



Effect of Fly Ash and Water in Hydrated Srpc-A Ftir Study

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Abstract

The present investigation, deals with the study of both hydrated Sulfate Resisting Portland Cement (SRPC) and fly ash (fly ash 20%, 30% and 50%) composite with two different waters. Among the three percentages of fly ash addition, 30% addition is found to be optimum. The samples (SRPC and 30% fly ash) were analyzed using the Fourier Transform Infrared Spectroscopy (FTIR) spectra. The relationship between compressive strength and molecular vibration changes were discussed using FTIR spectra. Also, the setting time is identified with the FTIR spectra and proper explanation with available literature for the kinetics is presented. It is inferred that increasing the fly ash concentration reduce the setting time. This is due to the calcium sulfoaluminate (CSA) present in the fly ash. Result of this study indicates that the blended paste better perform than the control paste hydrated with distilled water and effluent water.

Keywords: Fly ash, Cement, FTIR, Hydration, Setting

1. Introduction

Cement is an energy-intensive component of concrete. The unit cost of concrete can be reduced either by addition or partial replacement of cement with fly ash (Rafat Siddique, 2004). Recently the use of fly ash has dramatically increased due to an increase in environmental awareness and durability.

The ASTM C 595 define pozzolan as, “a silicious or silicious and aluminous materials, which itself possess little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with $\text{Ca}(\text{OH})_2$ at ordinary temperature to form compounds possessing cementitious properties (pozzolanic activity)”. Fly ashes mainly consist of SiO_2 , Al_2O_3 , Fe_2O_3 and CaO and some impurities. According to ASTM C 618, fly ash belongs to class C if $(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) > 70\%$. Usually class C fly ashes have a higher content of CaO and exhibit pozzolanic properties (Papadakis and Tsimas, 2002).

The variations in the property of the fly ash blended system through different concentrations under Indian condition are meager. Also the utility of the effluent water in the mixture is of considerable interest. The use of FTIR better characterize the amorphous and poorly crystalline phases that occur in the blended cement. Hence, the present study is aimed at in evaluating the performance of fly ash in blended cement paste using distilled water (DW) and Effluent water (EW) and finds the relationship between compressive strength and molecular vibrational changes.

2. Materials and Methods

ASTM Type V Sulfate Resisting Portland Cement (SRPC) and Fly ash (FA) collected from Neyveli Lignite Corporation, Neyveli, Tamil Nadu, India were used in this study and their chemical analysis are given below.

Composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O	K ₂ O	LOI	Others
SRPC	65.08	22.20	3.47	4.08	1.25	0.88	0.27	0.76	1.90	0.11
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 was mixed with SRPC in 20%, 30% and 50% quantity on weight addition basis. The control (SRPC) and blended samples (with fly ash) were hydrated with distilled water and effluent water in a water to solid ratio of (w/s) 0.4 at different intervals like 1hour, setting times, 1day, 7days, 28days.

The pelletised sample with KBr was made use of for recording FTIR spectra ($4000\text{--}400\text{ cm}^{-1}$) using Perkin Elmer-RX1 FTIR spectrometer available at Centralised Instrumentation and Service Laboratory (CISL), Annamalai University. Setting time and compressive strength of DW and EW pastes were carried out using ASTM C 191 and 109 procedure and the results are given in figure 1 and 2 (Lee and Van Deventer, 2002 and Natalaya Shannhan and Aba Zayed, 2007).

3. Results and Discussion

3.1 Setting time and Compressive strength study

Figure 1 and 2 shows the setting time and compressive strength of SRPC and fly ash composites (DW and EW). From the figure, the fly ash composite (20%, 30% and 50%) has a shorter setting time than the SRPC. This is due to $\text{C}_4\text{A}_3\text{S}$ which is responsible for producing more ettringite and ertringite to monosulfate conversion and also CSH gel. Hence strength of the paste at early age is increased. The result coincides well with the many observers (Malhotra and Ramezianpour, 1994, Raungrut Cheerarat and Chai Jaturapitakkul, 2004). The EW hydrated pastes have quick setting than DW due to the presence of accelerating ions in EW (Ghorab et al., 1990). The compressive strength of SRPC performs better than SRPC blend up to 7th days of hydration. This suggests that fly ash do not contribute notably for early strength development of the cement system. The results after 28th day indicate that there is a continuous and significant improvement in strength in the case of SRPC blend. This increase in strength may be due to the continuous production of CSH, the inert nature of fly ash particle and hence pozzolanic activity. The effluent water hydrated samples get an accelerating trend in early periods (up 7 days). At 28 days, the strength of EW control paste decreases whereas the strength of DW fly ash blend increases. From the result 30% fly ash blend gives a maximum compressive strength and hence it has been investigated through FTIR.

