

EFFECTS OF SULFATES ON THE HYDRATION OF PORTLAND CEMENT – A REVIEW

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ABSTRACT

Presented within is a critical overview of the effect of sulfates on cement hydration, properties, and optimum sulfate content in Portland cement. Calcium sulfate is used in Portland cement to control the C₃A reaction to induce the optimum hydration of C₃S to occur. The amount of calcium sulfate in the Portland cement influences the hydration, rheology, setting, phase assemblage, porosity distribution, and strength in cementitious materials. If added in excess, it can also lead to durability problems, thus a better understanding is needed about the mechanisms of sulfate on C₃A and C₃S hydration. The optimum sulfate content is well known as a key pathway to produce workable, good strength and durable concretes. Despite many years of research, questions regarding sulfate optimization remain. Further investigation on the influence of clinker and calcium sulfate characteristics, the use of different supplementary cementitious materials and chemical admixtures, and the curing conditions on the sulfate demand of Portland cement are needed. The main methods used to determine the optimum SO₃ content are reported, and the advantages and disadvantages are examined. Finally, recommendation for future research is also discussed.

Keywords: *Optimum sulfate content; Sulfate balance; Cement; Hydration; Supplementary Cementitious Materials*

1 INTRODUCTION

Portland cement is the most consumed building material worldwide; it has been in use for almost 200 years. The use of calcium sulfate to control the duration of the setting of cement began at the end of the 19th century and universally adopted by cement producers around 1930 [1,2]. Nowadays, the inclusion of calcium sulfate is an integral ingredient in Portland cement. Despite thousands of studies over several decades, many questions about the role of calcium sulfate on the cement phases (C_3A and C_3S) hydration, its mechanisms, and the so-called “optimum sulfate content” persists.

Gypsum ($CaSO_4 \cdot 2H_2O$) and/or natural anhydrite ($CaSO_4$) are usually added to clinker in the grinding stage. Depending on the temperature reached on the mill, the gypsum may dehydrate in hemihydrate ($CaSO_4 \cdot 1/2H_2O$) and/or soluble anhydrite ($CaSO_4$), which are more soluble and, therefore, will influence the cement hydration [3]. In this paper, the term “calcium sulfate” is used regardless of its composition; otherwise, the specific composition is mentioned.

Calcium sulfate is added to control the hydration of C_3A to avoid flash setting and extending the period in which the mixtures have fluidity and workability [1,4,5]. When all the sulfate from the solution is consumed—this moment is known as sulfate depletion—the renewed hydration of C_3A begins [6–9]. The amount of calcium sulfate to be added will determine when the renewed hydration of C_3A will occur. The amount required must be sufficient enough to delay the C_3A hydration until after the main C_3S hydration peak. Otherwise, the C_3S hydration is hindered, reducing the mechanical performance at early ages [10–13]. On the other hand, if too much calcium sulfate is added, the mechanical performance suffers [14–16]. Furthermore, increasing the sulfate content may lead to durability problems due to delayed ettringite formation (DEF), especially in cements submitted to high curing temperatures [14–16].

Although not as heavily investigated as C_3A -calcium sulfate systems, calcium sulfate also changes the C_3S hydration, the morphology of its hydration products, and its mechanical strength [6,8,11,17–19]. The effect of calcium sulfate on C_3S hydration needs to be properly understood as it can influence the sulfate optimization in Portland cements and, therefore, can influence cement properties.

Lerch [20] noted there is an optimum sulfate content for each cement, which results in the highest mechanical performance and lowest shrinkage. The optimum sulfate content (optimum SO_3 content or sulfate demand) is usually obtained empirically through isothermal calorimetry and compressive strength tests with cements with different amounts of calcium sulfate, as described in the ASTM C563 [21] standard.

Many questions regarding the effect of calcium sulfate in C_3A and C_3S hydration and the factors that may influence the optimum sulfate content remain. As discussed herein, many factors may influence this content, including clinker and calcium sulfate characteristics (fineness, chemical, and mineralogical composition), presence of supplementary cementitious materials (SCMs) and chemical admixtures, temperature, and time of hydration. Understanding of the sulfate demand on the system can address several problems in the fresh and hardened state and long-term performance (durability), a problem still quite common in the construction field. Without a complete understanding of the mechanism driving sulfate demand on the system, these problems might become increasingly common as the use of different SCMs and chemical admixtures on

cementitious materials increases. Recent investigations have provided insight on this subject. In this paper, the effect of calcium sulfate on C₃A, C₃S and Portland clinker hydration are reviewed, as well as the influence of the amount of sulfate on cement properties. Presented within are the main factors that may influence the optimum sulfate content and the methods that can be used to determine the sulfate demand. To the best of the authors' knowledge, a review focusing on the role of sulfate on Portland cement hydration and the optimization of the sulfate content is still extant. Despite the increase in such research, there remains several issues to be resolved and recommendations for future research is discussed.

2 EFFECT OF CALCIUM SULFATE ON CEMENT HYDRATION

To properly understand the sulfate optimization, it is fundamental to comprehend the influence of calcium sulfate on cement hydration. To lay the groundwork, first we present its influence on the two most important Portland cement phases concerning the initial hydration and sulfate optimization: C₃A and C₃S, focusing on studies using pure phases synthesized in laboratory. Next, we present the influence of calcium sulfate on cement hydration

2.1 Effect of calcium sulfate on C₃A hydration

Without the addition of calcium sulfate, C₃A reacts instantaneously once in contact with water, releasing a great amount of heat and resulting in the formation of a OH-AFm-type meta-stable product (C₄AH₁₃ and C₂AH₈) (see Eq. 1 [22], which is subsequently converted to katoite (Ca₂Al₂(OH)₁₂ or C₃AH₆) [22–24]. The formation of these products leads to “Flash-set,” i.e., stiffening and loss of workability in few minutes, making most practical Portland cement applications unfeasible [1,4].



To avoid Flash-set, gypsum (CaSO₄·2H₂O) and natural anhydrate (CaSO₄) are usually added. Depending on temperature of the cement mill, gypsum may be dehydrated to hemihydrate (CaSO₄·1/2H₂O) and soluble anhydrite (CaSO₄) [3]. The addition of calcium sulfate completely alters the C₃A reaction, and ettringite (C₆A \bar{S} ₃H₃₂) is formed in the first few minutes; see Eq. 2 [22,24]. The ettringite formation consumes the sulfates in the solution. When the sulfates are exhausted, the ettringite becomes unstable and reacts with the remaining C₃A to form a SO₄-AFm phase - monosulfate (C₄A \bar{S} H₁₂); see Eq. 3 [22,24]. Pourchet et al. [25] has reported the presence of OH-AFm phases in the first few minute when gypsum is used as calcium sulfate source; the presence of these phases is not observed when hemihydrate is used [25].



Figure 1 shows the typical heat flow curve resulting from the hydration of C₃A in the presence of calcium sulfate, divided into three stages. In stage I, an exothermic peak of heat release is observed, followed by a sharp reduction. The heat released at this stage results from the wetting of the particles, the dissolution of ions, and the formation of ettringite [24].

Then the reaction rate decreases dramatically, and the induction period (stage II) begins. The duration of this period of low heat release depends on the amount of calcium sulfate in the system. The higher the calcium sulfate content, the longer the duration of this period [25–27]. Finally, when all the added calcium sulfate is consumed, a new exothermic peak is observed due to the renewed C_3A dissolution and the formation of monosulfate (stage III) [24,26,28]. The peak shape has an almost vertical acceleration part, followed by an exponentially decaying shoulder [28]. Minard et al. [26] proposed that the hydrations kinetics of this period is controlled by dissolution. Quennoz and Scrivener [22] disagree and have suggested that it is related to the nucleation and growth of SO_4 -AFm. Further studies regarding this issue are needed to clarify the mechanism that controls the renewed C_3A dissolution and SO_4 -AFm formation.

The mechanism responsible for this delay is not yet fully understood. Several hypotheses have been proposed. The oldest theory is that the delay occurs due to the formation of an ettringite barrier on the particles of C_3A [29–31]; however, due to the needle-like crystalline morphology of the ettringite, it is improbable that this layer is responsible for hindering the diffusion of ions and the transport of water [4,32,33].

Other authors have suggested that the reason for the delaying of the reaction would be a “gel like” layer on the surface of C_3A [34]. This hypothesis is disputed according to the study of Minard et al. [26], this layer is an OH-AFm type phase, which also forms when C_3A is hydrated in the absence of calcium sulfate, in which the delay in the reaction is *not* observed. As noted earlier, this hydrate does not form when hemihydrate is used, but the reaction remains delayed [25]. Furthermore, the finer the C_3A , the greater the quantity of precipitated AFm, and the shorter the time for the sulfate ions to be consumed [26]. Finally, as shown by Geng et al. [32] ettringite forms after a few minutes of hydration when the C_3A surface is already covered by OH-AFm or SO_4 -AFm and, therefore, these phases do not retard C_3A hydration to any extent.

Joseph et al. [24] proposed that the C_3A hydration in the presence of gypsum is inherited by the surface coverage of ettringite on the active surface of C_3A . The authors suggest that the retardation is governed by a dissolution-controlled mechanism instead of a diffusion-controlled mechanism of the ettringite barrier hypothesis [24]. As recently showed by Liu et al. [27], however, the extraction of the sulfate of the solution (by adding $Ba(NO_3)_2$) leads to an abrupt end of the induction period (stage II), although ettringite is still present. Also, ettringite is more abundant in C_3A -gypsum systems, but the C_3A - $MgSO_4$ systems show the highest induction period [27]; thus the ettringite formation cannot explain the delay in C_3A hydration.

