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PROPERTIES OF A TERNARY CALCIUM SULFOALUMINATE -
CALCIUM SULFATE -FLY ASH CEMENT

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Abstract

In this paper, cement combinations based on calcium sulfoaluminate cement (CSAC) were developed and the effect of fly ash and the hemihydrate form of calcium sulfate on the properties of the systems were studied. Fly ash (FA), anhydrite (ANH), flue-gas desulfurization gypsum (FGDG) and plaster gypsum (PL) were used to develop appropriate CSAC/calcium sulfate and CSAC/calcium sulfate/addition systems, the hydration of which were studied. Tested properties of cements were the compressive strength and the setting times. The results suggest that the use of fly ash in the presence of anhydrite accelerates the formation of a strong ettringite-rich matrix that firmly accommodated unreacted fly ash particles, both synergistically contributing to a dense microstructure. At a given sulfate content, the use of anhydrite was shown to be favourable in terms of the setting times, heat patterns and strength development compared to the hemihydrate-based formulations.

Keywords:
D. Sulfoaluminate
D. Ettringite
D. Fly ash
Anhydrite
Hemihydrate

Abbreviations:
E=Ettringite
A=Anhydrite
Y=Ye'elimite
1. Introduction

The blending of by-products and additions with Portland cement (PC) is a well established approach to reducing the CO₂ emissions associated with the energy-intensive manufacture of cement. Currently 3.3 billion tonnes of PC are globally manufactured every year and it is estimated that the embodied CO₂ (eCO₂) for PC production is approximately 930kg of CO₂ per tonne of PC produced [1, 2]. An alternative way to reduce the eCO₂ of concrete is through the use of non-PC based systems as the binding ingredient. Calcium sulfoaluminate cements (CSAC), which have a lower eCO₂ than PC, have been developed and used in China on an industrial scale since the 1970s [3]. The primary raw materials are limestone, bauxite (or an aluminous clay) and gypsum, although by-products such as fly ash may be also used [4]. The preparation of clinker is achieved by burning the raw materials at temperatures in the range 1300-1350°C in rotary kilns. This is 100-150°C lower than PC production and thus the energy input requirement is lower. Manufacturing process is similar to that of PC although the resulting clinker has better grindability [5], leading to additional savings of 15-30 kWh with respect to energy consumption [6]. By considering the eCO₂ emissions of individual cement compounds as given in [7], it can be estimated that the eCO₂ of a typical pure CSAC, consisting of ye’elimite, belite and aluminoferrite, is approximately 600 kg/t. This represents a reduction in eCO₂ of approximately 35% when compared to PC.
The primary hydration product of CSAC is ettringite (3CaO.Al₂O₃.3CaSO₄.32H₂O) which forms at early ages (less than 48 hours) as prismatic needles. Ettringite forms in the presence of sufficient calcium sulfate (gypsum or anhydrite) which can be either blended with the ye’elimite-rich clinker or added in the raw meal intergrinding process. The optimum amount of calcium sulfate for dominant formation of ettringite depends on several parameters i.e. the ye’elimite content, the calcium sulfate content and their respective molar ratios [8]. If there is deficiency in calcium sulfate, then there is a tendency for monosulfoaluminate to form; whereas an excess of calcium sulfate may lead to unstable expanding systems. Other products of the hydration of CSAC are mainly aluminate hydrates, calcium silicate hydrates although unreacted ye’elimite is also typically present. Strengths of CSAC-based cements may reach over 40MPa at 24 hours [9] and they have been reported to exhibit very good resistance to aggressive environments, particularly to sulfate environments [10, 11]. This is because aluminate-based phases are bound as sulfoaluminates at early stages of hydration and these are not available for reaction with external sulfate agents to form expansive ettringite.

