FTIR and XRD Characterisation of CSAC Fly Ash Blended System

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Abstract - **In this paper, the study of both hydrated Calcium Sulfoaluminate Cement (CSAC) and Fly ash (FA) with different percentages of (0%, 10%, 20% and30%) composite with two different waters. The efficiency and maximum content of fly ash which that gives the maximum compressive strength were studied. The optimum value of fly ash is about 30% were found. The samples (CSAC with FA) analyzed using the Fourier Transform Infrared Spectroscopy (FTIR) spectra and XRD compared with compressive strength. The results between compressive strength and molecular vibration changes were observed using FTIR spectra. Also, the setting time is identified with the FTIR spectra and proper explanation with available literature for the kinetics is presented. The Result of this study indicates that the blended paste better performance than the control paste hydrated with distilled water and effluent water. To support this observation heat of hydration was carried out. The results indicated that CSAC blended with 30% FA is accelerates the initial reaction (setting), reduce the heat output and good performance to strength than that of CSAC.**

Keywords: **Fly ash, Cement, FTIR, hydration, setting**

1 INTRODUCTION

Cement is an energy intensive component in concrete. The utilization of waste industrial by-products possessing cementitious character in cement/concrete saves a lot of energy reduces the environmental problems and the cost of the cement substantially. The modern cement is commercialized with high early strength but with a questionable durability, whereas the addition of these admixtures develops a better durability [1,2]. Fly ash is one such pozzolan satistifying the conditions laid by ASTM C595.

In India the availability of fly ash is plenty and likely to be increase a manifold due to the installation of number of power stations.

The Calcium Sulfoaluminate Cement (CSAC) which is more suitable in different climate and which can with stood the sulphate attack. It has been used for construction on above-ground projects for years and exhibits properties uniquely suited to the harsh environment of underground construction. The character and its utility have been well studied at varied nature by many authors [3, 4, 5].

The admixtural effect of fly ash having special characters are of interest as it improves the quality to a high level of performance. In the present study one such fly ash having special characters are blended with CSAC in different proportions and its effects are analysed using Infrared spectroscopy and XRD as a tool. The results are confirmed through heat of hydration study.

2 MATERIALS AND METHODS

The commercial CSAC (ASTM C150) was utilized in this study. The fly ash was received from Neyveli lignite corporatin, Neyveli, Tamil Nadu, India. The chemical analysis for both has been carried out and reported in Table.1. Two different kind of waters namely Distilled Water (DW) and Effluent Water (EW) were used. EW was collected from synthesis chemical factory, Tripur, Tamil Nadu, India. These waters are analysed using standard procedures adopted by Tamil Nadu water and drainage Department, Tamil Nadu and are reported in Table. 2. A W/C of 0.4 is maintained for all studies.

TABLE.1.The chemiclal composition of CSAC and Fly ash (by wt%)

Composition	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**SO_3**	**MgO**	**Na_2O**	**K_2O**	**LOI**	**Others**
CSAC	43.2	5.8	28.30	1.20	14.3	0.88	0.25	0.34	4.6	1.2
Fly ash	7.64	53.38	27.40	3.04	1.69	4.03	0.74	0.12	1.70	0.26

The fly ash of 10%, 20% and 30% was added to cement by the method of addition to prepare the blended samples. The blended samples were hydrated with two different waters and hydrated to different time of intervals. Using a drop of methanol mixture at time intervals like 1h, near initial setting time, near final setting time, 1 day, 1 week and 4 week the hydration was stopped. The dehydrated samples were vacuum dried for one hour, and powdered using agate pestle mortar.

The initial and final setting times are computed using Vicat's apparatus adopting standard procedures suggested by ASTM191 and 109. The compressive strengths were determined at 3 days, 7 days, 28 days, 56 days and 90 days for all the samples using standard procedure. The infrared spectra for the samples were recorded at room temperature using Perkin Elmer RX-I available at CISL, Annamalai University, Annamalai Nagar. KBr pellet method is adopted, the spectra were recorded in the region 4000 cm^{-1} – 400 cm^{-1}with a resolution of ± 2 cm^{-1}.

Interdisciplinary science and Technology, Thiruvanathapuram, Kerala, India with cu–Kα_1 radiation (λ= 1.5405Å) at 40 KV and 30 mA. All the XRD patterns were recorded from 2θ =10˚ to 70˚ in the range 2˚/min.
The measured flowability, workability, consistency and strength suggest that 30% FA addition is more preferable. Hence 30% addition of blended system with DW and EW

X-ray diffraction is the most primary investigative technique in cement chemistry to identify and estimate the constituent mineral phase. XRD derive its strength by the very nature of absolute, measurement and direct representation of mineral structure and identification. The XRD pattern for all samples were recorded with X-ray diffractometer P Analytical (Philip-Netherlands–X'–pert), X' pert software, available in National Institute for alone are projected in the present study. Necessary plots are provided for useful and relevant discussion. The heat of hydration has been obtained using solution calorimetry adopting ASTM C 186 procedure with the help of AIML Ins. Co. Pvt. Ltd. Model instrument.

TABLE.2.The properties and contents (µg/g) of waters

Sl. No.	Contents	DW	EW
1.	Appearance	Colourless	Brounish
2.	Odour	Nil	Objectionable odour
3.	Total dissolved solids	95	9142
4.	Total hardness	4	2000
5.	Chloride	-	4731
6.	Sodium	-	800
7.	Magnesium	1	240
8.	Calcium	2	400
9.	Potassium	-	-
10.	Iron	-	0.89
11.	Sulphate	-	4.81
12.	Fluoride	-	0.1
13.	Electrical conductance (µs)	10	13060
14.	p^H	6.9	6.7

3 RESULTS AND DISCUSSION

A *Setting Time and Compressive Strength Study*

The setting time and compressive strength of CSAC and fly ash composites using (DW and EW) were measured (Fig.1,2,3 and 4). From the figure, the fly ash composite (30%) has a shorter setting time than the CSAC.