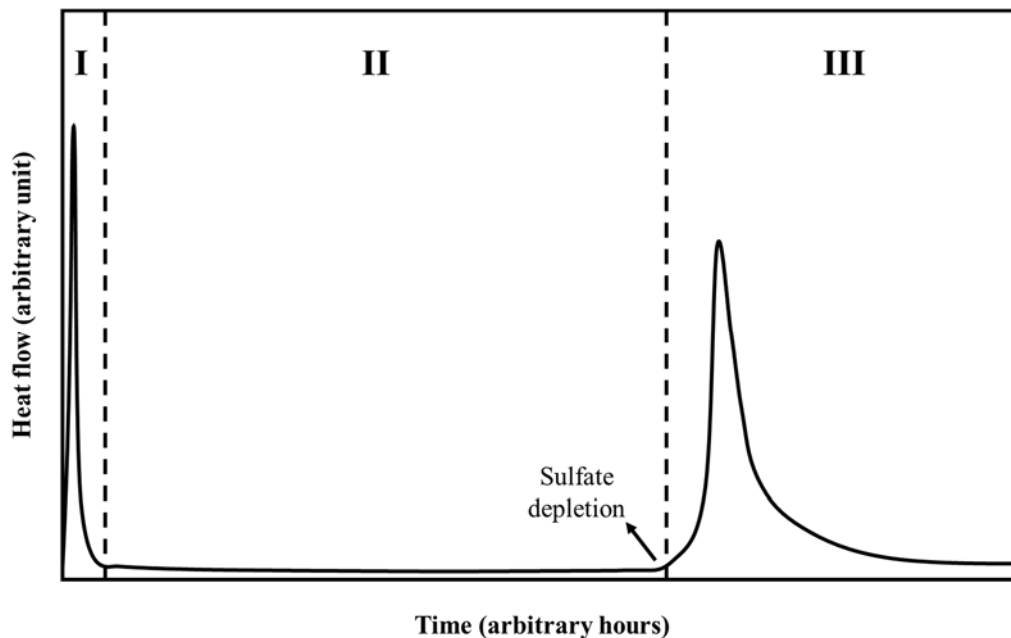
Another theory proposed by Minard et al. [26] is that the delay in hydration of C_3A occurs due to the adsorption of sulfate ions on its surface. According to Bullard et al. [28] the sulfates may be adsorbed at defect sites and inhibit the formation of etch pits, delaying the dissolution of C_3A . This theory may also explain why the reaction decreases more quickly in the presence of the highly soluble hemihydrate than in the presence of gypsum (which is less soluble) [28], as observed by Pourchet et al. [25].

Myers et al. [35] proposed that an Al-rich leached layer is formed at the partially dissolved C_3A surface, and Ca-S ion-pair complexes are adsorbed onto this layer, decreasing the active dissolution sites and the undersaturation of calcium ions, delaying the C_3A hydration. Recent experimental data reported in the literature [27,32,36,37] agrees with

the theory that the adsorption of S and/or Ca-S ion-pair complexes is correct mechanism that accurately describes the retardation on C₃A hydration.

In addition, the alkaline of the sulfate seems to play an important role in the retardation of C₃A hydration. As observed by Ye et al. [38], there is a cation-specific effect of sulfates on the delay of C₃A hydration. While most studies agree that calcium sulfate retards the C₃A hydration, there are contradictory results regarding the effect of other sulfate salts. Some authors have observed that magnesium sulfate retards the C₃A hydration [27,37,38], while others have noted an increase in C₃A hydration rate when adding magnesium sulfate [39]. The addition of sodium sulfate (Na₂SO₄) either does not result in a delay [29,40] or delays to a less extent compared to calcium sulfate [27,38]. Further studies regarding the effect of different sulfate salts on C₃A hydration are necessary.

Figure 1 – Typical calorimetry curve of C₃A-calcium sulfate mixtures.



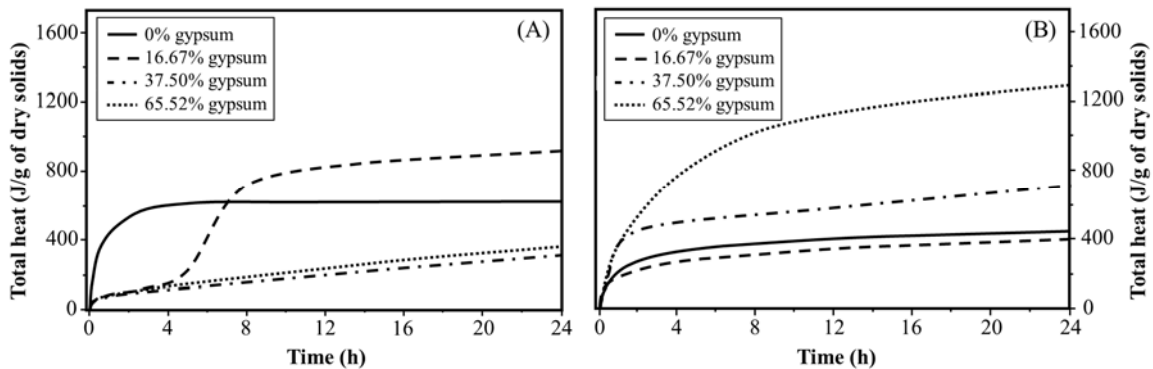
The crystalline structure of C₃A in the clinker depends on the alkali content present in the raw materials and on the alkali content incorporated during the clinker process (which is dependent on the fuel used). When Na⁺ ions are incorporated into the crystalline structure of C₃A—thus replacing Ca²⁺ ions—the formation of a solid solution with a general form of Na_{2x}Ca_{3-x}Al₂O₃ occurs, where x is the amount of Ca²⁺ that has been replaced by Na⁺. x values of up to 0.10 (2.4 wt% of Na₂O) result in only cubic C₃A, while values of x between 0.10 and 0.16 (2.4 – 3.7 wt% of Na₂O) result in the co-existence of the cubic and the orthorhombic polymorph. As the value of x increases to 0.16-0.20 (3.7 – 4.6 wt% of Na₂O), only the orthorhombic C₃A is presented. x values above 0.20 (4.6 wt% of Na₂O) result in a monoclinic polymorph [31,41–43]. In OPC, the monoclinic polymorph is not observed, and the clinker usually presents cubic and orthorhombic C₃A [31,44].

The crystalline structure has a great influence on the C₃A hydration process and, consequently, in the rheological properties (workability) of the cement paste. In the absence of calcium sulfate, both cubic and orthorhombic C₃A react with water, resulting

in the formation of metastable hydroxy-AFm phases, which then convert to katoite (C_3AH_6) [5,23]; however, cubic C_3A is more reactive than the orthorhombic C_3A [23,45,46].

In the presence of calcium sulfate, the behavior is inverted, and the orthorhombic C_3A is more reactive than the cubic one [5,23,36,45,47–49]. This is because despite retarding the cubic C_3A hydration, calcium sulfate accelerates the hydration process of orthorhombic C_3A [5,23,36,50]. As shown in Figure 2, the addition of gypsum decreases the heat released during the first hours of the hydration of cubic C_3A , indicating a delay in the reactions, while adding the same amounts of gypsum increase the heat released by the orthorhombic C_3A hydration.

Figure 2 – Total heat released during the first 24 h of hydration for (A) cubic C_3A and (B) orthorhombic C_3A with different amounts of gypsum, normalized by wt.% of dry solid (C_3A + gypsum). Source: adapted from Kirchheim et al. [23].



To date, it is not known why calcium sulfate is effective in delaying hydration of cubic C_3A but not orthorhombic C_3A . This may be related to the greater solubility of the ring structures of $Al_6O_{18}^{18-}$ in orthorhombic C_3A , which impacts the formation of the amorphous alumina layer on the C_3A particles, and thus affects the dissolution rate [23,36,46]. It may also be related to the sodium ions released in the dissolution of the orthorhombic C_3A , destabilizing the amorphous alumina layer [45] where the Ca-S ion-pair complexes are adsorbed according to the hypothesis of Myers et al. [35]. Further studies regarding the role of calcium sulfate on the hydration of the different C_3A polymorphisms are needed.

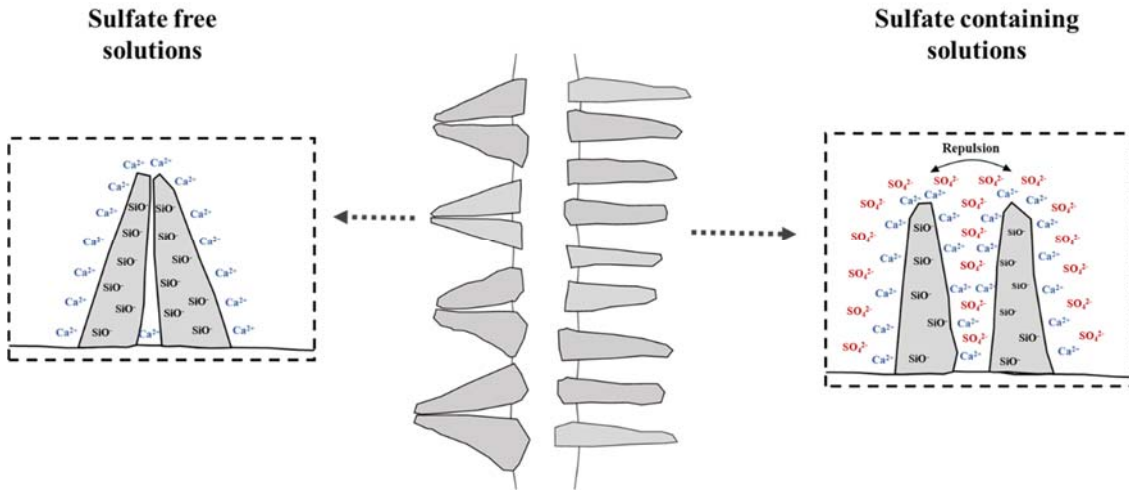
2.2 Effect of calcium sulfate on C_3S hydration

As calcium sulfate is normally added to control the C_3A hydration, their impact on C_3S hydration and strength are normally neglected. This ignores that fact that it has a great influence on C_3S hydration, which needs to be properly understood as it can influence the sulfate optimization in Portland cements, influencing the properties of the cement.

The addition of gypsum does not change the products formed during C_3S hydration, with the exception of the aluminum-doped C_3S where ettringite is formed [8,51]. The sulfate ions released from the gypsum dissolution are specifically absorbed on C-S-H, changing

their morphology [51,52]. As illustrated in Figure 3, a cloud of sulfate ions could be physically adsorbed by charge affinity in the positive charged C-S-H needles [51]. According to Mota et al. [51] this would result in the repulsion of the C-S-H needles and lead to a more divergent needle-structure instead of the convergent morphology observed in plain C₃S pastes.

Figure 3 – Schematic representation of the impact of sulfate ions on C-S-H morphology. Source: adapted from Mota et al. [51].



In addition, gypsum (and other soluble sulfates salts as Na₂SO₄) influence the C₃S hydration. Gypsum retards the initial hydration of C₃S, and a more extended induction period is observed [6,8,11,17]. According to Nicoleau et al. [11] and Juilland et al. [17] the sulfate ions are physically adsorbed on C₃S surface, decreasing the surface charge and lowering its dissolution rate.

After the induction period, the behavior changes and gypsum enhance the C₃S hydration [6,8,18,51–58]; see Figure 4. Yamashita et al. [59] have observed that increasing the clinker SO₃ content also accelerated the alite reaction but why it accelerates the reaction is still not known. Quennoz and Scrivener [8] proposed that the enhancement in C₃S hydration by gypsum is due to reactions between the sulfates and the aluminum present in C₃S structure, thus forming ettringite. These reactions remove the aluminum (which is known to retard C₃S hydration) of the solution and accelerate its hydration. Bergold et al. [60] suggest that this enhancement in aluminum-doped C₃S hydration is due to the seeding effect of very fine (nano-)ettringite, which might provide a suitable surface for heterogeneous nucleation of C-S-H, leading to a faster dissolution of C₃S.