The work reported in this paper aims to investigate the influence of two main aspects revolving around the optimization of hydration and performance of CSAC-based cement systems. The first is the form of calcium sulfate incorporated in the system recognising that the hemihydrate form is more readily available than anhydrite. The second aspect covered the development of a ternary system through the use of a low eCO₂ addition, particularly fly ash, which could provide a better balance between performance and eCO₂.
1.1 The calcium sulfate source

There is a considerable experimental activity on CSAC that has been focusing on the use of anhydrite as the calcium sulfate source in the CSAC system. Extensive work throughout the last decades is encapsulated in review articles [12-13]. Indeed, consensus indicates that anhydrous calcium sulfate is the predominant and preferable calcium sulfate source within the system. The use of other forms of calcium sulfate, particularly hemihydrate, however, are not fully documented so as to offer justifications of any cost-based, environmental-based or performance-based advantages associated with anhydrite preference in CSAC. Moreover, such lack of available data does not provide a clear indication of the influence of the hemihydrate of calcium sulfate on the hydration of CSAC. A more detailed look is therefore required at this type of calcium sulfate.

The intrinsic properties of both hemihydrate calcium sulfate and anhydrite are compared and established [14-15]. Setting times of the hemihydrate are known to be considerably short due to its high solubility (typically in the range of 7-9 g/l) and its reactivity, as opposed to that of anhydrite (approximately 2.5-3.0 g/l) [16]. Equations 1 and 2 suggest that during the reaction of both calcium sulfate forms with ye'elimite, the quantities of ettringite and Al(OH)$_3$ formed are comparable. The only changing parameter is the amount of water needed for complete phase formation.
Ye’elemite + Anhydrite:

\[ 4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3 + 2(\text{CaO} \cdot \text{SO}_3) + 38\text{H}_2\text{O} \rightarrow 6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 32\text{H}_2\text{O} + 2(\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}) \] (Eq. 1)

Ye’elemite + Hemihydrate:

\[ 4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3 + 2(\text{CaO} \cdot \text{SO}_3 \cdot 0.5\text{H}_2\text{O}) + 37\text{H}_2\text{O} \rightarrow 6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 32\text{H}_2\text{O} + 2(\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}) \] (Eq. 2)

Based on the available literature and data, it is therefore necessary to distinguish the beneficial characteristics offered by each form of calcium sulfate when incorporated in a CSAC system.

1.2 The use of fly ash in CSAC/calcium sulfate system

Although the eCO\(_2\) associated with the use of an optimized CSAC/calcium sulfate system may be lower than that of PC, potentially greater savings may be achieved based on the development of ternary CSAC-based systems with maintained performance properties.

By-products from coal combustion plants are associated with almost zero eCO\(_2\), whilst they may provide microstructural and mechanical advantages to cementitious systems when incorporated at optimum percentages. One advantage is the pozzolanic reaction. The use of low eCO\(_2\) pozzolanic by-products—particularly fly ash— in the CSAC system, may instigate reaction with Ca(OH)\(_2\).
yielding from belite hydration in CSAC thus providing additional C-S-H gel. Previous studies on compressive strengths of CSAC/fly ash blends suggest a slight decrease in strengths when fly ash contents are higher than 10% [17]. However, there is still limited understanding and lack of data on the hydration mechanisms of such systems. Given this, and by considering the advantageous effect of particle packing that fly ash may potentially provide when acting as a low-eCO$_2$ filler, then it is possible that a more sustainable system may be developed while maintaining its mechanical and microstructural properties.

2. Materials and methods

The materials used in this study are shown in Table 1. Particle size distribution was determined using a Malvern Mastersizer 2000 laser diffraction equipment. Anhydrite (ANH), plaster (PL) and flue gas desulfurization gypsum (FGDG), were used as the calcium sulfate sources in the CSAC system.

| Material                                               | Abbreviation | Particle density (kg/m$^3$) | Mean diameter size (μm) | Particle size distribution (μm) $d_{10}$ $d_{90}$ |
|--------------------------------------------------------|--------------|-----------------------------|-------------------------|-----------------------------------------------|
| Calcium sulfoaluminate cement                         | CSAC         | 2790                        | 25.3                    | 2.2 64.8                                       |
| Fly ash, category N to BS EN 450-1:2012 [18]           | FA           | 2290                        | 34.5                    | 2.4 81.6                                       |
| Calcium sulfate: Flue gas desulfurization gypsum       | FGDG         | 2520                        | 47.4                    | 8.7 119.2                                      |
| Calcium sulfate: Gypsum plaster                        | PL           | 2600                        | 27.5                    | 3.2 86.2                                       |
| Calcium sulfate: Anhydrite                             | ANH          | 2950                        | 24.5                    | 2.3 42.1                                       |