3.2 FTIR study

The spectra of Distilled water (DW) and effluent water (EW) hydrated Control (SRPC) and blended cement (SRPC+30 %FA) are shown in the Fig.3-6.

3.2.1 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 3. In 1 hour spectrum (Fig.3a), a medium intensity band around 3428 cm^{-1} and 1640 cm^{-1} may be assigned to the ν_1 and ν_2 water stretching and bending vibration respectively. A shoulder is emerging at 3640 cm^{-1} may be due to the formation of $\text{Ca}(\text{OH})_2$ (Abdul Aziz A Khalil, 1982). At 8th hour (Fig.3b), the ν_1 and ν_2 water bands are having a stronger intensity with a shift to higher wave number around 3430 cm^{-1} and 1642 cm^{-1} . The $\text{Ca}(\text{OH})_2$ peak is strong and sharp at 3640 cm^{-1} . At 15 hour (Fig. 3c) a growth in ν_1 and ν_2 bands and $\text{Ca}(\text{OH})_2$ are observed. As hydration time passes, the $\text{Ca}(\text{OH})_2$ peak increases in intensity up to 7th day (Fig.3e) and there after a constant intensity is observed. The ν_1 and ν_2 bands have a broad and strong intensity up to 28th day.
- In 1hour, a strong band near 1440 cm^{-1} is assigned to asymmetric stretching vibration of carbonate ($\nu_3\text{ CO}_3^{2-}$) band. After 1hour (up to 7th day), the ν_3 band at 1440 cm^{-1} has an increasing intensity and a new peak is observed (1day) at 873 cm^{-1}

due to out-of-plane bending vibration ($\nu_4 \text{CO}_3^{2-}$) of carbonate. The carbonation reactions are rapid but later (28th day) almost constant (Van Gervan, 2004).

- In 1 hour, a strong triplet band appearing between 1105 and 1137 cm^{-1} can be assigned to asymmetric stretching vibration of sulphate ($\nu_3 \text{SO}_4^{2-}$). Also, a weak doublet observed in lower region (around 600 cm^{-1} and 670 cm^{-1}) are due to in-plane bending ($\nu_2 \text{SO}_4^{2-}$) and out-of-plane bending ($\nu_4 \text{SO}_4^{2-}$) vibrations of sulphate (Rai and Singh, 2005). After 1 hour (at 15 hour), the ν_3 triplet merges to form a singlet at 1124 cm^{-1} . As time passes (28th day), the bands are absent. The changes suggest that the sulphate reaction is rapid between 1 hour and 1 day.

- In 1 hour, a strong and broad band around 925 cm^{-1} is due to asymmetric stretching vibration ($\nu_3 \text{SiO}_4^{4-}$) of C_3S and a medium intensity peak observed at 846 cm^{-1} is due to C_2S . In lower region a strong and sharp peak observed at 520 cm^{-1} is due to out-of-plane-bending ($\nu_4 \text{SiO}_4^{4-}$) vibration of C_2S and a weak peak observed at 465 cm^{-1} is due to in-plane-bending ($\nu_2 \text{SiO}_4^{4-}$) vibration of C_3S (Ghosh and Handoo, 1980, Mollah et al., 2000). At 15th hour (Fig.3c), the band at 925 cm^{-1} shifts to higher wave number at 970 cm^{-1} which indicate control gets setting (Fig.1a) (Mollah et al., 1999). From 1 day spectrum (Fig.3d), the ν_3 band grown stronger in intensity. At 28th days (Fig.3f), the ν_4 peak (520 cm^{-1}) decreases whereas the ν_2 peak (465 cm^{-1}) increases in intensity. The relative intensity change between ν_4 and ν_2 peak is faster. It indicates that the silicate polymerization and control gets strength and well coincide with the strength observation (Fig.1b) (Mollah et al., 1999). As hydration time passes the ν_4 peak is totally consumed at 180th day. In 28th day spectrum (Fig. 3f), the ν_2 and ν_3 band (469 and 990 cm^{-1}) has strong intensity.

