<th>MS(3-24)</th>
<th>MS(3-48)</th>
<th>MS(24-48)</th>
<th>MS(48-48)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumulative heat (J/g)</td>
<td>194</td>
<td>206</td>
<td>235</td>
<td>294</td>
<td>306</td>
</tr>
</tbody>
</table>

The fact that only two additions were used for mixtures MS, rather than titration, may explain the partially inconsistent results for MS(24-48). During separate addition of NaAlO₂ the time over which the total aluminum dosage is added is quite small. Consequently, the non-linear response to this dosage could indicate that the second addition takes place while etch pits are still opening. It could account for MS(24-48) being close to MS(48-48) rather than intermediate between it and M(3-48) in Figure 7.6b.

In line with our previous work, obtained results suggest that the coarse particle fraction reacts more extensively if the fine fraction has already reacted and is able to act as seeding agent, something that would depend mainly on the initial dosage rather than the total one ultimately titrated. We proposed that this can happen because the induction period of coarse particles is
more delayed by aluminates than that of the fine ones since they have a lower surface density of defects. Consequently, for a given dosage of aluminates, the coarser particles are more effectively inhibited. Given a high enough initial dosage, they may then only start to react after the finer fraction has largely hydrated.

Overall, these results suggest that if the reaction of the large particles is more effectively blocked than that of the finer fraction, then a substantial increase of the degree of hydration can be obtained between 10 and 24 h, which has clear implications for practical applications. Importantly also, these differences depend on what happens in the initial stages, which brings us to discussing more specifically our observations on the induction period in the next subsection.

7.4.2 Effect of NaAlO$_2$ on C$_3$S hydration during the induction period

Because of our bimodal size distribution, we have two induction periods rather than a single one. Resolving these is not trivial, but can be tentatively done by extrapolation of the two linear regimes in the global acceleration period [5].

The inflection point between these two regimes is particularly well visible in Figure 7.3a and 7.6d. The onset of the first linear regime (fine particle fraction) is determined by the total dosage of aluminates (see Figure 7.5 and 7.6f and comments in sections 7.3.1.1 and 7.3.1.2). In contrast, the induction period of the coarser fraction is more governed by the initial amount of added NaAlO$_2$ (Table 7.2). In particular, the second linear regime shifts almost parallel to later times when the initial concentration of aluminates increases (Figure 7.3a and 7.6d).

Attributing such difference to an effect of aluminates on dissolution is consistent with our SEM micrographs. These, firstly, also show that addition of NaAlO$_2$ inhibits hydration in the first minutes (Figure 7.8a_2). In contrast to the reference sample, the sample with aluminates is
characterized by C₃S surfaces that remain completely free of C-S-H. Instead, a different phase is formed less homogenously and in an amount that does not seem to grow over time (Figure 7.8a_2-c_2). This suggests that it could be an AFm phase, which was reported and qualitatively measured in the same conditions by ²⁷Al MAS NMR [5]. In addition, precipitation of AFm could also explain the lack of Ca identified on the surface of C₃S by XPS (see section 7.3.1.4).

Since the samples with aluminates are not initially covered with C-S-H, it is possible to observe the appearance of etch pits. For the sample M(48), this occurs only at 4 h (Figure 7.8c_2). This is a nice indication that the presence of NaAlO₂ affects dissolution of C₃S, thus resulting in the increased induction period observed during calorimetry measurements (Figure 7.3). In addition, it is clear that an increased dosage of aluminates acts more significantly on dissolution of silicates since at similar times (4 and 5 h respectively) the surface appears to be more pitted in M(48) (Figure 7.8c) than in M(184) (Figure 7.11b).

7.4.3 Effect of NaAlO₂ on C₃S hydration on the position of the main peak

We have also observed that the timing of aluminate additions has an important effect on the position of the main peak measured by calorimetry, which can also be referred to as onset of the deceleration. During titration (mixtures MT) as well as separate addition (MS) experiments we identified a clear dependence of the main peak position on the initial amount of NaAlO₂ present in solution (see section 7.3.1.2 and Figure 7.6c and 7.6d).

