Dielectric and Spectroscopic Studies
of A Fly Ash Blended Cement Paste

K.Thiruppathi

Department of Physics, AMET University

Chennai, TamilNadu, India

E-mail: thiruraj_ka@rediffmail.com

S.Barathan (Corresponding author)

Department of Physics, Annamalai University

Annamalainagar 608 002, Tamilnadu, India

E-mail: sbarathan_au@rediffmail.com

N.Anandhan

Department of Physics, SRM University

Chennai, 603 203, Tamilnadu, India

E-mail: anandhan_kn@rediffmail.com

D.Govindarajan

Department of Physics, Annamalai University

Annamalainagar 608 002, Tamilnadu, India

E-mail: degerajan@yahoo.com

Abstract

The dielectric constant (ε') of Sulfate Resisting Portland Cement (SRPC) blended with 30% of fly ash by addition is measured using microwave bench at 9.54 GHz, for initial 30 hours of hydration. The heat of hydration for the same blend using heat of solution calorimetry is also measured. It is observed that contrary to the usual trend of retarding of fly ashes, it shows an accelerating trend with increasing strength as times passes. SEM micrographs and XRD patterns are also recorded and observed that $C_4Al_2SO_{16}$ ($C_4A_3\bar{S}$) is found to be responsible for the accelerating trend of the mix. The hydration process in the early period is studied and it is suggested that suitable retarder should be adopted for the effective utilization.

Cement chemistry notations: C=CaO, A=Al_2O_3, $\bar{S}$=SO_3, H=H_2O, F=Fe_2O_3, S=SiO_2

Keywords: Composite materials, Dielectrics, Electrical properties, SEM, X-ray technique

1. Introduction

Industrial waste by-products create acute environmental problems. Their utilization in industry or in market sector may bring economical and ecological benefits, and impart technological developments. Fly ash is one such by-product possessing hydraulic and pozzolanic properties. It is used as an admixture along with cement and is having its own value in cement industry (Chai *et al*., 1999). Sulfate Resisting Portland Cement (SRPC) having a low value of alumina, reduces expansive product forming as well as sulfate attack. The short comings developed if any, by utilization of fly ash can be overcome by using a third or even fourth pozzolan into the system (Theerawat *et al*., 2006).

Generally, fly ash when mixed with OPC retards the reaction and develops more strength as day passes (Zhang *et al*., 1998). The fly ash chosen for the present study accelerates the reaction, and increases the strength with increase of time.

This peculiar behavior of the fly ash is interesting and needs a scientific approach. Since, such studies on fly ashes blended with SRPC are seem to be rarer, the authors have under taken the present work.

Cement paste is a high dielectric loss material. In the microwave range the dielectric losses due to moisture and water are much larger than that due to formation of hydrates (Yoon *et al.*, 1996). Since, microwave technique needs no electrodes it is preferred in this study along with XRD and SEM for conformation. The authors have made an attempt to study the blending of such a fly ash, with commercial SRPC hydrated with deionized water and the hydration process in terms of dielectric properties for first 30 hours. This helps to understand the behavior of this particular fly ash.

2. Materials and Method

Indian made commercial SRPC and fly ash collected from Neyveli Lignite Corporation, Neyveli, Tamil Nadu, India are used. The contents of SRPC and fly ash after chemical analysis in percentage are CaO 65.08; SiO_2 22.20; Al_2O_3 3.47; Fe_2O_3 4.08; MgO 0.88; SO_3 1.25; LOI 1.90 and CaO 7.64; SiO_2 53.38; Al_2O_3 27.40; Fe_2O_3 3.04; MgO 4.03; SO_3 1.69; LOI 1.70 respectively. Using Bogue's calculation major phases calculated in percentage are C_3S 63.44; C_2S 15.88; C_3A 2.30; C_4AF 12.40.