3.2.2 Hydrated FA Blends SRPC

Comparing the figures 3-6, the hydration reaction of 30%FA blends (Fig.4) and EW pastes (Figs.5 and 6) seems to be similar as that of DW control with a variation in reaction rate which are given below.

The strong and broad band (Fig.4a) observed at 1110 cm^{-1} and a small peak at 641 cm^{-1} are due to $\nu_3 \text{SiO}_4^{4-}$ and CSA stretching vibration of characteristic fly ash band (Benarchid et al., 2005 and Cheng Xin et al., 2001, Malhotra and Ramezani-pour, 1994). From 7th day (Fig.4e), the $\text{Ca}(\text{OH})_2$ peak gets a decrease in intensity, which may be due to starting of pozzolanic reaction of fly ash. The $\text{Ca}(\text{OH})_2$ peak is totally consumed within 28th day (Fig.4f) spectrum. The water bands (ν_1 and ν_2) have a higher intensity up to 28th day.

The carbonate bands are in increasing trend up to 7th day (Fig.4e) and beyond the band reduce in intensity as time elapses. The sulphate bands (ν_2 and ν_4) doublet merges to form a singlet exhibiting the setting of the blend. This result coincides with setting time observation (Fig.1b). After 1 day (Fig. 4d), the ν_2 and ν_4 peaks has continuous decreasing in intensity similar as that of SRPC.

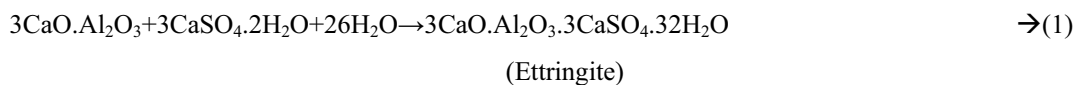
At 9th hour the ν_3 silicate band shifts to higher wave number with higher intensity than control. The characteristic fly ash band (at 1110 cm^{-1}) gets a stronger intensity up to 7th day (Fig.4e) spectrum. After 7th day a decreasing trend in intensity is observed indicate the starting of fly ash's reaction. The relative intensity changes between ν_4 and ν_2 are also faster. In 28th day, the ν_2 and ν_3 bands (465 and 990 cm^{-1}) gets an increased intensity than control. This may be due to higher rate of pozzolanic reaction with packing effect which increases the strength (Fig.1b).

In **effluent water hydrated control** (Fig.5), the ν_3 silicate band shifts from 925 cm^{-1} to higher wave number 985 cm^{-1} and is stronger in intensity and the relative intensity variation between ν_4 and ν_2 silicate are also faster than DW control at 7th day (Fig.5d). It indicates that the control paste gets a faster setting and strength (Fig.2a). After 7th day, the ν_2 and ν_3 silicate band has lesser intensity than (Fig.5d) DW control. This indicates that the EW control has a lesser strength than DW control and coincides with the compressive strength observation (Fig.2b).

In **effluent water hydrated fly ash blend** (Fig.6), the ν_3 silicate band shifts to higher frequency with intensity lesser than EW control (1day to 7th day) and also greater than DW fly ash blend. After 7th day, 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.

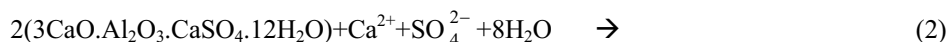
4. Discussion

The sulphate band 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 (1).



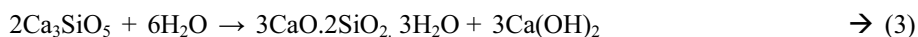
The shift of water bands (lower to higher wave number) indicates that conversion of ettringite to monosulphate (equation 2).



