Hydration of polyphase Ca_3SiO_5 – $\text{Ca}_3\text{Al}_2\text{O}_6$ in the presence of gypsum and Na_2SO_4

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Abstract

Alite (Ca_3SiO_5 : C_3S^*) and calcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$: C_3A) are the major phases in Portland cement, which have an essential role in the development of early age properties. The effects of gypsum content, fineness, and Na_2SO_4 addition on the early-stage hydration kinetics are investigated for polyphase (co-sintered) Ca_3SiO_5 – $\text{Ca}_3\text{Al}_2\text{O}_6$ model systems using calorimetry, X-ray diffraction, thermal analysis and solid-state ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy. The results demonstrate that the hydration of C_3A significantly affects the hydration of C_3S . The C_3S and C_3A hydration is hindered considerably in severely over-sulfated systems (where C_3A hydration is suppressed due to a very high gypsum content) and systems with additional Na_2SO_4 . Although there is a considerable amount of Al incorporation in the C-S-H phase, no clear trends with respect to gypsum content, hydration age or Na_2SO_4 addition are observed for the $\text{Al}_{\text{IV}}/\text{Si}$ ratios of the C-S-H phase determined from ^{29}Si NMR. With the addition of Na_2SO_4 , recrystallization of ettringite from the AFm phases is postponed from 1 day to 7 days.

* Cement chemistry notation: C – CaO , S – SiO_2 , A – Al_2O_3 , $\bar{\text{S}}$ – SO_3 , N – Na_2O

Keywords: Portland cement ; alite ; sodium sulfate ; kinetics ; hydration products

1. Introduction

Sodium sulfate (Na_2SO_4 , NS) acts as a potential activator to increase the reactivity and mechanical properties of blended systems with high Portland cement replacement levels. Previous studies have demonstrated a significant increase in the overall reactivity and mechanical properties, when high volume fly ash blends are activated with Na_2SO_4 ¹⁻⁵. However, the current understanding of the effect of Na_2SO_4 on the hydration of Portland cement systems is rather limited, and new knowledge is required to understand the fundamental mechanisms, potentials and limitations of such systems.

C₃S hydration. Alite/tricalcium silicate (Ca_3SiO_5 : C_3S) is the principal cement phase, constituting around 50 - 70% of Portland cement (PC), and its hydration is instrumental for the setting and hardening process as well as for the strength development. C_3S reacts with water to form calcium silicate hydrate ($(\text{CaO})_x\text{SiO}_2(\text{H}_2\text{O})_y$: C-S-H) gel and portlandite ($\text{Ca}(\text{OH})_2$: CH). Hydration of C_3S can be divided into 5 stages⁶ including periods of (I) dissolution, (II) induction, (III) acceleration, (IV) deceleration, and finally (V) a period of low hydration, following the heat evolution measured from isothermal calorimetry. The mechanisms that control the C_3S reaction kinetics in the different periods have been described in detail elsewhere⁷⁻⁹. It has been reported that Na_2SO_4 accelerates the hydration kinetics of C_3S in pure pastes, resulting in a higher degree of hydration (DoH) during the early ages and similar degrees of hydration at later ages^{10,11}. Mota *et al.*¹⁰ noted that the morphology of the C-S-H phase changed from convergent fibrils without sulfate addition to divergent bundles of fibrils when sulfate ions were present.

C₃A hydration. Although the amount of tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$: C_3A) is generally low in Portland cements (2 – 8 wt.%), it has a significant impact on the early-age heat release and in controlling the setting time⁷. When C_3A hydrates in the absence of gypsum, the hydration proceeds very fast, hence gypsum is added into the system to regulate the setting time. The hydration of C_3A – gypsum can be divided into two main stages. The first stage is a period of low heat release, where C_3A reacts with gypsum forming ettringite (AFt, $\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$: $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$). Although ettringite is expected as the only phase from a thermodynamic viewpoint, the presence of hydroxy-AFm ($\text{Ca}_4\text{Al}_2(\text{OH})_{14} \cdot x\text{H}_2\text{O}$: C_4AH_x , h-AFm) phases are also reported during this period¹²⁻¹⁴. In general, there is consensus on that the kinetics during this stage is controlled by a dissolution-controlled mechanism^{7,8,14}. The low reactivity of this period has been attributed to the adsorption of calcium-sulfur (Ca-S) ion pair complexes onto the surface of C_3A ¹⁵. With the depletion of gypsum, the C_3A hydration is enhanced by the removal of adsorbed Ca-S ion complexes, hence a high and a narrow peak of heat release is observed in isothermal calorimetry. With an increasing amount of gypsum, the second stage is delayed and the peak broadens with a reduction in the peak height^{16,17}. We have recently demonstrated that the broadening and lowering of the main peak with increased gypsum content can be explained by a dissolution-controlled mechanism¹⁴. At this stage C_3A reacts with ettringite, forming monosulfate ($\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{SO}_4 \cdot 6\text{H}_2\text{O}$: $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$, m-AFm). Water activity also plays a major role in the overall kinetics of C_3A reaction¹⁸. The addition of Na_2SO_4 to pure C_3A systems is considerably less effective on the retardation of hydration reactions compared to the addition of gypsum¹⁹. Nevertheless, even small amounts of Na_2SO_4 retards C_3A dissolution compared to neat C_3A -water systems^{20,21}. Although ettringite is not precipitated, the formation of monosulfate has been identified in C_3A – Na_2SO_4 systems^{19,22}.

