An Experimental Study on the SRPC and CSA Cement Systems Based on Flyash and Anhydrite

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Abstract— **This research paper deals, calcium sulfoaluminate based cement (CSAC) and Sulphate Resisting Portland Cement (SRPC) with fly ash (FA) was used and the effect of fly ash (which contains calcium sulfoaluminate) on the properties of the systems was studied with SRPC. Fly ash (FA), anhydrite (ANH) and flue gas desulfurization gypsum (FGDG) were used to develop appropriate addition systems, the hydration of which was studied. The compressive strength and the setting time properties of cements were tested. The results suggest that the use of fly ash (which contains calcium sulfoaluminate) accelerates the formation of a strong ettringite-rich matrix that firmly accommodated unreacted fly ash particles, and contributing to a denser microstructure. At CSAC in a given sulphate content, the anhydrite was shown to be favourable in terms of the setting times, heat patterns (higher) compared to SRPC blended with FA based formulations however in strength development in reverse order. The Scanning Electron Microscope (SEM), Thermo gravimetric (TG) analysis and XRD also shows similar results.**

Abbreviations-- E, Ettringite; A, Anhydrite; Y, Ye'elimite; S, Stratlingite; G, Gypsum;

Keywords— Sulfoaluminate, Ettringite, Fly ash, Hydration, C-S-H

I. INTRODUCTION

The mixing of cementitious materials and additives with Portland cement (PC) is a well established approach to reducing the CO_2 emissions associated with the energy-intensive manufacture of cement. At present around 3.5 billion tonnes of PC is globally manufactured every year and it is estimated that the embodied CO_2 (eCO_2) for PC production is approximately 900 kg of CO_2 per tonne of PC produced [1] and [2,3]. The way to reduce the CO_2 of cement is through the use of non-PC based systems as the binding ingredient. The calcium sulfoaluminate cement (CSAC) and fly ash (which contains calcium sulfoaluminate) with sulphate resisting Portland cement (SRPC) which have a lower emission of CO_2 than PC, have been used in the present work [7]. The emission of CO_2 of a typical pure CSAC and calcium sulfoaluminate rich fly ash with SRPC, consisting of ye'elimite, belite and aluminoferrite, is approximately 590 kg/t. This represents a reduction in emission of CO_2 approximately 30% to 35% when compared to PC.

The early hydration product of CSA rich fly ash with SRPC and CSAC is ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) which forms as primary product (within 24 h) as prismatic needles. The formation of ettringite in the presence of sufficient calcium sulfoaluminate in SRPC with fly ash and CSAC which can be either presence of the ye'elimite-rich clinker (during manufacturing) or added in the raw meal intergrinding process. The optimum quantity of calcium sulfoaluminate for dominant formation of ettringite depends on several parameters i.e. the ye'elimite, the calcium sulfoaluminate 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 [9]. Other products of the hydration of CSA rich fly ash with SRPC and CSAC are mainly aluminate hydrates and calcium silicate hydrates. Unreacted ye'elimite is also typically present. Strengths of CSAC and CSA rich fly ash with SRPC based cements may reach over 40 MPa at 28 days [10] and SRPC+30% FA over 50 MPa at 28 days and they have been reported to exhibit very good resistance to aggressive environments, particularly to sulfate environments [11] and [12]. This is because aluminate-based phases are bound as sulfoaluminates at early stages of hydration and these are not available for reaction with external sulphate agents to form expansive ettringite.

The aim of this paper to investigate the influence of two main aspects revolving around the optimization of fly ash with SRPC hydration and performance of CSAC based cement systems. The second aspect covered the development of a binary system through the use of a low emission CO_2 addition, particularly fly ash, which could provide a better balance between performance and emission of CO_2 with SRPC.
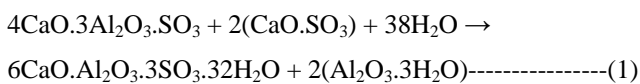
A. The calcium sulfoaluminate

There is a considerable experimental activity on development of CSAC and CSA rich fly ash blended SRPC that have been focusing on the use of anhydrite as the calcium sulphate source in the CSA system. Extensive work in the last decades is encapsulated in review articles[13,14]. 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, is 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
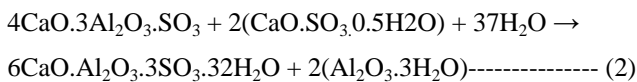
does not provide a clear indication of the influence of the hemihydrates of calcium sulfate on the hydration of CSAC. The CSA rich fly ash with SRPC also reported and compared with CSAC cements results. A more detailed look is therefore required at this type of calcium sulfate.

The intrinsic properties of both hemihydrate calcium sulfate and anhydrite are compared and established [15,16]. Setting times of the hemihydrate are known to be considerably short due to its high solubility (typically in the range of 7.5–9.5 g/l) and its reactivity, as opposed to that of anhydrite (approximately 3–4 g/l) [17]. Eqs. (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 parameter that varies is the amount of water needed for complete phase formation.

Ye'elemite + anhydrite:

$4CaO.3Al_2O_3.SO_3 + 2(CaO.SO_3) + 38H_2O \rightarrow$

$6CaO.Al_2O_3.3SO_3.32H_2O + 2(Al_2O_3.3H_2O)$----------------(1)

Ye'elemite + hemihydrate:

$4CaO.3Al_2O_3.SO_3 + 2(CaO.SO_3 0.5H2O) + 37H_2O \rightarrow$

$6CaO.Al_2O_3.3SO_3.32H_2O + 2(Al_2O_3.3H_2O)$-------------- (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 CSA system.

B. The use of fly ash in SRPC

Although the eCO_2 associated with the use of a fly ash in SRPC/calcium sulfate system may be lower than that of PC, potentially greater savings may be achieved based on the development of binary fly ash-based SRPC systems with maintained performance properties.

The CSA is formed as per the equation

$3CaCO_2 + 3Al_2O_3 + CaSO_4.2H_2O \rightarrow 4CaO.3Al_2O_3.SO_3 + 3CO_2 + 2H_2O$------------(3)
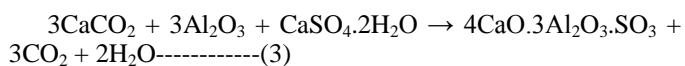
By-products from coal combustion plants are associated with almost zero eCO_2, whilst they may provide microstructural and mechanical advantages to cementitious systems when incorporated at optimum percentages. One advantage is the pozzolanic reaction. The use of low eCO_2 pozzolanic by-products – particularly fly ash – in the SRPC system, may instigate reaction with $Ca(OH)_2$ yielding from belite hydration in SRPC thus providing additional C–S–H gel. Previous studies on compressive strengths of SRPC/fly ash blends suggest a increase in strengths when fly ash contents are 30% [18]. 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-eCO₂ filler, then it is possible that a more sustainable system may be developed whilst maintaining its mechanical and microstructural properties[19].