This is due to C_4A_3S [5,6] which is responsible for producing more ettringite and hence ettringite to monosulfate Conversion and also CSH gel. Due to this setting and strength of the paste at early age, in fly ash blend, due to addition of fly ash is decreased [6,7]**.**

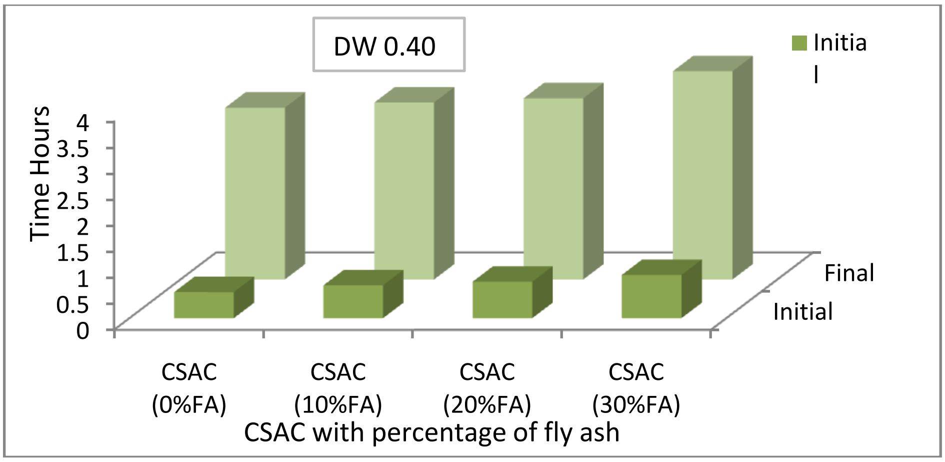

Fig.1. Setting time of DW-Control and blended CSAC

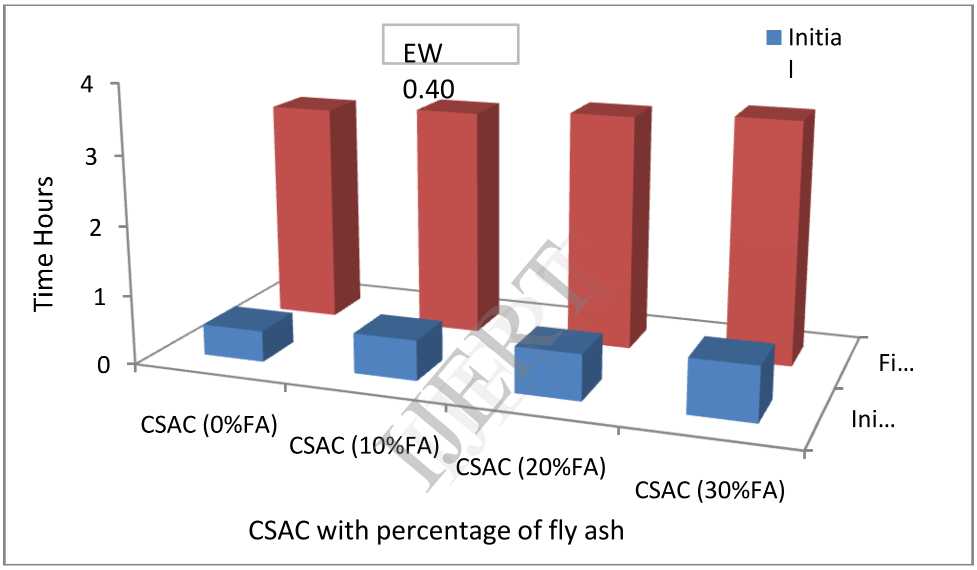

Fig.2. Setting time of EW-Control and blended CSAC

The result coincides well with the observations of Gartner [8]. The EW hydrated pastes have quick setting than DW in the early hydration which is due to the presence of accelerating ions in EW [9]**.** The compressive strength of CSAC performs better than CSAC blend up to 7days hydration. This may be due to the presence of retarding ion's effect surpassing the effect of CSAC in the system.

The results after 7 days indicate that there is a continuous and significant improvement in strength in the case of CSAC blend. This increase in strength may be due to the continued production of CSH, due to the fly ash particle pozzolanic activity. The effluent water hydrated all samples get an accelerating trend in early periods (up 7 days). At 28 days, the strength of EW control paste decreases and the strength of EW fly ash blend paste increases. From the result the 30% fly ash blend gives maximum compressive strength and hence it has been investigated through FTIR.