Unfortunately, interpreting this effect is not trivial since the reason for the onset of deceleration period is not well understood in the literature. Most recently, it has been suggested that it may be due to dissolution becoming limited either because of a reduction in the dissolving surface due to grains being covered by hydrates [3] or because of the coalescence of dissolution
pits [28]. Our results indicate that the position of the main peak is directly affected by the amount of aluminates initially present in solution, but does not depend on the amount added after that.

A few hours before the start of the deceleration stage, we can see by SEM, that in M(48) the surface of C₃S is still not uniformly covered by C-S-H (Figure 7.9a_2). This suggests that NaAlO₂ addition inhibits not only the dissolution rate due to later etch pits formation, but also modifies the nucleation and/or growth of C-S-H. In relation to this, we also observe that the morphology of the C-S-H appears to be affected by the presence of NaAlO₂. Needles seems to be longer and probably thinner (Figure 7.9), while their relative organization appears to be less dense.

7.4.4 Nature and role of aluminate phases

During investigation of the silicates surface by SEM, we observed the precipitation of the new phase in the presence of NaAlO₂, which as discussed in the previous sections was attributed to AFm. Based on our previous study [5], in the presence of NaAlO₂ the initial AFm formation is followed by the appearance of TAH and incorporation of Al in C-S-H. The knowledge of the relative organization of all these species in the sample would shed additional light on the origin of the proposed mechanism, by which aluminates passivates the silicates.

For this we attempted to develop a new experimental approach, in particular, $^{29}$Si{$^{27}$Al} CP NMR. The fact that a signal in the $Q^0$ range was obtained for the $^{29}$Si-enriched C₃S containing Al impurities insures the validity of the developed CP experiment, that to the best of our knowledge has never been applied to study cement hydration. At the same time, the fact that after 9 months of reaction there is no correlation observed between TAH and C-S-H phase is a bit surprising. Nevertheless, the explanation may be that Al in TAH and Si in C-S-H are too
far away to be detected by this approach. The same is true for the situation predicted by molecular modelling simulations [5] when aluminates ions adsorb on the surface of the initial hydroxylated C₃S by hydrogen bonds formation, thus as suggested inhibiting further hydration. Indeed, from those simulations we estimate the distance between Al and Si in Si–O···HO–Al which turns out to be around 6 – 7 Å. The concentration of the phases in the sample can be another limiting factor, but this could be overcome by using longer acquisition time during the measurements.

7.4.5 Effect of additions on the passivation of C₃S hydration by aluminates

The inhibitory effect of aluminates can be significantly reduced by the addition of sulfates (Figures 7.15, 7.16), which is in agreement with previous studies [9]. At the same time, addition of either Na₂SO₄ or gypsum to pure C₃S delays its hydration. In principle, addition of Na₂SO₄ to C₃S in water should complex Ca²⁺ thus creating higher undersaturation with respect to C₃S and consequently accelerating its dissolution. At the same time, promoted dissolution of C₃S can also activate Al ions in it to inhibit further reaction. For gypsum, an initial decrease in dissolution may be expected from the common ion effect on the undersaturation with respect to C₃S. Overall however, the main mechanism involved in the hydration delay in presence of both these sulfates remains unclear.

In the case of hydration with NaAlO₂ in the amount of 48 µmol/g of C₃S, sulfates cause the precipitation of ettringite, which decreases the amount of Al ions in solution. This increases the overall undersaturation and thus enhances the reactivity of C₃S (Figure 7.17).

In contrast to sulfates, CaCO₃ does not counteract the negative impact produced by NaAlO₂. Nevertheless, it significantly enhances the hydration rate of C₃S due to “filler” effect by providing more nucleation sites. In cement, limestone was proposed to react with aluminates
with the formation of calcium aluminate carbonates (AFm) [29,30]. In our case, this reaction most probably also takes place but much later, due to slow dissolution of CaCO$_3$, especially at lower pH.

Delayed reaction of CaCO$_3$ would explain observed retardation in presence of NaAlO$_2$, as well as slower transformation of AFm phases into TAH as revealed by $^{27}$Al NMR (Figure 7.20).

