JOURNAL OF MATERIALS SCIENCE 33 (1998) 4191–4199

# Study of hydration of OPC/PFA blend with various activators using microwave technique

X. ZHANG, Y. YANG, C. L. WONG, C. K. ONG
*Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore 119260, Republic of Singapore*

The early hydration of ordinary Portland cement (OPC) pulverized fly ash (PFA) blends with various PFA proportions was investigated using microwave technique and conduction calorimeter. It is found that PFA acts as almost inert filler in the OPC/PFA blends during the first 40 h of hydration, thus it retards the early hydration of the blends. To accelerate the pozzolanic hydration of the PFA, three different additives were studied. It is found that both $Ca(OH)_2$ and $Na_2SO_4$ can accelerate the early hydration of the OPC/PFA blends, but $Na_2SO_4$ is more effective than $Ca(OH)_2$, whereas NaOH is not suitable for the acceleration of the early hydration of the OPC/PFA blend. © *1998 Kluwer Academic Publishers*

## 1. Introduction

Pulverized fly ash (PFA) is an industrial waste produced by the combustion of finely ground coal in the furnaces of electricity generating stations. PFA consists mainly of glassy spherical particles and is being increasingly used as a replacement for cement in concrete, because of its low cost and it improves the workability of fresh concrete [1]. The concrete using PFA also possesses very high scaling resistance and can provide excellent durability in a freezing and thawing environment.

Huang [2] conducted a study on the strength development and hydration of fly ash cement, and the influence of the addition of gypsum at normal and elevated temperatures. He found that addition of a proper amount of gypsum to fly ash cement could accelerate the possolanic reaction between $Ca(OH)_2$ and fly ash, resulting in the increase in the strength of the fly ash cement paste after 28 days. The result is supported by the study of Gifford *et al.* [3]. They found that fly ash concrete met the requirements of 28-day strength. Torrii *et al.* [4] found that the replacement of Portland cement by a relatively large amount of fly ash effectively improved the resistance of concrete to sulphate attack. This result is supported by the work of Mangat *et al.* [5]. Ma *et al.* [6] performed a calorimetric study of cement blends containing fly ash at elevated temperatures, and found that the heat generated by fly ash blended cement is lower than that required by ordinary Portland cement (OPC). They reported that presence of low-lime fly ash might actually retard the hydration of Portland cement. Thus different ways of activating fly ash such as addition of $Ca(OH)_2$ or $CaSO_42H_2O$ were investigated. It was reported that the possibility of fly ash activation by $Ca(OH)_2$ mainly lies in facilitating the pozzolanic reaction which involves breaking of bonds and dissolution of the three-dimensional network structure of the glass [7, 8]. Another work showed that replacement of part of the cement by fly ash decreased early heat output and a good correlation between pozzolanic and hydration heat was found [9].

We have successfully developed a microwave technique to study the early hydration of OPC [10, 11], slag cement [10, 11], mortar [12] and OPC/high alumina cement (HAC) blend [13] by measuring the change in dielectric constant during cement hydration. We found [14] that there is a good correlation between the rate of change in dielectric constant ($-d\varepsilon/dt$) measured by our microwave technique and the heat evolution rate measured by the conduction calorimeter. Thus the traditional definition of the four periods of cement hydration based on the heat-evolution rate curve can be applied to the $-d\varepsilon/dt$ curve for monitoring cement hydration. We also found that the $-d\varepsilon/dt$ curve measured using the microwave technique provides more information than the heat evolution rate curve, which is useful for study of early hydration of cement systems.

In this work, we used a microwave technique, together with a conduction calorimeter, to study the early hydration of OPC/PFA blend and the effects of various activators on the acceleration of OPC/PFA blend.

## 2. Experimental procedure

Investigation of the hydration of OPC/PFA blend using a microwave technique was conducted by filling a rectangular wave-guide section with a sample of the material and then measured the variation of complex dielectric constant with time at a microwave frequency of 9.5 MHz. The details of the measurement are shown in references [10, 11].