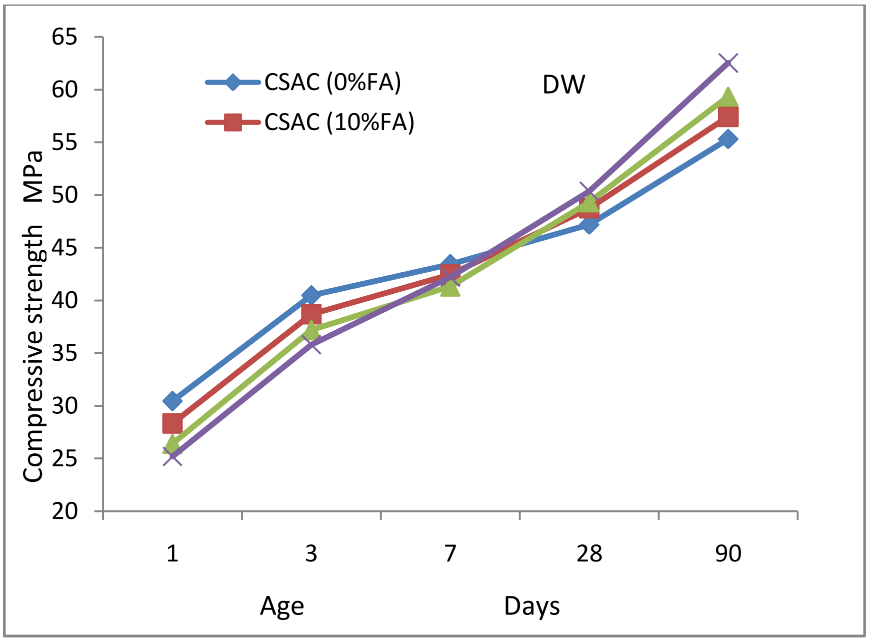

Fig.3. Compressive strength of DW-Control and blended CSAC

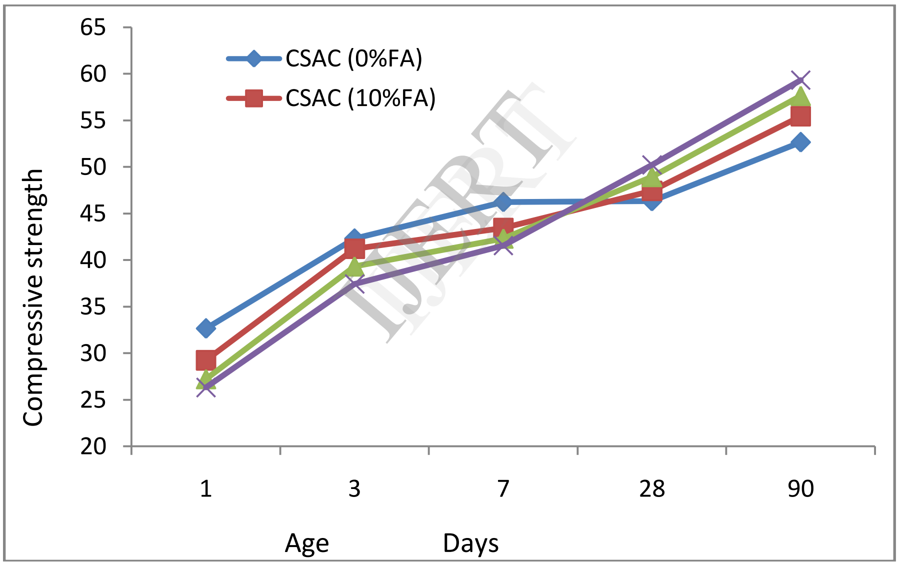

Fig.4. Compressive strength of EW-Control and blended CSAC

B FTIR Study

The spectra of Distilled water (DW) and Effluent water (EW) hydrated Control (CSAC) and blended cement (CSAC+ 30 %FA) are shown in the Fig.5-8.

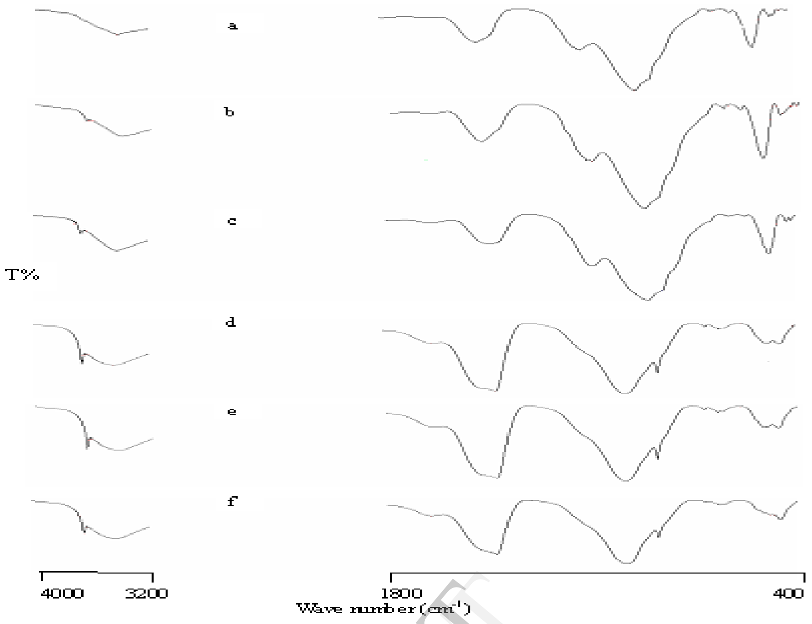

Fig.5. FTIR spectra of DW hydrated CSAC for (a) 30mins, (b) 3.5 hours, (c) 1 day,(d) 3days, (e) 7 days and (f) 28 days

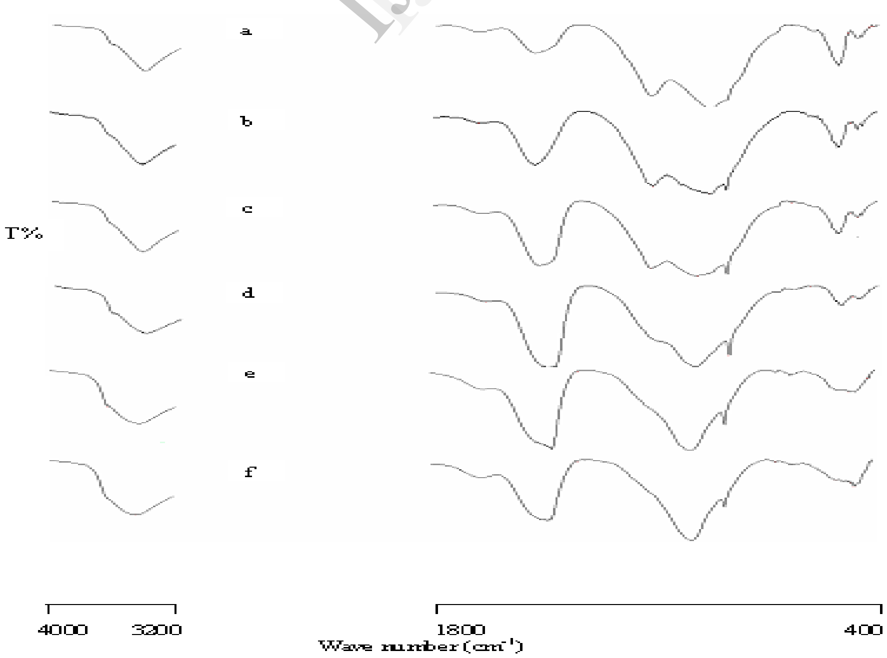

Fig.6. FTIR spectra of DW hydrated CSAC+30%FA for (a) 1hour, (b) 4 hours, (c) 1 day, (d) 3days, (e) 7days and (f) 28days

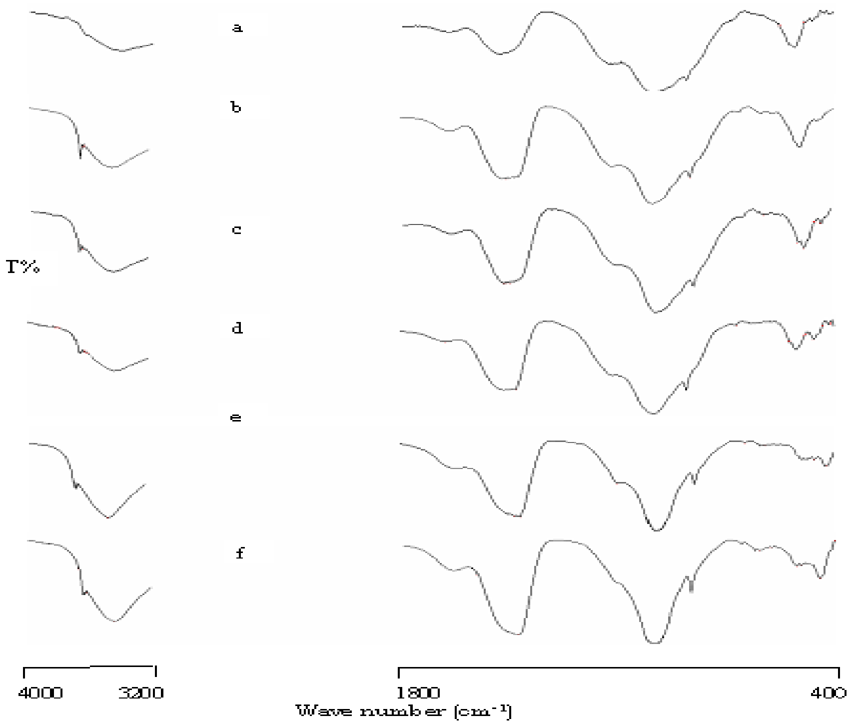

Fig.7. FTIR spectra of EW hydrated CSAC for (a) 30mins, (b) 3.5 hours, (c) 1 day, (d) 3days, (e) 7days and (f) 28 days