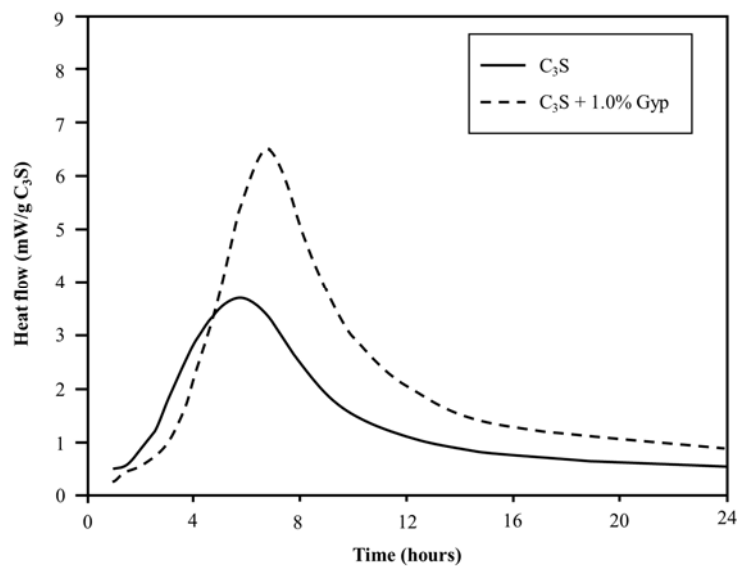
As observed by many researchers [6,53,55,58,61], however, including the example given in Figure 4, gypsum also accelerates the hydration of C₃S without alumina, where the formation of ettringite is not observed. Therefore, these hypotheses cannot explain the increase of C₃S hydration in the presence of calcium sulfate. According to Zunino and Scrivener [6], the enhancement of C₃S hydration by gypsum is probably a result of the interaction between this phase and C₃S and/or C-S-H, rather than interactions associated with the aluminates.

Due to the acceleration in C_3S hydration, the addition of gypsum usually increases the initial mechanical strength of C_3S pastes [18,56] but with a decrease in mechanical performance at later ages [18,56]. This is probably related to the decrease in C_3S content when gypsum is incorporated into the mixture, resulting in a lower amount of C-S-H at higher hydration degrees [56]. Besides, the intrinsic strength of the C-S-H gel is linearly related to its C/S mole ratio, and when gypsum is added, the C/S decreases as well as the intrinsic strength of C-S-H [18,62].

The enhancement in C_3S hydration by gypsum may be related to the change in morphology mentioned before. According to simulations performed by Gunay et al. [56], gypsum increases the C-S-H growth rate, but its mechanism is unknown as yet. Further studies on the impact of calcium sulfate on C_3S hydration are needed.

Note that all these studies were performed with gypsum. Therefore, it is also essential to study the effect of other calcium sulfate composition, e.g., hemihydrate and anhydrite, on C_3S hydration.

Figure 4 – Heat flow curves of C_3S and $C_3S + 1.0\%$ of gypsum pastes ($w/c = 0.5$) during the first 24 hours of hydration. Source: adapted from Zunino and Scrivener [6].



The C_3S can present in seven different polymorphs: (1) triclinic (T1, T2, and T3); (2) monoclinic (M1, M2, and M3); and (3) rhombohedral (R), which will depend on the temperature and doping with foreign ions [31,63–65]. Pure C_3S is T1, while the OPC usually presents M1 and/or M3 [31,63,65]. The SO_3 seems to stabilize the M1 polymorph, while the MgO favors the formation of M3 C_3S [66–69].

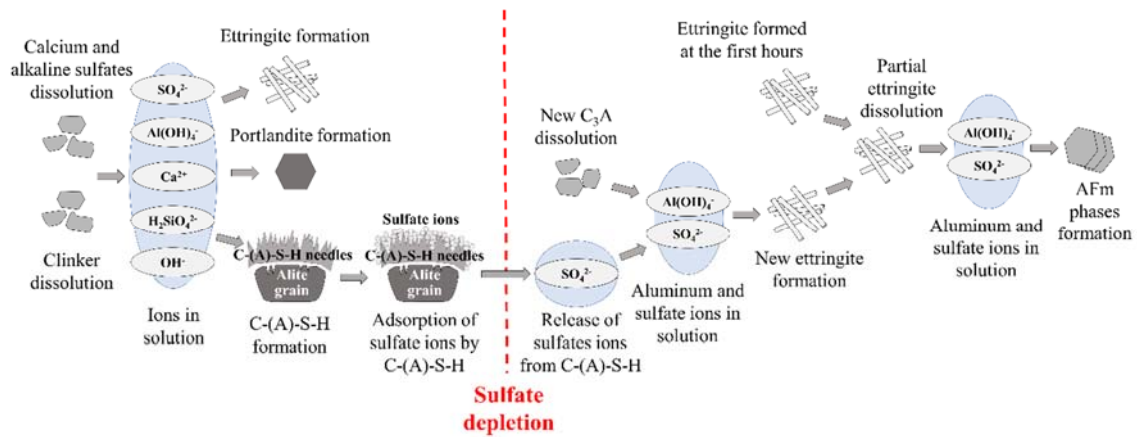
The change in C_3S crystalline structure might influence its hydration. The M1 polymorph seems to present a higher reactivity when compared to M3, resulting in higher mechanical strength [70]. This difference might be related to the higher non-bonding electrons in the M1- C_3S when compare to M3- C_3S [71]. Bazzoni et al. [72] has stated that there is no clear link between the polymorphism and reactivity, as the same polymorph can present

completely different reactivities depending on the foreign ion used to stabilize it. Thus, this difference between the M1 and M3 hydration rate might be related to the foreign ions usually incorporated in the alite structure during the clinker production, which can greatly influence C_3S hydration. The aluminum [73,74] and iron [74] doping decreases the C_3S hydration rate, while zinc increases the main hydration peak [72,75]. A study the effect of C_3S polymorphs (or the doping of foreign ions) on the interaction with gypsum remains to be conducted, despite some theories relating the presence of aluminum with the enhancement due to the presence of gypsum [8,60], as mentioned before. Further investigations on this topic are strongly recommended, as the interaction between C_3S and calcium sulfate might be a key factor to understand sulfate optimization.

2.3 Effect of calcium sulfate on Portland cement hydration

Figure 5 shows schematically the role of sulfate ions during Portland cement hydration. In the first few minutes, the dissolution of the calcium and alkaline sulfates release sulfate ions into the solution. A part of these ions reacts with the C_3A to form ettringite, while the other part is adsorbed—as $CaSO_3$ complexes—by the C-S-H needles. When all the solid sulfate has dissolved and the concentration of sulfates in solution decreases, reached the moment known as “sulfate depletion point,” the sulfate ions are desorbed from the C-S-H, leading to a renew dissolution of C_3A with a new and rapid formation of ettringite [8,76,77]. Then, the SO_3/Al_2O_3 ratio of the solution decreases, and the ettringite reacts with the remaining C_3A to form AFm phases [76,77].

Figure 5 – The role of sulfate on Portland cement hydration.



As discussed in Section 2.2, the morphology of C-S-H is influenced by the sulfate ions and changes with the sulfate depletion; see Bérodiér et al. [78]. During the first hours of hydration of the OPC, the sulfate ions are adsorbed on C-S-H, resulting in a divergent needle-like morphology (similar to the C-S-H formed in C_3S pastes with gypsum, shown schematically in Figure 3) [78]. After the sulfate depletion, the sulfate ions previously adsorbed on C-S-H are released into the solution, resulting in a change in C-S-H morphology that becomes “agglomerated” [78].

Figure 6 presents some examples of heat flow curves of ternary cements (OPC, blast furnace slag, and limestone) undersulfated, properly sulfated and supersulfated [79]. Figure 7 presents heat flow curves of undersulfated and properly sulfated pure C₃S-C₃A mixtures (92-8 wt%) [6]. The SD point shown in Figures 6 and 7 corresponds to the sulfate depletion point, leading to a renewed C₃A dissolution with a new and rapid formation of ettringite, followed by the beginning of AFm phases formation [6–9,80,81].

In the undersulfated systems, the sulfate depletion happens before or just after the main C₃S hydration peak, as shown in Figure 6. In the undersulfated sample, the amount of calcium sulfate added is not enough to delay the renewed C₃A hydration until after the main C₃S hydration peak. When this happens, the C₃S hydration is hindered and the peak becomes smaller and broader, influencing the strength development [6,33,60,80]. The heat flow curve from ternary cement pastes (Figure 6) differs from the heat curves of undersulfated pure C₃S-C₃A mixtures (Figure 7), where a higher and narrower peak (from the C₃A hydration) is observed, followed by a smaller and broader peak of heat (from the C₃S hydration) [8,81]. These differences are probably due to the C₃A availability (which will be higher in pure monophasic mixtures) [8] and the presence of iron in OPC (which decreases the reactivity of the aluminates). The reason for the delay of C₃S hydration in OPC pastes where the renewed C₃A hydration occurs early is not yet understood. This may be related to the release of aluminum ions into the solution due to the renewed C₃A dissolution, as the C₃S hydration in the aluminum containing solution is hindered [10–13]. There are several different hypotheses to explain this behavior.

In Al-containing solutions, aluminum incorporates to the bridging site and in the interlayer of C-S-H, resulting in C-A-S-H [82,83]. According to Garrault et al. [10] and Begarin et al. [84], C-A-S-H is not a suitable substrate for the C-S-H growth C-S-H nuclei themselves, and this may be the reason why the C₃S hydration is delayed. Another hypothesis is that the condensation of an aluminosilicate species at the C₃S surface, linked via hydrogen bonds to silicate surface groups, may be the reason for the inhibition of C₃S reaction [11,12]. Finally, Bergold et al. [60] suggest that this slow-down in C₃S hydration is due to AFm precipitation. These AFm phases could coagulate with the C-S-H and occupy C-S-H surface, which would become unavailable as a substrate for further C-S-H precipitation [60].

In the properly sulfated cements, the sulfate depletion point needs to be after the main C₃S hydration peak; see Figure 6. In these cements, the C₃S hydration occurs normally and the matrix has a proper mechanical performance.

In supersulfated cements, the sulfate depletion point occurs many hours later than the main peak of C₃S hydration. In these cements, the C₃S hydration is not negatively affected, but the mechanical performance is lower than in the properly sulfated systems, and the excess of calcium sulfate may lead to durability problems, as will be discussed in Section 4.

Figure 6 – Heat flow curves of ternary cements (OPC, slag and limestone). Undersulfated, proper sulfated, and supersulfated. SD represents the sulfate depletion point. Source: adapted from Adu-Amankwah et al. [79].