The ye'elimite content in the CSAC clinker was found to be 71% and the belite content was 15%, although no calcium sulfate was detected. To confirm the sulfate type in FGDG, PL, and ANH, TG
analysis (20°C to 300°C at a rate of 10°C/min) was conducted and mass losses of 5.43% and 5.16% respectively were obtained in the range of 135-137°C. No mass loss was observed in ANH.

In order to assess the hydration processes of the systems, cement pastes were prepared at a w/c ratio of 0.5 and cured in a 20°C water-curing tank until age of testing. TG and XRD analyses were performed after 1, 3, 7 and 28 curing days and SEM images of the pastes cured for 28 days were obtained, assuming that this period was adequate for allowing full formation of all hydration products. Acetone was used to arrest the hydration of the cements.

Setting times of the pastes were determined in accordance to BS EN 196-3:1995 [19]. Heat of hydration was determined using a Wexham developments JAF conduction calorimeter. Mortar samples were prepared to assess the mechanical properties and dimensional changes of the combinations. The compressive strength was conducted in accordance to BS EN 196-1:1995 [20] and the dimensional changes were monitored on air-cured mortar samples stored in conditioning chamber (maintained 20°C, 65% RH) at 1, 7, 28 and 90 days of age.

For the development of appropriate CSAC/calcium sulfate combinations, the following criteria were taken into consideration:

- Achievement of a cement strength class equivalent (or higher) to that of a 42,5N (or R) conventional cement as defined in BS EN 197-1:2000 [21]
A calcium sulfate content lower than that which creates dimensional instability. This was achieved experimentally by monitoring the dimensional change of CSAC/calcium sulfate cement pastes at increasing calcium sulfate contents.

A minimum content of calcium sulfate in the system to ensure ettringite formation and avoid monosulfoaluminate formation by using stoichiometric approach.

To examine the influence of the type and amount of the calcium sulfate sources on the mechanical properties and dimensional stability of the system, combinations were prepared at varying calcium sulfate contents, i.e. CSAC/calcium sulfate: 100/0, 80/20; 65/35; 50/50; 35/65 as shown in Table 2.

For the development and selection of appropriate CSAC/anhydrite/FA combinations (denoted as GAF in Table 2), FA was introduced at contents of 5%, 10% and 15% by mass of total combination, whilst maintaining the CSAC/anhydrite ratio that satisfied all criteria previously stated. The particular percentage range of FA was selected based on determining approximately the minimum amount of Ca(OH)\(_2\) likely to be formed from belite hydration so as to promote pozzolanic reaction.

To establish the minimum calcium sulfate content for sufficient ettringite formation, a stoichiometric approach was used. For complete ettringite formation in both cases, the molecular mass ratios of calcium sulfate to ye'elimite needed to be considered based on equations 1 and 2.
The ratios were determined as \( \frac{290}{607} = 0.477 \) and \( \frac{272}{607} = 0.448 \) for hemihydrate and anhydrite respectively. Based on the chemical composition of the as-received high-strength CSAC, the pure ye'elimite content was 71\% and no calcium sulfate was added and/or interground in advance during manufacturing. It was assumed that the full amounts of added calcium sulfate reacted solely with ye'elimite, therefore, the minimum calcium sulfate content required to promote ettringite formation and avoid monosulfoaluminate formation was calculated as \( 0.477 \times 0.71 \approx 34\% \) for the hemihydrate and \( 0.448 \times 0.71 \approx 32\% \) for the anhydrite respectively. The two contents were then considered as the limits for defining chemically stable CSAC/ANH and CSAC/hemihydrate combinations.
Table 2. Mix proportions and compressive strength development of combinations used