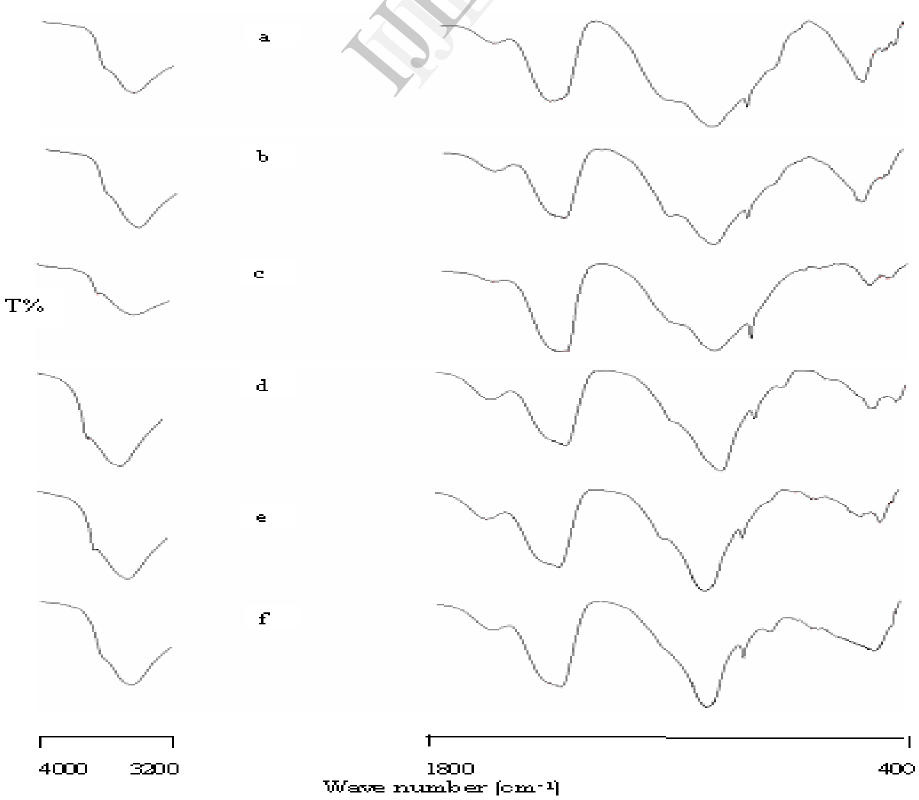

Fig.8. FTIR spectra of EW hydrated CSAC+30%FA for (a) 45mins, (b) 4 hours, (c) 1day,(d) 3days, (e) 7days, (f) 28 days

- *Dw Hydrated Control*

In cement hydration, water, carbonate, sulphate and silicate are the major bands identified through FTIR.

FTIR spectra of DW hydrated control are shown in figure 5. In 30 mins spectrum (Fig.5a), a medium intensity band around 3429 cm^{-1} and 1642 cm^{-1} may be assigned to the ν_1 and ν_2 water stretching and bending vibration respectively. A shoulder is emerging at 3642 cm^{-1} may be due to the formation of $Ca(OH)_2$ [10]**.** At 4th hour (Fig.5b), the ν_1 and ν_2 water bands having a stronger intensity with a shift to higher wave number around 3433 cm^{-1} and 1645 cm^{-1}. The sharp $Ca(OH)_2$ peak is observed at 3642 cm^{-1}. At 1day (Fig. 5c) a growth in ν_1 and ν_2 bands and $Ca(OH)_2$ are observed. As hydration time passes, the $Ca(OH)_2$ peak increases in intensity up to 7 days (Fig.5e) and there after a constant intensity is observed. The ν_1 and ν_2 bands have a broad and strong intensity up to 28 days.

In 30mins, a strong band near 1442 cm^{-1} is assigned to asymmetric stretching vibration of carbonate (ν_3□CO_3^{2-} □□□band. After 30 mins (up to 7 days), the ν_3 band at 1442 cm^{-1} has an increasing intensity and a new peak is observed (1day) at 873 cm^{-1} due to out-of-plane bending vibration (ν_4 CO_3^{2-}) of carbonate. The carbonation reactions are rapid but later (28 days) is almost constant.

paste gets setting (Fig. 1) [14]**.** From3 day spectrum (Fig.5d), the □□ band grows stronger in intensity. At 7th day (Fig.3e), the □□□ peak (520 cm^{-1}) decreases whereas the □□□peak (465 cm^{-1}) increases in intensity. The relative intensity change between □□□and □□□peaks is faster. It

- *Hydrated FA Blends CSAC*

Comparing the figures 6-8, the hydration reaction of 30%FA blends (Fig.6) and EW pastes (Figs.7 and 8) seems to be similar as that of DW control with a variation in reaction rate.

The strong and broad FA band (Fig.6a) observed at 1110 cm^{-1} is characteristic of fly ash and a small peak at 641 cm^{-1} is due to CSA stretching vibration in fly ash and cement band. In (Fig. 6d) the CSA is absent, indications its for consumption. From 7 days (Fig.6e), the $Ca(OH)_2$ peak gets a decrease in intensity, which may be due to starting of pozzolanic reaction of fly ash. The $Ca(OH)_2$ peak is totally consumed in 28 days (Fig. 6f) spectrum. The water bands (ν_1 and ν_2) have a higher intensity up to 28 days.

The carbonate bands are in increasing trend up to 7 days (Fig.6e) and beyond the band reduce in intensity as time ellapses. The sulphate bands (ν_2 and ν_4) doublet merges to form a singlet exhibiting the setting of the blend (Fig. 6b). This result coincides with setting time observation by Vicat's test (Fig.1). After 1day (Fig. 6c), the ν_2 and ν_4 peaks has continuously decreasing in intensity similar as that of CSAC. The ν_2 peak is not seen in 28 days (Fig.6 (e&f)) spectra.