Necessary amount of SRPC and fly ash are mixed in a proportion of (SRPC: Fly ash) 100:0, 95:5, 90:10, 85:15, 80:20, 75:25, 70:30 and 50:50% by addition, and mixed well with a mini vibrator. The mixture is hydrated with DW and made to a paste. Consistency, workability and flowability of the blended system were measured for all concentrations of fly ash addition. Though all the fly ash additions are studied the 30%addition is presented for the discussion in the present article as it is found to be more suitable and optimum. Using Vicat's apparatus, the initial and final setting times are determined (Fig. 1) adopting usual procedure (Shetty., 2004).

Investigation on hydration of SRPC plus fly ash blend using the microwave technique has been carried out using Vidyut Yantra X-band microwave bench coupled with a Computer available at PG and Research Department of Physics, Pachaiyppa's College, Chennai, Tamil Nadu, India. Its working principle has been explained elsewhere (Barathan *et al.*, 2006).

The blended paste is filled in the sample holder and butted against polystyrene to avoid leakage if any. The measurements are made during the first 30 hours of hydration at a frequency of 9.54 GHz which has been selected after a pilot study. The first measurement was carried out after 5 minutes from the start of hydration and is taken as zero. Further measurements are noted within 5-10 minutes during first 10 hours and then at an interval of 0.5-2 hours over the next 20 hours. With the help of these observations, the real part of dielectric constant (ε') are computed using C++ program. Measured values on both control and 30% fly ash blend are given as plots in Figure.2. It's imaginary part (ε'') is calculated and it is related to its electrical conductivity, σ, by the formula $\sigma = \varepsilon_0\varepsilon''\omega$, where ε_0 is the dielectric constant in vacuum and ω is the angular frequency. The computed conductivity values are plotted against the hydration time, and the representative curves are portrayed in Figure.3.

In order to substantiate the obtained results for 30%fly ash addition, heat of hydration is also measured using heat of solution calorimetry, following the methods suggested by Verbeck and Foster, and ASTM committee (Verbesk and Foester., 1949, ASTM committee., 1987). The results are plotted and given in Figure.4. The XRD analysis is carried out with PANalytical, X-ray diffractometer using Cu-K radiation available at NIIST Thiruvanathapuram, Kerala, India and the patterns are presented in Figure.5. The SEM micrographs are recorded using JEOL-SEM, model, JSM-5610 available at CISL, Annamalai University, Annamalai Nagar, Tamil Nadu, India and reported in Figure.6. The samples for these two studies were prepared as per the method described elsewhere (Sharma *et al.*, 1999)**.**

3. Results and Discussion

From the Figure.4 it is observed that 30% fly ash addition is associated with (i) decrease in heat output (ii) shortening of induction and dormant periods (iii) slight shift of the exotherm (maxima) towards lower time scale (iv)diffusion in shape of the peak and (v).decrease in FWHM. All these observations show an accelerated hydration of the blend than control (SRPC). The result through Vicat's test for setting time confirms these results.

From the Figure.2 it can be noticed that, upon addition of fly ash a drop in initial value of dielectric constant (ε') occurs. The time taken to attain a minimum from its initial value changes and hence the respective slope value decreases. The variation in rate of decrease of ε' in the duration 1–4 hours and rapid decrease between 4 and 15 hours depend on the percentage of fly ash. After 15 hours a linear change in ε' is noticed. Near the initial setting time, the ε' curve forms a slight shallow.

From Figure.3 it is inferred that with 30% fly ash the initial values of σ, become less compared to SRPC and increase up to 1 hour of hydration to reach a maximum value. After 1 hour of hydration, σ values decrease. During 4-10 hours of hydration, the decrease in σ is rapid and a linear variation in σ values is found. The observed shallow coincides with initial setting.

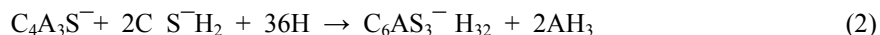In XRD pattern of fly ash (Fig.5), peaks at 2θ=33.8 and 41.7 are characteristics of $C_4A_3\overline{S}$ (Benarchid *et al.*., 2005, Malhotra *et al*., 1994). Upon hydration, as time increases the peak intensity decreases remarkably after setting time.