7.4.6 Mechanistic aspects

Some of the results presented are specifically dependent on the bimodal size distribution of our powder. Nevertheless, this characteristic turned out to be very useful in resolving the mechanism at stake of the impact of aluminates on C$_3$S hydration. In particular, as in our previous study, the ensemble of results presented appears to support the view according to which aluminates inhibit C$_3$S hydration by reducing its dissolution rate, and more specifically by delaying or hindering the opening of etch pits. Because of the important role of initial conditions in this process, it is not surprising that the aluminate dosage in the mixing water is found to play an important role.

Despite the strong support of an impact on dissolution, other issues should also be mentioned. For example, after the extended induction period, C-S-H needles can be found on the surface of C$_3$S as well as on the surface of the AFm phase. However, they do not grow uniformly and their morphology seems to be changed. Possibly this change in the packing density of needles may be beneficial for water to access the surface, which could also offer a possible explanation to the increased cumulated heat at 24 h. Nevertheless, whether this is a cause or an effect could be debated, since a lower dissolution rate would reduce the number of nuclei formed and potentially cause the observed changes in the packing of hydrates.
7.5 Conclusions

C₃S dissolution inhibited by NaAlO₂ was already proposed in our previous study to result from changes in dissolution rates. This work brings additional evidences for it. In particular, it was shown by SEM that addition of NaAlO₂ delays etch pits formation on the surface of C₃S and consequently the precipitation of the C-S-H. In addition, this delay is more evident for the coarser fractions of the particles, which is attributed to their lower surface density. This can be beneficial in systems for which long term hydration is more important than the initial one. Indeed, as discovered in this work, in the presence of NaAlO₂ and a bimodal distribution of particles, a seeding effect can be provided by fine particles for the coarser ones.

Furthermore, we investigated the different addition modes of NaAlO₂ thus obtaining information that appears to be more relevant to the one found in real cement system, where aluminates can be released over time rather than all at once. The effect of initial and total concentration of aluminates on hydration of C₃S observed during titration as well as delayed addition experiments is very intriguing. They reveal the complexity of the effect produced by aluminates. It appears that there are two different processes at stake: one responsible for the increase of the induction period and another for the position of the main hydration peak as well as the longer term hydration behavior. The dependence of the main peak position on the initial concentration of aluminates rather than their total dosage is not trivial to understand. Particularly not since for the induction period it is the total dosage of aluminates that matters rather than the initial concentration. Clearly these results suggest a combination of effects relating to surface state of C₃S in addition to the involvement of aluminum in chemical reactions.

It is mainly sulfate-based mineral additives that counteract the negative impact of aluminates even when added in the delayed way. Most likely, ettringite formation observed in this case
decreases the concentration of aluminate ions in the pore solution, displaces those inhibiting dissolution and reactives hydration independently of addition time. Addition of calcite enhances the hydration of C₃S but mainly due to filler effect. Alone it is not capable to act on aluminates at an early stage, most likely, due to its slow dissolution.

7.6 References


Figure 7.21. Effect of variable l/s ratio on C₃S hydration during first day. The sample “H₂O titr” refers to an experiment in which water is added over a period of 9 min thus varying the l/s from 0.4 to 0.8. For the sample “H₂O” l/s = 0.8 was used initially.
8. Conclusions and outlook

8.1 Conclusions

This work represents a fundamental study, that contributes to the understanding of different stages of tricalcium silicate (C\textsubscript{3}S) hydration as well as the effect of aluminate ions on it. New insights into the aluminate-silicates interplay were achieved by the combination of different techniques that provide information at different scales.

8.1.1 Hydration of C\textsubscript{3}S

\textsuperscript{29}Si-enriched C\textsubscript{3}S, synthesized with a very careful control of the structure and granulometry, together with well-defined experimental protocol insured \textit{in situ} step by step investigation of C\textsubscript{3}S hydration by magic angle spinning (MAS) nuclear magnetic resonance (NMR) technique. When high specific surface area (SSA) of the synthesized material was used, it was possible to study 90\% of the hydration process in 24 h of spectrometer time without external acceleration of the process. In this way, unique quantitative information pertinent to hydration mechanisms was obtained \textit{in situ} and with a time resolution down to 30 min. Results shed new light on the origin of the rate limiting steps, thereby resolving one of the central and century old questions about cement hydration because of the sensitivity enhancement that \textsuperscript{29}Si enrichment provides to understand chemical-kinetics at solid-liquid interfaces.