The compositions of the OPC and PFA used in this work are given in Table I. The OPC/PFA blends were prepared by mixing the required amounts of solids with de-ionized water at a water to solid ratio (*w*/*c*) of

TABLE I Component oxides (wt %) of OPC and PFA

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $Na_2O$ | $K_2O$ | $TiO_2$ | $Mn_2O_3$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OPC | 21.2 | 5.5 | 3.2 | 63.4 | 1.7 | 2.4 | 0.13 | 0.68 | | | |
| PFA | 59.9 | 24.5 | 3.7 | 7.6 | 1.3 | 0.17 | 0.45 | 0.60 | 0.72 | 0.07 | 0.25 |

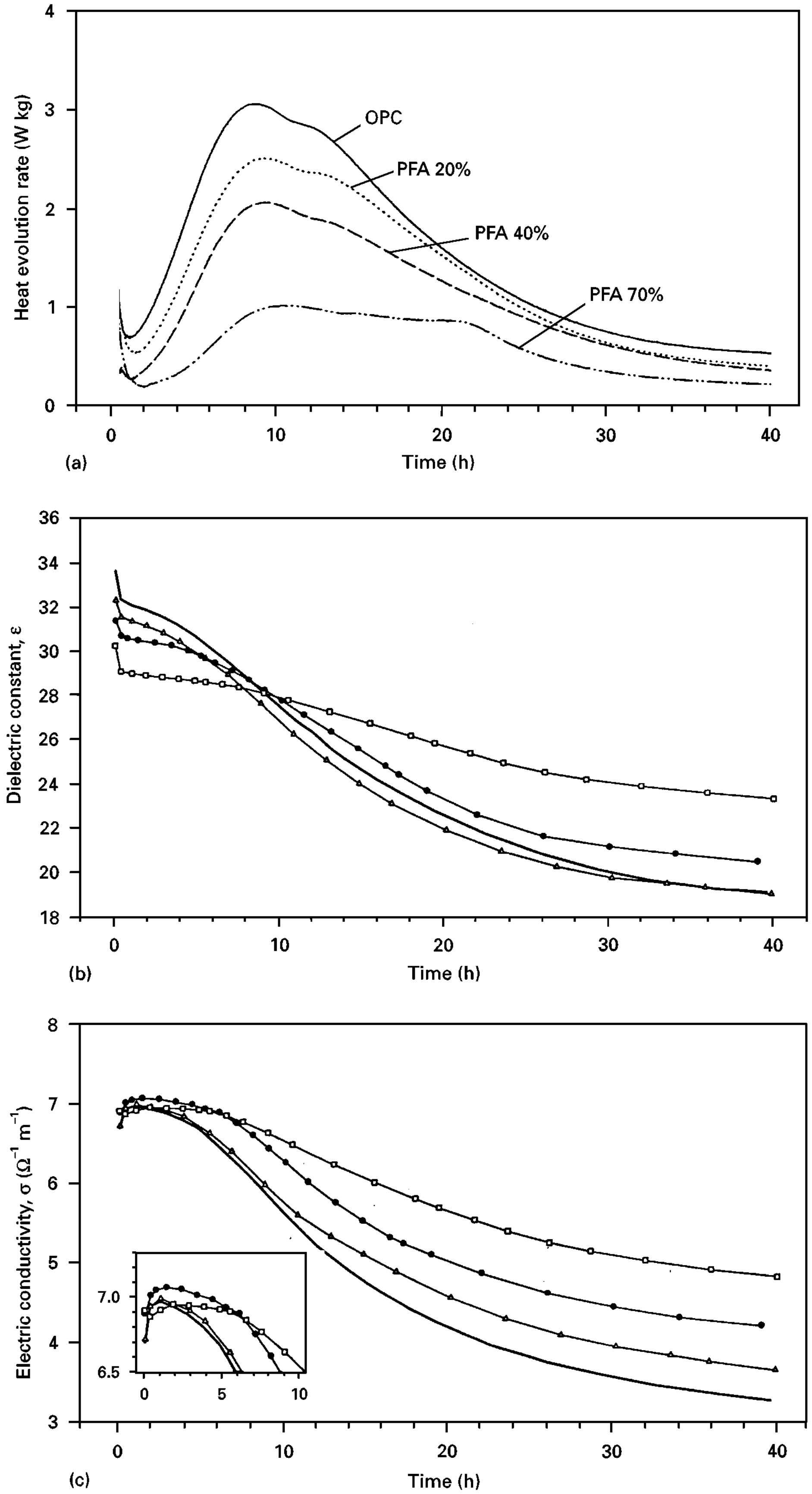


*Figure 1* Changes in (a) heat evolution rate; (b) dielectric constant ε; and (c) electrical conductivity σ of OPC/PFA blends with various PFA proportion during the early hydration. —, OPC; △ PFA 20%; ●, PFA 40%; □, FA 70%.

0.4. The first microwave measurement was made about 5 min after mixing with water. Further measurements were made at intervals of 5–10 min during the first 5 h and then at intervals of 0.5–2 h over the next 25 h. The heat evolution rate was measured using a JAF conduction calorimeter. All measurements were made at 23 °C.

## 3. Results and discussion

### 3.1. Hydration of OPC/FPA blend without additives

The effect of replacement of cement by different amounts of PFA on heat evolution rate is shown in Fig. 1(a). The ratios between the maximum heat evolution rate of OPC with 20, 40 and 70% PFA/OPC blends is 1 : 0.81, 1 : 0.68, 1 : 0.32, respectively, indicating that the decrease in the maximum heat evolution rate is approximately proportional to the PFA proportion in the blends, which is in agreement with the experimental results [6]. The length of the induction period is found to increase with increasing the PFA proportion in the blend, which agrees with the experimental result [6]. This result indicates that presence of PFA retards the hydration of OPC.

The time of the appearance of the first peak of the heat evolution rate curve is also slightly retarded as the PFA proportion increases whereas the time of the occurrence of the second peak is retarded significantly. With the increase of the PFA proportion the peaks of the heat evolution rate curve become more diffuse. It is also found that the