C₃S – C₃A model systems. Experimental studies on C_3S – C_3A systems have been previously studied in the presence of added calcium sulfates ($\text{CaSO}_4 \cdot x\text{H}_2\text{O}$: $\text{C}\bar{\text{S}}\text{H}_x$) for mixtures of

monophase C_3S and C_3A ^{23,24} and polyphase $C_3S - C_3A$ systems^{23,25}. In monophase systems, powders of C_3S and C_3A are mixed while in a polyphase system, they are mixed in the clinker (where phases are co-sintered) in a similar way as their occurrence in Portland cement. With increasing amounts of gypsum or calcium sulfates in general, the appearance of the main C_3A hydration peak in isothermal calorimetry is delayed, as also observed for $C_3A -$ gypsum systems^{23,24}. The main peak of C_3A hydration can occur before the onset of the acceleration period, during the acceleration period, in the deceleration period or after the deceleration period of the main peak of C_3S hydration when the gypsum content is varied. At very high gypsum contents, the main hydration peak of C_3A is not observed at all. In the present work, the following classification of the $C_3S - C_3A$ systems is used, based on their isothermal calorimetry curves:

- *Under-sulfated* ($U\bar{S}$): The main peak of C_3A hydration precedes the C_3S hydration peak (C_3A hydration peak forms before stage III of the C_3S hydration).
- *Slightly under-sulfated* ($sU\bar{S}$): The main peak of C_3A hydration appears during the acceleration period (stage III) of the C_3S hydration.
- *Properly sulfated* ($P\bar{S}$): In this system, which is the most commonly found in commercial PC, the main peak of C_3A hydration occurs during the deceleration period (stage IV) of the C_3S hydration.
- *Over-sulfated* ($O\bar{S}$): The peak of C_3A hydration will appear after the C_3S hydration peak (*i.e.*, at stage V of the C_3S hydration).
- *Severely over-sulfated* ($SO\bar{S}$): In this case the first stage of C_3A hydration does not end and a peak from C_3A hydration will not appear due to the very high gypsum content.

For both mono- and polyphase model systems, it has been observed that the reaction of C_3A and the sulfate content have a significant influence on the hydration of C_3S ^{23,24}. For the $U\bar{S}$

systems, the induction period appears to be longer and the rate of C_3S hydration after the induction period is retarded and broadened^{23,24,26}. After the C_3A hydration peak in $sU\bar{S}$ systems, the rate of C_3S hydration tends to decelerate and reaccelerates from a lower rate level and further decelerates leading to a double peak of C_3S hydration²⁴. Moreover, it was noted that although the kinetics is severely affected, the cumulative heat release from the $U\bar{S}$, $sU\bar{S}$ and $P\bar{S}$ systems does not show a significant difference after 48 hours²⁴. However, there are limited published studies on $O\bar{S}$ and $SO\bar{S}$ systems.

Although the effect of Na_2SO_4 has not been specifically studied for $C_3S - C_3A$ model systems, it has been investigated earlier for white Portland cements. With Na_2SO_4 addition to white Portland cement, there is a reduction in the DoH of C_3S beyond one day of hydration, although it is enhanced up to one day^{27,28}. On the other hand, the addition of Na_2SO_4 results in a significant retardation of the C_3A hydration²⁷. In this context, it is interesting that hydration of pure C_3A with the addition of Na_2SO_4 does not produce any ettringite, whereas ettringite is formed in blended cements when activated with Na_2SO_4 ²⁹. Regarding the compressive strength, addition of Na_2SO_4 increases the early-age strength while the later-age strength is only reduced marginally²⁷. It is important to note that while the effect of Na_2SO_4 on the durability of Portland cement (external sulfate attack) has been studied extensively, studies on its effect on hydration is rather limited. Curing Portland cement pastes immersed in Na_2SO_4 solutions leads to expansion and loss in strength^{30,31}. This is primarily attributed to ettringite formation, as a result of AFm phases consuming sulfates to form expansive ettringite crystals. Furthermore, Na_2SO_4 can react with portlandite to form gypsum, which is also expansive in nature³². The presence of carbonate ions from added limestone or carbonation combined with a low curing temperature ($\sim 5^\circ C$) can also lead to formation of thaumasite^{33,34} which drastically reduces strength and leads to disintegration of the cement matrix. Also, curing at high concentrations of Na_2SO_4

solutions leads to formation of a sodium substituted AFm phase, known as the ‘U-phase’, which also deteriorates the cement matrix^{35,36}.

This work investigates the hydration of polyphase C₃S – C₃A model systems at variable additions of gypsum (4-8 wt.%) in combination with and without Na₂SO₄. The effect of fineness of the model systems, and the synergy between the reactions of C₃S and C₃A are studied. Our work provides new findings on the model systems with high sulfate contents, which has not been clarified in the previous studies yet. Analytical techniques of isothermal calorimetry, QXRD, TGA, ²⁷Al and ²⁹Si MAS NMR are used to obtain quantitative information about the hydration kinetics and to characterize the hydration products until 7 days of hydration. The main deliverable of the present study is the quantitative data for the C₃S - C₃A model systems, in particular those based on solid-state ²⁷Al and ²⁹Si NMR measurements.