In particular, it was established that non-hydrated C\textsubscript{3}S particles surface predominantly consist of hydroxylated Q\textsuperscript{0} silicate species. During the induction and acceleration stages the amount of Q\textsuperscript{0}(h) remains constant and drops only after a significant amount of C\textsubscript{3}S has hydrated. This suggests that during dissolution, the surface decreases due to the reduction in particle size, but that this is compensated for by roughening (opening of etch pits and step retreat). The onset of silicate polymerization during the acceleration stage of hydration corresponds to the formation...
of dimeric (Q¹) units in calcium silicate hydrates (C-S-H). At the end of acceleration period longer chains containing (Q²) species are formed. Results suggest that during deceleration period the extent of silicate polymerization might be accompanied by an increased density of the C-S-H that consequently would present a diffusion barrier for mass transport and, thus, slow the hydration rate. Alternatively, the results obtained can also support the view according to which the deceleration takes place due to inhibition of hydration by hydrates themselves, impinging on each other’s growth.

Moreover, the developed approach also offers, for the first time, 2D J-mediated (through 29Si-O-29Si bonds) 29Si{29Si} NMR measurements that provide detailed insights regarding the different silicate species, their respective site connectivities, and relative populations, especially for previously unidentified discrete silicate moieties in the C-S-H. It was found that while the mean chain length is 5, there is a distribution mainly of dimers and octamers of which the proportion “happens” to give a mean chain length of 5.

The degree of C₃S hydration was determined based on the quantitative analyses of the NMR spectra and the obtained results showed a very good agreement with isothermal calorimetry measurements. NMR and isothermal calorimetry results confirm the importance of the surface area of the starting material showing that the degree of hydration decreases when coarser C₃S is used. Furthermore, a linear correlation between the parameters of the main hydration peak and SSA of the used C₃S was established.

Thus, in situ time-resolved solid-state NMR experiments coupled with original 29Si-enriched C₃S synthesis methods can provide ground-breaking information concerning the hydration of C₃S. Obtained results provide precious experimental data that could be used to evaluate existing and sometime conflicting hydration models.
8.1.2 Effect of NaAlO$_2$ on C$_3$S hydration

The addition of NaAlO$_2$ delays the hydration of C$_3$S and increasingly so with higher concentrations of aluminates in solution. In particular, the length of the induction period is extended and the position of the main hydration peak is shifted to later times. By molecular dynamics (MD) simulations, it was found that aluminate ions adsorb directly to the hydroxylated C$_3$S surface covered by dissolved calcium and hydroxide ions. This adsorption occurs through ionic interactions as well as the interfacial hydrogen bonds between aluminate and silicate ions, which can lead to the formation of hydrated calcium aluminate complexes on the surface of C$_3$S.

The ensemble of our results appears to support the view that C$_3$S hydration in presence of NaAlO$_2$ can be explained based on the dissolution control theory. In particular, we propose that the adsorption of aluminates evident during MD simulations takes place on the reactive sites of silicate surfaces, inhibiting further reaction by delaying or hindering the opening of etch pits. In support of this, we found by scanning electron microscopy (SEM) that addition of NaAlO$_2$ indeed delays the etch pits formation on the surface of C$_3$S and consequently the precipitation of the C-S-H. In addition, this delay is more evident for the coarser fractions of the particles than for the finer ones, which is attributed to their lower surface density of defects. The fact that annealing of the powder leads to more massive retardation also supports the view that aluminates inhibit C$_3$S hydration at active dissolution areas.

Because of the important role of initial conditions in this process, it is not surprising that the aluminate dosage, as well as pH in the starting mixing water play an important role. In particular, it is the initial concentration of aluminate ions that determines the position of the
main hydration peak and not the one added in total. Moreover, the observed delay occurs only when pH of the initial solution is below 13.