Also CSA peak at 641 cm^{-1} is observed, at 1 day due to which the ν_3 silicate band shifts to higher wave number with higher intensity than control. The characteristic fly ash band (at 1110 cm^{-1}) gets a strong intensity up to 7 days (Fig.6e) spectrum. After 7 days a

In 30mins, a strong triplet band appearing between 1106 and 1139 cm^{-1} can be assigned to asymmetric stretching vibration of sulphate (□□□SO_4^{2-} □□□□Also, a weak doublet observed in lower region (around 600 cm^{-1} and 670 cm^{-1}) due to in-plane bending (□□□SO_4^{2-} □□□and out-of-plane bending (□□□SO_4^{2-} □□□vibrations of sulphate [11] After 30 mins (at 1 day) , the ν_3 triplet merges to form a singlet at 1124 cm^{-1}. As time passes (28 days), the bands are absent. The changes suggest that the sulphate reaction is rapid between 30mins and 1day. The strong and broad band (Fig.5a) observed at 1110 cm^{-1} is characteristic of calcium sulfoaluminate (CSA) and a small peak at 641 cm^{-1} is due to CSA stretching vibration in CSAC

In 30mins **,** a strong and broad band around 926 cm^{-1} is due to asymmetric stretching vibration (□□□SiO_4^{4-}) of C_3S. In lower region a strong and sharp peak observed at 522 cm^{-1} is due to out-of-plane-bending (□□□SiO_4^{4-}) vibration of C_2S and a weak peak observed at 465 cm^{-1} is due to in-plane-bending (□□□SiO_4^{4-}) vibration of C_3S [12,13]. At 3.5 hours (Fig.5b), the band at 926 cm^{-1} shifts to a higher wave number at 966 cm^{-1}. This indicates that the control

indicates that the silicate polymerization and control gets strength and well coincide with the strength observation (Fig.3) [15]. As hydration time passes the □□□peak is totally consumed. In 28th day spectrum (Fig. 5f), the □□□and □□□band (465 and 990cm^{-1}) has strong intensity. decreasing trend in intensity is observed indicating the starting of fly ash's reaction. The relative intensity changes between ν_4 and ν_2 are also faster. In 28 days, the ν_2 and ν_3 bands (465 and 995 cm^{-1}) get an enhanced intensity than control. This may be due to higher rate of pozzolanic reaction with higher packing effect which increases the strength (Fig.3).

In effluent water hydrated control (Fig.7), the ν_3 silicate band shift from 925 cm^{-1} to higher wave number 982 cm^{-1} is stronger in intensity and the relative intensity variation between ν_4 and ν_2 silicate are also faster than DW control at 1 day (Fig. 5c). It indicates that the control paste gets faster setting and strength (Fig.2). After 7 days, the ν_2 and ν_3 silicate band has lesser intensity than (Fig.7d) DW control. This indicates that the EW control has a less strength than DW control and coincides with the compressive strength observation (Fig.4).

In effluent water hydrated fly ash blend (Fig.8), the ν_3 silicate band shift to higher frequency with intensity is lesser than EW control (1day to 7days) and also greater than DW fly ash blend. After 7 days, the ν_3 silicate band has a stronger intensity and the relative intensity changes between ν_4 and ν_2 band is faster than EW control.

C XRD Study

From the XRD patterns of fly ash admixtured CSAC, it is observed that (Fig.10(c-f)), as percentage of fly ash is increased, the intensity of C_3S peak increases up to 30% fly ash addition but decreases for 50% addition (diagram not provided) and the intensity of ye'elimite is also increased. The variation in intensity of the peaks observed for other phases (C_3S, C_2S, C_3A and C_4AF) is in accordance with fly ash addition.

On hydration, the XRD patterns recorded a reduction in intensity of peaks of main phases accompanied by an increase in intensity of peaks of their hydration by products.

The XRD patterns of hydrated FA free and FA admixtured CSAC at different time intervals with DW in a W/C of 0.4 are shown in Figs. 9 and 10. The 35 mins pattern (Fig. 9(a)) has peaks at $2\theta=30.51^\circ$(gypsum) and $2\theta=26.51^\circ$(C_3A). As time eludes the intensity of the peak at $2\theta=23.12^\circ$(ettringite) emerges and $2\theta=30.51^\circ$ and $2\theta=26.51^\circ$ observe a slight decreases. This is an evidence for the interaction between gypsum and C_3A phase. In the 3.5hour pattern (Fig. 9(b)) a sharp peak at $2\theta=47.05^\circ$ $Ca(OH)_2$ is seen. Peaks at $2\theta=23.12^\circ$ (d= 3.31) have increase the intensity. This suggest the ettringite formation. Hence this may be consider asfinal setting time [16,17]**.** This result supplements the IR studies. In 1 day XRD pattern (Fig. 9(c)) the peaks at $2\theta=29.38^\circ$ and $2\theta=31.34^\circ$ due to C-S-H and monosulphate respectively are found emerging where as the peak at $2\theta=23.12^\circ$ is decrease. The conversion of ettringite to monosulphate occurs. These are responsible for transforming the paste from stiffen to plastic. These peaks are observed to increase in intensity as time advances, implying the reaction proceeding faster. This period corresponds to the by product formation.

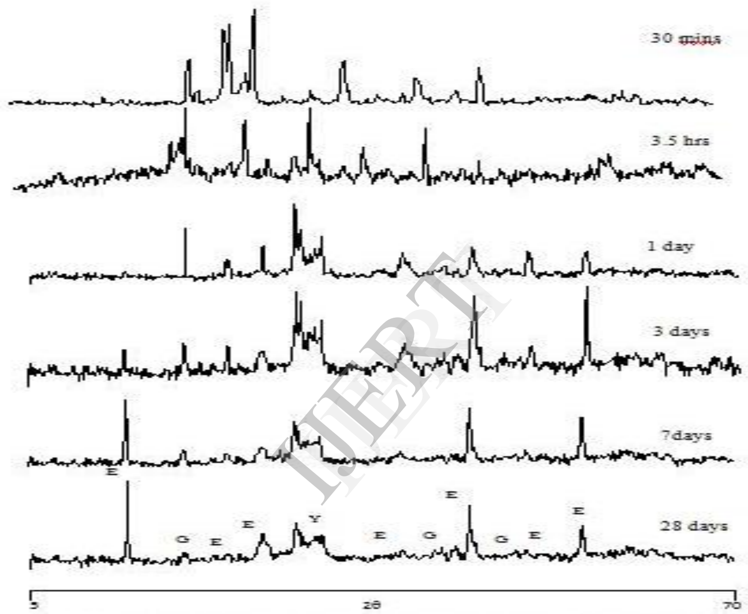

Fig.9. XRD pattern of CSAC hydrated with DW for (a) 30mins (b) 3.5hrs (c) 1d (d) 3d (e)7d (f) 28d