2. Experimental protocol

2.1. Materials

Polyphase C₃S – C₃A model cements (*i.e.*, where C₃S and C₃A are present in the same grains, similar to Portland cement clinker) with two different compositions of C₃S and C₃A and with different fineness were purchased from SARL Minerals (France). According to the manufacturer, the model cements were produced by mixing appropriate fractions of CaO, Al₂O₃ and SiO₂ and heating the mixtures at 1450 °C, resulting in Al₂O₃ being dissolved in C₃S. ²⁹Si MAS NMR confirmed the presence of the monoclinic M1 form of C₃S³⁷ whereas XRD showed the cubic polymorph of C₃A.

The compositions and fineness of the polyphase C₃S – C₃A samples used in this study are given in Table 1. The particle size distributions are measured by laser diffraction (Malvern Mastersizer 2000) after dispersing the samples in ethanol (Fig. S1, Supplementary

information). Analytical grade gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and technical grade sodium sulfate (Na_2SO_4) were used. Table 2 shows the compositions of the mixtures used in this study, specifying the additions of gypsum (4-8 wt%) and sodium sulfate solution (0.75 M).

2.2. Methodology

Gypsum was mixed with the polyphase C_3S – C_3A systems by dry mixing using a Turbula blender for 8 hours. The pastes were prepared with deionized water in a temperature-controlled room at 20 °C and 60% RH, using a solution to binder ratio of 0.5 in all blends. The pastes were prepared using a mechanical mixer at 750 rpm for 2 minutes to ensure homogeneous mixing.

For the quantitative analyses by X-ray diffraction, thermal analysis and NMR, the hydration of the pastes was stopped after 1 and 7 days using a freeze drier, operating at 0.025 mbar pressure and -60°C for 2 hours after grinding the samples in an agate mortar. Freeze drying may partially deteriorate hydrate phases such as ettringite and monosulfate³⁸. However, each of the techniques for arresting hydration are associated with some damages on the system with respect to physical or chemical properties³⁹⁻⁴¹.

2.2.1. Isothermal calorimetry

A TAM air 8-channel isothermal calorimeter was used to monitor the heat release for 7 days at 20 °C. Around 3-4 g paste transferred into the calorimeter which was prepared externally. The initial period of 30 min was omitted because of a potential of high error, arising from the temperature difference between the sample and the calorimeter.

2.2.2. Thermogravimetric analysis (TGA):

TGA was carried out on a NETZSCH STA 409 PC instrument, using a heating rate of 10 °C/min, a temperature range of 20 – 600 °C (under N₂ flow), and approx. 25 – 40 mg sample for each measurement. Selected samples were analyzed up to 1000 °C to ensure the absence of carbonation reactions. The portlandite content was calculated using the tangent method⁴², which corrects for contributions from other dehydrating phases and physically bound water in C-S-H in the range 20 – 600 °C⁴³, and is expressed in g per 100 g anhydrous cement using the relation (Eq. 1)

$$CH_{per\ 100g\ anhydrous} = \frac{100CH_{measured}}{100 - BW} \quad (1)$$

where BW is the bound water content (mass loss until 600 °C⁴³).

2.2.3. Quantitative X-ray diffraction:

X-ray diffraction (XRD) was carried out from 5 to 70° 2θ on a Bruker D2 PHASER diffractometer with a CuK anode. The samples were front loaded, implying that preferred orientation was detected for the (0 2 0) peak of gypsum and the (0 0 2) peak of portlandite. Quantification of the phases was obtained by Rietveld analysis using the Topas (Academic) software. The mass absorption coefficient (MAC) of the sample were calculated considering the bound water content measured by TGA and corundum (α-Al₂O₃) was used as an external standard^{25,44}. The quantities of different phases were further corrected, considering the incorporation of the bound water content from TGA, as described in ref.⁴⁵. The degrees of C₃S and C₃A hydration are estimated by determining the fraction of the initial masses reacted.

2.2.4. ²⁹Si and ²⁷Al MAS NMR

^{29}Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy was used to obtain the DoH for C_3S and to characterize the formed C-S-H phases. The ^{29}Si MAS NMR measurements were recorded at 59.6 MHz on a Varian-INOVA 300 MHz (7.05 T) spectrometer, using a home-built CP/MAS probe for 7 mm outer diameter (o.d.) partially sintered zirconia (PSZ) rotors (220 μl sample volume) and a spinning speed of 6.0 kHz. Single-pulse excitation with a 3.0 μs pulse width ($\sim 45^\circ$ flip angle) for a radio frequency field strength of $\gamma B_1/2\pi \approx 40.0$ kHz was employed along with a 60-s repetition delay and typically around 2816 scans. Neat tetramethyl silane (TMS) was used as the ^{29}Si chemical shift reference, employing larnite ($\beta\text{-Ca}_2\text{SiO}_4$, $\delta = -71.33$ ppm⁴⁶) as a secondary standard. The deconvolutions were carried out using the *dmfit* program⁴⁷, providing intensities for the different Si sites, denoted as Q^0 , Q^1 , $Q^2(1\text{Al})$ and Q^2 , using the conventional nomenclature. The Q^0 peaks (from anhydrous C_3S) were fixed with respect to frequency and line width in the deconvolutions based on the ^{29}Si MAS NMR spectra of the anhydrous model cements. For the C-(A)-S-H phase, the average chain length of aluminosilicate tetrahedra (MCL) and the fraction of tetrahedrally coordinated Al in the C-S-H phase (molar $\text{Al}_{\text{IV}}/\text{Si}$ ratio) are calculated from the expressions (2) and (3)^{48,49}.

