



Factors influencing the sulfate balance in pure phase C₃S/C₃A systems

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ABSTRACT

Understanding the sulfate balance mechanism of cement is needed for an effective use of sustainable blended cements. Pure phase systems allow to study the interaction between sulfate and each of the phases involved in early age hydration separately. This paper explores the effect of different factors on sulfate requirement in C₃S/C₃A systems. It was observed that reaction rates of both C₃S and C₃A have an influence on the overall sulfate balance, as they affect the amount of sulfate adsorbed on C-S-H and the amount of ettringite formed, respectively. Furthermore, the type of sulfate source used (gypsum or hemihydrate) can also significantly change the position of the aluminate peak for the same total sulfate in the system.

1. Introduction

Calcium sulfate is added to clinker during grinding in order to control the reaction of tricalcium aluminate (C₃A) and prevent flash setting [1]. In the presence of gypsum, the hydration reaction of C₃A shifts from the precipitation of platey calcium aluminate hydrates and ettringite is formed [2]. As more gypsum is incorporated in the system, more retardation of the C₃A reaction can be achieved [3]. If the level of sulfate addition is insufficient, the aluminate peak may occur before the tricalcium silicate (C₃S) peak and the later becomes smaller and broader with lower degrees of hydration and strength at early ages [4,5]. The optimum amount of sulfate required is usually determined on the basis of compressive strength tests at 1 or 28 days.

The widespread adoption of blended cements necessitates better understanding of the sulfate requirement for these systems. Recently, we showed that the surface area provided by the addition of supplementary cementitious materials (SCMs), rather than the amount of alumina in the anhydrous blend, explains the increased sulfate requirement of limestone calcined clay cement (LC³) [6]. Sulfate is adsorbed in C-S-H during the acceleration part of the C₃S peak. A faster rate of C-S-H precipitation due to the “filler effect” consequently leads to an earlier depletion of solid gypsum. After this point, sulfate is desorbed from C-S-H and is available to react with aluminates to form ettringite. A linear relationship was found between the SO₃ content of the system and the heat released until the onset of the aluminate peak.

Model mixtures of pure C₃S and C₃A powders allow the effects of the finenesses of the different phases to be studied. By adjusting the fineness of each pure phase independently, the effect of the rate of reaction of C₃S and C₃A on the sulfate balance of the overall system can be

studied. In addition, C₃S/C₃A systems behave similarly to OPC in terms of sulfate balance. More gypsum leads to a retardation of the onset of the aluminate peak, and C-S-H precipitation influences the balance. Quennoz et al. [7] observed significant differences in the time of gypsum depletion between pure C₃A and C₃S/C₃A systems showing that C-S-H also participates in the sulfate balance of these systems, as in the case of OPC and blended cements [8].

The mechanism by which gypsum slows down the reaction of C₃A has been extensively studied, but is still a matter of debate. Recent studies support the idea of adsorption of sulfate or sulfate complexes in C₃A surface as the most tenable mechanism explaining the observed retardation [9–11]. The common textbook view that ettringite forms a diffusion barrier is not supported by the evidence [12,13].

In addition to the well know effect of sulfate on C₃A, an enhancement effect of gypsum over alite hydration has also been reported [5,14]. Mota et al. proposed that sulfate adsorbed in the C-S-H needles can modify the growth process by promoting repulsion between the growing needles [14]. Gunay et al. also concluded that the adsorption of calcium sulfate on C-S-H modifies the nucleation and growth process [15], in agreement with previous findings of Bentur [16] that showed an increase in the amount of C-S-H formed.

In this study, C₃S/C₃A pure phase systems are used to assess the influence of different mixture design and kinetic factors on the sulfate balance of the system. In particular, the influence of the C₃A and C₃S rate of reaction are explored, along with the dissolution rate of the sulfate source used. The heat release at the onset of the aluminate peak versus the SO₃ content of the system is revisited, and an explanation of this trend based on measurable properties of the system is given.

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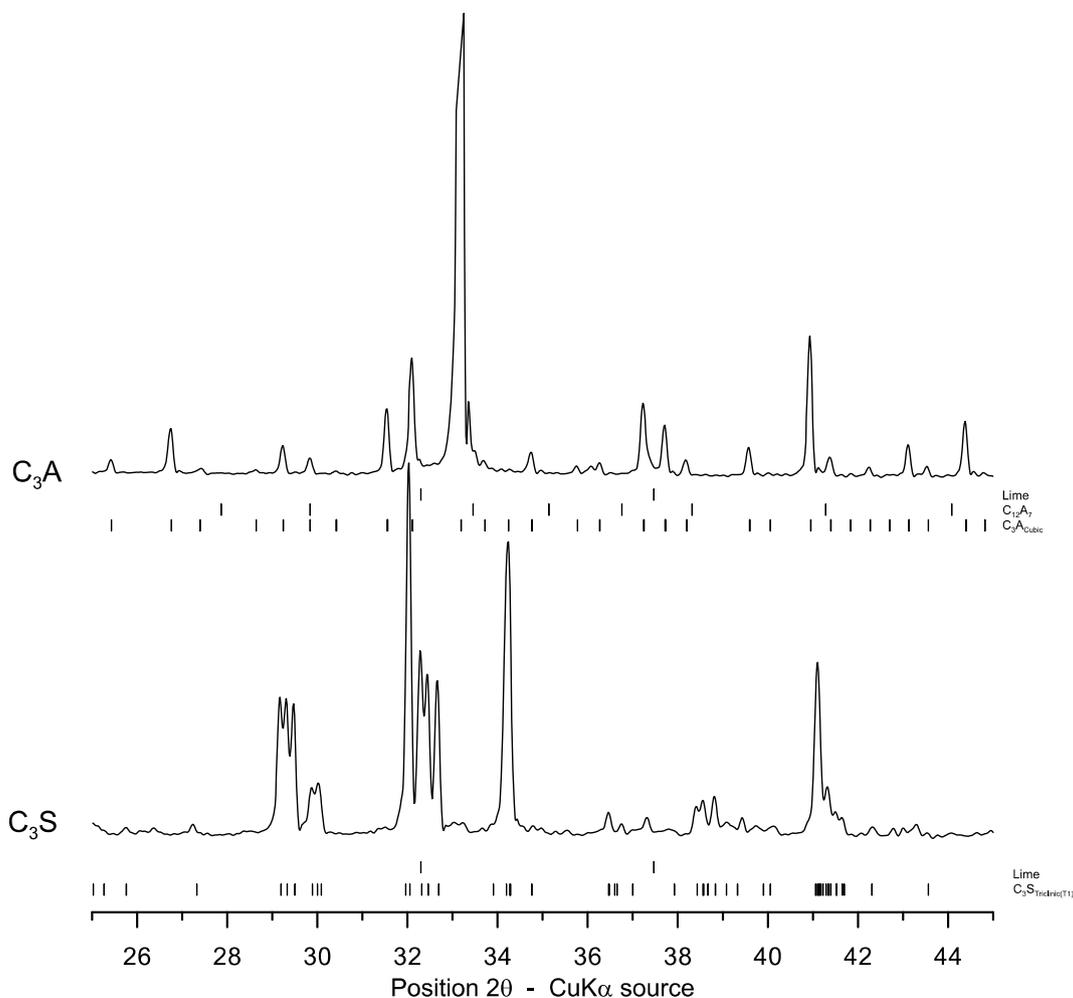


Fig. 1. Diffractograms of the pure triclinc C_3S and cubic C_3A synthesized in this study.