From SEM micrograph (Fig.6) just before the initial setting time (8hour), needle like ettringite crystals are observed in control paste. As the fly ash is added, this occurs earlier (2hour), indicating early setting.
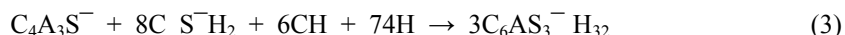
Fly ash under investigation contains $C_4A_3\overline{S}$ phase (Malhotra *et al*., 1994) as it is evidenced from XRD. During burning the lignite coal at around 1200ºC in presence of high pressure CSA is formed. The composition of lignite is Al:34.72, Ca:14, Cu:12, Fe:6, Mg:4, Mn:3, Na:4, S:14, Zn:6.50, Si:14.52 and other minor compounds are Ag, Cd, K, Pb, Ti<1. From this composition, CSA is formed as per the equation

$$3CaCO_2 + 3Al_2O_3 + CaSO_4.2H_2O \rightarrow C_4A_3\ \overline{S} + 3CO_2 + 2H_2O \qquad (1)$$

The hydration of $C_4A_3\overline{S}$ is a rapid reaction with gypsum which induces formation of needle like ettringite crystals. The exact reactions in the absence and presence of calcium hydroxide are given below:

$$C_4A_3\overline{S} + 2C\ \overline{S}H_2 + 36H \rightarrow C_6A\overline{S}_3\ H_{32} + 2AH_3 \qquad (2)$$
$$\text{Ettringite}$$

$$C_4A_3\overline{S} + 8C\ \overline{S}H_2 + 6CH + 74H \rightarrow 3C_6A\overline{S}_3\ H_{32} \qquad (3)$$
$$\text{Ettringite}$$

The sulfate present both in SRPC and fly ash produces ettringite and this is similar to the presence of yeelimite in sulfoaluminate cement (Péra and Ambroise, 2004), which is responsible for quick hydration. Hence, as fly ash is added the reaction gains momentum reducing the dormant period. It is evidenced from heat of hydration curve (Zhi Ge).

The hydration kinetics of the system can be categoriesed into four stages (Jawed *et al*., 1983, Mindess *et al*., 1981, Zhang *et al* 1998)**.** The first stage falls up to 1 hour from the moment of mixing water. The instant the water is in contact with cement or blend, the following reactions occur and the ettringite gets formed.

$$C_3S \rightarrow C_2S + Ca^{2+} + OH^- \qquad (4)$$

$$C_3A + 6H + 3\overline{CSH_2} \rightarrow 6Ca^{2+} + 2Al(OH)^-_4 + 3SO_4^{2-} + (OH)^- \qquad (5)$$
$$6Ca^{2+} + 6H + 2Al(OH)^-_4 + 3SO_4^- + (OH)^- \rightarrow C_6\overline{AS}_3H_{32} \qquad (6)$$
$$\text{(Ettringite)}$$

In this stage most of the ions like Al^{3+}, Ca^{2+}, Si^{4+} are unbound charges in the aqueous phase. Leaching of ions from calcium silicate and tricalcium aluminate to the grain surface results in a large dielectric constant and electrical conductivity. As time passes, the contribution of ion concentration increases and decrease the ε' rapidly. This is true for both control as well as blended system.

The CSA present in the FA acts more rapidly than all the other phases. While hydrating there is every possibilities of detachment of calcium aluminium sulphate thereby forming products quickly. Hence, the decrease in ε' is very rapid and a lower value than SRPC control result. This can be given by the equation (7 & 8).

$$C_4A_3\ \overline{S} + 2\overline{CSH_2} + 36H \rightarrow C_6\overline{AS}_3H_{32} + 2AH_3 \qquad (7)$$

$$C_4A_3\ \overline{S} + 8\overline{CSH_2} + 74H + 6CH \rightarrow 3C_6\overline{AS}_3H_{32} \qquad (8)$$

Stage II The period form 1 – 4 hour can be considered as stage II and this is usually called as induction period. The continuous production and occupation of Ca^{2+} make its concentration increases, attain a super saturation level which makes a decrease of both ε' and σ. A hydro silicate rich solution and cement grains slows down the hydration by forming a electrical double layer, in the case of control. Where as in the blended system as CSA activates the reactions the thickness of the double layer will be higher and further delay the wandering there by reducing further ε' and σ. So a lower value than control is obtained.