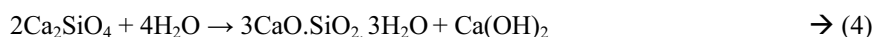


(Monosulphate)

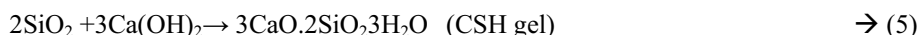
This is indication of the control paste being converted from plastic to hardened state and coincides with the setting time (Fig.1&2) (Tong Liang and Yang Nantu, 1994). The shift of silicate band (920 to 975 cm^{-1}) indicates the formation of CSH and $\text{Ca}(\text{OH})_2$ (equation 3 and 4) (Puertas and Fernández-Jiménez, 2003).



(CSH-gel)



30% fly ash composite (Fig.4f) has higher content of CSH due to the 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 $\text{Ca}(\text{OH})_2$, forming hydrates of CSH as given in eqn. 5.



The reduction in $\text{Ca}(\text{OH})_2$ with fly ash content, increases the CSH gel, are 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 longer time.

In effluent water control, the early hydration is accelerated due to chloride ions present in the EW. The $\text{Ca}(\text{OH})_2$ content is slightly less after 7 day. It is due to the control paste had suffered sulphate, magnesium ions etc., attack. Consequently, brucite (eqn.6), and recrystallisation of gypsum, ettringite (670 cm^{-1}) are also formed (Lee et al., 2005). It may cause the deterioration of the paste. Brucite is produced by the reaction with Mg^{2+} ions and $\text{Ca}(\text{OH})_2$.



The effluent water hydrated fly ash (30%) composite has higher strength than EW control paste. This result is well supported by the earlier reports of Sunil Kumar (2000) who showed that the blending fly ash in OPC has higher strength than control and increased resistance against sea water. This may be due to chloride ion diffusion of paste decreases with increasing replacement of OPC. The decrease may be attributed to change in pore size distribution, increasing CSH gel formation and increasing alumina level enabling more chloride to be fixed as Friedel's salt ($\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$) (Leng et al., 2000). EW hydrated fly ash composite has lesser strength than DW hydrated fly ash blends composite but higher than EW control paste.

5. Conclusion

The EW control has faster setting because of the formation of higher amount of ettringite than DW control. Fly ash blend reduces cementitious materials and hence slow hydration and less strength at early periods. After 7th day, 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 SRPC. It seems that suitable addition of fly ash and reduction of chloride ions concentration may bring an equivalent paste that of SRPC both in character and strength.

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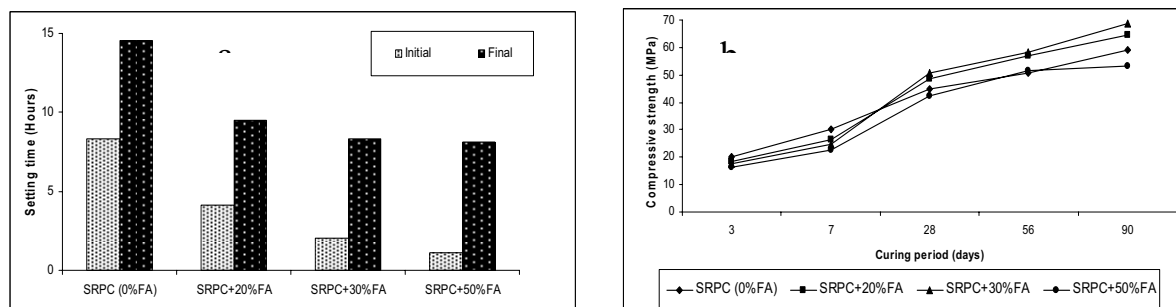


Figure 1. (a) Setting time and (b) Compressive strength of DW-Control and blended SRPC