$$\text{MCL} = \frac{2[Q^1 + Q^2 + \frac{3}{2}Q^2(1\text{Al})]}{Q^1} \quad (2)$$

$$\text{Al}_{\text{IV}}/\text{Si} = \frac{Q^2(1\text{Al})}{2[Q^1 + Q^2 + Q^2(1\text{Al})]} \quad (3)$$

The degree of hydration (*DoH*) of C_3S is calculated as $\text{DoH} = 1 - Q^0$ (in%), where Q^0 is the relative intensity of the peaks from non-reacted C_3S .

Solid-state ^{27}Al MAS NMR spectra were recorded at 156.3 MHz on a Varian Direct-Drive VNMR-600 (14.09T) spectrometer using a home-built CP/MAS probe for 4 mm o.d. PSZ rotors. The experiments employed a spinning speed of 13.0 kHz, single-pulse excitation (0.5 μs pulse width for $\gamma B_1/2\pi \approx 60.0$ kHz), ^1H decoupling (TPPM, $\gamma B_2/2\pi \approx 42.0$ kHz) during acquisition, a relaxation delay of 2 s, and typically 4096 scans. ^{27}Al chemical shifts are given relative to a 1.0 M aqueous solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Deconvolutions of the centerband regions were carried out using the *dmfit* program⁴⁷, assuming a combination of Gaussian and Lorentzian line shapes.

3. Results

3.1. Hydration kinetics by isothermal calorimetry

3.1.1. Effect of sulfates on the hydration kinetics

The rates of heat release measured by isothermal calorimetry at 20 °C on p90 with 4 %, 6 % and 8 % of gypsum and with/without Na_2SO_4 added are shown in Fig. 1. With increasing amount of gypsum, the heat release peak from the aluminate reaction is consistently delayed and broadened. This is consistent with the observed effect of increasing gypsum content on the hydration of pure C_3A systems^{14,17} and the hydration of C_3A in $\text{C}_3\text{S} - \text{C}_3\text{A}$ model systems^{23,24}. Employing the definitions proposed above (*c.f.* Introduction), the blends of p90_4g, p90_6g and p90_8g can be classified as $\text{U}\bar{\text{S}}$, $\text{sU}\bar{\text{S}}$ and $\text{O}\bar{\text{S}}$, respectively. With the addition of Na_2SO_4 (p90_4g_NS and p90_8g_NS), only a single peak appears instead of two distinct peaks from C_3S and C_3A hydration, which is more narrow and exhibits a higher intensity as compared to the peak of the hydration of pure C_3S .

Fig. 2 shows the cumulative heat release up to 7 days of hydration for the same blends as studied in Fig. 1. The under-sulfated ($\text{U}\bar{\text{S}}$) system (p90_4g) exhibits a lower heat release in the early hours of hydration, but the measured overall heat release is similar in these blends after

7 days, which is in agreement with the earlier results²⁴. With the addition of Na₂SO₄, there is a clear increase in the heat release in the early hours but after that, the total heat release stagnates and is significantly lower by 7 days, as compared to the samples without Na₂SO₄.

The effect of sulfates on the C₃S and C₃A hydration was further investigated with a different system composed of 93 wt.% C₃S and 7 wt.% C₃A (p93). In this system (Fig. 3), p93_4g is properly sulfated (P $\bar{S}$) whereas p93_8g is severely over-sulfated (SO $\bar{S}$). This is expected when compared to p90, since the C $\bar{S}$ /C₃A ratio is further increased in this system. In p93_8g, a peak of C₃A hydration does not exist (at least until 7 days of hydration) as the gypsum content is too high compared to C₃A content. The cumulative heat release for the p93 systems (Fig. 3, right) reveals a significant reduction in the overall heat release of p93_8g as compared to p93_4g. Moreover, there is a clear reduction in the overall heat release of p93_8g_NS as well, when compared to p93_4g_NS. These results show that severely over-sulfated systems (SO $\bar{S}$) have a reduced DoH after the initial hydration. However, in contrast to the p90 mixtures (Fig. 2), p93_8g and p93_8g_NS have similar overall heat release after 7 days of hydration.