In the stage III (4 – 15 hours called as acceleration period) the secondary reaction starts with anhydrated cement grains being hydrated and rupturing the double layer (Mindness and Young, 1981) and rapid formation of C-S-H, and conversion of ettringite to monosulphate occur, due to which stiffening of the paste occurs, visual observation shows the same.

In the blended system the hydration products are accelerated and quick conversion of ettringite to monosulphate occur resulting in a sharp decrease of ε' and σ.compared to control. More accumulation of hydration products accelerates and hence earlier setting (Eqn. 5, 6, 7, 8).

Stage IV is called (15 – 30 hours) as post acceleration period. In this period more hydration products are formed. Only a small amount of products have to be formed. Due to minimum availability of the media, the reactions are slow and hence a straight line with minimum slope is obtained.

In the case of blended system the products to be formed are too less and hence a asymptotic line. The reaction of C_4A_3S is similar to that of yeelimite present in the CSA cement (Ambroise et.,2008) responsible for quick hydration. Due to increase in percentage of FA, the reaction gains momentum and sets quickly and as is evidenced from heat of hydration curve. The particle to paste to aggregate bonds developed at this surface. At this all the CSA are consumed as is evidenced from XRD. The reaction of blended system is equal to the control and hence the line coincides.

Due to endothermic process or evaporation of excess water the heat of hydration curve falls well below the baseline. The addition of fly ash increases the concentration of $C_4A_3\bar{S}$ resulting in ε' values to fall off rapidly.

During the induction period the products formed with $C_4A_3\bar{S}$ and C_3A are available again which react with cement producing ettringite and the process is continuous. Hence, a low variation in ε' values and the same is almost maintained a constant.

During the acceleration period, more C_3A, C_4AF and $C_4A_3\bar{S}$ phases interact, resulting in large and early ettringite formation than SRPC. Due to this the ε' falls of slowly to attain the minimum value. This minimum corresponds to maximum ettringite crystal formations which can be well visualized from the SEM picture (Fig.5). The conductivity graph is also well marked as per the above observation (Zhang X *et al*., 1999). As fly ash concentration increases the reaction becomes faster and hence the rate of dε'/dt becomes less and is constant in the post acceleration period.

The visual observations and microstructure study reveals an unaffected nature of this blended system even a after one year. This confirms the behavior of CSA in the fly ash equivalent to a natural material, causing no harm and regulates high performance in terms of mechanical strength and durability.

4. Conclusion

The study of this blended system using microwave suggests an accelerating trend. This microwave study analysis the hydration kinetics well. This reduction in setting time is evidenced due to the presence of CSA in the fly ash. Heat of hydration study, XRD, analysis and the SEM analysis confirms the above results. The reaction seems to be continuous, yielding more ettrigite products there by shortening the setting time. However in order to control the accelerating trend of the fly ash as admixture, a suitable retarder is to be added. Not only the flow ability, consistency workability results favored this 30% addition but also the setting and hydration kinetics supplemented this addition. With suitable retarder this will be more useful in under water construction.

Acknowledgement

References

Ambroise J and Péra J. (2008). Immobilisation of calcium sulphate contained in demolition waste. *J Hazard Mater*, 151: 840-846.

ASTM Committee C-1, C 186-86, Annual book of ASTM Standards (Cement, Lime, Gypsum 1987); Vol.04.01: 188.

Barathan S, Govindarajan D, Sivakumar G,Raghu K. (2006). Microwave study of hydration of cement with different waters. *Indian Journal of Pure and Applied Physics*, 44, 334-338.

Benarchid My. Y, Rogez J, Diouri A, Boukhari A, Aride. (2005). Formation and hydraulic behaviour of chromium-phophorous doped calcium sulphoaluminate cement. *J. Thermochimica Acta*, 433:183-186.