| Cement / Combination | Notation | CSAC | FGDG | PL  | ANH | FA | Compressive strength N/mm² at day |
|----------------------|----------|------|------|-----|-----|----|----------------------------------|
|                      |          |      |      |     |     |    | 1     | 3     | 7     | 28    | 90    |
| CSAC                 | 100      | -    | -    | -   | -   | -  | 36.2 | 43.7  | 57.4  | 76.1  | 72.2  |
| CSAC/FGDG            | FGDG1    | 35   | 65   | -   | -   | -  | 6.8  | 8.1   | 9.4   | 16.3  | 10.2  |
|                      | FGDG2    | 50   | 50   | -   | -   | -  | 14.3 | 18.1  | 19.9  | 32.3  | 30.7  |
|                      | FGDG3    | 65   | 35   | -   | -   | -  | 24.0 | 31.8  | 37.6  | 42.7  | 46.9  |
|                      | FGDG4    | 80   | 20   | -   | -   | -  | 28.2 | 36.6  | 45.9  | 61.0  | 62.1  |
| CSAC/ANH             | ANH1     | 35   | -    | -   | 65  | -  | 4.2  | 6.3   | 9.1   | 11.6  | 11.5  |
|                      | ANH2     | 50   | -    | -   | 50  | -  | 11.9 | 21.9  | 25.8  | 43.3  | 47.1  |
|                      | ANH3     | 65   | -    | -   | 35  | -  | 22.9 | 29.0  | 39.5  | 46.0  | 49.7  |
|                      | ANH4     | 80   | -    | -   | 20  | -  | 31.9 | 39.4  | 50.0  | 67.1  | 67.2  |
| CSAC/PL¹             | PL1/2/3  | 80/65/50 | -  | 20/35/50 | - | -   | -    | -     | -     | -     | -     |
| CSAC/ANH/FA          | GAF5     | 61   | -    | -   | 34  | 5  | 29.3 | 37.8  | 39.7  | 51.1  | 51.2  |
|                      | GAF10    | 58   | -    | -   | 32  | 10 | 30.8 | 36.2  | 39.2  | 49.6  | 49.4  |
|                      | GAF15    | 55   | -    | -   | 30  | 15 | 31.5 | 35.1  | 38.9  | 48.8  | 48.2  |

¹ The preparation and study of CSAC/PL-based mortars in certain techniques was not possible because of the rapid setting that occurred.
3. Results and discussion

3.1. Dimensional stability

Dimensional changes of CSAC/ANH and CSAC/FGDG mortars at varying contents of calcium sulfate are shown in Figures 1 and 2 respectively. Due to rapid setting that occurred in CSAC/PL combinations, preparation and tests were not possible. It can be seen that at calcium sulfate contents below 50%, both FGDG and ANH-based formulations exhibited similar and almost dimensionally neutral patterns at early ages. These were followed by a slight shrinkage on the region of $5 \times 10^{-4}$ on the 28th day, reaching the maximum values on the 90th day. When calcium sulfate contents reached above 50%, expansion occurred to both combinations with severe cracks forming at a sulfate content of 65% which is a characteristic of ettringite’s instability when ye’elimite is introduced in exceedingly high sulfate concentrations. Based on these results, the value of 50% was considered as the maximum content when selecting stable CSAC/calcium sulfate combinations. Shrinkage patterns of CSAC/FGDG were less than those observed CSAC/ANH at a given proportion, with a difference ranging from approximately 50 to $180 \times 10^{-4}$ strains. This was because, for the two calcium sulfate types to yield the same molecular weight of ettringite upon their reaction with ye’elimite, the hemihydrate content requirement was higher than that of anhydrite, according to Equation 2 and Figure 3. Towards the 90th day of examination, slight shrinkage was observed at both CSAC/ANH and CSAC/FGDG samples at calcium sulfate contents less than 50%, probably due to a small degree of ongoing water evaporation occurred after complete ettringite formation.
3.2. Compressive strength development

Compressive strength development of water-cured CSAC/FGDG, CSAC/ANH and GAF mortars at increasing calcium sulfate contents are shown in Table 2.