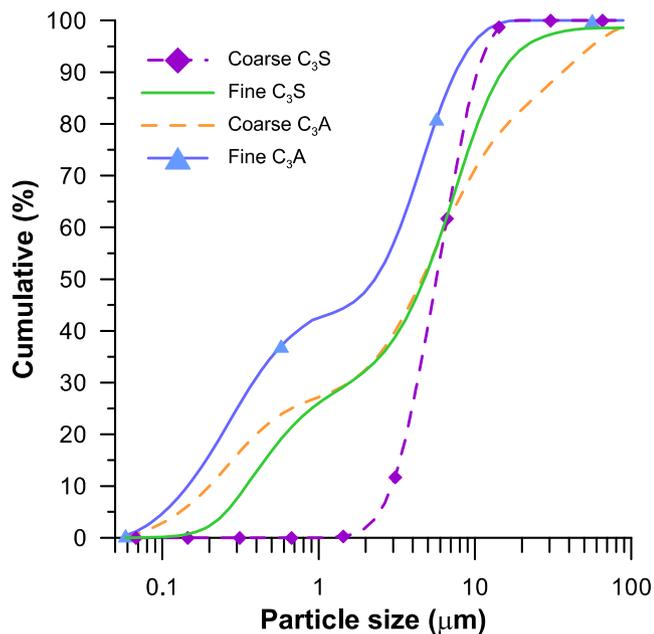


Fig. 2. Particle size distribution of the pure phase materials used in this study.

2. Materials and methods

2.1. Synthesis of pure phases

The synthesis of pure tricalcium silicate (C_3S) and tricalcium aluminate (C_3A) was conducted following the procedure described in [17] for the production of large amounts of material. For the synthesis of C_3S , calcium carbonate (VWR) and fumed silica (0.2 μm , Sigma-Aldrich) were used. The sintering temperature was maintained at 1600 $^{\circ}C$ for 4 h, and the samples were air quenched subsequently. The result was triclinc (T_1) C_3S with a free lime content below 0.5% in all batches, as quantified by Rietveld refinement.

For the synthesis of C_3A , the same calcium carbonate as for C_3S was combined with aluminum oxide (Al_2O_3 , Merck), keeping the CaO content of the raw mix fixed at 62.5% (slightly above the stoichiometric amount) to prevent the formation of mayenite ($C_{12}A_7$). The sintering temperature was maintained at 1450 $^{\circ}C$ for 4 h, and the samples were air quenched subsequently. As a result, cubic C_3A was obtained, with free lime content of 0.4–0.7% measured by Rietveld refinement in the different batches. A representative diffractogram of both materials is shown in Fig. 1.

2.2. Raw materials characterization

After synthesis, the pure phases were ground in a concentric disc mill in batches of 100 g. For the production of coarse C_3S and C_3A , 30 s of grinding was applied twice. The grinding rounds were kept short to

Table 1
Distribution values, span (width), specific surface area and specific gravity of raw materials.

	Coarse C ₃ S	Coarse C ₃ A	Fine C ₃ S	Fine C ₃ A
D _v 90 (μm)	10.5	35.6	14.5	7.7
D _v 50 (μm)	5.7	4.9	4.9	2.3
D _v 10 (μm)	2.9	0.2	0.4	0.2
Span (–)	1.33	7.22	2.88	3.26
SSA (m ² /g)	1.09	1.03	2.87	4.53
Sp. gravity (g/cm ³)	3.15	3.05	3.15	3.07

prevent excessive heating of the material. In the case of fine C₃S and C₃A, the process of grinding for 30 s was repeated 6 times. Subsequently, particle size distribution was measured by laser diffraction using isopropanol as dispersant, Fig. 2.

The specific surface area (SSA) of each raw material was measured by nitrogen adsorption, using the BET method. In all cases, samples of around 1.5 g were degassed for 2 h at 200 °C under a N₂ flux before the measurement. The specific gravity was measured using a helium pycnometer. The measured values of the raw powders are summarized in Table 1.

2.3. Mixture design and experimental methods

The base mixture was a pure C₃S system with a water to binder ratio of 0.5 by mass (1.570 w/s ratio by volume). From this reference, all other mixtures were prepared keeping constant the volumetric w/s ratio. For the C₃S/C₃A systems, a ratio of 92/8 by mass was selected, which is similar to the ratio found in many Portland cement clinkers. Mixtures were prepared by combining C₃S and C₃A and different amounts of gypsum (CaSO₄·2H₂O) or hemihydrate (2CaSO₄·H₂O) as sources of sulfate. The sulfate source was incorporated by replacing part of the C₃S/C₃A mixture.

The heat evolution was measured in a TAM Air isothermal calorimeter at 20 °C for up to 6 days. Paste samples were mixed with a high shear mixer at 1600 rpm for 2 min, 10 g of paste was placed in a glass ampoule, sealed and introduced in the calorimeter.

For in-situ XRD experiments, paste specimens were prepared in the same manner as the isothermal calorimetry samples. The paste samples were mounted on a disc shaped sample holder, and covered with a 12.7 μm thick Kapton film which was secured on top with a ring. The temperature was controlled at the base of the sample holder with a Peltier stage and kept constant at 20 °C. The samples were analyzed in a Bragg-Brentano configuration in a PANalytical X'pert pro diffractometer working at 45 kV and 40 mA with a copper source. A 1° soller slit was used, and scans were acquired between 7 and 70° 2θ in 14 min, equivalent to a step size of 0.0167° 2θ. The external standard method was used to compute the K-factor of the device and account for the amorphous phases present. The scans were collected every 30 min up to 24 h of hydration. Rietveld refinement was conducted using the HighScore Plus v4.8 software.

3. Results and discussion

3.1. The effect of gypsum addition on C₃A and C₃S hydration

The influence on hydration kinetics of different additions of gypsum on the two C₃As studied (fine and coarse) are shown in Fig. 3. As seen, the duration of the first stage of hydration (before the main peak), corresponding to the precipitation of ettringite, depends on the amount of gypsum added for the same C₃A, but also on the fineness of the material, in good agreement with previous studies [3]. In pure C₃A-gypsum systems, the observed peak corresponds to the transformation of ettringite to AFm, and is triggered by gypsum depletion from the system [7]. In the results presented, 30% gypsum addition to fine C₃A

leads to a similar retardation of the peak as 20% addition to coarse C₃A. Finer C₃A is able to react faster with gypsum and therefore, there is an earlier depletion.

The effect of different gypsum additions on pure triclinic C₃S (fine and coarse) are shown in Fig. 4. In this case, the amounts of gypsum added are much lower than the ones used in pure C₃A systems. It is observed that the induction period is slightly longer in the systems with gypsum as compared to pure C₃S. In addition, gypsum leads to an enhancement of the main peak of hydration for both particle sizes studied. These effects are observed even at low gypsum additions. After around 6 h of hydration, the degree of hydration (DoH) of C₃S with gypsum addition is significantly higher than plain C₃S. Further discussion on the effect of gypsum addition on C₃S hydration is presented in section 3.6.

3.2. The effect of C₃A fineness on C₃S/C₃A systems

The influence of the C₃A fineness on the sulfate balance of C₃S/C₃A systems was studied by comparing the calorimetry curves of systems combining fine C₃S with either coarse or fine C₃A, and different levels of gypsum addition. As in the case of pure C₃A, the aluminate peak occurs after solid gypsum is depleted from the system. However, in this case it is associated with a second formation of ettringite, similar to that observed in OPC [5]. Fig. 5 shows the heat flow and heat curves for fine C₃S mixed with coarse C₃A, while Fig. 6 contains the results for fine C₃S mixed with fine C₃A systems.