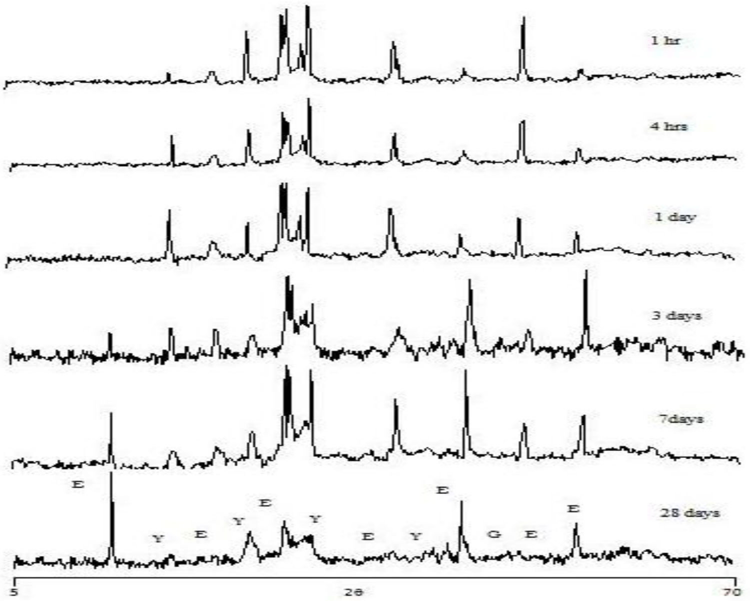

Fig. 10. XRD pattern of CSAC +30%FA hydrated with DW for (a) 1hr (b) 4 hrs (c) 1d (d) 3d (e)7d (f) 28d

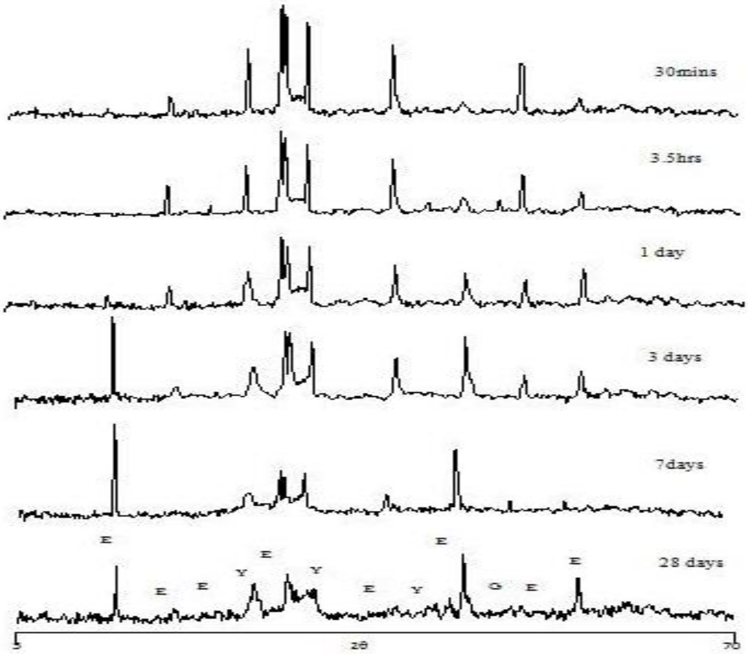

Fig. 11. XRD pattern of CSAC hydrated with EW for (a) 30mins (b) 3.5hrs (c) 1d (d) 3d (e)7d (f) 28d

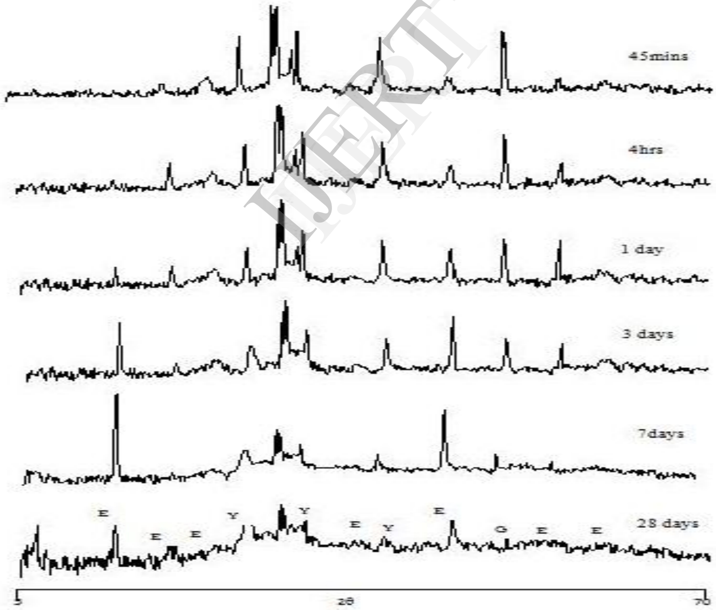

Fig. 12. XRD pattern of CSAC+30%FA hydrated with EW for (a) 45mins (b) 4hrs (c) 1d (d) 3d (e)7d (f) 28d

In 1 hour spectrum Fig.10(a) the calcium sulfoaluminate peaks at 2θ=33.8˚ and 2θ=41.7˚ are of medium intensity. As time proceeds, from 1 hour onwards the peak at 2θ=23.12˚ starts emerging. The SiO_2 peak also appears with less intensity at 2θ=26.6˚. This period corresponding to initial setting of cement paste.

In the 4th hour spectrum Fig. 10(b) the intensity of the peaks at 2θ=33.8˚ and 2θ=41.7˚ due to CSA have decreased. This may be attributed to the more reaction of calcium sulfoaluminate with gypsum resulting in higher production of ettringite, which is observed from the increase in intensity of the ettringite peak at 2θ= 23.12˚. The emerging of peak at 2θ= 47.05˚ due to Ca(OH)2. This result well supports IR observations. This period may correspond to final setting of cement paste. There is no change in intensity of SiO_2 peak. The intensity of the peak at 2θ= 32.26˚ and 2θ= 51.81˚ is little decreased compared to 1 hour.

The peak at 2θ=29.38˚ due to C–S–H is shows and CH at i day spectrum. The conversion of ettringite to monosulfate occuring in this stage observed from variation in peak intensity at 2θ=23.12˚ and 2θ=31.34˚. The CSA peak intensity at $2\theta=33.8^\circ$ and $2\theta=41.7^\circ$ is lesser than that of 4th hour hydration. This implies that the by product begins to form. Slight change in SiO_2 peak due to crystallisation of SiO_2 is observed.