II. 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 desulphurization gypsum (FGDG) were used as the calcium sulfate sources in the CSAC system.

Table 1. Materials used in the research.

Material	Abbreviation	Particle density (kg/m³)	Mean diameter size (µm)	Particle size distribution (µm)	
				d₁₀	d₉₀
Sulphate Resisting Portland cement	SRPC	2780	25.1	2.1	64.6
Calcium sulfoaluminate cement	CSAC	2792	25.4	2.3	64.9
Fly ash, category N to BS EN 450-1:2012 [18]	FA	2293	34.6	2.6	81.8
Sulphate Resisting Portland cement with fly ash	SRPC+FA	2653	30.6	2.5	75.2
Calcium sulfate: flue gas desulfurization gypsum	FGDG	2525	47.6	8.9	118.2
Calcium sulfate: gypsum plaster	PL	2650	26.5	3.4	86.2
Calcium sulfate: anhydrite	ANH	2950	23.5	2.1	42.9

The ye'elimite content in the CSAC clinker was found to be 65% and the belite content was 20%, although less amount of calcium sulfate was detected. To confirm the sulfate type in FGDG, PL, and ANH, TG analysis (30 °C to 350 °C at a rate of 10 °C/min) was conducted and mass losses of 5.23% and 5.06% respectively were obtained in the range of 140–145 °C. less mass loss was observed in ANH. The ye'elimite content in the fly ash doped SRPC was found to be 30% to 35% [20].

The hydration processes of the systems, cement pastes were prepared at a w/c ratio of 0.4 and cured in a 25 °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 stop the hydration of the cements.

Setting times of the pastes were determined in accordance to BS EN 196-3:1995 [21]. Heat of hydration was determined using a Wexham development 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 [21] and the dimensional changes were monitored on air-cured mortar samples stored in conditioning chamber (maintained 25 °C, 60% RH) at 1, 7, 28 and 90 days of age.

For the development of appropriate CSAC/calcium sulfate combinations, and percentage of fly ash doping with SRPC 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 ASTM Committee C-1, 1987[23]

 •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 FGDG,ANH and FA sources on the mechanical properties and dimensional stability of the system, combinations were prepared at varying FGDG,ANH contents, i.e. CSAC/FGDG: 100/0, 80/20; 70/30; CSAC/ANH:80/20; 70/30 and SRPC/FA : 70/30 as shown in Table 2.

Table 2.Mix proportions and compressive strength development of combinations used.

Cement/combination	Notation	SRPC	CSAC	FGDG	PL	ANH	FA	Compressive strength N/mm^2 at day				
								1	3	7	28	90
CSAC		–	100	–	–	–	–	32	40.7	55.2	70.2	75.4
CSAC/FGDG	FGDG1	–	70	20	–	–	–	22.3	29.8	34.6	40.7	45.6
	FGDG2	–	80	30	–	–	–	25.3	33.4	43.6	58.1	60.2
CSAC/ANH	ANH1	–	70	–	–	20	–	20.9	26.3	35.5	43.2	45.7
	ANH2	–	80	–	–	30	–	28.2	37.4	48.2	64.2	63.2
SRPC	SRPC1	100	–	–	–	–	–	21.58	32.47	43.56	49.74	57.53
SRPC	SRPC2	70	–	–	–	–	30	18.44	26.39	49.98	57.48	66.34

For the development and selection of appropriate CSAC/anhydrite and SRPC/FA combinations (denoted in Table 2), FA was introduced at contents of 5%, 10%,15%, 20% and 30% by mass of total cement, among them 30% was the best one, in the same way CSAC/anhydrite, whilst maintaining the CSAC/anhydrite ratio that satisfied all the 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 Eqs. (1),(2) and (3). 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.

III.   RESULTS AND DISCUSSION

A.   Dimensional stability

Dimensional changes of CSAC/ANH and CSAC/FGDG and SRPC/FA mortars at e shown in Fig. 1. It can be seen that at below 30%, 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 $5–10 \times 10^{-4}$ on the 28th day, reaching the maximum values on the 90th day. When FGDG and ANH contents reached above 30%, expansion starts occurred to both combinations with lighter cracks forming at a characteristic of ettringite's instability when ye'elimite is introduced in exceedingly high sulfate concentrations, so that is not good proportion to discuss, it is neglected. Based on these results, the value of 30% was considered as the maximum content when selecting stable CSAC/ FGDG and ANH combinations. Shrinkage patterns of CSAC/FGDG were less than those observed CSAC/ANH at a given proportion, with a difference ranging from approximately 40 to 160×10^{-4} strains. This was because, for the calcium sulfate 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 Eq. 1 and 2. Towards the 90th day of examination, slight shrinkage was observed for both CSAC/ANH and CSAC/FGDG samples contents less than 30%, probably due

to a small degree of ongoing water evaporation occurred after complete ettringite formation. In the same way SRPC/FA contents less than 30%, slight shrinkage was observed probably due to a small degree of ongoing water evaporation occurred after complete ettringite formation.
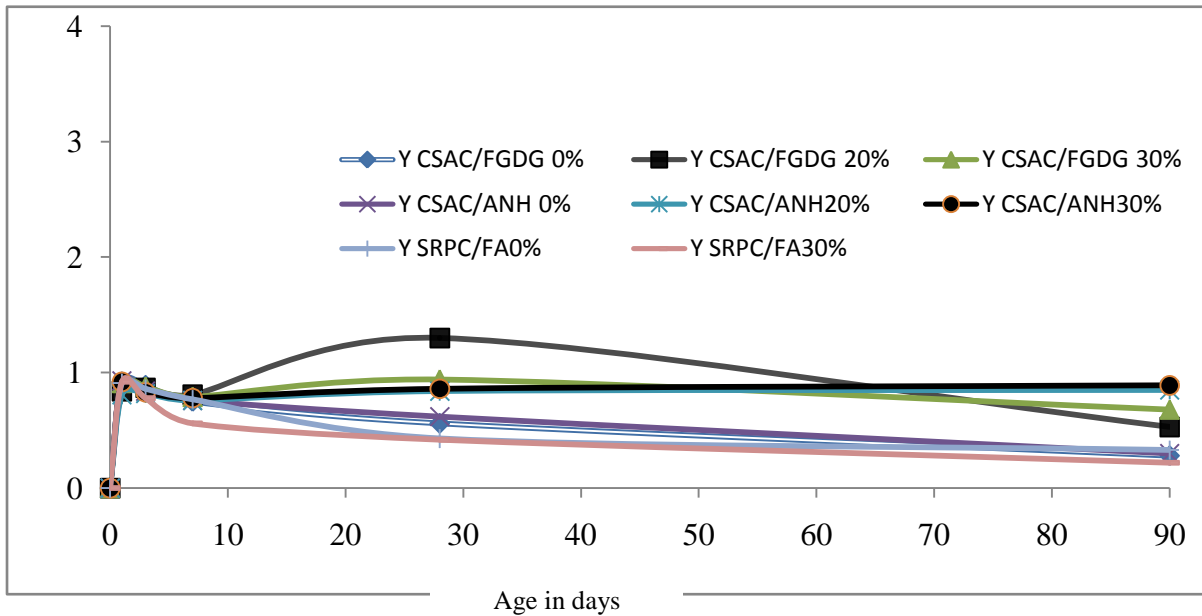