3.1.2. Effect of fineness on the hydration kinetics

It is well known that the fineness of the reactants plays an important role on the hydration kinetics for cementitious systems. However, the fineness of p90 and p93 measured by the Blaine method and laser diffraction gave contradicting results (Table 1) and hence it cannot be conclusively judged which sample contains particles with highest fineness. Hence to quantitatively study the effect of fineness on the hydration kinetics, the coarse fraction of p93 (p93_C) has been used. Fig. 4 shows the rate and cumulative heat release for the p93_C systems. The peak of C₃A hydration for p93_C_4g is located further in the deceleration period of C₃S, as compared to p93_4g, although both can be considered as P $\bar{S}$, whereas p93_C_8g is found to be SO $\bar{S}$, as expected. This implies that in addition to the C $\bar{S}$ /C₃A ratio and temperature,

the fineness also plays an important role for the peak position of C_3A hydration in the heat release curves. The addition of Na_2SO_4 does not induce a particular difference in the hydration rate for the p93_C_4g_NS and p93_C_8g_NS samples up to 36 hours, while thereafter a slight reduction is observed in the cumulative heat release of the latter. This difference is actually marginal when compared to heat release of the finer fractions of p93 (Fig. 3). Interestingly, hydration of p93_C_8g is considerably retarded compared to p93_C_8g_NS, which contains additional sodium sulfate, even after 7 days of hydration.

3.2. Studies of paste samples after hydration stoppage

3.2.1. ^{29}Si MAS NMR

The hydration of $C_3S - C_3A$ model systems can conveniently be studied by ^{29}Si MAS NMR, since this method allows quantification of the crystalline anhydrous components as well as the less-ordered/amorphous C-(A)-S-H phase, following the deconvolution approaches commonly used in ^{29}Si MAS NMR studies of Portland cement hydration, see for example references⁴⁸⁻⁵¹. The deconvolutions of the ^{29}Si NMR spectra for the $C_3S - C_3A$ systems is simplified, as compared to the analysis of spectra of hydrated Portland cements, due to the absence of belite which results in a Q^0 resonance that overlaps with the resonances from C_3S . A typical example of a deconvolution is shown for the ^{29}Si MAS NMR spectrum in Fig. 5, whereas Table S1 (Supplementary information) summarizes all intensities derived from the deconvolutions of the ^{29}Si MAS NMR measurements obtained for all samples hydrated for one and seven days. Furthermore, all the ^{29}Si MAS NMR spectra are given in Fig. S2. Generally, the deconvolutions used six Q^0 sites to account for anhydrous C_3S (resonances at -69.1, -70.4, -71.4, -72.6, -73.6, -74.8 ppm), whereas the Q^1 sites of the C-(A)-S-H phase were simulated by two peaks at -77.1 and -78.9 ppm. The $Q^2(1Al)$ was simulated by a single resonance at -80.9 ppm, and two peaks at -83.1 and -85.1 ppm were used for the Q^2 sites. These sites and this procedure are in

accordance with the deconvolution approach used earlier for analysis of the C-(A)-S-H phase resulting from white Portland cement hydration⁵¹. The use of two distinct peaks for the Q¹ and Q² sites reflects that distinct sites of these types are present in the C-(A)-S-H structure. These sites cannot be clearly distinguished from the present spectra, i.e., Q¹ resonances from dimeric units and end groups of chains and Q² peaks from bridging (-83.1 ppm) and pairing (-85.1 ppm) sites of the chains. The degrees of C₃S hydration (DoH) represents the most important information obtained from the ²⁹Si NMR spectra. However, additional information on the C-(A)-S-H composition can also be derived from calculations of the average chain length of aluminosilicate tetrahedra (MCL) and the molar ratio of tetrahedral Al incorporated in the C-(A)-S-H phase (Al_{IV}/Si) from Eqs. (2) and (3), respectively (Table 3). The Al_{IV}/Si ratios (Fig. S3 provides a visual representation), which range from 0.08 to 0.14 for all blends studied after 1 and 7 days of hydration, match with the Al_{IV}/Si ratios reported earlier for the C-(A)-S-H phase in hydrated ordinary Portland cements⁵²⁻⁵⁴. Considering the observed small range of Al_{IV}/Si ratios and the estimated error limits of ± 0.02 for the individual measurements, no clear trends can be derived between the Al_{IV}/Si ratios of the C-(A)-S-H phases and the sample compositions in the samples studied.

3.2.2. ²⁷Al MAS NMR

Numerical analysis of the ²⁷Al MAS NMR spectra is complicated by the presence of non-symmetric line shapes, caused by second-order quadrupolar broadening of the central transition for the ²⁷Al quadrupole ($I = 5/2$) nucleus. In particular, this holds for the two tetrahedral Al sites in C₃A⁵⁵, which at 14.1 T exhibit quadrupolar line shapes for the centerband that cover the spectral range from 80 to 25 ppm. However, the octahedral Al sites of ettringite (AFt), monosulfate (AFm) and the so-called third aluminate hydrate (TAH), from octahedral Al sites