For the CSAC/calcium sulfate combinations the results show that, regardless of the calcium sulfate type introduced, the compressive strength values tend to decrease at increasing ANH or FGDG contents. Highest strengths were observed in pure CSAC mortars. This is in coherence with previous work [22] when considering 7-day and 28-day values. During the first 24 hours of hydration, the formation of ettringite in the CSAC/calcium sulfate systems would be mainly responsible for the systems' strength development as evidenced from TG, XRD and SEM analyses in Figures 4-11. In pure CSAC, where the ye'elimite content is highest compared to all other formulations, the strength evolution at very early ages would be dependent on the formation of other hydration products, most probably C-A-H, Al(OH)$_3$ and little amounts of ettringite due to absence of calcium sulfate. The effect of this possible set of hydration products on the strength development of pure CSAC could potentially be greater than that of ettringite upon the CSAC/calcium sulfate systems. This is because, according to dTG curves in Figures 5, 8 and 9, the ANH and FGDG in the CSAC/calcium sulfate systems did not appear to be fully depleted from day 1 so as to give full amounts of ettringite and provide high strengths - possibly due to low reactivity of the calcium sulfate materials. Complete ettringite formation for most of the systems did not seem to occur at least until the 7th day and this may have caused the systems to exhibit lower 1-day strengths than CSAC.
The use of both FGDG and ANH in CSAC at a proportion of 35% or 50% by mass of the combination gave 28-day strength values meeting the target 42.5 N/R class (Figure 3) and no strength loss was observed up to 90 days. Based on these results and by considering the chemical and dimensional criteria discussed on section 1.1, the selected CSAC/calcium sulfate combinations were those containing 35% FGDG or ANH. The particular content was sufficient to ensure complete ettringite formation and avoid monosulfoaluminate formation as in stoichiometric calculations. In addition, the content was such that did not appear to cause dimensional instability according to Figure 3.

Compressive strength development of GAF combinations showed that within a maintained CSAC/ANH ratio, the increase of FA at a 15% content gave an increase in 28-day strengths of approximately 3-6 MPa compared to GAF5 and GAF10. Therefore the chosen GAF formulation was the one consisting of 15% by mass of FA, 55% CSAC and 30% ANH as it met the target strength class at maximum percentage of the addition.

### 3.3. Hydration

The hydration processes of CSAC/FGDG, CSAC/PL, CSAC/ANH and GAF15 mixes were investigated through TG, XRD and SEM analyses and each system is discussed below.
3.3.1 65%CSAC/35%FGDG

X-ray diffractograms and dTG curves of the stable CSAC/FGDG system are shown in Figures 4 and 5 respectively. SEM images of 28-day sample are shown in Figures 6a and b. Based on the diffractograms, the main hydration product was ettringite, and unreacted ye'elimite, gypsum, and gehlenite peaks were also detected. Ettringite corresponding XRD peaks and dTG curves occurred from the first 24 hours of hydration. SEM images showed a homogeneous microstructure with rich amounts of needles within a pore. The prismatic needles had a thickness of approximately 0.5 - 2 μm and a length ranging from 60 - 100 μm.

Based on the TG analysis, the corresponding weight loss at 115-135°C and the mass loss was progressively increasing towards the 7th day. At slightly higher temperatures (150-157°C), an additional mass loss was observed, which was assigned to the amounts of gypsum formed in the combination [14]. At 28 days, however, overlapping occurred between corresponding decomposition temperatures of ettringite and gypsum.

In temperatures between 265°C - 272°C, alumina hydrates were detected by TG analysis with a mass loss progressively increasing with time (4.25 - 5.46%). This phase was not detectable by XRD analysis due to its non-crystalline structure.
3.3.2 65%CSAC/35%PL

X-ray diffractograms and dTG images of CSAC/PL are shown in Figures 7 and 8 respectively. Hydration products were found to be identical to those of CSAC/FGDG at all ages of examination, namely ettringite, gypsum, unreacted ye'elimite and gehlenite. On the first day of hydration, gypsum amounts were excess and a dTG mass loss of this peak reaching almost 6% was observed. Onwards the 28th of hydration, the gypsum amounts were reduced and only a broad peak between gypsum and ettringite was detected. This occurred due to overlapping between the two phases, showing a combined mass loss of the two products. Consequently, the mass loss recorded could not be quantitatively ascribed to ettringite mass loss. The Al(OH)$_3$ had an increasing dTG mass loss reaching up to almost 6.6%, which was comparable to the pattern observed in 65%CSAC/35%FGDG.