Fig. 1. Dimensional changes of CSAC/FGDG, CSAC/ANH and SRPC/FA combinations at varying contents
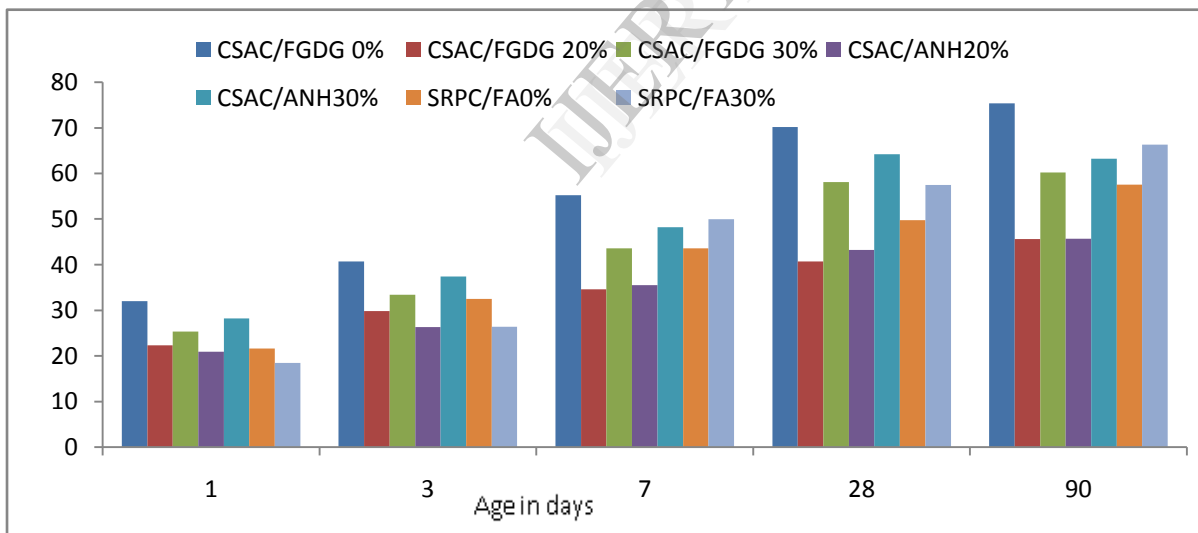

Fig.2 The compressive strength of CSAC/FGDG, CSAC/ANH and SRPC/FA at varying limits of stability.

B.   Compressive strength development

Compressive strength development of water-cured CSAC/FGDG, CSAC/ANH and SRPC/FA mortars at increasing days as shown in Table 2 and Fig.2.

The CSAC/FGDG, CSAC/ANH and SRPC/FA combinations the results show that, regardless of the type introduced, the compressive strength values tend to increase at increasing ANH or FGDG and FA contents. The highest strengths were observed in pure CSAC and SRPC/FA in 30% mortars. This is in coherence with previous work [22] when considering 7-day and 28-day values. During the first 24 h of hydration, the formation of ettringite in the CSAC or SRPC systems would be mainly responsible for the systems' strength development as evidenced from TG, XRD and SEM analyses in Fig. 3, Fig. 4, Fig. 5, Fig. 6, Fig. 7, Fig. 8, Fig. 9, Fig.10 and Fig. 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 small amounts of ettringite due to the 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/FGDG, CSAC/ANH and SRPC/FA systems. In the similar way, the strength development most probably C–A–H, Al(OH)$_3$ and small amounts of ettringite due to the absence of calcium sulphate in SRPC systems. In SRPC/FA, 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 [23]. According to dTG curves in Fig. 4, Fig. 7 and Fig. 10, the ANH and FGDG in the CSAC and SRPC/FA 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 and fly ash. 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 and SRPC.
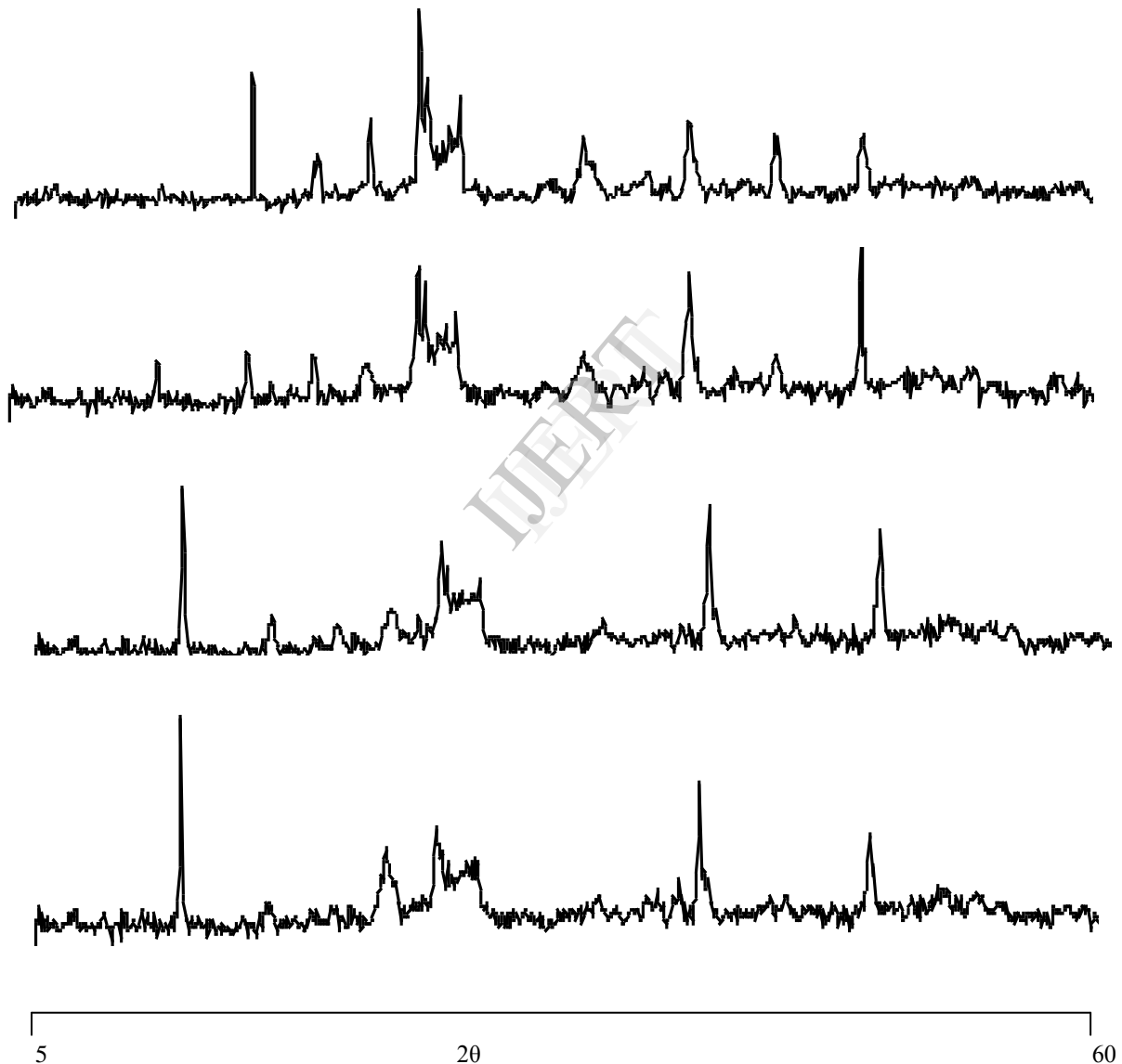