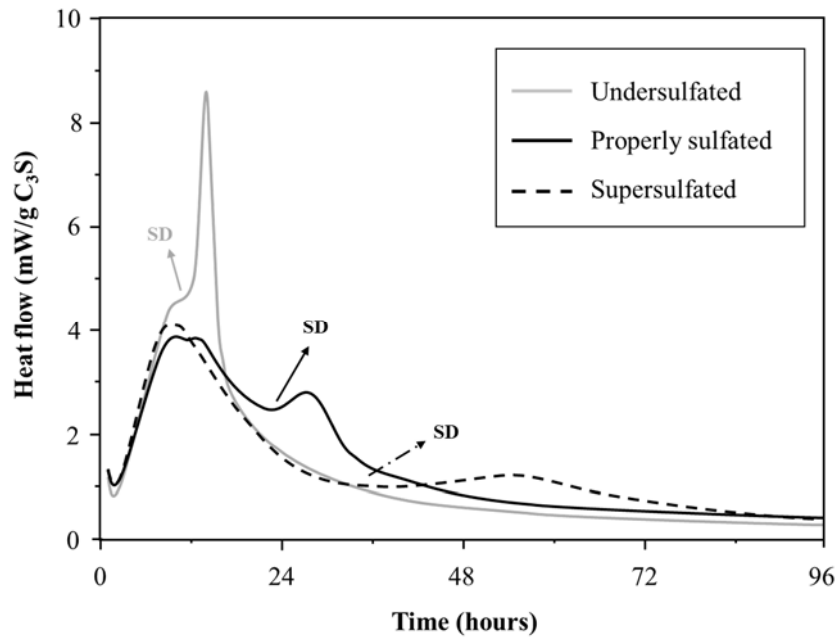
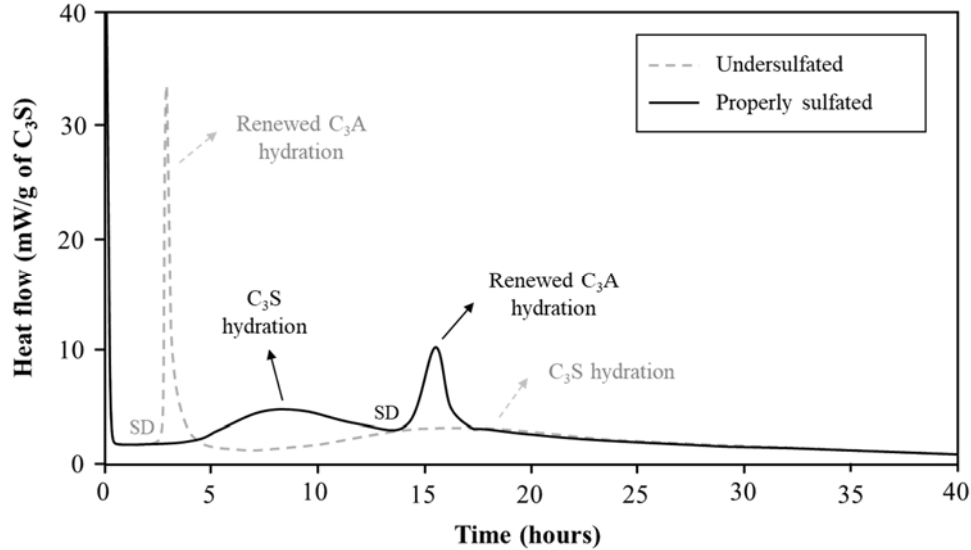


Figure 7 – Heat flow curves of C_3S - C_3A pastes (92-8 wt%) undersulfated and properly sulfated. SD represents the sulfate depletion point. Source: adapted from Quennoz and Scrivener [8].



3 FACTORS THAT INFLUENCE THE SULFATE DEMAND

As mentioned earlier, good mechanical strength in concrete requires obtaining proper C_3S hydration; sulfate depletion needs to occur after the main alite hydration peak. Any factor that changes the sulfate supply to the solution and/or the sulfate consumption will change the optimum sulfate content. The sulfates in solution come mainly from the sulfate source (gypsum, hemihydrate, anhydrate, alkaline sulfates, etc.) dissolution. If the dissolution is

accelerated, more sulfate will be supplied, increasing its depletion and the optimum sulfate content will rise and vice versa. The sulfate of the solution is consumed by ettringite formation and C-S-H adsorption [6]. Thus, factors that increase the ettringite and/or C-S-H formation will increase the sulfate consumption, thus increasing the optimum sulfate content.

3.1 Physic-chemical and mineralogic properties of clinker

The fineness of cement has a significant influence on sulfate demand. Increasing the C_3A fineness increases the ettringite formation [6] Increasing the C_3S fineness results in higher C-S-H precipitation in the first hours of curing [6]. Thus, sulfate consumption is enhanced, and sulfate depletion is accelerated. Therefore, the higher the cement fineness, the higher the amount of sulfate needed to obtain a proper sulfated system [6,85].

The C_3A content of the clinker also influences the sulfate demand. The higher the C_3A content, the higher the ettringite formation, which consumes more sulfate ions from the solution and, therefore, will increase the demand for sulfate [6,86]. According to Damidot et al. [86], in cements with more than 10 wt% of C_3A , the optimum sulfate content for maximum strength often exceed the limits of cement standards (e.g., 3.5 wt% in ASTM C150 [87], and 4.5 wt% in Brazilian standard NBR 16697 [88]). The C_4AF content excites a similar behavior as the C_3A content, but its influence is lower due to its lower reactivity [89].

The C_3S content also has a significant role in sulfate demand. More C_3S results in more C-S-H formed and more sulfate adsorbed [8]. Therefore, an increase in C_3S content might lead to a higher optimum sulfate content.

Another factor, which influences the sulfate demand, is the alkali content of cement. The higher the alkali content, the higher the amount of sulfate needed [89,90]. The alkali in cement occurs as alkali sulfates and/or are incorporated in the cement phases, mainly in C_3A and in the silicate phases. Among the alkali sulfates, different phases can be present in clinker, as thenardite (Na_2SO_4), arcanite (K_2SO_4), apthitalite ($3K_2SO_4 \cdot Na_2SO_4$), syngenite ($CaSO_4 \cdot K_2SO_4 \cdot H_2O$), and calcium langbeinite ($2CaSO_4 \cdot K_2SO_4$) [91,92].

In the presence of alkali sulfates, which are very soluble, the hydration of C_3S is accelerated in the first few days, increasing the amount of C-S-H formed [91,93], which increases the amount of sulfate absorbed by C-S-H and thus increases the sulfate demand. As observed by Fu et al. [94], the addition of 2.5% of Na_2SO_4 anticipated the sulfate depletion in two hours.

Conversely, alkaline sulfate might retard the C_3A hydration (to a lesser extent compared to calcium sulfate), thereby decreasing the sulfate demand. This delay in C_3A hydration will depend on the alkaline sulfate polymorph. Calcium langbeinite seems to greatly retard the C_3A hydration, followed by syngenite, and thenardite. Arcanite and apthitalite also result in lower delays on C_3A hydration [91,92,95]. With the increase of calcium langbeinite content, the amount of calcium sulfate necessary for obtaining proper sulfated mixtures decreases [91]. Therefore, the higher the SO_3 of the clinker, the lower the amount of calcium sulfate that needs to be added to obtain proper sulfated cements.

On the other hand, as observed by Wistuba et al. [47] an increase in the alkali content of clinker favors an increase in orth- C_3A /cub- C_3A ratios, which anticipates the sulfate

depletion. The crystalline structure of C_3A depends on the alkali content incorporated. High alkali contents favor the orthorhombic phase rather than the cubic one. As mentioned in Section 2.1, when studying pure phases, orthorhombic C_3A reacts much faster than cubic C_3A in the presence of calcium sulfate, increasing the amount of ettringite formed and increasing the consumption the sulfate of solution. Thus, the orth- C_3A /cub- C_3A ratio of clinker probably influences the optimum sulfate content, but further studies are needed to verify this assumption, as there are differences between pure C_3A polymorphs and C_3A polymorphs from industrial clinker, which might influence its reactivity.

The C_3S polymorphism and/or the ions doping changes its reactivity [70,74,84]. As discussed in Section 2.2, the M1 polymorph seems to be more reactive than the M3 polymorph [70]. Regarding ion doping, Al_2O_3 [74,84] and Fe_2O_3 [74] retards the C_3S hydration, while the MgO slightly increases it [74]. Therefore, these factors will influence the C-S-H formation rate and affect the sulfate consumption by its adsorption. Thus, it will probably alter the optimum sulfate content.

3.2 Physics, chemical, and mineralogic properties of the sulfate source

The optimum sulfate content is related to the SO_3 content rather than to the solid sulfate content. Therefore, the higher the SO_3 content of the sulfate source, the lower the amount of the solid sulfate source needed to obtain proper sulfated cements. Sulfate solubility plays a huge role in the sulfate demand. Generally, the higher the calcium sulfate solubility, the higher the optimum sulfate content. The solubility of calcium sulfate varies with its fineness (surface area) and its chemical/mineralogical composition. The higher the sulfate source surface area, the higher its solubility. Therefore, as observed by Barbosa et al. [96], the increase in gypsum fineness anticipates the sulfate depletion and renewed C_3A hydration. Thus, a higher calcium sulfate fineness tends to increase the sulfate demand of the cement.

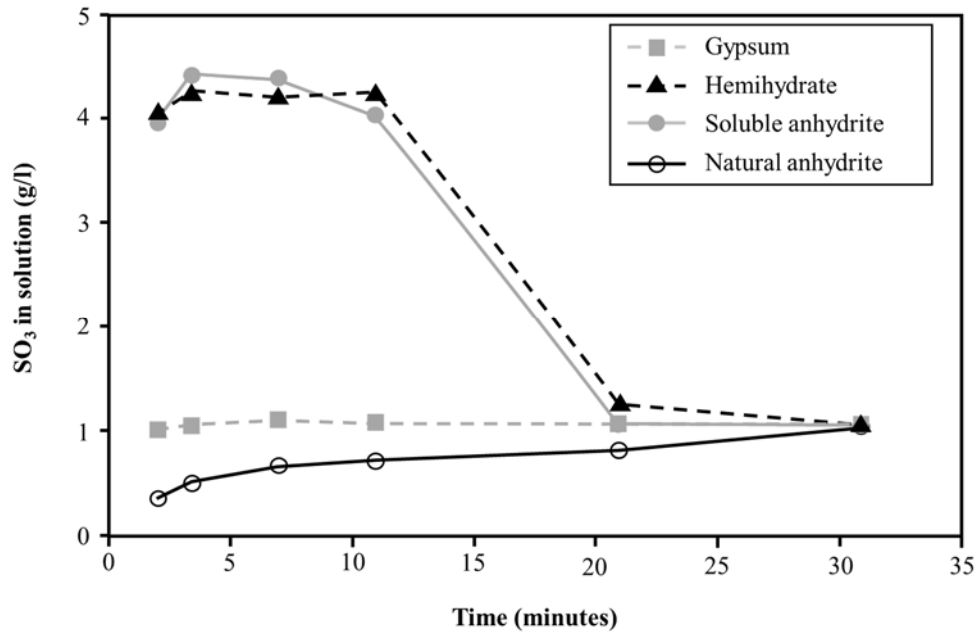
Regarding the calcium sulfate source, gypsum ($CaSO_4 \cdot 2H_2O$) and natural anhydrite ($CaSO_4$) are commonly used in cement production; however, depending on temperature of the cement mill, gypsum may be dehydrated to hemihydrate ($CaSO_4 \cdot 1/2H_2O$) and soluble anhydrite ($CaSO_4$) [3]. The crystal structure and composition of calcium sulfate impact its solubility [25,97], as shown in Figure 8; hemihydrate and the soluble anhydrite are the most soluble, followed by gypsum and then natural anhydrite [3].