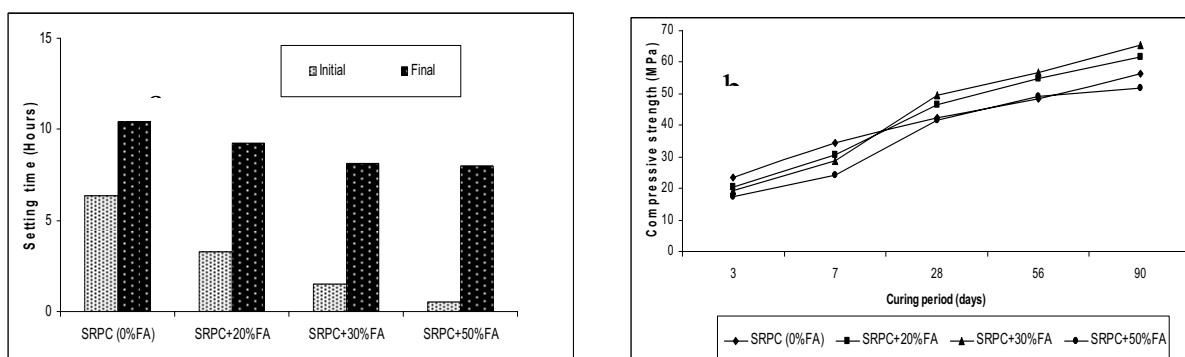


Figure 2. (a) Setting time and (b) Compressive strength of EW-Control and blended SRPC

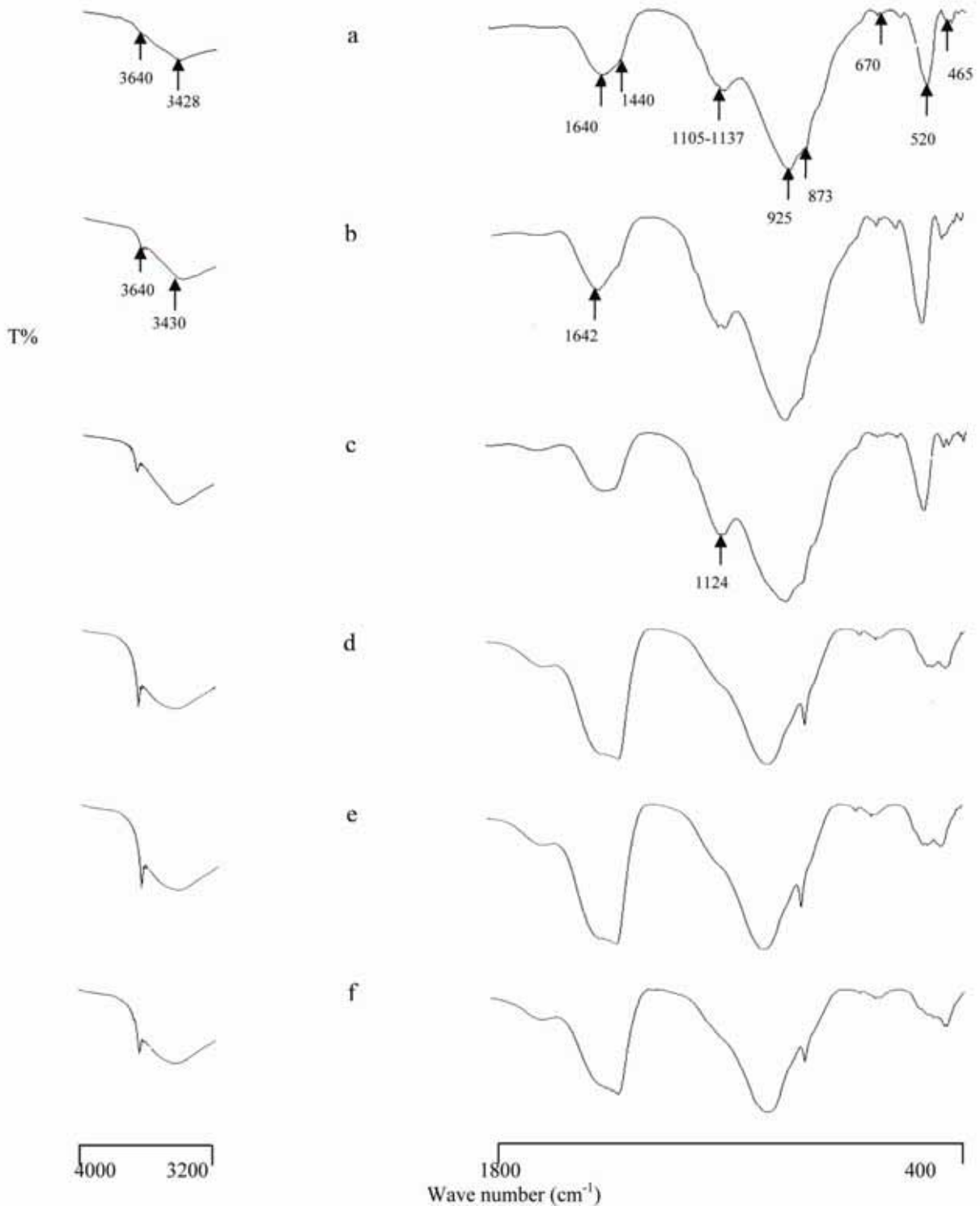


Figure 3. FTIR spectra of SRPC hydrated with DW for (a) 1 hour (b) 8 hours (c) 15 hours (d) 1 day (e) 7 days (f) 28 days