Fig. 3. X-ray diffractograms of 70%CSAC/30%FGDG obtained at 1, 3, 7 and 28 days of hydration.
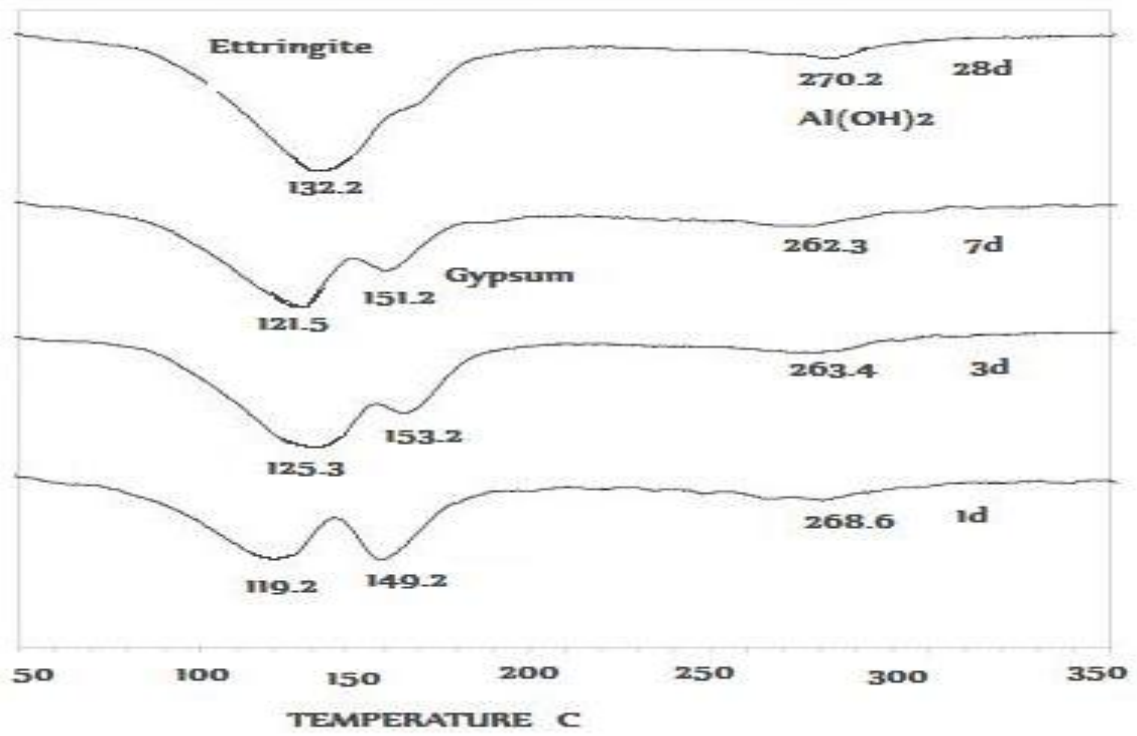
Fig. 4. dTG curves and mass losses in 70%CSAC/30%FGDG obtained at 1, 3, 7 and 28 days of hydration.
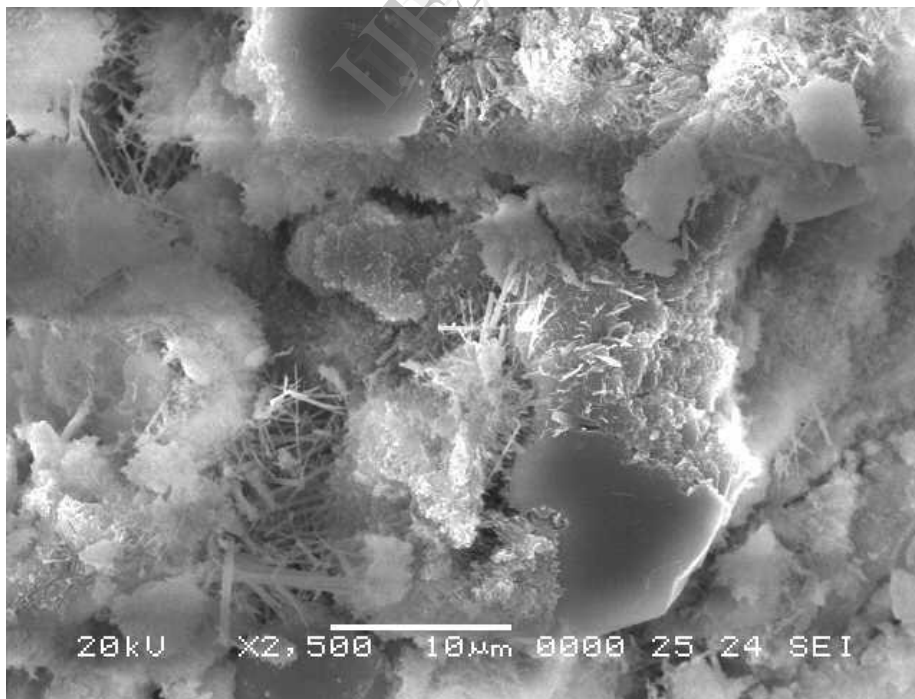