Mixtures with hemihydrate form more ettringite in the first hours, increasing the sulfate consumption and anticipating sulfate depletion [6,25,98]. Thus, from these observations, it is expected that the use of a more soluble calcium sulfate polymorph (i.e., hemihydrate and/or soluble anhydrite) will increase the optimum sulfate content. The use of natural anhydrite or gypsum, which have similar solubility, seems to result in the same optimum SO_3 content [99].

Note: it is essential to have a correct adjustment between C_3A reactivity and sulfate solubility. If gypsum or natural anhydrite is used to control the hydration of cements with high C_3A activities (high content and/or the orthorhombic form), a flash set may occur due to the insufficient amount of sulfate in solution, causing the formation of OH-AFm or SO_3 -AFm [86,100,101]. On the other hand, if a more soluble calcium sulfate (hemihydrate or soluble anhydrite) is used in cements with low C_3A activity, false set may occur due to the formation of gypsum [100,101]. Therefore, to obtain properly

sulfated mixtures, a rule of thumb would be to use more soluble calcium sulfates (hemihydrate or soluble anhydrite) in cements with high C_3A reactivity and less soluble calcium sulfates (gypsum or natural anhydrite) in cements with low C_3A reactivity. Further studies on this subject are required to fully understand this mechanism.

Figure 8 – Dissolution rates of gypsum, hemihydrate, soluble anhydrite, and natural anhydrite. Source: adapted from Dodson and Hayden [3].



The influence of sulfate ions on pure cubic C_3A hydration depends on the type of cation (Na, Mg or Ca). Liu et al. [27] have shown that $MgSO_4$ causes the most significant retardation, followed by $CaSO_4 \cdot 2H_2O$, and Na_2SO_4 . In addition, Fu et al. [94] observed that the addition of Na_2SO_4 anticipates the sulfate depletion point in slag-cement mixtures, thus increasing the sulfate demand. This probably occurs due to the increase in alite hydration and, as a result, in C-S-H formation in the presence of Na_2SO_4 . Therefore, the cation in sulfate probably influences the optimum sulfate content in Portland cements, as observed by He et al. [102] when studying $MgSO_4$, $CaSO_4 \cdot 2H_2O$, Na_2SO_4 and K_2SO_4 . Further investigations are needed to verify and provide more information regarding this process.

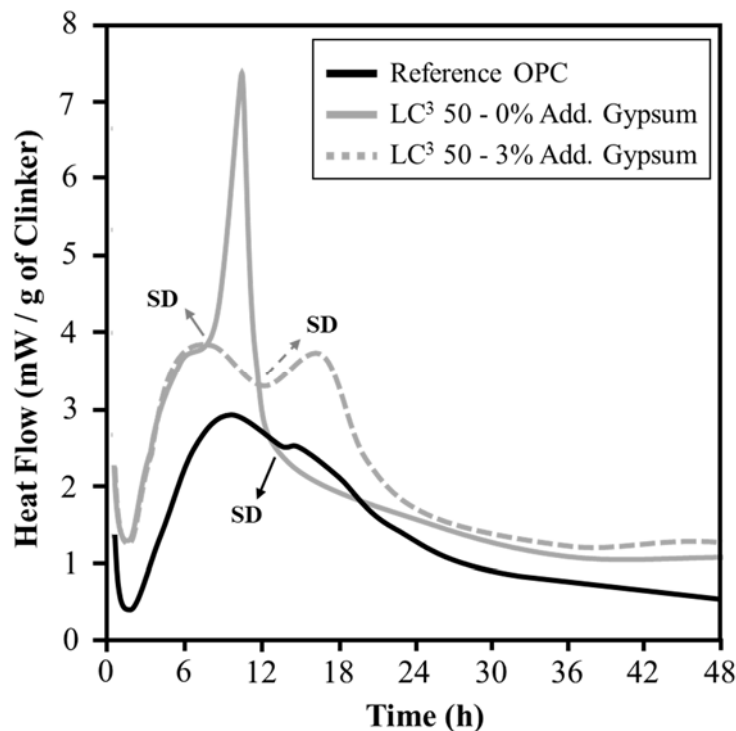
Many studies also have shown the potential of using phosphogypsum as a replacement for gypsum [103–105]; however, the presence of impurities (P_2O_5) in phosphogypsum delays the C_3S hydration [105], changing the sulfate consumption rate, which may influence the optimal sulfate content. A study Radwan and Heikal [106] phosphogypsum impurities actually accelerate C_3A hydration. To the best of the authors' knowledge, no systematic study regarding the sulfate optimization with phosphogypsum has been published yet. This is an area that should be studied without delay as phosphogypsum as a setting regulator seems to be a future trend. It is also essential to verify Radwan and Heikal [106] results regarding the effect of phosphogypsum impurities on C_3A hydration and shed light on this mechanism.

The distribution of sulfates seems to be as important as the other factors already mentioned. As showed by Tang and Gartner [92], the C_3A hydration rate is much lower in cements where clinker and gypsum were interground when compared to cements which they were interblend. Intergrinding increases the sulfate supply rate by reducing the diffusion distances between the sulfate and aluminate phases [92]. Thus, when testing to determine the optimum sulfate content is important to intergrind the calcium sulfate with clinker (as is typically done by the cement industry), as the intergrinding results in lower sulfate demand, and the results obtained with interblend will not be representative of the intergrinding cements [92].

3.3 Supplementary Cementitious Materials (SCMs)

As reported by many researchers, replacing cement (clinker + calcium sulfate) by SCMs as slags [107,108], fly ash [100,109–112] (especially high calcium fly ashes [109,112]), silica fume [113], calcined clay [9,114–117], limestone [9,118], red mud [119,120], zeolite [121], and ground waste expanded perlite (highly reactive pozzolan) [113], usually anticipate sulfate depletion, thus increasing the sulfate demand per clinker. Because of the high amounts of calcined clay and limestone, LC^3 cements usually require more gypsum in comparison with plain Portland cement [9,122–127]. As demonstrated by Zunino and Scrivener [9] (Figure 9), replacing approximately 50% of the OPC with a mixture of calcined clay and limestone (2:1), i. e. the LC^3 50 cement, anticipates sulfate depletion and, in this case, the mixture became slightly undersulfated. To adjust the sulfate balance here, required adding 3 wt% of gypsum to the LC^3 50 cement [9].

Figure 9 – Heat flow curves of OPC and LC^3 50 cement. SD is the sulfate depletion point. Source: adapted from Zunino and Scrivener [9].



Note that by replacing OPC (cement + calcium sulfate) with SCMs, the content of calcium sulfate concerning cement mass decreases, but remains the same in regard to clinker. Usually, this anticipates sulfate depletion, and the mixture could become undersulfated, requiring more sulfate. In these situations, the optimum sulfate content per clinker will be higher than the OPC, but the optimum sulfate content per cement will be lower. The lower optimum sulfate content in relation to cement mass is expected and by replacing clinker with SCMs will result in the mixture having less C_3A and less C_3S . Note: the increase of the optimum sulfate per clinker by SCMs is possibly related to two main factors: filler effect and alumina content.

First, when SCM replaces a portion of clinker, the C_3S hydration is accelerated due to more space available for the hydrates of clinker phases to form in and adhere to the surface of the SCM particles, which act as sites for heterogeneous precipitation and growth of hydrates [9,80]. Thus, as more C-S-H is formed, more sulfate is adsorbed, increasing the sulfate demand per clinker [9,80].

Generally, C_3S hydration increases with the increase in SCM content, directly influencing the sulfate demand. Also, the higher the SCM surface area, the higher the enhancement in C_3S hydration and C-S-H formation [9,80]. Thus, SCMs with higher surface areas have a higher sulfate demand [80,108,110,114,116,119,120,125].

The aluminum content of the SCMs may also influence sulfate demand [9]. Using SCMs with higher aluminum contents, increases the amount of ettringite formed, which increases the sulfate consumption and anticipating sulfate depletion. Using SCMs with higher amounts of alumina seems to increase the sulfate demand. Zunino and Scrivener [9] disagree despite the majority of the studies indicating that the alumina content influences the optimum sulfate content. They contend that the aluminum content of calcined clay does not influence the sulfate demand. They studied two different clays with different aluminum contents and different surface areas. The clay with higher aluminum content and lower surface area presented a lower sulfate requirement than the other clay [9]. Although this clearly shows the great impact of surface area on sulfate demand, it is impossible to conclude that aluminum content does not influence the optimum sulfate content as SCMs with higher aluminum content usually increase the amount of ettringite formed.

Whittaker et al. [108] studied slags with similar particle size distribution but different alumina contents. The sulfate depletion occurred early in the cement with slag with the higher alumina content, indicating that the alumina content influences sulfate demand. In a study by Avet et al. [125], the sulfate depletion occurred early in the mixture with the calcined clay, which contained 95.0 wt% of kaolinite (43.8 wt% of Al_2O_3) when compared to the mixture with the calcined clay, which contained 50.3 wt% (32.3 wt% of Al_2O_3), despite its much lower B.E.T. surface area (9.6 m^2/g for the clay with higher alumina content and 45.7 m^2/g for the other). Based on these results, the alumina content seems to have significant influence on the sulfate demand. Additional study on the role of SCM aluminum content on the optimal sulfate content is required to confirm the finding of Zunino and Scrivener [9].