In the 3 day pattern, peaks at $2\theta=32.26^\circ$ and $2\theta=51.81^\circ$ are less intense than in 1 hour, 4 hours and 1 day patterns Fig.10(d). CSA has almost been consumed at this stage which can be confirmed from less availability of its peaks at $2\theta=33.8^\circ$ and $2\theta=41.7^\circ$. The intensity of the peak at $2\theta=47.05^\circ$ (CH) has decreased marginally after one day with a corresponding marginal enhancing of C–S–H peak. This may be attributed to the presence of fly ash particle serving as an extra nucleation points for more hydration products to be precipitated.

The intensity of C_2S peak at $2\theta=32.26^\circ$ and $2\theta=51.81^\circ$ have a little variation, due to its less contribution for early hydartion. After one week, it undergoes reactions to yield more CH and C–S–H at a much slower rate than C_3S. It is quite possible that maximum products are obtained using C_3S within one week. The later period contribution to C–S–H and CH is mainly from C_2S and partly from C_3S [18,19,20]. The above qualitative analysis well supports the interpretation through IR absorption.

In the 28 days XRD pattern (Fig.10(f)) the intensity of the CH peak ($2\theta=18.1^\circ$ and $2\theta=47.05^\circ$) is well reduced than that of 7 days pattern (Fig.10(e)). This may be probably due to amorphous silica available in fly ash further reacting with calcium hydroxide to form additional C-S-H gel. This process is called as pozzolanic reaction. It is clearly observed in 4th week of hydration and there is every possibility of the reaction to be started occurring any where between 1 and 4th week. It is understandable that the physical presence of fly ash particle serving extra nucleation points for hydration also favours more products to be precipitated,. so higher strength is observed than that the control. The pozzolanic reaction is

$$CH + S \rightarrow C\text{-}S\text{-}H$$

For better comparison of the effects of different environment on CSA cement Effluent Water (EW) taken into consideration on hydration of CSAC and CASC+30% fly ash addition, the XRD pattern of pastes hydrated with EW water at different time intervals are shown in Figs.11 and Figs.12.

At 30mins, the silicate phases have not contributed to the formation of C–S–H and CH considerably. This can be evidenced from non appearance of $2\theta=47.05^\circ$ and $2\theta=18.10^\circ$ peaks and $2\theta=29.38^\circ$ peak. However the effects of water are visualised with the formation of early ettringite. The effluent water water which is rich in sulphate than distilled water, have given rise to higher ettringite crystallisation and is evidenced from relatively intense ettringite peaks with these waters as compared to distilled water. The CSA reacts faster with other reactants compared to DW treated samples.

At 3.5 hour in Fig.11(b) for EW, the C–S–H gel peak at $2\theta=29.38^\circ$ is seen. The production of ettringite at the above periods, leads final setting of cement system. The 1 day spectrum (Fig.11(c)) shows a variation in peak intensity i.e., peak at $2\theta=23.12^\circ$ decreases, while the peaks at $2\theta=31.34^\circ$, $2\theta=56.64^\circ$ and $2\theta=29.38^\circ$ increase for EW waters. This indicates the formation of C–S–H gel and conversion of ettringite to monosulphate. This conversion takes place earlier with EW than with DW paste. This may be attributed to the accelerating nature of EW owing to the presence of Na^+, K^+, Ca^+, SO_4^- etc.,

At 3days, all the XRD patterns exhibit CH Peak. The intensity of this peak ($2\theta=47.05^\circ$) is higher in paste made with GW followed by EW and DW. Though the hydration is accelerated in the presence of EW, the observed CH crystallization is lower. Carbonation also tends to lower $Ca(OH)_2$ amount, by forming $CaCO_3$. But it is rather difficult to confirm or rule out the presence of $CaCO_3$ in the hydrated samples, since some of the these peaks overlap with C_3S and C_2S peaks. However, the $Ca(OH)_2$ peak at $2\theta=18.1^\circ$ starts emerging from 1 day onwards.

At 7 days and 28 days of hydration, the intensity of C-S-H and CH peak has been reduced for all waters. This may be attributed to the effect of carbonation. The peak at $2\theta= 38.00^\circ$ is become visible as a shoulder at 28 days. This may be due to $Mg(OH)_2$ or due to traces of heavy metals present in the water. Hence the strength of paste get reduced. This is evidence from strength measurement. Also the reduction of strength compared to DW less by only 2.4%.

The XRD patterns of CSAC + Fly ash treated with EW is shown in Figs.12. In EWwater treated pastes, as percentage of fly ash increases, the acceleration effect is well pronounced up to 1 day. This may be due to presence of CSA in fly ash and yeelimite in the cement, whose amount increases as percentage of fly ash increases. Also the effect of water (acceleration than that of DW) seen up to 7days (peak intensity variation) may also be associated with various impurity ions (Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, Fe^{2+} etc.,) present in the water (Table.2.). These results are in favour of compressive strength and setting time observations. These observed compressive strength more or less equal to DW control sample at 28 days.

The pozzolanic reaction occurring between 7 and 28 days, is observed through intensity of CH and CSH peaks in 7 days(at intensity CSH peak and strong intensity CH peak) and 28 days (higher intensity CSH peak and lower intensity CH peak). This reaction is little faster with EW compared to DW treated samples.

Though EW have accelerated the hydration reactions, the compressive strength of EW sample are lower compared to DW treated samples at 28 days. This can be attributed to more C-S-H precipitated in DW treated pastes than in EW treated pastes. This fact is ascertained from more intense C-S-H peaks in DW pastes than in other pastes. The reduction in the C-S-H amount in EW may be attributed to the deleterious effects of impurity ions present in these waters. As C-S-H amount is lowered, correspondingly compressive strength of EW pastes get lowered. All this observations well coincide with compressive strength and observed IR results.

D Heat of Hydration

The heat evolved during the period of first 24 hours is determined using solution calorimetry. The rate of heat evolution is plotted for all samples CSAC and CSAC + 30% FA with DW and EW. From the curves (Fig. 13) it is observed that 30% percentage of fly is associated with (i) decrease in heat output **[**21], (ii) shortening of induction and dormant period, (iii) A slight shift of the peak (maxima) towards lower time scale (iv) diffusion in shape of the peak and (v) decrease in FWHM. All these observation showed an accelerating trend of the fly ash. As fly ash percentage increases the heat of hydration curve falls well below the baseline.