Concerning the longer term impact, it was discovered that in the presence of NaAlO$_2$ and a bimodal distribution of particles, a seeding effect can be provided by the fine fraction for the coarser one. This results in an increased degree of C$_3$S hydration at 10-24 hours, which can have important practical implications.

By $^{27}$Al one-pulse MAS NMR it has been established that the increase in the NaAlO$_2$ dosage promotes the formation of AFm phases, enhances Al incorporation in C-S-H and increases the amount of third aluminate hydrate (TAH) at later times. However, in our experiments we did not resolve any resonances that could be attributed to covalent bonds between silicon and aluminium. In the presence of Na$_2$SO$_4$ ettringite formation was detected, which, most likely, decreases the concentration of aluminate ions in the pore solution, causing partial desorption of the adsorbed aluminates responsible for retardation and thus, as observed, reactivates hydration independently of addition time.

In summary, we have seen that the effect of aluminates on the hydration of C$_3$S is complex and can depend on several parameters. All results can be consistently interpreted with the view that aluminates have an impact on C$_3$S dissolution and surface state of C$_3$S.

8.2 Future outlook

A well-designed approach of using in situ NMR to study hydration of cementitious materials serves as one of the main outcome of this work. Nevertheless, it can be further improved. For instance, to avoid the disparities between the set temperature and the true sample temperature inside the probe, the use of the NMR spectrometer equipped with temperature control unit
would be beneficial, especially, for $^{27}$Al NMR experiments where high spinning speeds are required.

Results obtained in this study will serve as a basis for the further development of the cement hydration models and understanding of the influence of aluminates on the development of mechanical strength. At the same time, a number of open questions remain which would be interesting to study in further research.

- The properties of cement depend not only on the coordination and local environment of silicon, but also of calcium ions. Thus the role of Ca examined by $^{43}$Ca solid-state NMR could potentially play a significant role in structural and chemical studies. However, limitations of this technique should be considered due to low natural abundance of $^{43}$Ca (0.135%) and its quadrupolar nature, as well as the very high cost of $^{43}$Ca if enrichment is to be considered.

- Isothermal calorimetry measurements do not provide reliable data on the kinetics of $\text{C}_3\text{S}$ hydration during the pre-induction period due to the necessity of ca. 40 min for temperature equilibration inside the cell after the sample is introduced. To overcome this problem an internal mixing system could, probably, be used thus providing the missing information about the initial dissolution. Furthermore, this study could be complemented by the analyses of the changes in the composition of the pore solution during this stage, for example, with the help of inductively coupled plasma – optical emission spectrometry (ICP – OES), thus correlating kinetics of $\text{C}_3\text{S}$ dissolution with the quantitative composition of the dissolved ions. If successful, addition of NaAlO$_2$ could be done to further examine the mechanism proposed in this work and, in particular, to monitor the change in the undersaturation of the system.
Further investigations by SEM applying different sample preparation procedures should be considered. For instance, hydrated samples of C₃S, embedded in an epoxy resin and polished, would make it possible to see the hydration front and compare more explicitly the different advancements in reaction of finer and coarser particles with and without the presence of NaAlO₂. Other microscopy techniques, such as cryo-FIB-nanotomography in combination with image-based modelling could be also considered to gain 3D information on hydrate distribution during hydration. This technique, in principal, is able to provide quantitative microstructural analysis of particles in dense suspensions as fresh cement paste, thus avoiding possible artifacts from dilution.

Annealed samples showed a very interesting behavior, apparently eliminating reactivity differences between particles of different size classes. Therefore, from an experimental point of view, annealing appears to be a useful treatment to further examine the action of aluminates on silicates dissolution.

In this work, mainly a C₃S with a bimodal particle size distribution was studied. It turned out to be beneficial helping in differentiating the effect of aluminates on different particles size fractions. Nevertheless, the study of monodispersed systems could be of potential interest and an alternative to the wider spread use of annealing.

This study was done on a model system. The next essential step would be to gradually increase the system complexity, shifting the composition of the investigated paste more close towards the real cement.
Annex

In this chapter we report the results of additional experiments done in relation to the investigated topic. Obtained results are only preliminary studies and at this stage are not conclusive yet. Therefore, they are not included in the main text of the thesis.