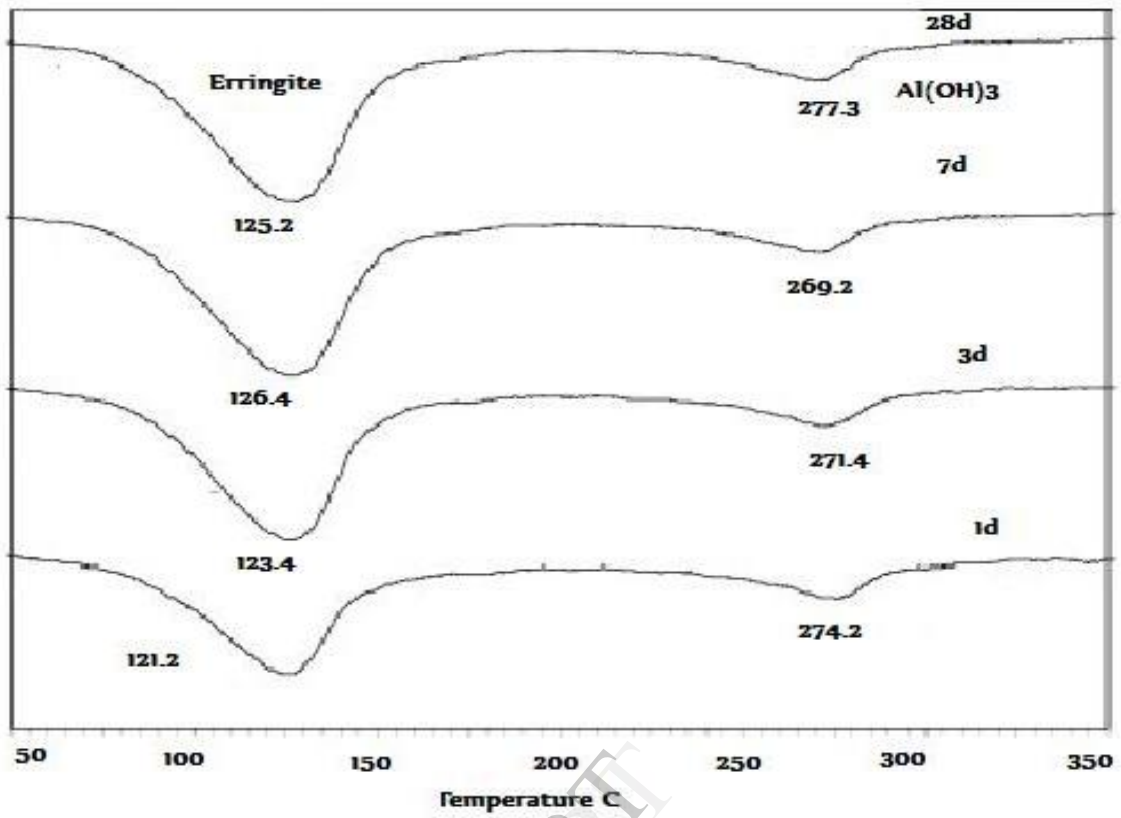Fig.5. SEM image of 70%CSAC/30%FGDG obtained at 28 days.

Fig. 7. dTG curves of 70%CSAC/30%ANH at 1, 3, 7 and 28 days of hydration.
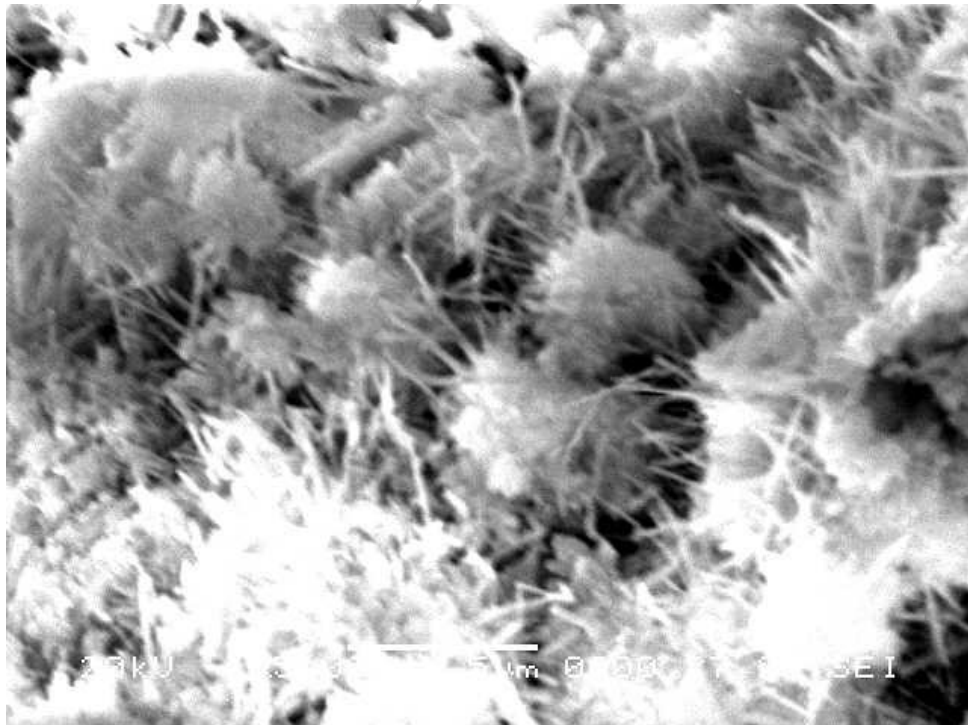