4 DISCUSSION

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.

$$4CaO.3Al_2O_3.SO_3 + 2(CaO.SO_3) + 38H_2O \rightarrow 6CaO.Al_2O_3.3SO_3.32H_2O + (Al_2O_3.3H_2O) \qquad (1)$$

The change in sulphate bands change indicate that the ettringite formation of the paste. It is indicative of early faster dissolution of gypsum and other alkali sulphates, and according to the equation (2).

The shift of water bands (lower to higher wave number) indicate that conversion of ettringite to monosulphate (equation 3).

$$3CaO.Al_2O_3+3CaSO_4.2H_2O+26H_2O \rightarrow \underset{\text{(Ettringite)}}{3CaO.Al_2O_3.3CaSO_4.32H_2O} \qquad (2)$$

$$3CaO.Al_2O_3+3CaO.Al_2O_3+32H_2O \rightarrow \underset{\text{(Monosulphate)}}{2(3CaO.Al_2O_3.CaSO_4.12H_2O)}+Ca^{2+}+SO_4^{2-}+8H_2O \qquad (3)$$

This also indicates that the control paste converting from plastic to hardened state and coincides with the setting time (Fig.1&2) [18]**.** The shift of silicate band (920 to 975cm^{-1}) indicate the formation of CSH and $Ca(OH)_2$ (equation 4 and 5) [16]**.**

$$2Ca_3SiO_5 + 6H_2O \rightarrow \underset{\text{(CSH-gel)}}{3CaO.2SiO_2.3H_2O} + 3Ca(OH)_2 \qquad (4)$$

$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO.SiO_2.3H_2O + Ca(OH)_2 \qquad (5)$$

In 30% fly ash blend has higher content of CSH due to elevated pozzolanic reaction. When fly ash is mixed with water, together with cement, it induces pozzolanic reaction, in which glass phase silica and alumina progressively react with $Ca(OH)_2$ formed by cement hydration, producing hydrates of CSH as given in eqn. 6.

$$2SiO_2 + 3Ca(OH)_2 \rightarrow \underset{\text{(CSHgel)}}{3CaO.2SiO_2 3H_2O} \qquad (6)$$

The reduction of $Ca(OH)_2$ (3640 cm^{-1}) with fly ash content (1110 cm^{-1}), while increasing CSH gel (995 cm^{-1}), is responsible for the formation of the structure of hardened cement. Therefore, in paste containing fly ash, the hydration of cement forms the hardened structure and the pozzolanic reaction of fly ash improves the structure, ensuring strength development at a long time.

Effluent water hydrated control, accelerates the early hydration due to chloride ions present in the EW. The $Ca(OH)_2$ content is slightly less after 7 days. It is due to the control paste being suffered by sulphate, magnesium ions etc., attack. Consequently, brucite (eqn.6), and recrystallisation of gypsum, ettringite (670 cm^{-1}) also formed [19]. It may cause the deterioration of the paste. Brucite produced by the reaction with Mg^{2+} ions and $Ca(OH)_2$.

This is seen as a small peak, as the main substance is CSAC. The effluent water hydrated fly ash (30%) composite has higher strength than EW control paste. This result is well supported with the earlier reports of Thiruppathi [22] who showed the blending fly ash in SRPC has higher strength than control and increased resistance against sea water. It may be due to chloride ion diffusion of paste decrease with increasing replacement of SRPC with fly ash. The decrease may be attributed to the change in pore size distribution, increasing CSH gel formation and increasing alumina level enabling more chloride to be fixed as

$$MgSO_4+Ca(OH)_2+2H_2O\rightarrow \quad Mg(OH)_2+CaSO_4+2H_2O \qquad (7)$$

Friedel's salt ($C_3A.CaCl_2.10H_2O$) [23]. This is why EW hydrated fly ash composite has lesser strength than DW hydrated fly ash blends composite but higher than EW control paste.
To support these observations, the chemical composition of lignite is given. Al: 34.72, Ca: 14, Cu: 12, Fe: 6, Mg: 4, Mn: 3, Na: 4, S: 14, Zn: 6.5, Si: 14.52 and other minor compounds are Ag, Cd, K, Pb, Ti<1. This composition favours the formation of CSA according to the above equation. The hydration of CSA leads to the rapid formation of ettringite. The ettringite formation depending on the portlandite present ($Ca(OH)_2$) in the system.

If excess calcium hydroxide is present along with excess sulfate, yet a new reaction could occur giving a higher yield of ettringite. It is the reaction that occurs with cement.

$$3CaO.3Al_2O_3.CaSO_4+ 8CaSO_4 + 6Ca(OH)_2 + 90H_2O \rightarrow 3[3CaO.Al_2O_3.3CaSO_4.32H_2O] \qquad (9)$$

$$3CaO.3Al_2O_3.CaSO_4+2CaSO_4+38H_2O\rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O+4Al(OH)_3 \qquad (8)$$

These above reactions occur within one day and hence accelerate the initial hydration.

During the initial stage a problem which has been encountered during the calorimetry study is associated with the base line. CSAC containing large amount of fly ash, the curves were below the baseline after the initial heat output. This suggest that an endothermic reaction is dominating the exothermic reactions normally associated with cement hydration. This phenomenon is also be referred in the literature [19-21 and 24]. These processes are associated with two effects: one is the evaporation of excess water and second, the dissolution of C_3S. The excess water might evaporate thereby removing excess of heat initially and exothermic hydration reactions dominate. Alternatively an endothermic process possibly favours the dissolution of C_3S, may dominate during the part of induction period and endothermic effect is most apparent in the CSAC systems and all these observations well supported by XRD analysis.

5 CONCLUSION

- The use of FA in CSAC 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 hydrated cement phases appeared to synergistically contribute to a dense microstructure. Accumulated heat outputs and later strengths reached higher values than those of the pure. The incorporation of FA in the CSAC appeared to be more mechanically beneficial than that of pure form of CSAC. In the very early hydration stages and this was detectable by FTIR and XRD.
- In the CSAC systems the EW control has faster setting because of the formation of higher amount ettringite than DW control. Fly ash blend reduces cementitious materials and hence slows the hydration and less strength at early periods. After 7 days, pozzolanic activity of DW hydrated fly ash blend produces more amount of CSH than control. EW hydrated fly ash composite also has higher strength (28 days) than EW control. The 30% fly ash is a suitable percentage against sulphate attack as well as strength gain in CSAC later ages with water consumption through aggressive environment. It seems that suitable addition of fly ash and reduction of chloride ions concentration may bring an equivalent paste that of CSAC both in character and strength.

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