In general, two main cases can be distinguished regarding the sulfate balance of the C₃S/C₃A systems: one where the aluminate peak occurs before the C₃S peak (undersulfated), characterized by a lower and broader C₃S peak following the aluminate peak, and others where the aluminate peak occurs after the C₃S one (properly sulfated), characterized by a higher and narrower C₃S peak preceding the aluminate one.

As in the case of pure C₃A systems (Fig. 3) more gypsum is required to retard the aluminate peak in the systems with fine C₃A (Fig. 6) as compared to coarse C₃A (Fig. 5). In all cases, the C₃S peak is similar, thus the contribution of sulfate adsorption on C-S-H to gypsum depletion can be considered similar in systems with an aluminate peak occurring at a relatively similar hydration time (for example, C₃S_{Fine}C₃A 3.0% gypsum compared to C₃S_{Fine}C₃A_{Fine} 4.0% gypsum). This suggests that, in addition to sulfate adsorption on C-S-H, there is another factor linked to the rate of reaction of C₃A itself that should be considered in the sulfate balance of the system.

3.3. The effect of C₃S fineness on C₃S/C₃A systems

The influence of the C₃S fineness on the sulfate balance of C₃S/C₃A systems was studied by comparing the calorimetry curves of systems combining fine and coarse C₃S with coarse C₃A (Fig. 5 and 7 respectively), and different amounts of gypsum. As observed, more retardation of the aluminate peak is observed in the systems with coarse C₃S for the same gypsum addition. As an example, the system with 3.0% gypsum has the maximum of the aluminate peak at around 14 h in the fine C₃S system and 31 h in the coarse C₃S one. Similarly, 2.0% gypsum addition leads to an undersulfated system in the system with fine C₃S, while it is properly sulfate in the case of coarse C₃S. These differences are linked to the amount of sulfate that is adsorbed on C-S-H before the aluminate peak. Finer C₃S reacts faster, and therefore more C-S-H is precipitated before this point, increasing the amount of sulfate adsorbed and triggering and earlier depletion of solid gypsum.

3.4. Heat release vs SO₃ content

Quennoz and Scrivener [5] showed that sulfate adsorption on C-S-H plays a major role in the sulfate balance of C₃S/C₃A systems. Recently, Zunino and Scrivener [6] showed that the sulfate balance can be affected by the incorporation of SCMs due to the increase in the rate of C-

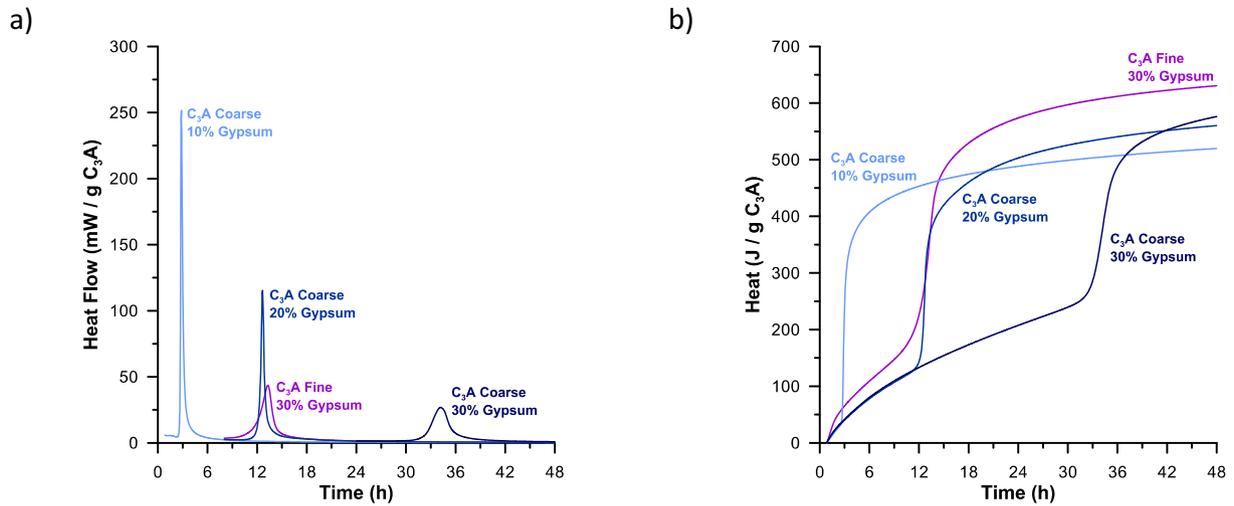


Fig. 3. Heat flow (a) and total heat (b) of pure fine and coarse C_3A systems with different gypsum additions.

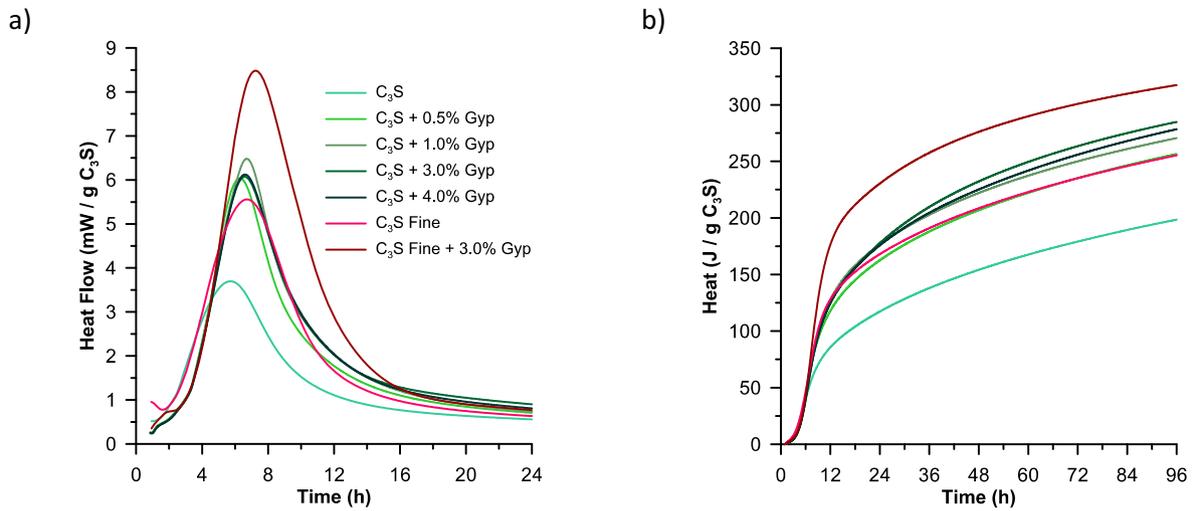


Fig. 4. Heat flow (a) and total heat (b) of pure fine and coarse C_3S systems with different gypsum additions.