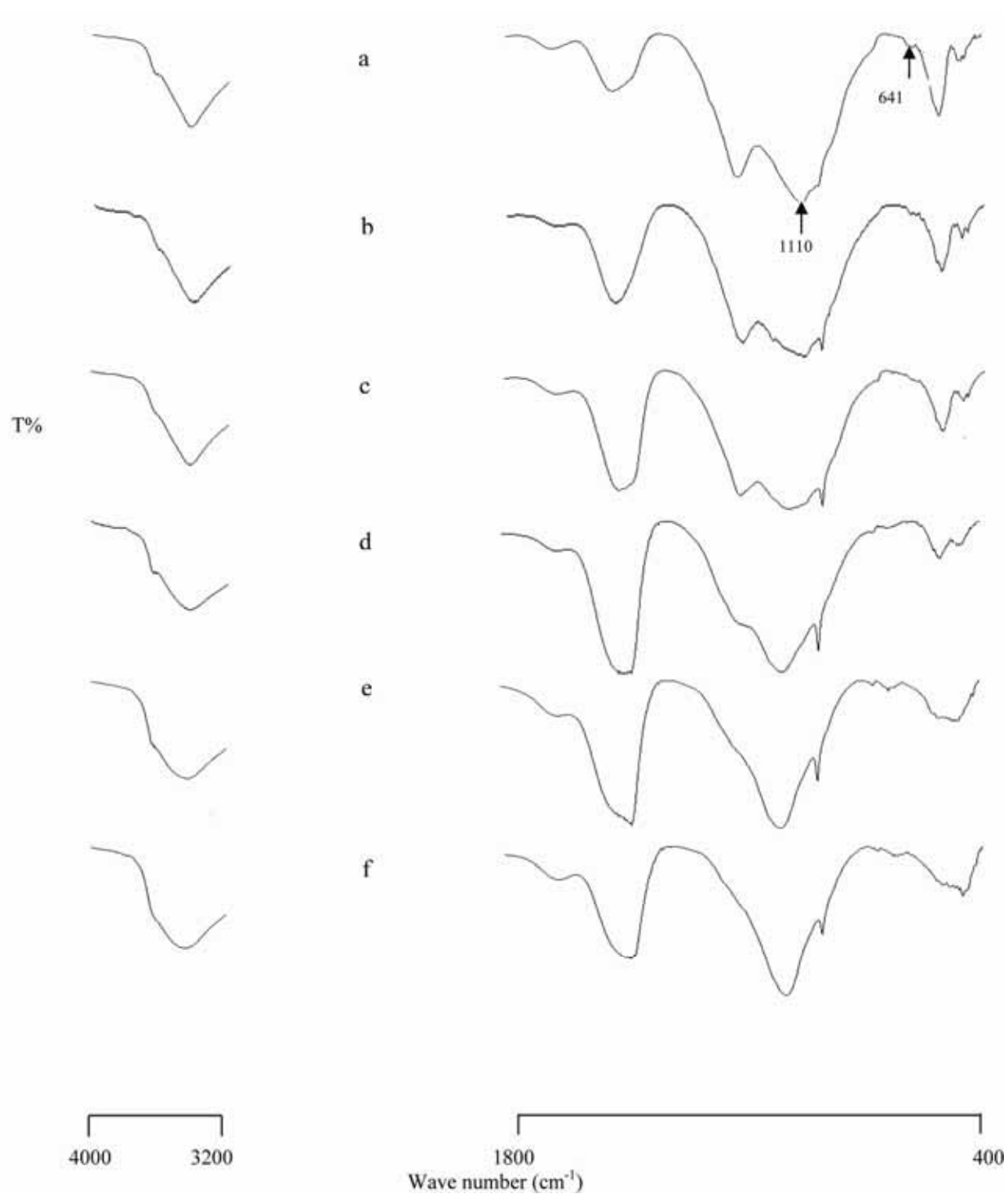


Figure 4. FTIR spectra of SRPC +30%FA hydrated with DW for (a) 1 hour (b) 2 hours (c) 9 hours (d) 1 day (e) 7 days (f) 28 days