3.3.3. 65%CSAC/35%ANH

Hydration of CSAC/ANH as determined through TG, SEM and XRD is shown in Figures 9, 10a-b and 11 respectively. XRD results showed that the crystalline products of 65%CSAC/35%ANH were equivalent to those of the other two calcium sulfate-based systems, i.e. ettringite, unreacted ye'elimite and gehlenite. Ettringite peaks as shown in Figure 11 became progressively stronger as with the other systems, reaching a maximum on the 28th day of hydration. In this system, no overlapping occurred between dTG gypsum peaks and ettringite peaks, as calcium sulfate was provided solely in the form of anhydrite. Consequently, no hemihydrate dTG peaks were available and therefore quantitative dTG mass losses were entirely ascribed to the amount of ettringite.
Towards the 28th day, ettringite mass loss was increasing from approximately 13% to approximately 21.5%. An increase in mass loss of Al(OH)$_3$ was observed (almost 1% increase) on the 28th day compared to day 1.

SEM images (Figure 10a-b) showed rich amounts of prismatic ettringite needles within a pore, and no significant difference in morphology and mineralogy was observed compared to 65%CSAC/35%FGDG images.
dTG curves at 1, 3, 7 and 28 days and SEM images at 28 days for GAF15 are shown in Figures 12 and 13a -b respectively. X-ray diffractograms at 1, 3, 7 and 28 days of hydration are shown in Figure 14.

According to the results, ettringite was formed from the first day of hydration, with a 4.2% increase in mass loss when reached the 28th day. In particular, the patterns obtained in dTG analysis were similar as in 65%CSAC/35%ANH combination. Crystalline products detected from XRD were ettringite, unreacted ye'elimite, anhydrite and some additional peaks were attributed to the presence of quartz and mullite from the addition of FA and stratlingite appearing onwards the 28th day. The formation of small amounts stratlingite may probably be a result of a reaction between hydrated belite and aluminate-based phases. The XRD peaks of anhydrite were less intense compared to the other systems as the anhydrite was added in lesser amounts in the system (15% calcium sulfate instead of 35% as in the other combinations). Al(OH)₃ amounts were comparable to the other combinations, having a dTG mass loss in the range of 5 - 6.6% throughout the period of examination.

SEM images of GAF15 in Figures 14a and b showed a dense, homogeneous microstructure consisting of rich amounts of prismatic ettringite needles with unreacted FA particles. The microstructure observed showed a synergistic effect between FA and ettringite. The observed FA particles were immobilized and appeared to be firmly wedged into spaces in-between the formed sulfoaluminate phases, denoting that an effective void filling had occurred.
By comparing XRD patterns of CSAC/FGDG, CSAC/PL, CSAC/ANH and GAF15 it can be seen that common hydration products detected were ettringite and unreacted ye'elimite although $\text{Al(OH)}_3$ could not be detected due to its non-crystalline structure. Gypsum was detected at CSAC/FGDF and CSAC/PL, whereas anhydrite was detected in GAF15 and CSAC/ANH. Ettringite XRD peaks were more intense in CSAC/ANH and GAF15 than in CSAC/PL and CSAC/FGDG, particularly at an angle of 26.5º, probably due to the overlapping peak of anhydrite. In the GAF15, quartz and mullite were additionally detected due to the FA incorporated in the combination.
3.4. Isothermal conduction calorimetry

Heat patterns and accumulated output rates of CSAC/ANH, GAF15 and CSAC/FGDG systems are shown in Figure 15. Measurements of heat of hydration for the CSAC/PL could not be obtained as the combination suffered from rapid setting and no time was given for preparation of the sample.