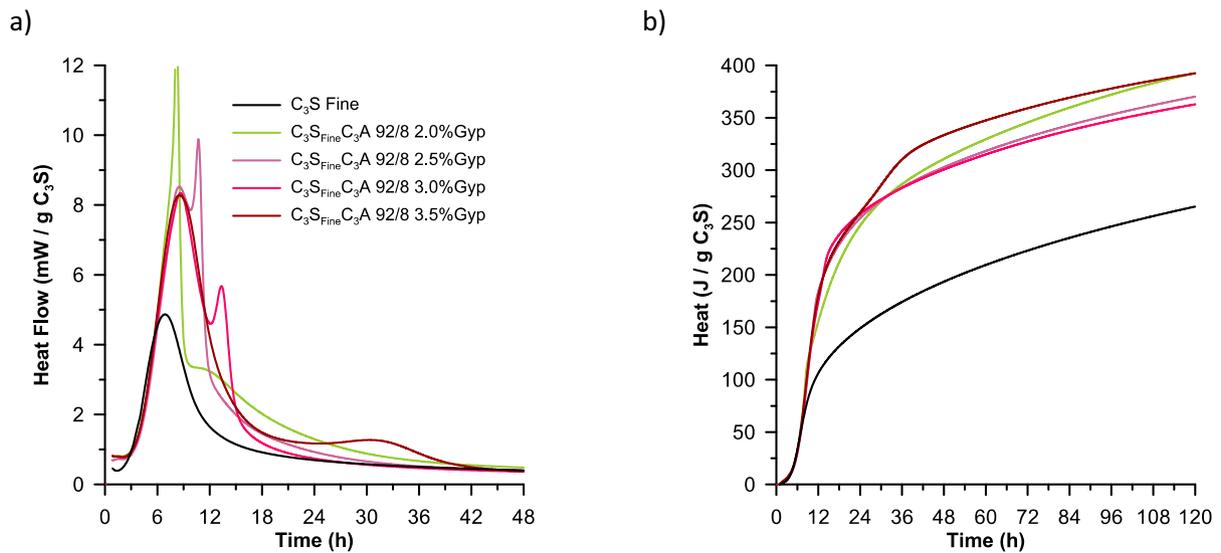


Fig. 5. Heat flow (a) and total heat (b) of C_3S/C_3A systems 92/8 with coarse C_3A and different gypsum additions.

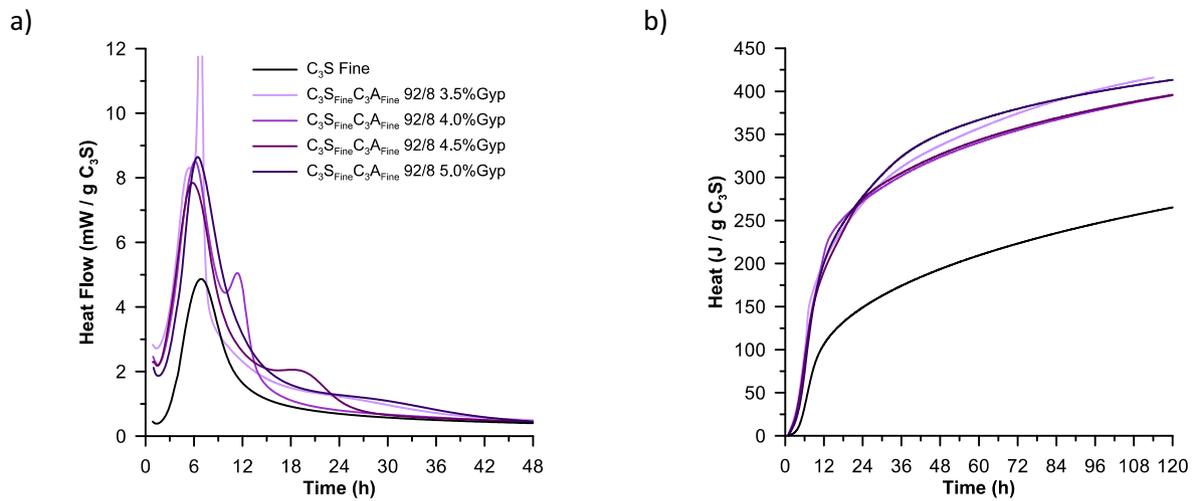


Fig. 6. Heat flow (a) and total heat (b) of C_3S/C_3A systems 92/8 with fine C_3A and different gypsum additions.

S-H precipitation by the filler. A linear correlation between the total SO_3 content of the system and the heat release up to the onset of the aluminate peak, taken as an indication of the amount of C-S-H formed, was found. In this study, the same correlation was obtained for the different C_3S/C_3A systems, as shown in Fig. 8.

Two linear trends were found in this case: one grouping the systems with coarse C_3A , and one for the systems with fine C_3A . An important observation is that the slope of both linear trends is almost the same, and they just differ on the intercept with the SO_3 axis.

The fineness of C_3S leads to an enhancement of the C_3S peak (see Fig. 4), which can be considered an analogue effect to the addition of SCMs. In Fig. 8, it can be seen that this effect does not change the heat- SO_3 correlation between the systems if the C_3A fineness and quantity remains the same. This is in good agreement with the results shown in [6], as in that case all the systems were prepared with the same OPC (i.e., same C_3A) and at relatively similar levels of OPC replacement.

In [6], it was suggested that the intercept with the SO_3 axis represented the amount of sulfate consumed before the aluminate peak due to the precipitation of ettringite. In pure phase systems, this hypothesis can be verified experimentally, and it will be discussed in subsection 3.4.1. As discussed in [6], the total heat released before the onset of the aluminate peak also includes the heat associated with ettringite precipitation during this period. As in the case of blended cements shown in the referenced study, this amount is similar among

systems following the same trendline, as shown in the next subsection.

Even considering that the C_3A fineness shifts the linear trend obtained, the slope remains constant, suggesting that the slope of the regression could be related to another property of the system that remains constant among the different systems. This will be addressed in subsection 3.4.2.

3.4.1. Intercept with SO_3 axis: link with the amount of ettringite formed before the aluminate peak

As seen in Fig. 8, an increase in the fineness of C_3A leads to a shift to the right of the regression line obtained. Based on the observation of pure C_3A and C_3S/C_3A systems with fine and coarse C_3A , it is inferred that the difference might be associated to the amount of ettringite formed before the onset of the aluminate peak (gypsum depletion point). To study the relationship between the amount of ettringite formed before the onset and the intercept of the regression lines with the SO_3 axis, in-situ XRD experiments were conducted on a system with fine and coarse C_3A . The gypsum content was adjusted in each case so that the aluminate peak occurs between 12 and 18 h. This led to a mixture design with 2.5% gypsum in the coarse C_3A system, and 3.75% gypsum in the fine C_3A one. In both cases fine C_3S was used.

Fig. 9 shows the phase assemblage of the coarse (a) and fine (b) C_3A system. The amount of ettringite formed before the onset of the aluminate peak is significantly higher in the fine C_3A system. The amounts

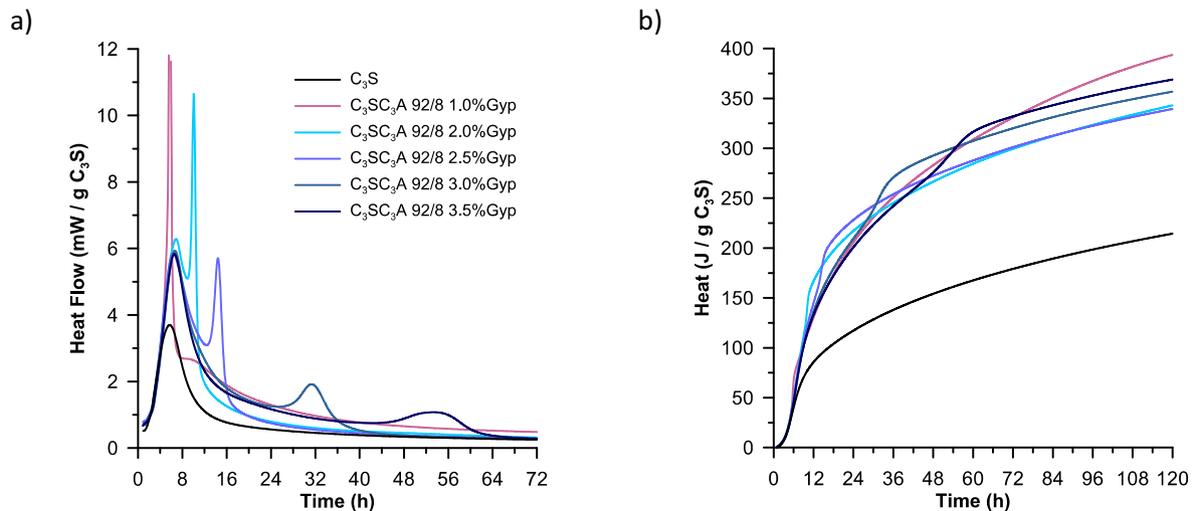


Fig. 7. Heat flow (a) and total heat (b) of C_3S/C_3A systems 92/8 with coarse C_3S and C_3A , and different gypsum additions.