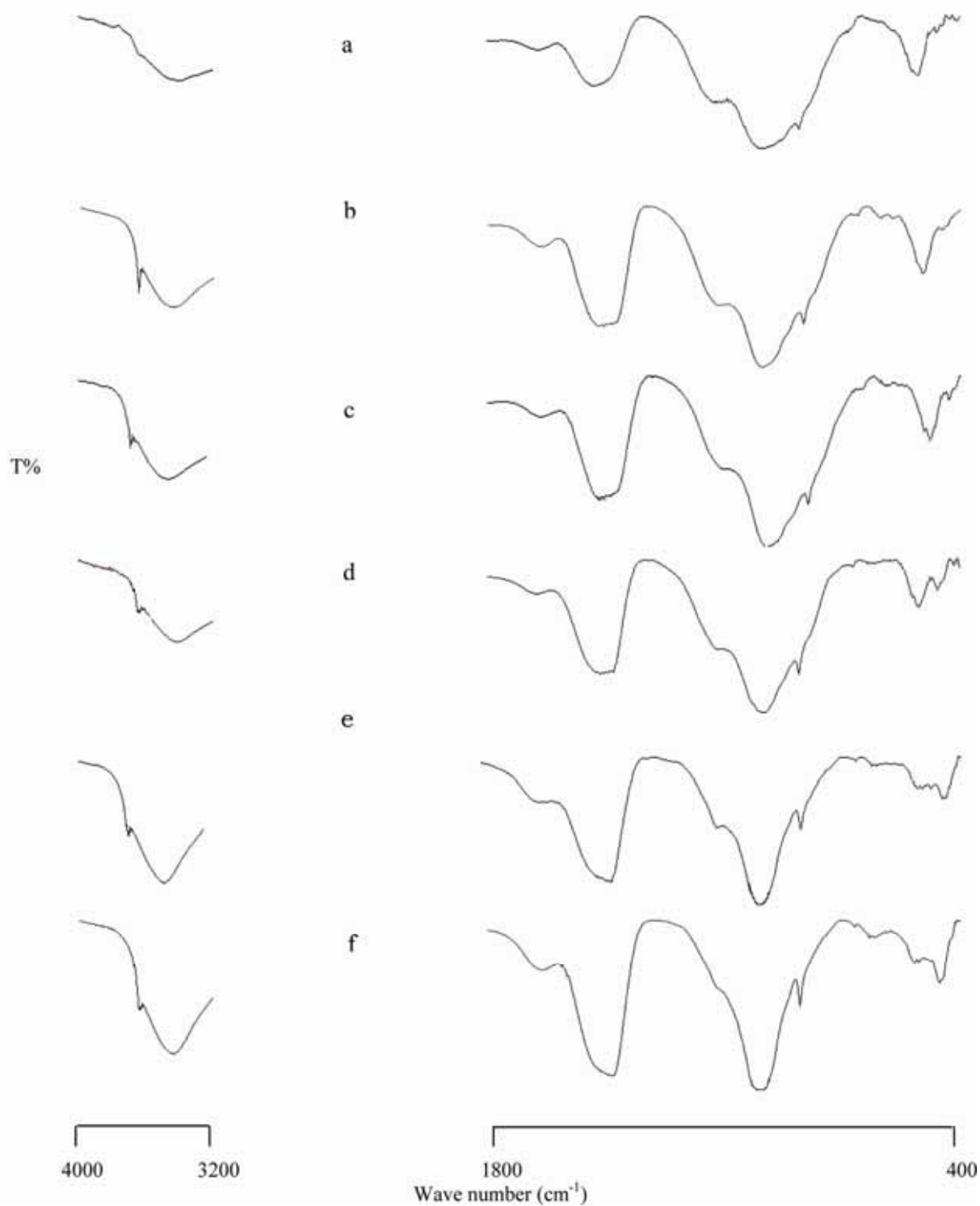


Figure 5. FTIR spectra of SRPC hydrated with EW for (a) 1 hour (b) 6 hours (c) 11 hours (d) 1 day (e) 7 days (f) 28 days