GAF15 heat pattern showed an initial shoulder peak occurring in less than 2 hours, followed by a maximum heat rate between the 5th and the 6th hour. Peaks were associated with the depletion of calcium sulfate and the formation of sulfoaluminate and aluminate hydrates. Output peak rates were higher in GAF15 combination. CSAC/ANH showed a heat pattern similar to that of GAF15 but with lower maxima and equivalent peaks delayed at approximately 2 hours compared GAF15. Both the combinations showed the same tendency of exhibiting an initial shoulder followed by a heat peak maximum. In CSAC/FGDG, only one main peak was detected 2 and 4 hours earlier than those of GAF15 and CSAC/ANH respectively. This reflected the tendency of hemihydrate to accelerate the formation of both sulfate hydrate and sulfoaluminate hydrate phases simultaneously. The particular peak was attributed to the formation of gypsum and ettringite, both having occurred at the same period. A smooth curve was also observed after a period of dormancy, having a maximum heat output rate of less than 2 W/kg at 17 hours, probably due to the precipitation of further sulfoaluminate and aluminate-based phases.
Comparison of the initial and final setting times between all examined cements is shown in Figure 16.

Generally, the initial setting of almost all cements/combinations occurred at the beginning of their accelerating heat pattern period and final setting times occurred before the corresponding heat output maxima. In all CSAC/calcium sulfate combinations regardless of the presence of FA, setting times were shorter than those of a typical Portland cement-based combination, mainly because of the high water demand during ettringite formation. It is known that 32 molecules of water are attracted on the ettringite skeletal structure according to the phase chemical composition. In contrast, the C-S-H is associated with fewer molecules regardless of its stoichiometric variations. Main factors influencing the water adsorption rate in ettringite are mainly the morphology, the crystalline structure, the phase size (larger than C-S-H) and the interlocking effect between the compounds. Comparing the behaviour of CSAC/FGDG to that of typical CEM I systems, the results suggest that setting times would not normally raise concerns in construction processes when considering transportation and casting. By comparing, however the setting behaviours of the CSAC/FGDG and CSAC/PL systems (i.e. two CSAC/hemihydrate systems), it can be seen that there is a notable difference in initial and final sets. This may be attributed to the reactivity and solubility of the two materials which might have been affected by the presence of moisture from the production process and/or any impurities present [14].
The incorporation of FA in the CSAC/ANH combination (i.e. the GAF15) caused a reduction on the final setting time -approximately 40 minutes- whilst no effect on initial setting times occurred. The explanation for these results lies on the calorimetric curves and the cumulative heats of the two combinations (Figures 15). It can be seen that the initial shoulder peak in GAF15 was higher and occurred faster than that of CSAC/ANH. This reflected an earlier consumption of calcium sulfate and formation of the hydrates. Consequently a higher water demand caused final sets to reduce in GAF15. Moreover, cumulative heats of GAF15 were still higher than those of CSAC/ANH, regardless of the fact that ettringite amounts were lesser in GAF15 (a TG mass loss approximately 2.5% lower than that of CSAC/ANH), due to the reduced CSAC and anhydrite contents in the combination,

The incorporation of PL in CSAC had the most considerable effect on setting times. Values were unacceptably short and during the mixing process, rapid setting occurred without allowing any margin for sample preparation, compaction and finishing. The final setting time was taken as less than 5 minutes. As evidenced, most of the techniques adopted for investigation of the cements could not be conducted for this particular combination. This may likely reflect the particular hemihydrate's impractical use and it may probably raise concerns when considering applications. Such behaviour would most probably be associated with the substantially high reactivity of calcium sulfate hemihydrate, therefore plaster-based CSAC combinations may not constitute the most appropriate solution for use in construction unless admixtures that retard the setting times and prolong the fresh semi-plastic state of the paste are introduced.