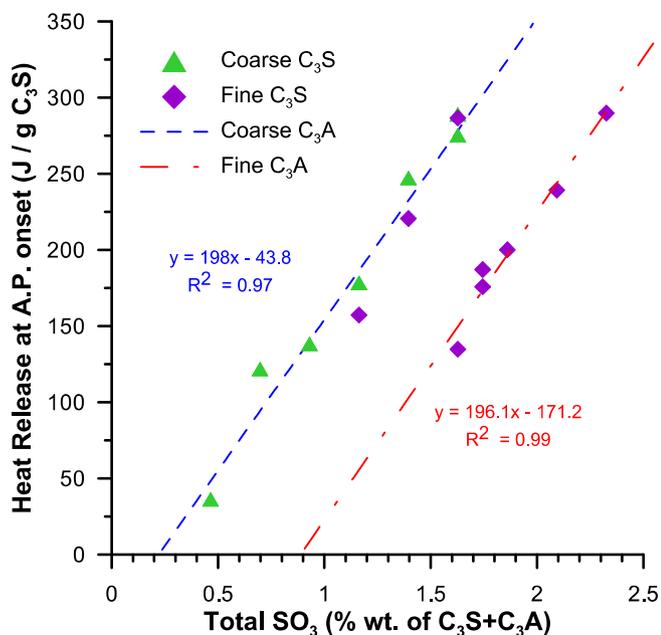


Fig. 8. Heat release at the aluminate peak (A.P.) onset vs total SO₃ content for all the C₃S/C₃A 92/8 systems with different gypsum additions studied.

of ettringite measured at the onset of the aluminate peak for each system are shown in Table 2. Even considering the inherent error associated with this type of measurements, these figures provide at least an idea of the order of magnitude of the ettringite content. Stoichiometrically, 3 mol of SO₃ are required to form 1 mol of ettringite, leading to a mass ratio of 0.191 g SO₃/g ettringite formed. This value can be used to compute the amount of SO₃ required to form the ettringite measured by in-situ XRD, which are summarized in Table 2, along with the intercepts computed from the regression lines shown in Fig. 8.

The computed SO₃ required to form the observed ettringite are in within 10% variation of the intercept of the corresponding regression lines in Fig. 8 for both systems. Thus, the intercept is indeed linked to the amount of ettringite formed before the occurrence of the aluminate peak, and a shift right can be triggered by an increase of this amount (finer C₃A and/or higher C₃A content).

The heat associated with the formation of ettringite before the

aluminate peak is included in the values shown in Fig. 8. A variation of the actual correlation obtained could be presumed. However, the amount of ettringite formed before the aluminate peak onset is similar for systems with the same C₃A fineness. This was also observed in OPC-based blended systems [6]. The high correlation coefficients obtained in Fig. 8 indicate that systems with the same C₃A share the same intercept despite their different SO₃ content, and consequently the ettringite content formed before the aluminate peak (see Table 2). If the amount of sulfate added is beyond the amount that is able to be adsorbed in C-S-H and consumed by ettringite precipitation, gypsum depletion would not be reached (i.e. the aluminate peak is not visible) and thus, the parameters for determining a point in Fig. 8 cannot be obtained.

3.4.2. Slope: relation to \$/Ca ratio of C-S-H

Previous studies have reported values for the sulfur-to-calcium (\$/Ca) ratio of C-S-H before the aluminate peak for C₃S/C₃A systems [5] and also in blended OPC [8]. These datasets were acquired using SEM/EDS. The values reported for the \$/Ca ratio of C-S-H before the aluminate peak vary from 0.04 to 0.06. Another study measured by STEM/EDS the \$/Ca ratio evolution of cement at early ages, reporting values over the same range during the first hours of hydration [18].

As it was shown in Fig. 8, while the different systems have different heat-SO₃ relationships depending on the amount of ettringite formed before the aluminate peak, the slope remains constant. The amount of C-S-H formed was computed at a DoH equivalent to the heat release of the slope, assuming an enthalpy of reaction of 524 J/g C₃S [19]. The sulfur content equivalent to the addition of 1% SO₃ (per gram of C₃S + C₃A) to this obtained amount of C-S-H was used to compute the theoretical \$/Ca ratio. As there might exist uncertainty of the value of the slope obtained by regression of the heat-SO₃ correlation, a sensitivity analysis of the \$/Ca ratio was made for different values of the slope, Fig. 10. Furthermore, the value \$/Ca ratio was computed for a variety of Ca/Si ratio values of C-S-H. As seen, the computed \$/Ca are in good agreement with the measured values of \$/Ca found in the literature [5,8,18] for typical values of Ca/Si during this period of hydration. Thus, the slope of the heat-SO₃ correlation is linked to the sulfur amount adsorbed into C-S-H before the aluminate peak.

3.4.3. Sulfate adsorption in C-S-H and the initial amount of ettringite formed influence sulfate balance

The results presented indicate that the overall sulfate balance of these systems is controlled by two factors: first, the adsorption of sulfate

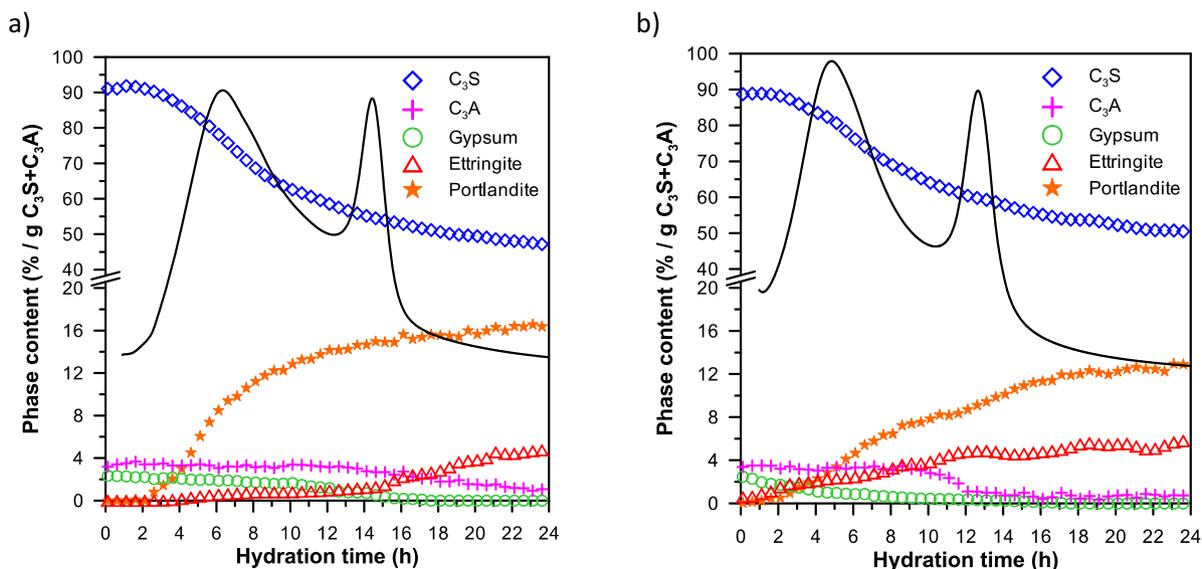


Fig. 9. Initial phase assemblage measured by in-situ XRD of C₃S/C₃A 92/8 systems with coarse (a) and fine (b) C₃A.