associated with the C-(A)-S-H phase, have very small ^{27}Al quadrupole couplings⁵⁵⁻⁵⁷ that result in Gaussian-like line shapes for the centerband at 14.1 T. In addition, resonances from tetrahedral and five-fold coordinated Al in the C-(A)-S-H phase are observed, which can be deconvoluted with two overlapping Gaussian peaks at 72.1 and 67.3 ppm for the Al_{IV} site and a Gaussian resonance at 35.4 ppm from the Al_{V} site. The Al_{IV} and Al_{V} sites from the C-(A)-S-H phase and TAH result from less-ordered structural sites and may exhibit a distribution in electric field gradients at the ^{27}Al nuclear sites. This results in a characteristic tail towards lower frequency in the ^{27}Al NMR spectra, which is best described in simulations by the so-called Czjzek model⁵⁸. However, the use of Gaussian peaks in the present deconvolutions is an acceptable approximation, considering the relative high magnetic field used for the ^{27}Al NMR spectra. The resonance frequencies are in good agreement with those reported earlier for the Al_{IV} sites in the silicate chains⁵⁹⁻⁶¹ and the interlayer Al_{V} sites^{57,61,62} of the C-(A)-S-H structure. As an example, a typical ^{27}Al MAS NMR spectrum is shown in Figure S4. All ^{27}Al MAS NMR spectra have been analyzed by a combination of spectral integration and deconvolution to extract the fractions of AFt, AFm and TAH phases (c.f. Table 3), which are of principal interest in the present study. The fractions of the hydrate phases are given as the molar fractions (%) of Al in AFt, AFm and TAH. Note that different AFm phases (m-AFm and h-AFm) are not distinguished, as they exhibit very similar ^{27}Al chemical shifts in the range 9 – 11 ppm⁵⁵. The degrees of C_3A hydration are not reported as they are difficult to accurately estimate due to the quadrupolar broadening of the C_3A resonances as well as the overlap with the Al_{IV} and Al_{V} peaks from the C-(A)-S-H phase.

3.2.3. TGA

Table 4 reports the portlandite (CH) content per 100 g anhydrous C_3S and the total bound water content. The mass losses from de-hydroxylation of the C-(A)-S-H, ettringite and AFm phases

cannot be quantified individually as they tend to overlap. Also, the peaks of these phases shift depending on the DoH, mass of sample, etc.⁴³. A typical example of a thermogravimetric curve (TG) and its differential (DTG) is provided in Fig. S5.

3.2.4. X-ray diffraction

Table 4 reports XRD data associated with the degrees of hydration of C₃S and C₃A as well as the quantity of portlandite present per 100 g anhydrous binder calculated from Rietveld analysis. One of the major challenges in using XRD in this study is the presence of C₃S in its monoclinic M1 form. Since a well-tested crystal structure is lacking for this polymorph, the crystal model proposed by de Noirfontaine *et al.*⁶³ was used. For the Rietveld refinements, the structures ICSD 202220 for portlandite, ICSD 1841 for C₃A cubic, ICSD 409581 for gypsum and ICSD 155395 for ettringite from the Inorganic Crystal Structure Database⁶⁴ were used. The poorly crystalline short-range ordered C-S-H structure reported by Snellings *et al.*⁶⁵, developed from C-S-H in hydrated white Portland cement, was used. Hydrogarnet (C₃AH₆) was not detected in any of the systems. The quality of quantification of gypsum and portlandite is low because these crystals are highly subjected to preferred orientation as a result of their crystal morphology. Additionally, the samples were front loaded in the XRD experiments, which increases risks of preferred orientation, and hence gypsum and portlandite quantities are not reported. Moreover, the AFm phases, which are poorly crystalline and lack proper XRD crystal-structure files, are not reported. The presence of a sodium substituted AFm phase, commonly known as the ‘U-phase’³⁵, which is typically found in Portland cements exposed to Na₂SO₄, was not detected in any of the samples (Fig. S6).

4. Analysis

4.1. Heat of hydration

Fig. 6 compares the measured heat release from isothermal calorimetry after 1 and 7 days of hydration with the theoretical heat release calculated from the DoH of C₃S based on XRD and ²⁹Si NMR, and DoH of C₃A measured from XRD. For the calculation of the theoretical heat release, the measured degrees of C₃S hydration is multiplied with the enthalpies of reaction, assuming that the enthalpy of C₃S reaction is 517 J/g⁴². As the enthalpy of C₃A hydration when precipitating ettringite (1672 J/g_{C₃A}) and AFm (1144 J/g_{C₃A}) is different, the effective enthalpy of C₃A hydration is calculated based on the ratio of ettringite and AFm contents obtained from ²⁷Al NMR (*c.f.* Table 3).

As clearly seen in Fig. 6, there is a good correlation between the measured and calculated heat releases, although there seems to be a systematic underestimation of heat calculated from the ²⁹Si NMR data (particularly at lower heat) and a systematic overestimation of the data from XRD. Also, the degree of C₃S hydration measured from XRD is higher compared to the values from ²⁹Si NMR (*c.f.* Tables 3 and 4). These systematic differences may reflect the following effects: (i) *The crystallinity of C₃S*: The anhydrous powders of p90 and p93 have degrees of crystallinity around 90% based on the total non-detected/amorphous content in the samples from XRD. As the quantitative XRD approach, employed here, only calculates the crystalline C₃S, this could potentially lead to an overestimation of the degree of C₃S reaction by XRD. (ii) *The model crystal structure of C₃S*: Errors could potentially arise from the choice of the crystal structure for the M1 form of C₃S used in the Rietveld refinement. (iii). *Overlap of Q⁰ and Q⁰(h) sites*. It is well-known that a few percent of hydrated Q⁰ silicate sites, Q⁰(h), may form during the early hydration of C₃S⁶⁶⁻⁶⁸. The intensities from these sites will overlap with the Q⁰ resonances from C₃S and thereby contribute to an underestimation of degree of C₃S hydration from ²⁹Si NMR. A similar discrepancy between results from ²⁹Si NMR and XRD has been reported for the quantification of alite hydration in a hydrated white Portland cement – silica fume blend⁶⁹. Furthermore, there will be lower calculated heat release due to the partial

decomposition of ettringite by the hydration stoppage, as the enthalpy of formation of ettringite is much higher than for the AFm phases. The discrepancies with measured heat may also arise from inaccuracies in enthalpy of hydration, errors from the calorimeter, etc.