CSAC/FGDG setting times were higher than those of CSAC/ANH and GAF15 probably due to the variability of the commercial product, in combination with the presence of impurities that ultimately affected its reactivity.
4. Conclusions

Given the need for the utilization of alternative cementitious systems to reduce the environmental impact associated with Portland cement manufacture, alternative cementitious systems of lower eCO₂, when optimally proportioned and based on calcium sulfoaluminate- calcium sulfate-fly ash, may potentially offer environmental benefits. The following conclusions are made according to the results of this paper:

- The use of FA in CSAC in the presence of anhydrite promoted an earlier formation of a strong ettringite-rich matrix, firmly accommodating FA particles with earlier final sets. Both the FA particles and the formed hydrated phases appeared to synergistically contribute to a dense microstructure. Accumulated heat outputs and early strengths reached higher values than those of the pure CSAC/ANH and CSAC/FGDG combinations.

- The use of hemihydrate and anhydrite calcium sulfate in combination with CSAC had a notable effect on the rate of hydration, setting times, and to a lesser extent the mechanical performance of the system. The incorporation of anhydrite in the CSAC appeared to be more mechanically beneficial than that of any hemihydrate form. No significant differences were found in the mineralogy and morphology of the hydration products at different introduced forms of calcium sulfate at 35% by mass. In the hemihydrate-based systems, gypsum formation occurred at very early hydration stages and this was detectable by TG and XRD. Al(OH)₃ quantities were comparable at all CSAC/calcium sulfate systems as shown by TG. The use of hemihydrate (FGDG) was found to accelerate the formation of phases, based on the heat patterns.
The incorporation of hemihydrate in CSAC caused unacceptably short setting times of the CSAC/PL combination without allowing a time margin for sample preparation in most techniques. This may render the use of hemihydrate impractical within CSAC/calcium sulfate systems and it may raise concerns when considering applications. Such behaviour is associated with the substantially high reactivity and solubility of hemihydrate compared to that of anhydrite. Therefore, plaster-based CSAC combinations may not be regarded as the most appropriate solution for certain applications unless admixtures that retard the setting times are introduced. The most advantageous form of calcium sulfate for the CSAC system appeared to be the anhydrite form.

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LIST OF FIGURES

Figure 1. Dimensional changes of CSAC/ANH combinations at varying ANH contents

Figure 2. Dimensional changes of CSAC/FGDG combinations at varying FGDG contents

Figure 3. 28-day strength of CSAC/FGDG and CSAC/ANH at varying calcium sulfate content and limits of stability

Figure 4 X-Ray diffractograms of 65%CSAC/35%FGDG obtained at 1, 3, 7 and 28 days of hydration

Figure 5 dTG curves and mass losses in 65%CSAC/35%FGDG obtained at 1, 3, 7 and 28 days of hydration.

Figures 6a and b SEM image of 65%CSAC/35%FGDG obtained at 28 days.

Figure 7. X-ray diffractograms of 65%CSAC/35%PL at 1,3,7 and 28 days of hydration

Figure 8. dTG curves of 65%CSAC/35%PL at 1,3,7 and 28 days of hydration

Figure 9. dTG curves of CSAC/ANH at 1, 3, 7 and 28 days of hydration
Figures 10a and b  SEM Image of 65%CSAC/35%ANH at 28 days of hydration

Figure 11. X-ray diffractograms of 65%CSAC/35%ANH at 1,3,7 and 28 days of hydration

Figure 12. dTG curves of GAF15 at 1,3,7 and 28 days of hydration

Figure 13a and b  SEM image of GAF15 at 28 days of hydration

Figure 14. X-ray diffractograms of GAF15 at 1,3,7 and 28 days of hydration

Figure 15. Heat patterns and accumulated heat output rates of CSAC/FGDG, CSAC/ANH, and GAF15

Figure 16. Initial and final setting times of the investigated cements
Figure 8

The diagram shows the temperature and relative dTG for Ettringite, Gypsum, and Al(OH)₃ at different time points (1d, 3d, 7d, and 28d).

- **Ettringite**
  - 114.05°C, 7.91%
  - 147.29°C, 5.95%

- **Gypsum**
  - 140.98°C, 26.28%
  - 132.80°C, 21.37%
  - 121.44°C, 11.75%

- **Al(OH)₃**
  - 276.80°C, 6.59%
  - 271.33°C, 6.08%
  - 271.20°C, 6.05%

The temperature range is from 50°C to 350°C.
Figure 13b

Fly ash

Ettringite in pore