A.1 Hydration of pure C₃S and C₃S containing Al impurities

In this section of the work we further investigate by isothermal calorimetry and nuclear magnetic resonance (NMR) measurements the effect produced by NaAlO₂ on hydration of tricalcium silicate (C₃S). In particular, it is interesting to see if Al impurities that are initially present in the synthesized C₃S contribute to the observed behavior.

A.1.1 Isothermal calorimetry

Synthesized pure C₃S and containing Al impurities C₃S-al were hydrated in pure water and with 48 µmol NaAlO₂/g of C₃S. It can be seen that despite the difference in the granulometry (Figure A.1), the reaction of these two powders with water is quite similar. The evolution of the heat rate as well as cumulated heat during the reaction are compared in Figure A.2. The addition of 48 µmol of NaAlO₂ results in clear induction period for C₃S-al hydration, whereas for pure C₃S there is no period of total inactivity visible.

Furthermore, although the position of the main hydration peak is retarded less for pure C₃S than for C₃S-al (Figure A.2a), the amount of the heat released after 10 h of hydration is much higher for the C₃S-al (Figure A.2b). This is difficult to rationalize with different particle size distribution (PSD), but it looks like the C₃S-al has the well-defined fraction of the fine particles and the pure C₃S not, thus suggesting that C₃S-al is prone to seeding in presence of NaAlO₂ more than pure C₃S (seeding effect is discussed in chapters 6 and 7 of the main text).
Figure A.1. Particle size distribution of pure C₃S and C₃S containing Al impurities.

<table>
<thead>
<tr>
<th></th>
<th>C₃S</th>
<th>C₃S-al</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₁₀, µm</td>
<td>1.3</td>
<td>2.8</td>
</tr>
<tr>
<td>d₅₀, µm</td>
<td>6.4</td>
<td>14.7</td>
</tr>
<tr>
<td>d₉₀, µm</td>
<td>15.1</td>
<td>28.1</td>
</tr>
</tbody>
</table>

Figure A.2. Hydration of C₃S with and without Al impurities.
A.1.2 Nuclear magnetic resonance

$^{29}\text{Si one-pulse NMR}$

The impact of NaAlO$_2$ on the hydration of C$_3$S was also studied by one-pulse $^{29}$Si magic angle spinning (MAS) NMR. To insure high resolution in a short period of time pure $^{29}$Si-enriched C$_3$S was used. Thanks to the 100% enrichment all experiments were done in situ monitoring hydration up to 98 h. Selected spectra of this experiment together with the quantitative analyses of all obtained resonances are shown in Figure A.3 and A.4, respectively. As can be seen from Figure A.3, it was not possible to resolve a resonance corresponding to Al in calcium silicate hydrates (C-S-H) by $^{29}$Si NMR. This signal ($Q^2(1\text{Al})$) normally appears around -81.5 ppm and in our case it is so broad and small that hardly can be detected and distinguished from the noise level. Based on the integrated intensities of the observed resonances (Figure A.4) we can conclude that on the one hand, the presence of Al promotes the formation of hydrated products (mainly $Q^1$) after 9 h of reaction. But on the other hand, at earlier stage of hydration we can observe that more C$_3$S remains unreacted ($Q^0$) when NaAlO$_2$ is added, what is in agreement with the calorimetric data for pure C$_3$S showed before (Figure A.2). In addition, in agreement with the main study it is dominantly $Q^1$ species formation that determines the advancements of hydration during acceleration period. Amount of $Q^2$ is appeared to be too low in this system what does not really allow to discuss them.
Figure A.3. Selective spectra obtained during \textit{in situ} hydration of $^{29}$Si-enriched C$_3$S in presence of NaAlO$_2$ (48 $\mu$mol/g) studied by $^{29}$Si one-pulse NMR.