Table 2

Ettringite formed before the aluminate peak measured by in-situ XRD, computed SO₃ required and intercept of the Heat-SO₃ regression with the SO₃ axis.

System	Ettringite at A.P. onset (% C ₃ S + C ₃ A)	SO ₃ required (% C ₃ S + C ₃ A)	Intercept Heat-SO ₃ with SO ₃ axis (% C ₃ S + C ₃ A)	Variation (%)
C ₃ S + C ₃ A 92/8 Coarse C ₃ A	1.1	0.211	0.22	4.1
C ₃ S + C ₃ A 92/8 Fine C ₃ A	4.5	0.852	0.87	2.1
C ₃ S + C ₃ A 92/8 Fine C ₃ A Hemi	9.5	1.820	1.99	8.5

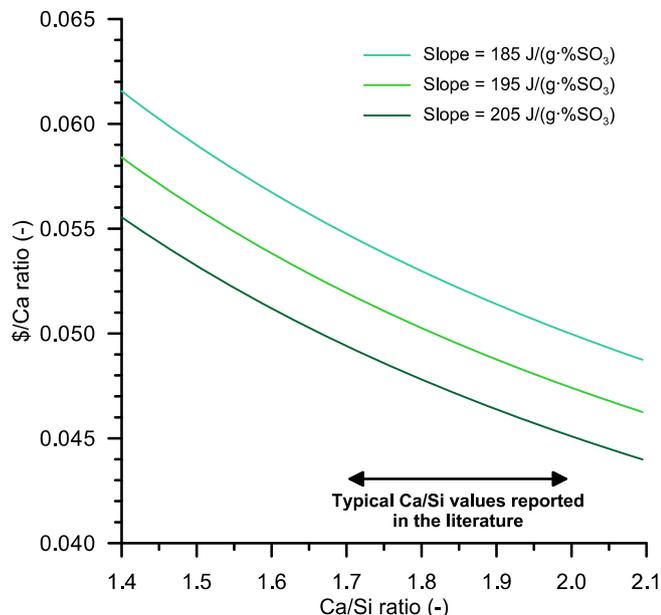


Fig. 10. S/Ca as a function of Ca/Si ratio of C-S-H for different slope values of the heat-SO₃ regression trendline (b).

on C-S-H and second, the rate of precipitation of ettringite before the aluminate peak.

The contribution of both factors to the sulfate balance of the system should be considered simultaneously. This can be concluded based on the calorimetry results shown in Fig. 11. In these systems, the gypsum/C₃A and gypsum/C₃S ratios were adjusted by varying the gypsum content in system with C₃S/C₃A ratios of 94/6, 92/8 and 90/10. Fig. 11a show that the gypsum/C₃A ratio cannot be solely used to

predict the sulfate demand, as the position of the aluminate peak in all cases is different. In this case, the differences are explained by the reduction in the amount of C-S-H formed (due to a lower content of C₃S as the amount of C₃A increase) and the consequent lower adsorption of sulfate. In fact, the systems with more C₃A (less C₃S) exhibit a more retarded aluminate peak. This is in agreement with the experiment of Quennoz and Scrivener on alite [5].

Fig. 11b shows systems where the gypsum/C₃S ratio was fixed. As seen, the position of the aluminate peak is different in all the systems, showing that adsorption of sulfate on C-S-H neither can solely explain the position of the aluminate peak. In this case, the systems with less C₃A exhibit a more retarded aluminate peak, as the amount of ettringite that is formed is lower. In the 94/6 system, the aluminate peak is not seen even after 6 days, indicating that the amount of C₃A and the adsorption on C-S-H were not able to deplete solid gypsum from the system.

3.5. The effect of the sulfate source on the sulfate balance of C₃S/C₃A systems

The amount of ettringite that is formed before the onset of the aluminate peak is one of the factors that explains the sulfate balance of C₃S/C₃A systems. More ettringite can be precipitated during this period by increasing the fineness of C₃A and/or the amount of C₃A. In addition, it has been shown in previous studies that the source of sulfate can also influence the initial reactivity of C₃A. Hemihydrate has a faster rate dissolution compared to gypsum [20].

To study the influence of the dissolution rate of the sulfate source, some replicates of the systems containing fine C₃S and fine C₃A were prepared using hemihydrate instead of gypsum. As the SO₃ content of these compounds is different (SO₃Gyp/SO₃Hemi = 0.84) the content of hemihydrate was adjusted to match the SO₃ content of the gypsum (noted as GypSO₃EQ), Fig. 12. An addition of 4.0% GypSO₃EQ leads to an undersulfated system, which is not the case for the same SO₃ content if

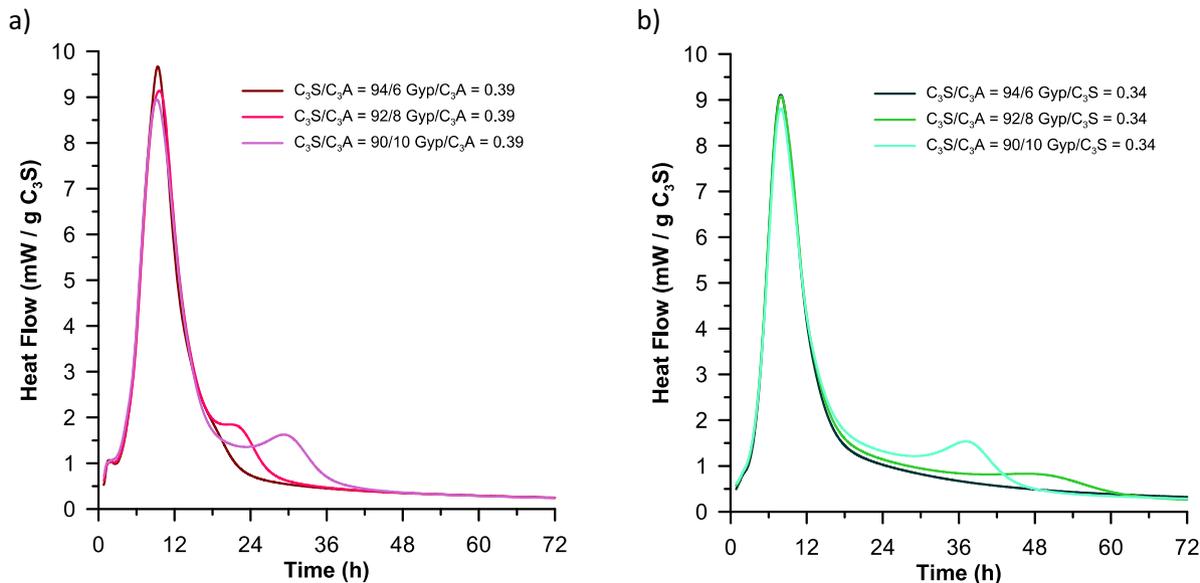


Fig. 11. Heat flow curves of C₃S/C₃A systems with fine C₃S and coarse C₃A, with varying Gypsum/C₃A (a) and Gypsum/C₃S (b) ratios.