The effect of limestone on optimum sulfate content is also not clear. Some authors [9] state that an increase in limestone increases the optimum sulfate content due to filler effect for the other SCMs. The enhancement in cement hydration is generally higher when using limestone compare to others SCMs, as the limestone surface seems to have a stronger

bond interaction with calcium ions [9,115]. According to Campitelli et al. [85] the limestone actually decreases the optimum sulfate content for maximum strength. This behavior may be related to the change in phase assembly when using limestone, which stabilizes hemicarboaluminate and monocarboaluminate instead of monosulfate, thus increasing the ettringite formation [54,128]. This changes the volumes of solid and, therefore, the strength. Thus, the optimum SO_3 content for maximum strength may differ in cements with limestone compared to plain cements. Further investigations are needed to verify the results postulated by Campitelli et al. [85] and understand why a decrease in the sulfate demand occurs in the presence of limestone.

Some SCMs—e.g., fly ash [109,112] and in particular circulating fluidized bed combustion (CFBC) fly ashes [129,130]—contains sulfates in their composition. The sulfates from SCM, if available in the early hours of hydration, will help control C_3A hydration by reducing the amount of calcium sulfate and obtaining a properly sulfated mixture. Unfortunately, as sulfates are present in different phases of the chemical reaction, with different solubilities, the decrease in the calcium sulfate to obtain maximum performance is not straightforward. Sulfates can be found in fly ash and other SCMs as alkali sulfates and calcium sulfate (dihydrate, hemihydrate, or anhydrous), which are relatively soluble and will contribute to the sulfate demand of cement. Alternatively, sulfates can be present in the glassy phase, which would not be necessarily be soluble at the early ages; therefore they could not contribute to the sulfate demand of the cement [109,112]. More investigation on this subject is encouraged to properly understand the effect of the sulfates from SCMs on the sulfate demand of OPC.

Note that the influence of SCMs on the sulfate demand of Portland cement is not straightforward, as it may depend on the particle size, chemical composition, and solubility, among other factors. Therefore, when analyzing a new SCM, it is important to verify its impact on the sulfate demand of the cement in order to obtain the best performance and avoid incompatibilities.

In some countries, such as the United States, it is common to add the SCMs in the concrete stage instead of during cement production [131]. This can become problematic as the SCM may increase the sulfate demand of the cement, which would render the mixture undersulfated and cause problems such as setting, workability, and strength development. When added to the mix during cement production, the industry can control the sulfate demand and adjust the sulfate content in a much better way.

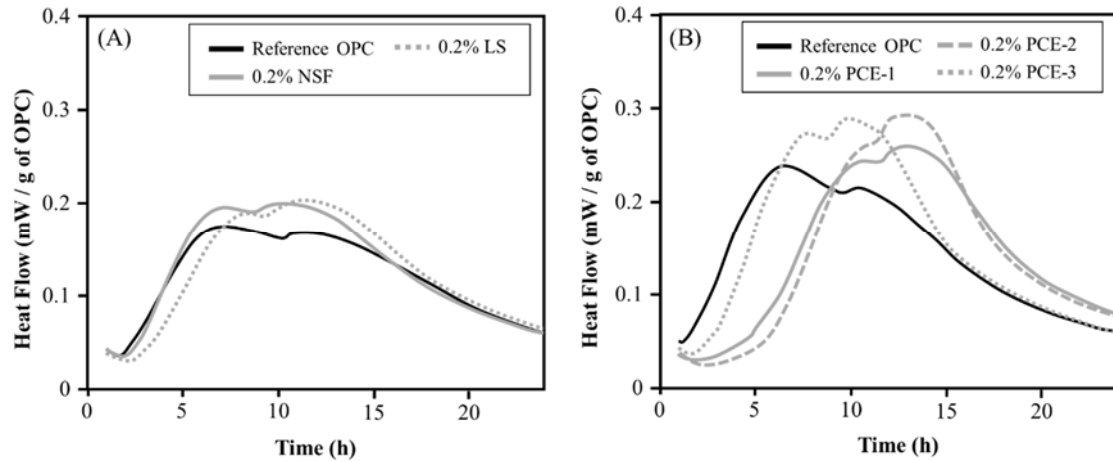
3.4 Chemical admixtures

Many chemical admixtures used in mortars and concrete influence the reactivity of cement phases and the dispersion and wetting of cement grains. In addition, they may affect the dissolution of sulfates [100], i.e., the optimum sulfate content.

Water reducers, plasticizers, or superplasticizers affect cement hydration. Polycarboxylate-ether (PCE), naphthalene sulfonate formaldehyde polycondensate (NSF) and lignosulfonate (LS) admixtures result in retarding alite hydration, thus prolonging the induction period and lowering the C-S-H formation rate [132–135]. According to Kishar et al. [136] however, the NSF accelerates the conversion of ettringite to monosulfate. The same behavior was observed by Rosa [137] and by Jiang et al. [138] when studying pure C_3A pastes with PCE admixtures. As observed by Ng and Justnes [134] and Jansen et al. [135], the presence of PCE, NSF, or LS admixtures approaches

the sulfate depletion point from the main hydration peak of alite, as shown in Figure 10 [134], indicating that these chemical admixtures increase the sulfate demand.

Figure 10 – Heat flow curves of reference OPC without chemical admixture and with 0.2 wt% (in relation to OPC) of naphthalene sulphonate-formaldehyde (NSF), lignosulfonate (LS), and polycarboxylate superplasticizers of short side chains (PCE-1), long side chains (PCE-2), and long and very long side chains (PCE-3). Source: adapted from Ng and Justnes [134].



There are three main hypotheses to explain this behavior [139]. First, the adsorption of the superplasticizer on the sulfates may slow down the dissolution of the calcium sulfate, thereby decreasing the supply of sulfate ions to the solution [3,135,139,140]. The lower the rate of sulfate ions supplies into the chemical admixture solution might not be enough to “feed” the dissolution of C_3A , creating a “false” sulfate depletion [135,139].

The second hypothesis is that the presence of superplasticizer leads to a faster sulfate consumption due to the better dispersion of anhydrous particles [139]. The third hypothesis is that the PCEs-based admixtures enhance ettringite nucleation, providing a large surface area for the growth of the hydration products, resulting in faster consumption of sulfates [139]. Why PCE admixtures enhance ettringite nucleation is not well understood [139]. Additional investigations are needed to understand this mechanism and the chemical admixture’s influence (e.g., chain length, etc.) on the optimum SO_3 content.

Also worth mentioning is that the sulfate amount added may interfere with the efficiency of the chemical admixture. At the optimum SO_3 content, C_3A reacts with the sulfates in solution, forming ettringite, and the superplasticizer admixtures adsorb onto aluminate hydrates and silicates phases, increasing the fluidity of the mixture [133,141]. That said, the superplasticizer effect of PCE decreases with an increase in the content of sulfate added, being most significantly influenced by the alkali sulfates (Na_2SO_4 and K_2SO_4) when compared to gypsum and $MgSO_4$ [102,141]. When the content of sulfate in cement paste increases, the amount of sulfate ions in solution increases and is competitively adsorbed onto cement surfaces, thereby reducing the adsorption of PCE and decreasing its superplasticizer effect [49,102]. If the soluble sulfate/ C_3A ratio is too low, hydration of C_3A occurs, resulting in the formation of aluminate hydrates that adsorb the chemical admixtures and form organo-mineral phases, thus reducing the superplasticizer effect of PCE [49,133,141]. These “incompatibilities” between superplasticizer and cement can be

avoided if the amount of calcium sulfate and the solubility of the sulfate source is well adjusted.

The use of accelerators and retarders also changes the sulfate demand of the cement. The accelerators enhance the C_3S and C_3A hydration, increasing the sulfate consumption and accelerating the sulfate depletion [100,142,143]. This effect is higher in aluminum-containing accelerators with high Al_2O_3/SO_4^{2-} due to the reaction between the sulfate and the alumina from the chemical admixture [142]. Salvador et al. [143] have observed this behavior in mixtures with both main types of accelerators, alkaline and alkali-free. Note: the sulfate depletion occurs early in the mixtures with alkaline accelerators. The accelerators compositions explain this result. As the alkali-free accelerator is based on an aluminum sulfate solution (while the alkaline type is based on sodium aluminate solution), the sulfates from the chemical admixture provide more sulfate to the solution even though the sulfate concentration in solution was always lower than that in the reference paste [143].

As for other chemical admixtures, the amount and composition of calcium sulfate added might influence the accelerator efficiency. Maltese et al. [144] have observed that the lower the dissolution rate of the calcium sulfate, the more efficient is the accelerator.

Retarders might also influence the sulfate demand for cement. Although all retarders delay the C_3S hydration, the effect on C_3A hydration is different depending on the type of retarder used. As observed by Bishop and Barron [145], while tartaric acid retards the C_3A hydration and ettringite formation, sucrose and the lignosulfonate-based admixture accelerate it. Thus, retarders probably have different effects on optimum sulfate content. Studies on this subject are quite scarce and this should be the subject of future research.

Grinding aids are commonly used during the comminution of clinker to reduce electrostatic forces and minimize agglomeration between clinker and SCM grains [146,147]. The chemical composition of the grinding aids includes glycols—propylene glycol (PG), monoethylene glycol (MEG), and diethylene glycol (DEG); alkanolamines—triethanolamine (TEA), triisopropanolamine (TIPA), and diethylisopropanolamine (DEIPA); and polycarboxylate ethers (PCEs) [146]. The use alkanolamines promotes the reaction of C_3A , thus increasing the amount of ettringite formed (which anticipates the sulfate depletion) and enhancing the aluminate reaction [146,148]. More investigations are needed to fully understand the effect of the alkanolamines on the sulfate demand and investigate the impact of other types of grinding aids (such as the glycols) on cement hydration and sulfate optimization.