Figure A.4. Quantitative analyses of the data obtained for $^{29}$Si-enriched C$_3$S hydration with (48 $\mu$mol/g) and without NaAlO$_2$ addition studied by $^{29}$Si one-pulse NMR.
**$^{27}$Al one-pulse NMR**

To further examine if there is any effect produced by Al in C₃S on the coordination of Al in the formed hydration products, the $^{27}$Al MAS NMR spectra were recorded during *in situ* hydration in NaAlO₂ solution of pure $^{29}$Si-enriched C₃S and C₃S-al (Figure A.5). As for $^{29}$Si NMR measurements the same dosage of NaAlO₂ was added. Being in agreement to what has been reported before, we can observe in both cases the formation of AFm phases (9.8 ppm) right from the first hours of hydration. With progress of reaction amount of AFm phases continuously decreases and we start to observe the formation of third aluminate hydrate (TAH) (5 ppm) and incorporation of Al into C-S-H phase (69 ppm). It is also possible to detect a small amount of 5-fold Al around 30 ppm. Despite the fact that the same species are formed during hydration of both powders, the observed kinetics is different. For instance, based on the quantitative analyses of the obtained spectra it can be clearly seen that the presence of aluminum in C₃S provides faster disappearance of AFm phases, it promotes formation of TAH and also more Al gets incorporated in C-S-H when there is additional source of Al from C₃S (Figure A.6). Formation of TAH is associated with the formation of the C-S-H phase. This correlates well with our observations from isothermal calorimetry experiments where we could clearly see more C-S-H resulted from the hydration of C₃S-al.
Figure A.5. Al one-pulse NMR spectra of the hydrated $^{29}$Si-enriched (a) and C$_3$S-al (b) in presence of NaAlO$_2$ (48 µmol/g).

Figure A.6. Quantitative analyses of the $^{27}$Al NMR spectra obtained during hydration of $^{29}$Si-enriched and C$_3$S-al in presence of NaAlO$_2$ (C = 60 mM): 82 ppm (Al in C$_3$S), 69 ppm (Al in C-S-H), 35 ppm (Al$^{3+}$ substituting Ca$^{2+}$ in the interlayer of C-S-H), 10 ppm (AFm) and 5 ppm (TAH).

A.2 Influence of TIPA addition
We investigated by isothermal calorimetry the effect of triisopropanolamine (TIPA) on C$_3$S hydration in presence of NaAlO$_2$. Amount of TIPA added varied between 0.06 and 0.9 wt.%.
To fully understand the possible effects of the chemical it was also important to examine different addition modes.

Results showed that regardless of the addition mode no positive effect can be observed due to TIPA addition. As can be seen from Figure A.7, even when TIPA first mixed with NaAlO₂ solution, thus allowing enough time to form possible chelates, no cancelation of the retardation can be observed when later added to C₃S. Moreover, when concentration of TIPA is increased up to 0.9 wt.%, this provides further decrease in silicates reactivity. In addition, presence of TIPA decreases cumulative heat when compared with the reference sample (Figure A.7b).

Figure A.7. Effect of TIPA on C₃S hydration when added together with NaAlO₂ solution studied by isothermal calorimetry. The used concentrations of TIPA are a) 0.06%, b) 0.2%, c) 0.9%.

A.3 Effect of metakaolin addition
Addition of metakaolin provides similar effect if compared to the hydration in presence of NaAlO₂ solution (Figure A.8). When 25 wt.% of C₃S is replaced by metakaolin induction period is increased for about 2 h and 1.5 h retardation of the main peak is observed. Furthermore, despite the initial decrease in the cumulated heat of the paste with metakaolin its increase after 8 h of hydration is detected being the same trend as in the case of NaAlO₂
addition.

$^{27}$Al NMR measurements on the system containing metakaolin were also performed but the very broad and intense resonance in the area of 6-fold Al arising from pure metakaolin makes the analyses impossible.

![Figure A.8. Effect of metakaolin on the hydration of C₃S.](image-url)
Curriculum Vitae

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SCHOLARSHIPS AND AWARDS

2016
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2013
• Scholarship of French Embassy in Switzerland

2009
• Essay competition sponsored by Saint-Gobain Recherche (2nd award) Titel: “Mesoporous inorganic fibers”
• MSU competition in Mathematic (1st award)
• Winner of the national project “Conquer Vorobiev mountains” organized by MSU (in chemistry, physics, mathematic and philology)

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