4.2. Degree of hydration (DoH)

Fig. 7 shows the average DoH for C_3S from the XRD and ^{29}Si NMR measurements, and DoH for C_3A measured from XRD. Comparing the blends without Na_2SO_4 , the mixes p90_4g, p90_6g and p90_8g, which are $U\bar{S}$, $sU\bar{S}$ and $O\bar{S}$, respectively, have similar DoH of C_3S after 7 days. When comparing p93_4g ($P\bar{S}$) and p93_8g ($SO\bar{S}$), a consistent reduction of DoH for C_3S DoH are seen for both 1 and 7 days. Similar results are also apparent for the coarser blends p93_C_4g ($P\bar{S}$) and p93_C_8g ($SO\bar{S}$). As expected, a reduction in degree of hydration is observed for coarser systems for both 1 and 7 days with and without Na_2SO_4 as compared to the systems with the same gypsum content.

In general, the DoH of C_3S is higher with Na_2SO_4 after 1 day, except for p90_8g where the DoH is rather similar. After 7 days of hydration, the DoH of C_3S with Na_2SO_4 is lower, particularly for the systems where the DoH of C_3S without Na_2SO_4 is higher than 0.6. It seems that there is a tipping point for the degree of C_3S hydration with and without Na_2SO_4 around DoH 0.5 to 0.6. On the other hand, the DoH for C_3A does only marginally increase from 1 to 7 days of hydration. A clear decrease in the DoH of C_3A after 1 and 7 days are visible with the addition of Na_2SO_4 for all mixtures, except for those of $SO\bar{S}$ (p93_8g and p93_C_8g) and $U\bar{S}$ (p90_4g) systems.

4.3. Aluminate hydrates

The relative amounts of ^{27}Al in ettringite/Aft and AFm measured by ^{27}Al MAS NMR at 1 and 7 days of hydration are plotted in Fig. 8. These results should be interpreted with caution as the actual method for hydration stoppage may affect the results^{39,40}. A good correlation between the ettringite content determined by XRD and ^{27}Al NMR is observed (Fig. S7). The total ettringite content in the samples p90_4g, p93_4g, p90_6g and p90_8g is low (< 3% Al) at both 1 and 7 days. This is in agreement with the results from Fig. 1, as the main peak of C_3A has appeared well before 24 hours of hydration for these samples. Hence, the ettringite content is expected to be low. Small deviations of the Aft and AFm content from 1 day to 7 days may not be limited to ongoing hydration, but it could also arise from the hydration stoppage and experimental error. An increase in the ettringite content is clearly visible in $\text{SO}\bar{\text{S}}$ systems (p93_8g and p93_C_8g). These features are expected as a C_3A peak has not occurred after 7 days, and therefore, ettringite is favored as the main hydration product from C_3A hydration.

With the addition of Na_2SO_4 , there is an increase in the ettringite content at 7 days compared to 1 day for all samples except p90_4g_NS. This increase in the amount of ettringite is mostly compensated by a reduction in AFm content rather than an increase in DoH of C_3A . Thus, a recrystallization of ettringite seems to occur, which may be similar to the delayed ettringite formation⁷⁰. Stability of ettringite at later ages should be carefully followed in the systems in particular those with added Na_2SO_4 in order to assess their potentials and limitations.

5. Discussion

Our results demonstrate that the C_3S hydration is significantly influenced by the hydration of the C_3A – gypsum component. Following C_3S hydration by the peak of C_3A reaction in isothermal calorimetry, a significant retardation is observed in the rate of heat release. However, except for the $\text{SO}\bar{\text{S}}$ systems, the other systems ($\text{U}\bar{\text{S}}$, $\text{sU}\bar{\text{S}}$, $\text{P}\bar{\text{S}}$, $\text{O}\bar{\text{S}}$) achieve similar degrees of hydration after 7 days. In the case of $\text{SO}\bar{\text{S}}$ systems, there is a clear reduction in the

DoH of both C₃S and C₃A beyond 1 day, which has not been previously reported for model systems. On the other hand, the addition of Na₂SO₄ results in an accelerated hydration compared to similar systems without Na₂SO₄ at low degrees of hydration and vice versa.