3.5 Water/binder ratio

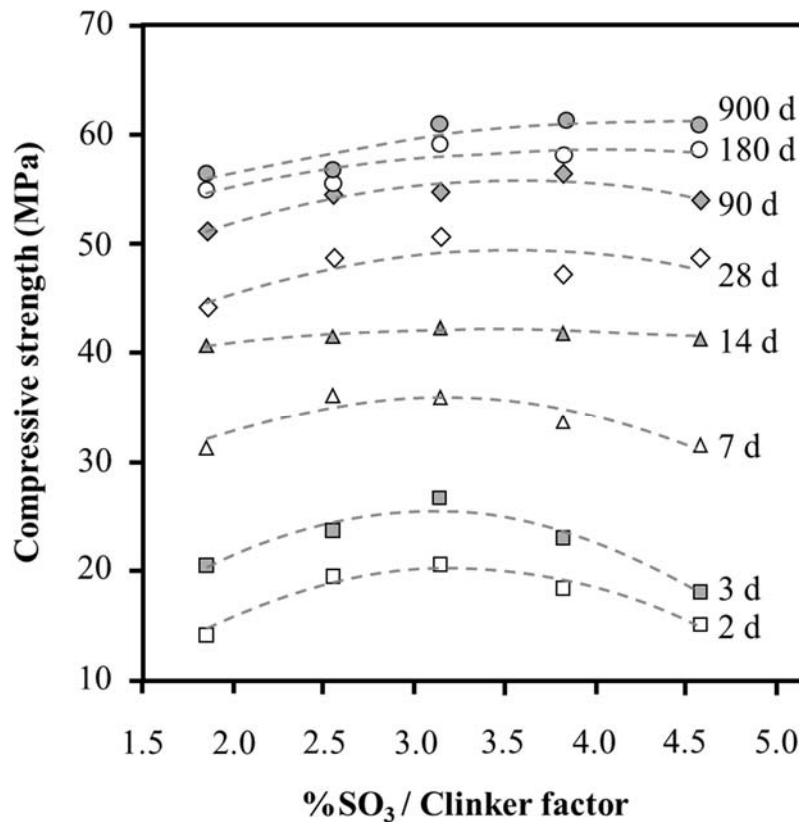
The water/binder ratio (or water/cement ratio) influences cement hydration. Generally, when the w/c ratio decreases, the concentration of alkalis in the solution increases, increasing the cement hydration rate [149]; however, due to the lower space available for the hydrates to grow and the lower amount of water available to hydrate, the long-term degree of hydration is decreased [90,100,111,150]. If the water/binder (w/b) ratio alters cement hydration, it probably influences the sulfate demand. In the study Wyrzykowski and Lura [151] the OPC that was properly sulfated at a w/b ratio of 0.30 became under-sulfated at a w/b ratio of 0.16. As observed by Zunino and Scrivener [126], the sulfate depletion occurred slightly early in the LC^3 system, with a w/b ratio of 0.4 compared to the mixture w/b ratio of 0.8. Despite delaying the sulfate depletion, the increase in w/b

ratio enhanced the aluminate peak of LC³ systems [126]. More investigation on this subject is needed to properly understand the effect of w/b ratio on the sulfate demand of OPC.

3.6 Hydration age

At later ages, although the optimum sulfate content seems to be higher [149,152], it is less pronounced [13] (see Figure 11 [111], demonstrating that there is a different optimum sulfate content for each age. The reason for this is not clear and is counterintuitive. The opposite effect would be expected, i.e., the optimum sulfate content decreases with age, as calcium sulfate enhances the hydration of C₃S, resulting in higher initial strength, but lowers the final strength due to the decrease in C-S-H density and the lower amount of C-S-H formed as less clinker (hence less C₃S and C₂S) is present in the cement. It is speculated that this behavior might be related to the SO₃ content needed to result in the maximum volume of aluminate phases at each age, which impacts the volume of solids, the porosity, and the strength. As observed by Cottin and Vibert (1976)¹ and cited by Kurdowski [152], the gypsum content needed for the maximum volume of aluminate phases increases with time, which could explain the higher optimum sulfate content at later ages. Further studies regarding the variation of optimum sulfate content with the age are required to understand this phenomenon properly.

Figure 11 – Mechanical strengths vs sulfate factor. Example of the procedure to determine the optimum sulfate content. Source: adapted from Tsamatsoulis and Nikolakakos [111].



¹ B. Cottin, C. Vibert. Poisoning of tricalcium silicate hydration by soluble alumina Cement-Wapno-Gips, 7 (1976) 193-196.

3.7 Curing conditions

The dissolution of gypsum [153] and anhydrous cement, and the precipitation of hydrates increases with the temperature [154,155], prompting the rapid consumption of sulfates from the solution and anticipating sulfate depletion [152,156]; simply, high curing temperatures results in higher optimum sulfate content [89,111,152,156].

The relative humidity (RH) also plays a vital role in cement hydration, especially when low water/binder ratios ($w/b < 0.30$) are used. As observed by Wyrzykowski and Lura [151], water-saturated cement pastes hydrate faster than the sealed ones. It stands to reasons that a change in RH might influence sulfate demand. Further investigations are needed to fully understand this mechanism.

As discussed in Section 4.5, DEF formation occurs in mortars and concretes that have been cured at high temperatures ($> 65\text{ }^{\circ}\text{C}$) and in moist environments. As observed by Al Shamaa et al. [157], RH greatly influences the probability of DEF. Clearly, as the curing temperature and RH are predominant factors in DEF; they should be considered together with the sulfate content to prevent durability problems.

3.8 Summary of the effects that influence sulfate optimization

Table 1 summarizes the main factors that may influence the optimum sulfate content in Portland cement (direct, inverse, or unknown) and the state-of-knowledge (well known or needs further investigation).

Table 1 – Main factors that may influence the optimum sulfate content.

| Type | Sub-type | Relationship | Status |
|-------------------|------------------------------------------------|--------------|-----------------------------|
| Clinker | Fineness | Direct | Well known |
| | Alkali content | Direct | Well known |
| | SO ₃ content | Inverse | Well known |
| | C ₃ A and C ₄ AF content | Direct | Well known |
| | C ₃ S content | Direct | Well known |
| | C ₃ A polymorphism | Unknown | Needs further investigation |
| | C ₃ S polymorphism | Unknown | Needs further investigation |
| Sulfate source | SO ₃ content | Inverse | Well known |
| | Fineness | Inverse | Well known |
| | Composition (solubility) | Inverse | Needs further investigation |
| | Impurities (phosphogypsum) | Unknown | Needs further investigation |
| | Cation | Unknown | Needs further investigation |
| | Distribution in cement | Inverse | Well known |
| SCMs | Content | Inverse | Well known |
| | Fineness | Direct | Well known |
| | Aluminum content | Uncertain | Needs further investigation |
| | Sulfate content | Uncertain | Needs further investigation |
| Admixtures | Plasticizers | Direct | Needs further investigation |
| | Setting accelerators | Direct | Needs further investigation |
| | Retarders | Unknown | Needs further investigation |
| | Grinding aids - alkanolamines | Direct | Needs further investigation |
| | Grinding aids - glycols | Unknown | Needs further investigation |
| | Water/binder ratio | Inverse | Needs further investigation |
| | Hydration age | Direct | Needs further investigation |
| Curing conditions | Temperature | Direct | Well known |
| | Relative humidity | Unknown | Needs further investigation |

4 INFLUENCE OF SULFATE CONTENT ON THE CEMENTITIOUS MATRIX PROPERTIES

As discussed in Section 2.3, the sulfate content has a significant effect on cement hydration kinetics. It also changes the composition of the phase assemblage and influences other properties, e.g., setting time, workability and rheology, mechanical performance, and drying shrinkage, and may impact a cement's long-term performance, i.e., durability.

4.1 Effect of sulfate content on setting time

The increase of calcium sulfate content delays the initial and final setting times until a limit is reached. Further addition of calcium sulfate does not influence the setting time [158]. In addition, the inadequate amount/type of sulfate may lead to two types of premature setting: flash set and false set.

Undersulfated systems may present a “flash set” due to the quick reaction of C_3A , with the formation of calcium-alumina hydrates, making most practical applications of Portland cement unfeasible [4]. When the flash set occurs, further mixing cannot break apart the microstructure that has formed, and subsequent strength development is poor [31,159].

The presence of hemihydrate ($CaSO_4 \cdot 1/2H_2O$) in OPCs—that can be formed from the dehydration of gypsum during grinding—can result in premature stiffening known as “false set,” in the first few minutes due to its rehydration and formation of gypsum ($CaSO_4 \cdot 2H_2O$) [159,160]. Stiffening results from interlocking needle-like gypsum crystals and the reduction in free water available to lubricate the system and promote fluidity [31]. Further mixing can overcome this premature stiffening, and the subsequent strength development is not greatly affected [31,159].

4.2 Effect of sulfate content on workability and rheology

Typically, increasing the sulfate content of the cement increases the water demand [158], the viscosity [102], and the yield stress [102] of cementitious mixtures. Gypsum is softer than clinker; therefore, when it is interground with clinker it usually shows a higher surface area, which is responsible for the increase in the water demand [158]. In addition, more ettringite is formed at higher sulfate contents, which has a prismatic/needle shape and high surface area, and greatly impacts the viscosity of cement paste [97].

The composition of the calcium sulfate added also influences the rheology of the cement paste. The use of hemihydrate, which has a higher solubility than gypsum, increases the amount of sulfate on the solution and changes the ettringite morphology from spherical or stubby rod to elongated ettringite [161]. According to Mbasha et al. [161], this change in the ettringite morphology is responsible for increasing the yield stress and plastic viscosity of the cement pastes.

4.3 Effect of sulfate content on the degree of hydration and chemical shrinkage

As discussed in Section 2.3, the amount of sulfate greatly influences the cement hydration and, consequently, the degree of hydration. Usually, the degree of hydration of the cement

increases with the increase of the amount of sulfate until a certain content is reached—the optimum SO_3 content—and then decreases. In this sense, chemical shrinkage related to the degree of the hydration of the cement is influenced in the same way by the sulfates; i.e., the cement with the optimum SO_3 content presents the highest chemical shrinkage [79].

4.4 Effect of sulfate content on porosity and mechanical strength

The sulfate content also influences the porosity and the mechanical strength of the cement. The optimum sulfate content shows the lowest porosity with the highest strength [62,79,158]. As mentioned in Section 2.3, in undersulfated systems, the C_3S hydration is inhaled, greatly impacting the porosity and the strength mainly in the first days. Adding more calcium sulfate increases the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio in the cement, resulting in relatively more ettringite and less monosulfate [86]. Ettringite has a higher volume compared with monosulfate; therefore, as the volume of solids increases, it modifies the porosity distribution, lowers the total porosity and increases the mechanical strength [62,79]. The higher the sulfate content, the higher the solid volumes, and, until a determined value (i.e., the optimum sulfate content), the lower the porosity and the higher the strength.

Further additions of calcium sulfate—over the optimum content—increase the porosity and thus decrease the mechanical strength. This behavior probably is due to the decrease in the C-S-H amount, as the clinker content is lower. Moreover, it may also be related to the reduction of density and increase of C-S-H gel porosity with an increase of sulfate added and the consequent decrease in C/S mole ratio [79], leading to a decrease in the intrinsic strength of C-S-H gel [18,62].

A higher volume of solids means there is less liquid available to evaporate. Thus, an increase in the sulfate content usually decreases drying shrinkage until a certain value is reached. The optimum SO_3 content for maximum cement mortar strength usually coincides with the optimum sulfate level for minimum concrete shrinkage under normal curing conditions [100].

4.5 Effect of sulfate content on long-term performance (durability)

The excess of sulfate can be deleterious to a concrete's durability, as the increase in the SO_3 content of cements increases the risk of delayed ettringite formation (DEF) [14–16], which is the formation of ettringite in a cementitious material after the concrete has set. This formation may occur in cementitious materials that have been cured at elevated temperatures (above $65\text{ }^\circ\text{C}$) or in massive concrete structures [162–164]. Delayed ettringite formation causes expansion and cracking, increasing the porosity and permeability, facilitating the entry of aggressive agents as CO_2 and chlorides, and reducing the lifetime of concrete structures [157,162,163]. Thus, cement standards usually limit the maximum content of SO_3 in cements, depending on the type of cement. The threshold of 5 to 6% SO_3 is commonly accepted in the literature for expansion [31].