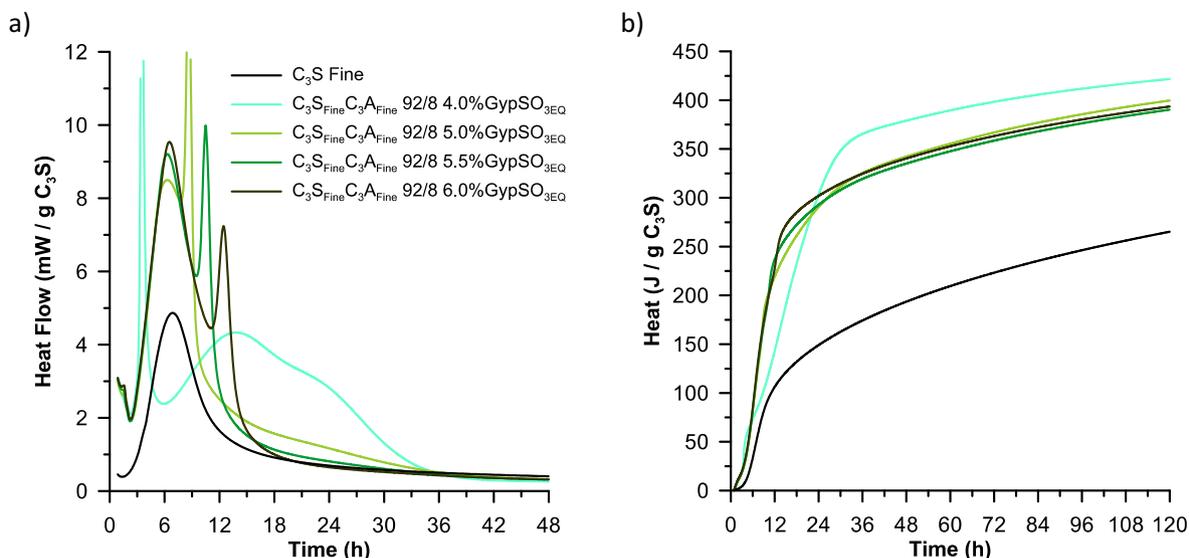


Fig. 12. Heat flow (a) and total heat (b) of C₃S/C₃A systems 92/8 with fine C₃A and different hemihydrate additions.

the sulfate source is gypsum (see Fig. 6). As the observed ability to retard the aluminate peak was lower as compared to gypsum at the same sulfate addition, higher SO₃ contents were also prepared (5.5% and 6.0% GypSO_{3EQ}). These results also show that the retardation of the C₃A reaction by the addition of gypsum or hemihydrate depends on the type of sulfate source used for the same added SO₃ content. Therefore, the dissolution rate of the sulfate source is another factor to be accounted for to determine the position of the aluminate peak.

Since the C₃S used for the systems shown in Fig. 6 and Fig. 12 is the same and the observed C₃S peaks are similar, the difference in the retardation of the aluminate peak observed is attributed to the early formation of ettringite before the onset of the aluminate peak. The heat-SO₃ regression was also performed and compared to the gypsum systems prepared with the same pure phases, Fig. 13. As observed, the systems containing hemihydrate as sulfate source fall in a different line shifted right respect to the mixtures with gypsum.

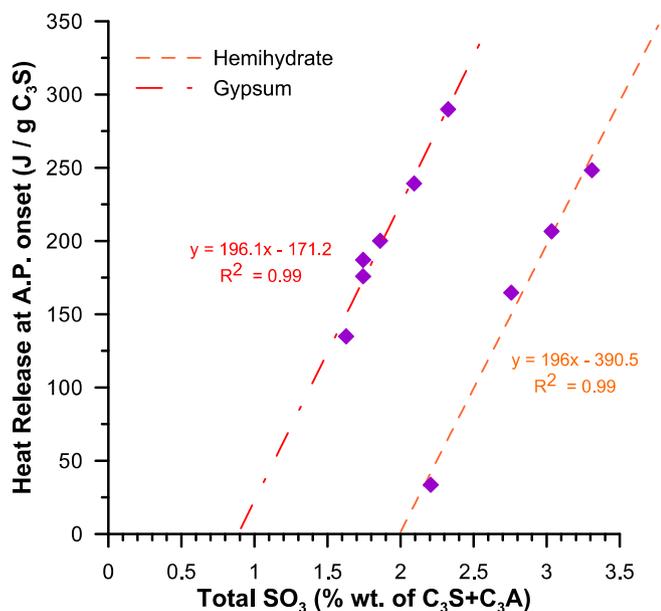


Fig. 13. Heat release at the aluminate peak (A.P.) onset vs total SO₃ content for C₃S/C₃A 92/8 systems with fine pure phases and different gypsum or hemihydrate additions.

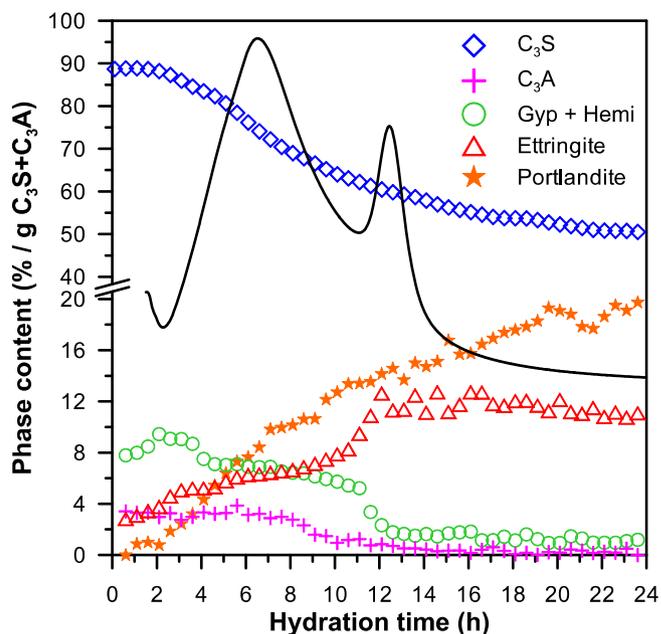


Fig. 14. Initial phase assemblage measured by in-situ XRD of C₃S/C₃A 92/8 system with fine pure phases and 6.0% hemihydrate addition.

The initial ettringite content was verified by an in-situ XRD measurement on the system containing 6.0% hemihydrate, Fig. 14. Hemihydrate turns into gypsum during the first hours of hydration. The initial amount of ettringite is significantly higher as compared to the gypsum system (Fig. 9b). The first point is acquired between 6 and 10 min after initial contact of the materials with water, and the difference shows that indeed hemihydrate is able to provide more sulfate ions in solution, which react quickly with C₃A to form ettringite, before the slowing down of the C₃A reaction. Afterwards, the rate of ettringite precipitation is controlled by the rate of reaction of C₃A which is similar among systems with the same C₃A fineness, in agreement with the similar slope observed for ettringite content over time in Fig. 9b for the system with gypsum and Fig. 14 for the system with hemihydrate.