A major hypothesis that addresses this retarding effect of C₃A on C₃S hydration is the inhibiting effect of Al ions in the solution. It is proposed that when gypsum is present in the system, the Al ions are bound in the form of ettringite, and once gypsum is completely consumed, Al can be freely available in the solution^{23,71}. One explanation for the inhibiting effect of Al on C₃S hydration could be the reduction of active sites of dissolution at the C₃S surface by adsorption of Al ions at lower pH (<13)^{72,73}. This could lead to an increase in the induction period for the C₃S reaction. Hence, this could be attributed to the prolongation of the induction period in U $\bar{S}$ systems (p90_4g). A second explanation for the inhibiting effect of Al could be the formation of C-(A)-S-H instead of C-S-H⁷⁴ as pure C-S-H acts as better nucleation seeds⁷⁵. Quennoz²³ reported an increase in the Al/Ca ratio measured by EDS analysis for samples after the hydration peak of C₃A reaction had occurred in the isothermal calorimetry curves. However, the Al_{IV}/Si ratios determined in the present study from ²⁹Si MAS NMR (Table 3, Fig. S1) clearly show that there is a significant amount of Al incorporated in the C-(A)-S-H phase but no clear variations in the incorporated amount of Al with different gypsum contents. Since EDS measurements carried out at high voltages (15kV)²³ are subjected to high interaction volumes, and hence could lead to significant errors, the results are not always conclusive⁷⁶. The coagulation of AFm phases on the C-S-H would further increase the Al/Si ratio measured by EDS. On the other hand, the Al_{IV}/Si ratios from ²⁹Si NMR do not account for five- and six-fold coordinated Al in the C-(A)-S-H phase.

Bergold *et al.*²⁴ proposed that consumption of ettringite, which acts as nucleation seeds, and coagulation of C-S-H with AFm phases after the main hydration peak of C₃A being the reason

for the retardation of C_3S reaction. As a result, the free surface area is reduced, which retards the nucleation and growth process. Although this could explain the current results on $sU\bar{S}$, $P\bar{S}$ and $O\bar{S}$ systems, this does not explain the reduced DoH of C_3S in $SO\bar{S}$ systems. According to this hypothesis, as there is no C_3A hydration peak, the higher amount of ettringite and lower precipitation of AFm phases should ensure faster hydration of C_3S . Similarly, inhibition of Al ions hypothesis also does not explain the current results as in $SO\bar{S}$ system. As gypsum is not depleted, Al concentration in the solution should not rise. While it is clear that the previous studies have overlooked an important parameter regarding the synergetic hydration of $C_3S - C_3A$ systems, it is still not clear which parameter is that exactly.

Similarly, the reason for the reduced DoH of C_3S with Na_2SO_4 in the later age of hydration remains unclear²⁸. The reduction of AFm phases for recrystallization of ettringite (c.f. Fig. 8) does not seem to have a positive impact on the hydration kinetics. Nevertheless, a strong synergy exists between the hydration of C_3S and C_3A phases, while further in-depth studies are required to unlock the underlying reaction mechanisms.

6. Conclusions

In this work, the hydration of polyphase $C_3S - C_3A$ model cement systems with different gypsum content, additional Na_2SO_4 , fineness and composition have been analyzed. Special attention was given to over sulfated systems, which have not been studied for model synthetic cements before. The analytical techniques of isothermal calorimetry, QXRD, TGA, ^{27}Al and ^{29}Si MAS NMR have been used to follow the hydration and for quantification of the different phases at one and seven days. The main conclusions from the present work are summarized as follows:

- Hydration of C_3S is largely dependent on the hydration of C_3A in a polyphase system.

- The amount of gypsum and the fineness of the cement have a significant influence on the position of the main peak of C₃A hydration with respect to the C₃S hydration peak measured by isothermal calorimetry. An increase in fineness is found to result in a faster occurrence of C₃A hydration peak compared to the main peak of C₃S hydration.
- While changes in gypsum content have a large influence on the early hydration kinetics, the overall degrees of hydration are found to be similar by 7 days for all systems except the severely over-sulfated (SO $\bar{S}$) systems.
- The SO $\bar{S}$ systems are found to have lower degrees of C₃S and C₃A hydration after 7 days of hydration for the studied mixtures.
- Addition of Na₂SO₄ accelerates the hydration with respect to the mixtures without Na₂SO₄ at lower degrees of hydration, but hydration is hindered at higher degrees of hydration, similar to the SO $\bar{S}$ systems.
- No correlation was found with respect to gypsum and Na₂SO₄ contents and fineness for the Al_{IV}/Si ratios of the C-(A)-S-H phase for the studied blends.
- The DoH of C₃S determined from XRD was found to be consistently higher than the DoH measured by ²⁹Si NMR.
- The addition of Na₂SO₄ results in a significant increase in the amount of ettringite and a corresponding reduction of AFm phases from 1 day to 7 days of hydration.

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Figure 1: Effect of gypsum content and Na_2SO_4 on the rate of heat release for the early hydration of the p90 systems up to 30 hours. Left: blends without Na_2SO_4 and right: blends with Na_2SO_4 (c.f. Table 2).

Figure 2: Effect of gypsum content and Na_2SO_4 on the cumulative heat release of hydration for the p90 mixtures up to 7 days of hydration.

Figure 3: Effect of gypsum content and Na_2SO_4 on the heat evolution for the hydration of the p93 systems. Left: rate of heat release up to 24 hours, and right: cumulative heat release up to 7 days of hydration.

Figure 4: Heat release curves (left) and cumulative heat release (right) for the p93_C sample, illustrating the effect of fineness when compared to Fig. 3

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Figure 6: Heat releases calculated from the degrees of C_3S hydration based on XRD and ^{29}Si NMR is compared to the heat release measured by isothermal calorimetry. Heat release from C_3A hydration is estimated by the degree of hydration from XRD with aid of ^{27}Al NMR for the estimation of ettringite and AFm phases (for determining the effective enthalpy of hydration) for both series.

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