4.6 Summary of the effects of sulfates on cement properties

It is important to keep in mind that the amount needed to optimize each property (rheology, setting time, porosity, drying shrinkage, and mechanical strength) may not be the same, and different “optimum sulfate content” can exist for each cement [31,158].

Table 2 summarizes the effects of sulfate content on the properties of cementitious mixtures.

Table 2 – Effects of sulfate content on the properties of cementitious mixtures.

| Property | | Effect | References |
|---------------------|----------------------------------------------------------------|-------------------------------------------------------------------|-------------|
| Setting time | Increase of SO ₃ content | Increase of initial and final setting times until a plateau value | [158] |
| | Insufficient amount of SO ₃ (undersulfated systems) | Flash set | [4,31,159] |
| | Use of hemihydrate (CaSO ₄ ·1/2H ₂ O) | False set | [31,159] |
| Rheology | Increase of sulfate content | Increase of viscosity, yield stress and water demand | [102,158] |
| | Use of hemihydrate (CaSO ₄ ·1/2H ₂ O) | Increase of viscosity, yield stress and water demand | [161] |
| Porosity | Increase of sulfate content | Decreases until an optimum content and then increases | [62,79] |
| Mechanical strength | Insufficient amount of SO ₃ | Poor mechanical strength | [62,79,158] |
| | Increase of sulfate content | Increases until an optimum content and then decreases | [62,79,158] |
| Chemical shrinkage | Increase of sulfate content | Increases until an optimum content and then decreases | [79] |
| Drying shrinkage | Increase of sulfate content | Decreases until an optimum content and then increases | [100] |
| Durability | Increase of sulfate content | Increases the risk of DEF | [14–16] |

5 METHODS TO DETERMINE THE OPTIMUM SULFATE CONTENT

The determination of the initial and final setting times by the Vicat needle [165] is the most popular method used by the cement industry to adjust the calcium sulfate content. This method can verify setting problems as flash set or false set, and if the amount of calcium sulfate added provides an adequate setting time. As discussed in Section 4.1, the setting times increase with the increase in calcium sulfate content until a plateau value. In this test, the amount of SO₃ is chosen as the amount that results in a specific initial and final setting time. This method cannot determine the optimum sulfate content, which will result in the highest mechanical strength and lowest shrinkage.

There are some empirical equations in the literature to determine the optimum SO₃ content [31,152]. Because many factors influence the optimum sulfate content (as discussed in Section 3), these formulae have limited practical importance [13]. The best and most used way to determine the optimum sulfate content is to test different mixtures and varying the sulfate content.

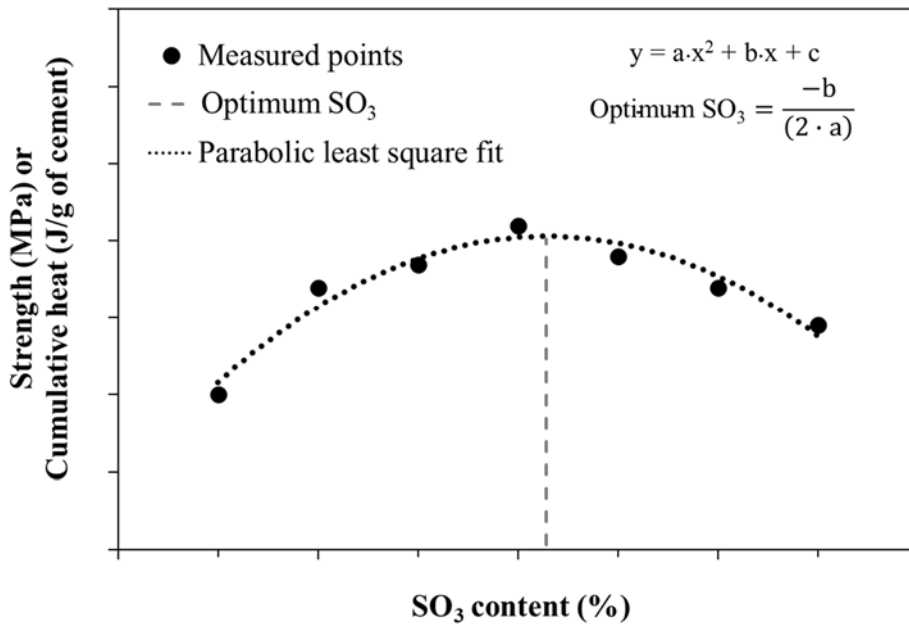
The optimum sulfate content is usually defined by measuring the mechanical strength or the heat released by mixtures of the same components (clinker or SCM) with different calcium sulfate contents. ASTM C563 [21] describes the method to determine the optimum sulfate content by using either isothermal calorimetry and/or measuring mechanical strength. This standard [21] recommends that at least five mixtures with different SO₃ contents should be tested. The SO₃ should differ more than 0.20 wt% between the individual mixes, and the maximum and minimum SO₃ content of the blended samples must differ by at least 2.0 wt%. The higher the number of samples with different SO₃ contents tested, the more accurate the optimum sulfate content will be. The cement fineness should be as similar as practically possible [13,149,166].

Isothermal calorimetry is a simple, convenient, and rapid way of determining the optimum sulfate content [13,109,166]. The optimum sulfate content is determined by plotting the cumulative heat at determined age (i.e., 1, 3, or 7 days) as a function of the SO₃ content in the cement; see Figure 12. The heat recorded before the end of the induction period should not be considered in this cumulative heat due to the lower reproducibility of the initial peak [13]. Due to the low amount of heat released after 7 days, the calorimetry should not be used to determine the optimum sulfate content at later ages.

Measuring mechanical strength, the most common method to gauge the optimal sulfate content, is widely used by the cement industry. It is simple and does not need expensive equipment. It does demand a higher amount of material, which can be problematic for some studies with limited materials. The strength of each formulation is plotted, and a parabolic least square fit is realized in a similar method to isothermal calorimetry. The optimum sulfate will then be the x values that provide the highest strength; see Figure 12.

Although not as popular compared to isothermal calorimetry and compressive strength tests, ASTM C563 [21] describes the determination of the optimum sulfate content by the drying shrinkage of mortars. In this case, the optimum content is usually defined as the content of calcium sulfate, resulting in the lowest drying shrinkage. Similarly, the chemical shrinkage test, described by Geiker [167], can also be used to optimize the amount of sulfate in Portland cement [79]. In this test, the optimum SO₃ content is that which results in the highest chemical shrinkage at a specific age—indicating the highest degree of hydration.

Figure 12 – Example of the procedure to determine the optimum sulfate content.



Note: none of the previous tests assess the long-term performance/durability of the cement paste, mortar, and/or concrete. As discussed in Section 4.5, the sulfate content might significantly influence the durability of the cement matrix, especially when an excess of sulfate is used that can lead to delayed ettringite formation (DEF). Therefore, the determination of the optimum sulfate content should be combined with durability tests that evaluate the probability of DEF, per the Duggan test [15,168] or similar method [16,169].

Table 3 summarizes the different methods that can be used to optimize sulfate content, in addition to the advantages and disadvantages of each method. The optimum sulfate content may not be a specific number but rather a range of SO₃. In addition, the optimum sulfate content might vary according to the performance criteria (mechanical strength, shrinkage, etc.) and with the age; see Section 3.6. Therefore, the optimum SO₃ content should be a compromise between the different performance criteria and the different ages.

Table 3 – Methods to determine the optimum sulfate content.

| Method | Advantages | Disadvantages |
|---------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Mechanical strength | <ul style="list-style-type: none"> • Quite common. • Do not require expensive equipment. | <ul style="list-style-type: none"> • Requires more material than calorimetry (600 g of cement per SO₃ content per age). • Time-consuming. • Do not evaluate long-term performance (durability). |
| Calorimetry | <ul style="list-style-type: none"> • Easy to test. • Rapid. • Can be carried out at a wide range of temperatures. • Requires less material than the other tests (depend on the equipment used, but usually between 5-50 g of cement per content of SO₃). | <ul style="list-style-type: none"> • Inaccurate in determining the optimum SO₃ content at later ages (> 7 d). • Require a calorimeter, which may not be available in all laboratories. • Do not evaluate long-term performance (durability). |
| Setting time | <ul style="list-style-type: none"> • Most common. • Verifies setting problems (flash set or false set). | <ul style="list-style-type: none"> • More laborious than the other techniques (as calorimeter). • Do not determine an optimum SO₃ content (only determines the SO₃ content, resulting in a specific setting time). • Requires more material than calorimetry (at least 1000 g of cement per SO₃ content). • Do not evaluate long-term performance (durability). |
| Chemical shrinkage | <ul style="list-style-type: none"> • Do not require expensive equipment. • Requires less material than the other tests (depend on the setup used, but usually between 5-30 g of cement per content of SO₃). | <ul style="list-style-type: none"> • Time-consuming. • Do not evaluate long-term performance (durability). |
| Shrinkage | <ul style="list-style-type: none"> • Do not require expensive equipment. | <ul style="list-style-type: none"> • Requires more material than calorimetry (750 g of cement per SO₃ content). • Time-consuming. • Do not evaluate long-term performance (durability). |
| Probability of DEF | <ul style="list-style-type: none"> • Evaluates the probability of occurrence of DEF, which will influence the long-term performance (durability). | <ul style="list-style-type: none"> • Time-consuming. • Do not determine optimum SO₃ content. |

6 SUMMARY AND PERSPECTIVES FOR FUTURE RESEARCH

Calcium sulfate greatly influences C₃A, C₃S, and OPC hydration, influencing the properties of the concrete. This paper has summarized the most important research findings to date on this topic. Further investigation regarding the effect of calcium sulfate on C₃A and C₃S hydration is needed, especially with the C₃A and C₃S polymorphs, as the mechanism by which calcium sulfate influences the hydration is not yet fully understood.

The calcium sulfate content added to the cement influences the properties of the cement. An optimum SO₃ content results in concrete with the highest strength and lowest shrinkage. This content will depend on many factors, including the characteristics of the clinker and calcium sulfate, the presence of SCMs and admixtures, the water/binder ratio, curing conditions, and the age of hydration. Many knowledge gaps remain on this subject, and further investigation is highly recommended.

Despite being used for more than a century and the subject of hundreds of studies, many questions on the influence of calcium sulfate on cement properties remain. Additional studies on this subject are required to provide a complete understanding of its influence on the rheology, setting, mechanical performance, and durability of OPC.

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