The slope of the heat-SO₃ regression remains the same as for gypsum, Fig. 8. Thus, the S/Ca ratio of C-S-H is not significantly affected by a change in the sulfate source of the system, but rather the

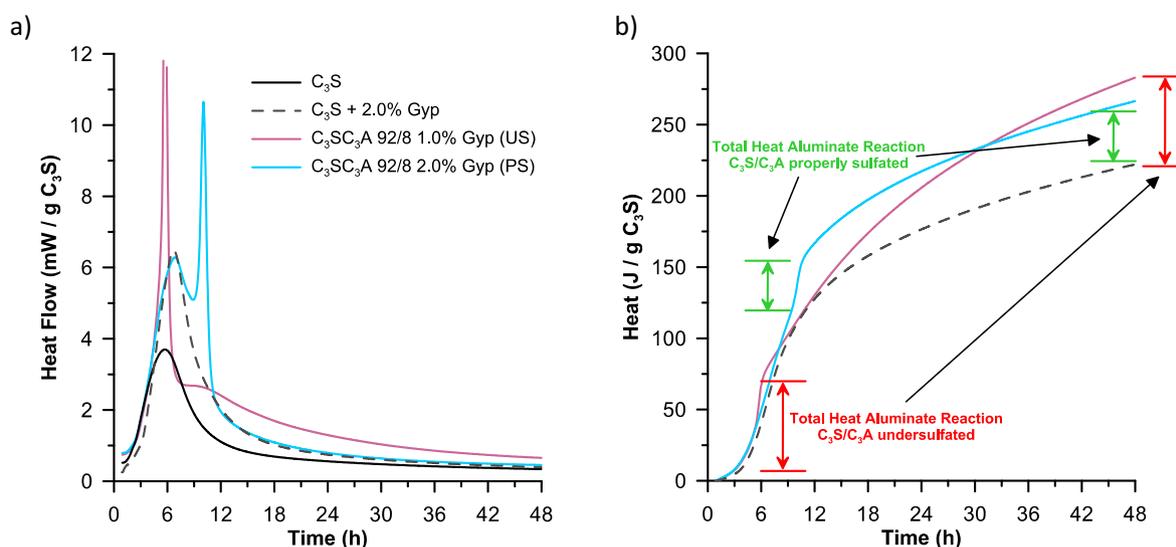


Fig. 15. Heat flow (a) and total heat (b) of under and properly sulfated C₃S/C₃A systems, in addition to pure C₃S and sulfated C₃S.

initial ettringite content increases. The intercept for the regression of the systems with hemihydrate was also compared with the theoretical SO₃ required to form the ettringite measured by in-situ XRD, being is also within 10% variation of the computed intercept, Table 2.

3.6. Further insights on the effect of gypsum addition on C₃S hydration

As it was shown in Section 3.2, in undersulfated systems where the aluminate peak precedes the C₃S one, a lower and broader C₃S peak is observed. Several hypotheses have been formulated to explain this observation. Quennoz and Scrivener [5] suggested that the re-acceleration of the alite reaction was slowed down due to the presence of aluminum in the pore solution of undersulfated system. Bergold et al. [4] proposed that the aluminate reaction interfered with C-S-H precipitation due to interactions with AFm.

While the actual mechanism explaining the change in the kinetics of the C₃S reaction in undersulfated systems is still unclear, some insights can be gathered from the results of this study. It was shown that gypsum addition can have an enhancement effect on pure triclinc C₃S (see Fig. 4). Fig. 15 shows two C₃S/C₃A systems, one undersulfated (1.0% gypsum) and one properly sulfated (2.0% gypsum), and also the curves for the corresponding C₃S and C₃S + gypsum with the same sulfate content as the properly sulfated C₃S/C₃A system.

The DoH of C₃S in C₃S/C₃A properly sulfated is significantly higher to the one of pure C₃S. On the other hand, the peak of the C₃S + gypsum system matches the one of the properly sulfated C₃S/C₃A system. Therefore, a big part of the difference between the peaks of C₃S alone and in the C₃S/C₃A system with 2.0% gypsum can be explained by the enhancement effect of sulfate on C₃S hydration.

In the undersulfated C₃S/C₃A system, the C₃S peak is lower and broader compared to the properly sulfated case. To compare the DoH of C₃S in both C₃S/C₃A systems, the calorimetry curves were decoupled. The aluminate peak was then integrated, and the total heat associated with it is shown as vertical arrow markers in Fig. 15b. This shows that after 48 h of hydration, the DoH of C₃S in properly and undersulfated systems is similar, despite the significantly different kinetics during the first hours of hydration. This is in agreement with data from Bergold et al. [4], where virtually the same DoH of C₃S was computed from in-situ XRD data of under and properly sulfate systems after 46.5 h.

The difference of heat release associated with the aluminate reaction between the properly and under sulfated system can be explained by the different types of phases precipitated during the aluminate peak in undersulfated (precipitation of AFm) and properly sulfated (second

formation of ettringite) systems [5].

The results of this study showed that an enhancement of the C₃S peak is observed with gypsum additions, leading to an increased DoH. Quennoz and Scrivener [5] observed the same effect on alite (C₃S with additions of alumina and magnesium oxide) with similar levels of gypsum addition. However, they did not observe the same effect on their pure C₃S material. It should be noted that the height of the peak of pure C₃S reported in their study is close to 11 mW/g C₃S, much higher than even the fine C₃S with 3% gypsum system reported here. This indicates that their material was very fine, and therefore the overall enhancement effect of gypsum is less significant in such fast reacting material. An analogue observation was made on a fine alite from a commercial OPC by Adu-Amankwah et al. [21].

Several hypotheses have been proposed to explain the observed enhancement of gypsum on C₃S/alite. Bergold et al. [4] proposed a seeding effect of (nano-)ettringite to explain the higher DoH measured in alite systems with gypsum addition. In light of the results of this study, this hypothesis is unlikely, as the enhancement of the peak is observed as well in pure C₃S system, where no aluminates (and consequently, ettringite) are present. This suggests that the cause of the enhancement of C₃S hydration by gypsum is an interaction exclusively between this phase and C₃S (and/or C-S-H), rather than one that involves the aluminates. Further research is required to clarify the mechanism behind this interaction.

4. Conclusions

This study compared the effect of different factors that affect the rate of sulfate consumption during the early stages of hydration of C₃S/C₃A systems, modifying their sulfate balance. As it was shown, the interaction between C₃S, C₃A and sulfate is complex and therefore the sulfate balance cannot be explained by a single factor.

Based on the results presented, the following conclusions can be drawn:

1. Two main factors explain the sulfate balance of C₃S/C₃A systems: first, the amount of ettringite precipitated before the onset of the aluminate peak and second, the adsorption of sulfate into C-S-H.
2. The fineness of C₃A modifies the amount of ettringite precipitated before the aluminate peak, while the fineness of C₃S affects the rate of C-S-H precipitation. Both factors can consequently play a role in the final position of the aluminate peak in C₃S/C₃A systems.
3. The intercept with the SO₃ axis of the heat-SO₃ curve is linked to the

amount of ettringite precipitated before the onset, while the slope is driven by the S/Ca ratio of C-S-H during this period. The intercept can be modified by changing the kinetics of reaction of C₃A or the type of sulfate source.

4. The addition of sulfate enhances the hydration of C₃S. The DoH of C₃S in C₃S/C₃A systems is higher as compared to pure C₃S. This can be explained by the enhancement of C₃S hydration by the addition of gypsum.
5. Undersulfated C₃S/C₃A systems exhibit a lower and broader C₃S peak as compared to properly sulfated systems. At 48 h, the DoH of C₃S in under and properly sulfated system is the same, thus, the effect of the different kinetics of C₃S reaction on the overall DoH is constrained to the first two days of hydration.

CRediT authorship contribution statement

Franco Zunino: Conceptualization, Methodology, Writing - original draft, Writing - review & editing. **Karen Scrivener:** Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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