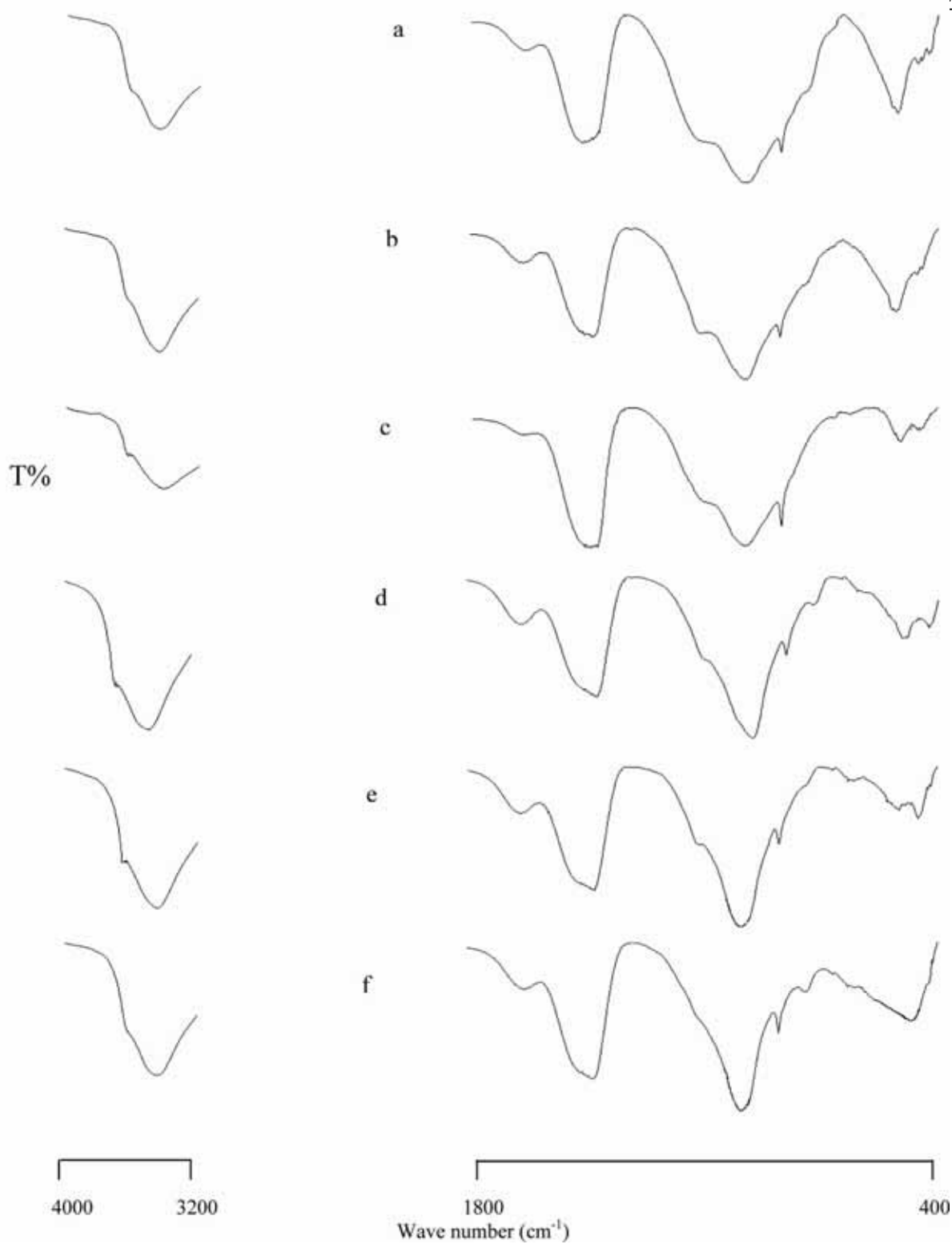


Figure 6. FTIR spectra of SRPC +30% hydrated with EW for (a) 1 hour (b) 2 hours (c) 8 hours (d) 1day (e) 7 days (f) 28 days