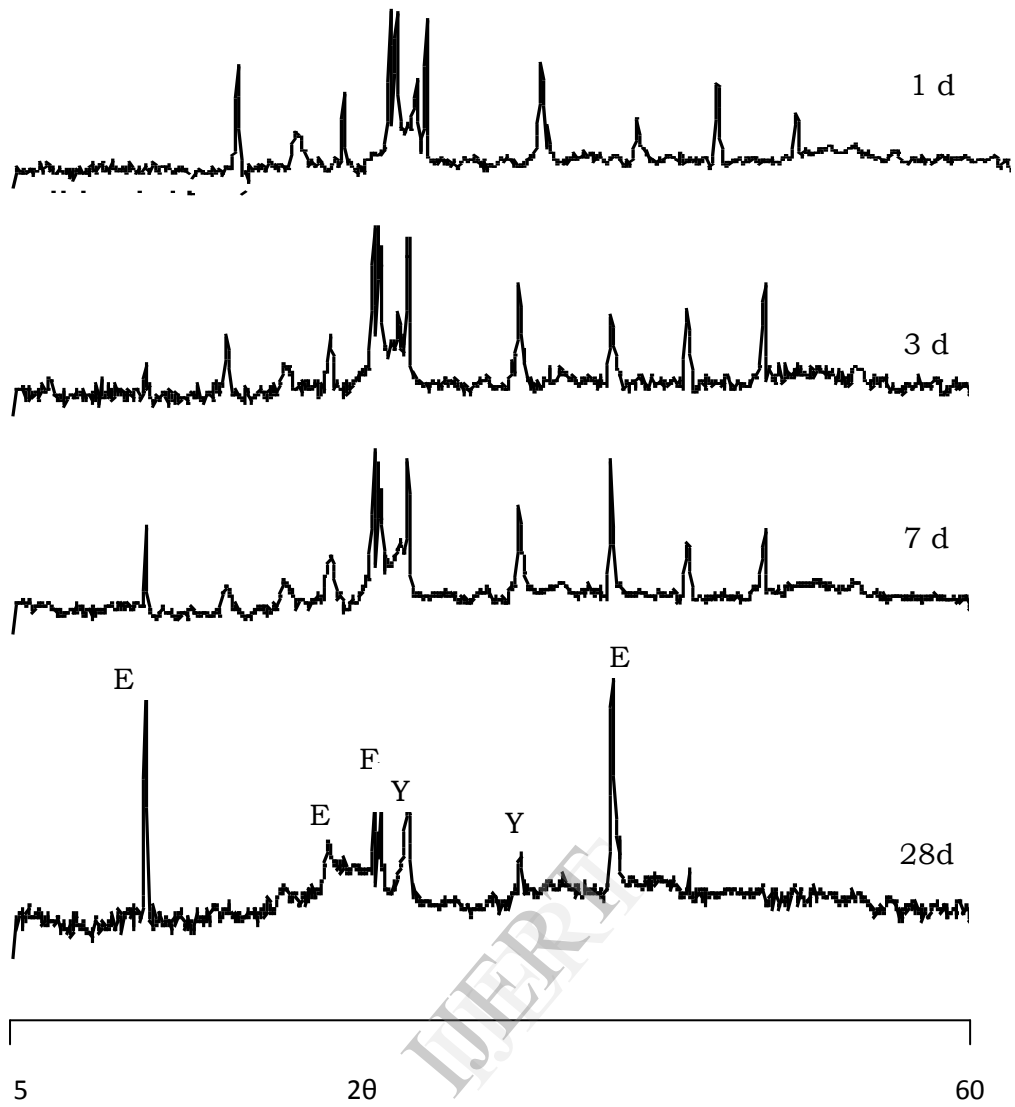Fig. 8. SEM image of 70%CSAC/30%ANH at 28 days of hydration.

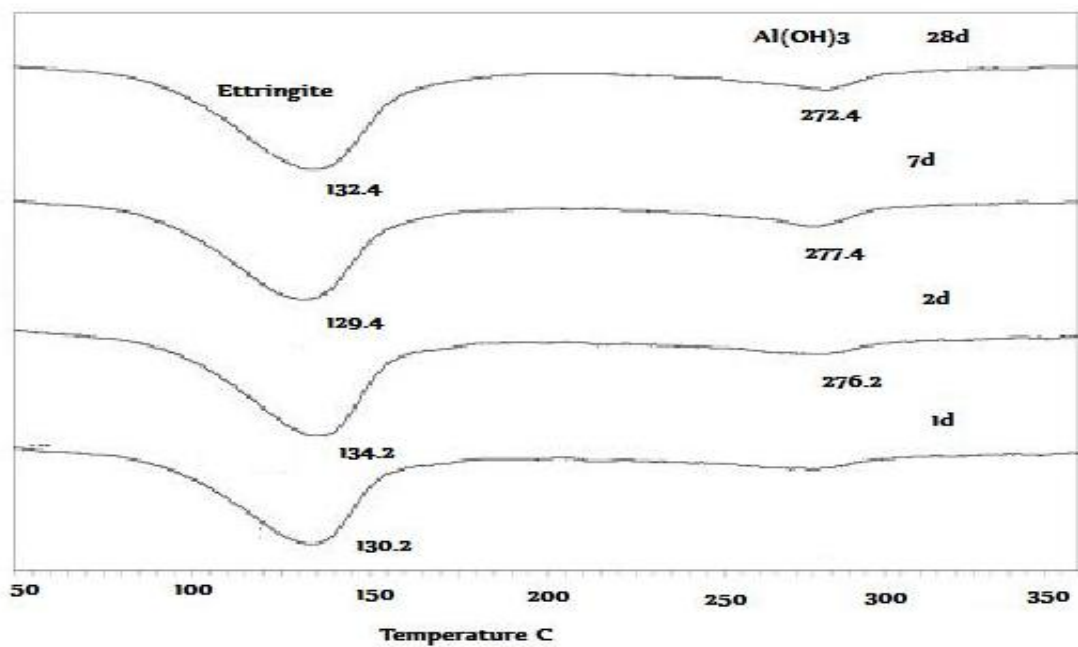Fig. 9. X-ray diffractograms of 70% SRPC/30% FA at 1, 3, 7 and 28 days of hydration.