Chai Jaturapitakkul, Kraiwood Kiattikomol and Smith Songpiriyakij. (1999). A study of strength activity index of ground coarse flyash with portland cement. *Science Asia*, 1999; 25: 223-229.

Freiesleben Hansen.P, Mejlhede Jense O. (1998). *Materials and Structure*, 31 Mars: 133.

Jawed I, Skalny J. and Young J.F. (1983). In Structural and performance of cements, Edited by P. Barnes (Elsevier Science, London); 237.

Malhotra V.M. and Ramezanianpour A.A. (1994). Fly ash in Concrete, CANMET, second Edition, Canada.

Mindess S and Young J.F. (1981). *Concrete*, 76-77.

Sharma R.L, Pandey S.P. (1999). Influence of mineral additives on the hydration characteristics of ordinary Portland cement. *Cem. Concr. Res*., 29: 1525-1529.

Shetty M.S. (2004). Concrete Technology Theory and Practice, S. Chand & Company Ltd, New Delhi.

Theerawat Sinsiri, Pichaya Teeramit, Chai Jaturapitakkul and Kraiwood Kiattikomol. (2006). effect of fineness of fly ash on expensive of mortar in magnesium sulphate. *Science Asia*, 32, 63-69.
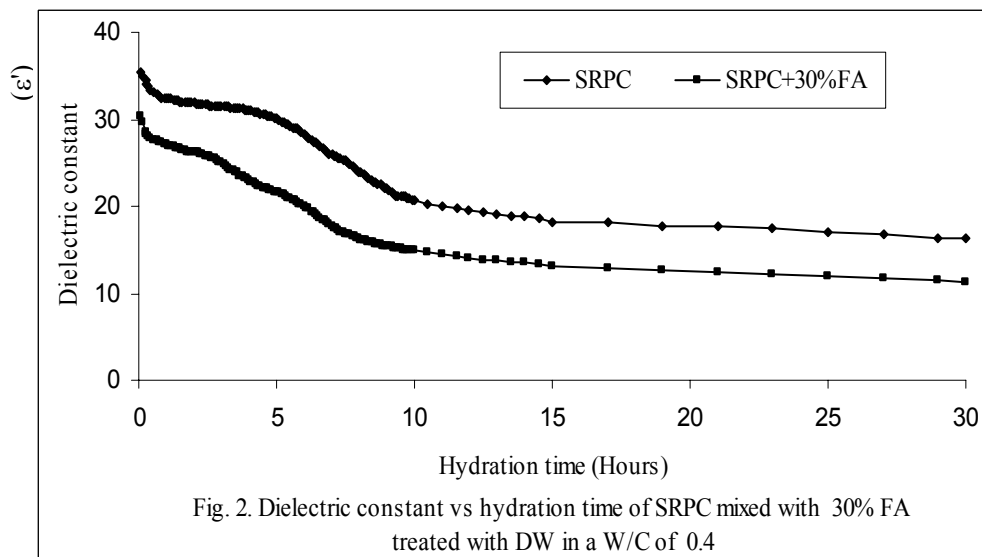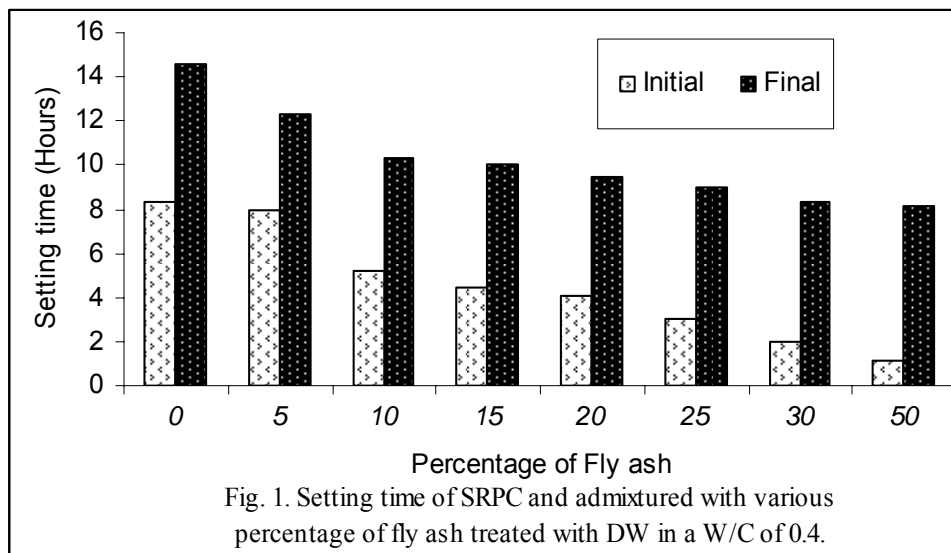
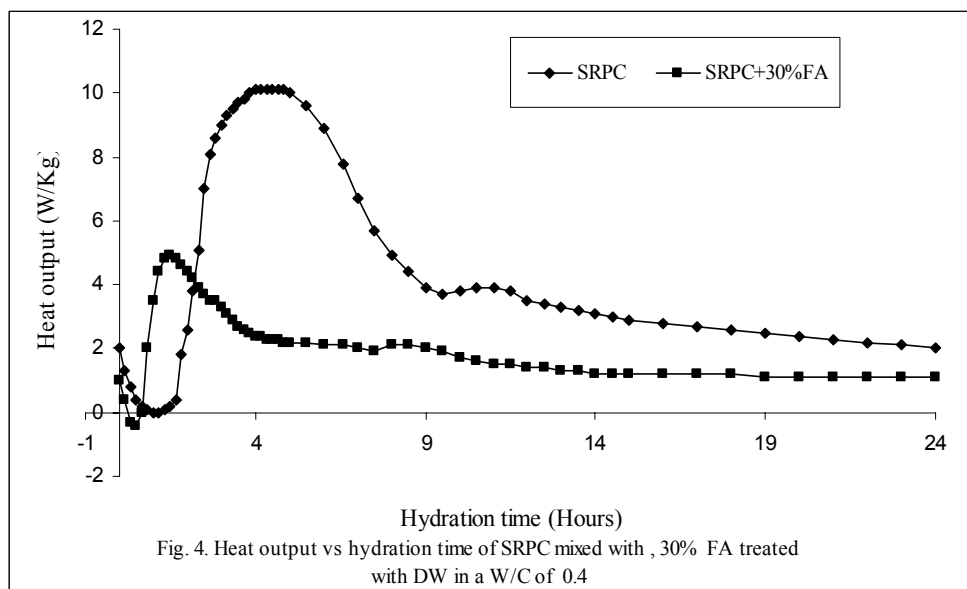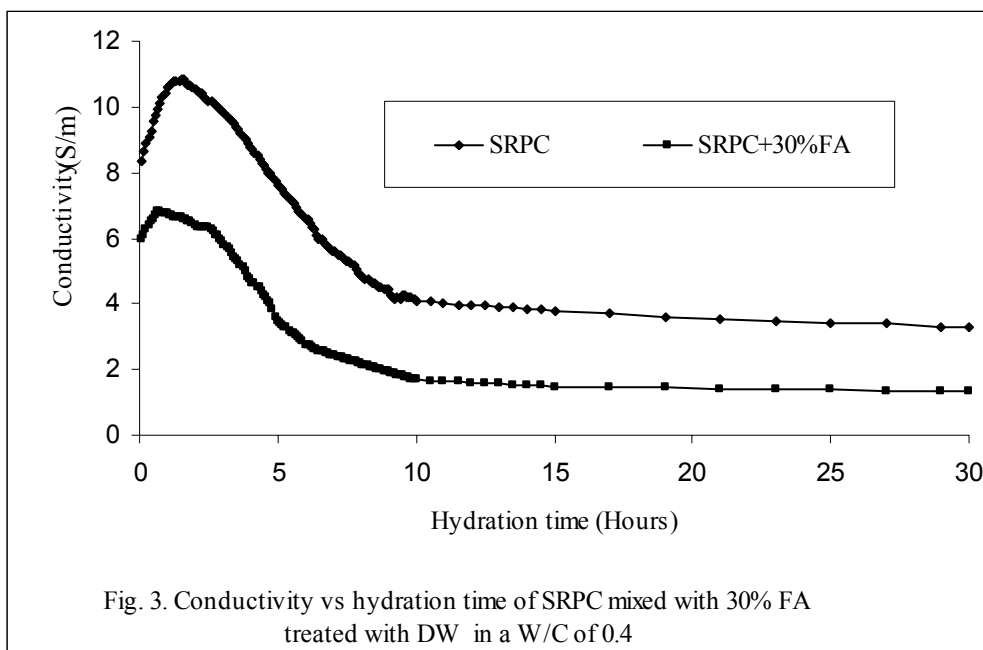Verbeck G.J, Foster C.W. (1949). Bulletin No.32, (Portland cement Association).

Yoon S.S, Kim H.C, Hlll§ R. M. (1996). the dielectric response of hydrating porous cement paste. *J.Appl Phy*, 29, 869-875.

Zhang X, Yang Y, Ong C.K. (1999). A noval way of estimation of the apparent activation energy of cement hydration using microwave technique. *J. Mater, Sci.*, 34, 3143-3147.

Zhang X, Yang Y, Wong C.L and Ong C.K. (1998). Study of hydration of OPC/PFA blend with various activators using microwave technique, *J. Mater. Sci*, 33: 4191-4199.

Zhi Ge, 138 Town Engineering Building, Civil, Construction and Environmental Department, Iowa State University, Ames, IA 50010.
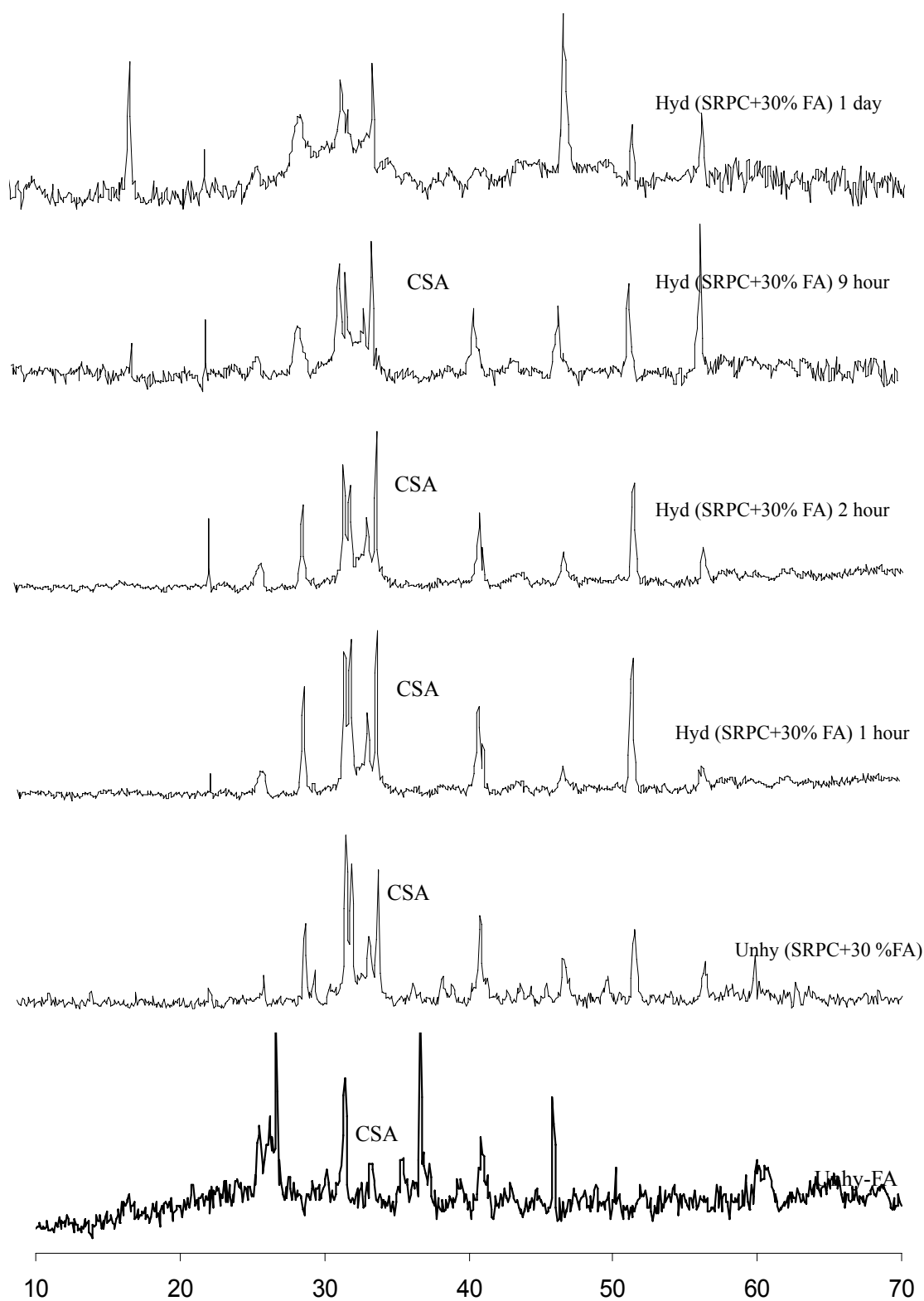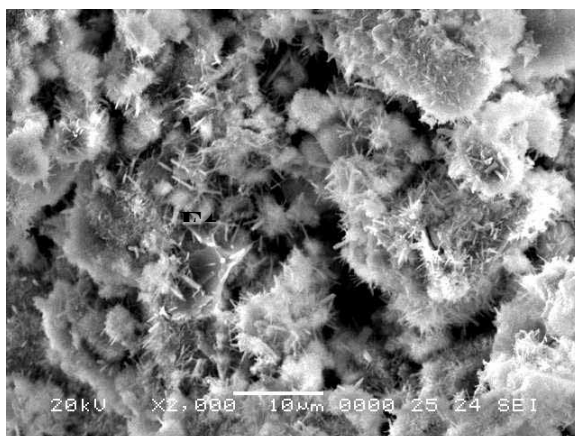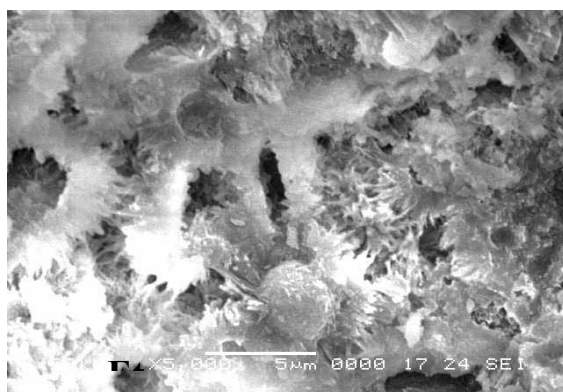
Fig. 1. Setting time of SRPC and admixtured with various percentage of fly ash treated with DW in a W/C of 0.4.

Fig. 2. Dielectric constant vs hydration time of SRPC mixed with 30% FA treated with DW in a W/C of 0.4

Fig. 3. Conductivity vs hydration time of SRPC mixed with 30% FA
treated with DW in a W/C of 0.4

Fig. 4. Heat output vs hydration time of SRPC mixed with , 30% FA treated
with DW in a W/C of 0.4

Figure 5. XRD spectra for Unhydrated FA, SRPC+30%FA, SRPC+30%FA hydrated 1h, 2h,9h. (CSA= Calcium Sulfoaluminate)

a

b

Figure 6. SEM micrograph of (a) SRPC (hydrated for8 hour)

(b)SRPC + 30% (Hydrated for 2 hour)