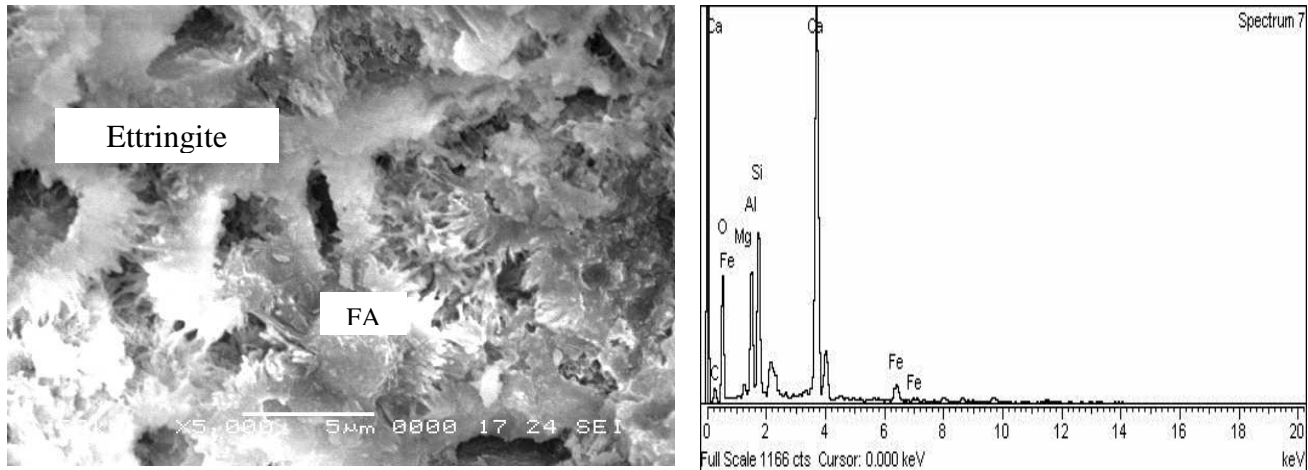Fig. 10. dTG curves of 70% SRPC/30% FA at 1, 3, 7 and 28 days of hydration.

Fig. 11. SEM image of 70%SRPC/30%FA at 28 days of hydration with EDX

The use of both FGDG and ANH in CSAC at a proportion of 20% and 30% by mass of the combination gave 28-day strength values (40.7, 43.2 N/mm^2 and 58.1,64.2 N/mm^2) and SRPC/FA of 30% (57.48 N/mm^2 meeting the target 40.5N/mm^2 (Fig. 2) and no strength loss was observed up to 90 days. Based on these results and by considering the chemical and dimensional criteria discussed in above section, the selected CSAC/ 30% FGDG or ANH. This particular content was sufficient to ensure complete ettringite formation and avoid monosulfoaluminate formation as in stoichiometric calculations. The SRPC combination with FA at 30% is sufficient to develop required strength at 28 days. In addition, the content was such that did not appear to cause dimensional instability according to Fig.1.

Compressive strength development combinations showed that within a maintained CSAC/ANH ratio, CSAC/FGDG and SRPC/ FA at a 30% content gave an increase in 28-day strengths compared to20%. Therefore the chosen percentage formulation was the one consisting of 30% by mass of FA, FGDG and ANH as it met the target strength class at maximum percentage of the addition.

C. Hydration

The hydration processes of CSAC/FGDG, CSAC/ANH and SRPC/FA mixes were investigated through TG, XRD and SEM analyses and each system is discussed below.

→ **CSAC/FGDG**

X-ray diffractograms and dTG curves of the stable CSAC/FGDG system are shown in Fig. 3 and Fig. 4, respectively. SEM images of 28-day sample are shown in Fig. 5. 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 h of hydration. SEM images showed a homogeneous microstructure with rich amounts of needles within a pore. The prismatic needles had a thickness of approximately 1–2 μm and a length ranging from 40 to 80 μm.

Based on the dTG analysis, the corresponding weight loss at 110–125 °C and the mass loss were progressively increasing towards the 7th day. At slightly higher temperatures (140–150 °C), an additional mass loss was observed, which was assigned to the amounts of gypsum formed in the combination and excess loss of water content [24]. At 28 days, however, overlapping occurred between corresponding decomposition temperatures of ettringite and gypsum.

The alumina hydrates were detected by TG analysis with a mass loss progressively increasing with time (4.1–5.2%) between 260 °C–270 °C,. This phase was not detectable by XRD analysis due to its non-crystalline structure.

→ **CSAC/ANH**

Hydration of CSAC/ANH as determined through XRD, TG and SEM is shown in Fig. 6 and 7 and 8 respectively. XRD results showed that the crystalline products of 70%CSAC/30%ANH were equivalent to those of the other two systems, i.e. ettringite, unreacted ye'elimite and gehlenite. Ettringite peaks as shown in Fig.6, 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 10% to approximately 20.5%. An increase in mass loss of $Al(OH)_3$ was observed (almost 2% increase) on the 28th day compared to day 1.

SEM images (Fig. 8) showed rich amounts of prismatic ettringite needles within a pore, and no significant difference in morphology and mineralogy was observed compared to 70%CSAC/30%FGDG images.

→ 70%SRPC/30%FA

The X-ray diffractograms, dTG curves at 1, 3, 7 and 28 days and SEM images at 28 days for SRPC/FA of 30% are shown in Fig.9, 10 and 11 respectively.

In 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 of stratlingite may probably be a result of a reaction between hydrated belite and aluminate-based phases. The XRD peaks clearly indicates that different phases present in the mixture during the 28 reaction. $Al(OH)_3$ amounts were comparable to the other combinations, having a dTG mass loss in the range of 4.1–5.2% throughout the period of examination.

SEM images with EDX of SRPC/FA of 30% in Fig. 11 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/ANH and SRPC/FA it can be seen that common hydration products detected were ettringite and unreacted ye'elimite although $Al(OH)_3$ could not be detected due to its non-crystalline structure. Gypsum was detected at CSAC/FGDF whereas anhydrite was detected in CSAC/ANH. Ettringite XRD peaks were more intense in CSAC/ANH than in CSAC/FGDG and SRPC/FA particularly at an angle of 24.5°, probably due to the overlapping peak of anhydrite. In the SRPC/FA little quartz and mullite were additionally detected due to the FA incorporated in the combination.

→ Isothermal conduction calorimetry

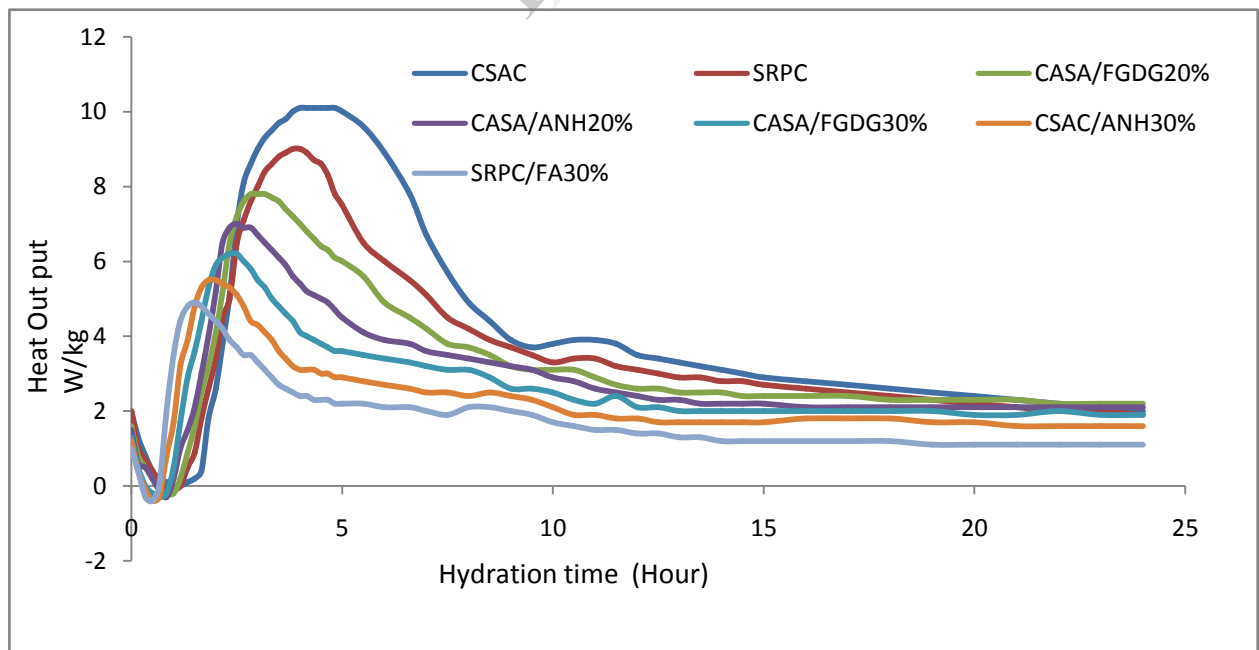Heat patterns and output rates of CSAC/ANH, CSAC/FGDG and SRPC/FA systems are shown in Fig. 12.

Fig. 12.Heat patterns and heat output rates of CSAC/FGDG, CSAC/ANH and SRPC/FA.

The heat pattern showed an initial shoulder peak occurring in less than 2 h in very low rate, followed by a maximum heat rate between the 3th and the 5th hour for all combinations. Peaks were associated with the depletion of calcium sulfate and the formation of sulfoaluminate and aluminate hydrates. Output peak rates were higher in CSAC and SRPC where as other combinations. The SRPC/FA showed a heat pattern similar to that of others but with lower maxima and equivalent peaks accelerates at approximately 2 h compared with other maximas. All 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 h earlier than those of SRPC/FA 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 between 13 h and 14 h, probably due to the precipitation of further sulfoaluminate and aluminate-based phases in all cases.

→ Initial and final setting times

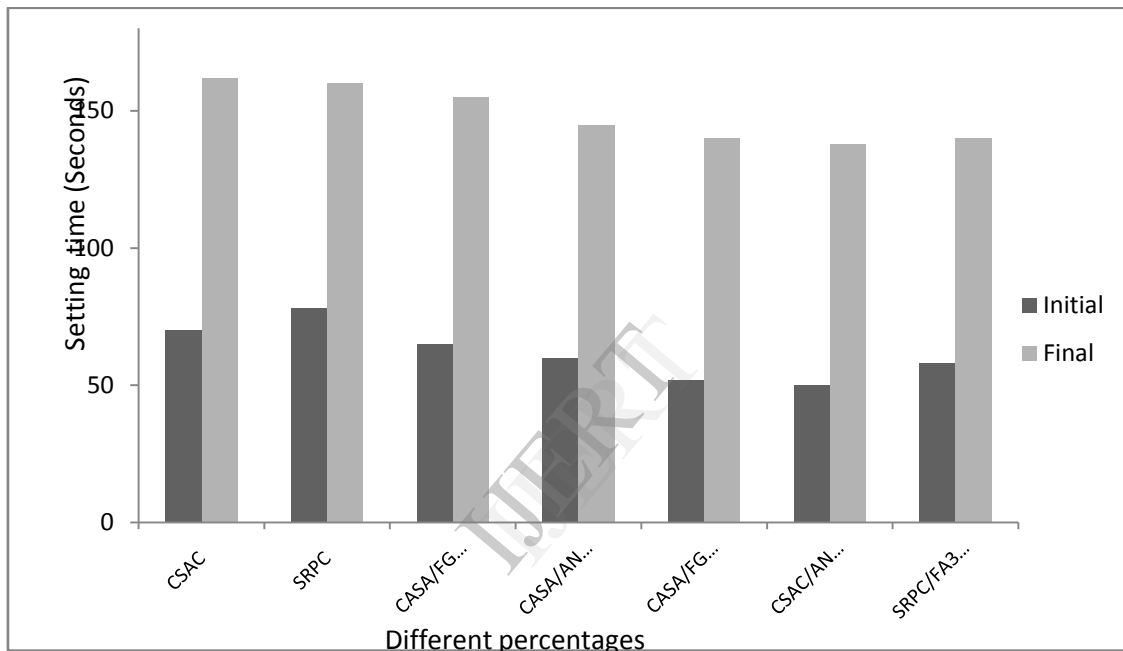Comparison of the initial and final setting times between all examined cements is shown in Fig. 13

Fig. 13.Initial and final setting times of the investigated cements.

The initial setting of almost all cements and combinations occurred at the beginning of their accelerating heat pattern period and final setting times occurred before the corresponding heat output maxima. In all 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, the molecules of water are attracted on the ettringite skeletal structure according to the phase chemical composition. In contrast, the C–S–H gel 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 behaviours of cement 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 SRPC/FA, it can be seen that there is a notable difference in the 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 [24].

The incorporation of FA in the SRPC/FA combination caused a reduction on the initial and final setting time. The explanation for these results lies on the calorimetric curves and the cumulative heats of the two combinations (Fig. 12). It can be seen that the initial shoulder peak in SRPC/FA was 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 it all these due to presence of ye'elimite in fly ash.CSAC/FGDG setting times were higher than those of CSAC/ANH and SRPC/FA probably due to the variability of the commercial product, in combination with the presence of impurities that ultimately affected its reactivity [25].

IV. 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 eCO$_2$, when optimally proportioned and based on calcium sulfoaluminate SRPC-fly ash, may potentially offer environmental benefits. The following conclusions are made according to the results of this paper:

•The use of FA in SRPC in the presence of ye'elimite 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 incorporation of anhydrite in the CSAC appeared to be more mechanically beneficial than that of hemihydrate form. 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 systems as shown by TG. The use of hemihydrate (FGDG) was found to accelerate the formation of phases, based on the heat patterns.

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