full-width-half-maximum (FWHM) of the peak in the heat evolution rate curve increases with increasing the PFA proportion. This retarding effect of PFA on cement hydration is also reflected in the microwave responses of the OPC/PFA blends. The initial value of $\varepsilon$ is reduced as the PFA proportion increases (Fig. 1b). After that, the $\varepsilon$ enters the slow change stage and the length of the slow change stage varies with the PFA proportion. The higher the PFA proportion, the longer the slow change stage lasts. At the end of the 40-h hydration, the 70% PFA/OPC blend has the highest value of $\varepsilon$, followed by the 40% PFA/OPC blend, 20% PFA/OPC blend and OPC.

The rate of decrease in $\varepsilon$ ($-\mathrm{d}\varepsilon/\mathrm{d}t$) is found to be dependent on the PFA proportion in the blends (Fig. 2a). It is also found that the number of peaks in the $-\mathrm{d}\varepsilon/\mathrm{d}t$ curves for the blends with 40 and 70% PFA differs from that of the OPC and the blend with 20% PFA. It is found that the electrical conductivity $\sigma$ of the PFA/OPC blends increases quickly immediately after mixing with water (Fig. 1c). After the initial increase, the $\sigma$ value of all blends remains fairly constant for a period of time. The duration of this slow change stage in $\sigma$ increases with increasing the PFA proportion. The rate of the decrease in $\sigma$ ($-\mathrm{d}\sigma/\mathrm{d}t$) is also found to be dependent on the PFA proportion in the blends (Fig. 2b). The higher the PFA proportion, the fast the $\sigma$ decreases. The overall decrease in $\sigma$ is similar to the overall decrease in $\varepsilon$: the more PFA in the PFA/OPC blend, the larger the decrease in $\sigma$ during the early stage of hydration.

From the results of the microwave studies, it is obvious that increasing the PFA proportion in OPC/PFA blend will result in small value and slow change in both the dielectric constant $\varepsilon$ and the electrical conductivity $\sigma$. This is because of the low reactivity of the PFA compared with the OPC. It seems that the PFA makes little contribution to the hydration in the early period.

### 3.2. The effect of additives on the hydration of PFA/OPC blends

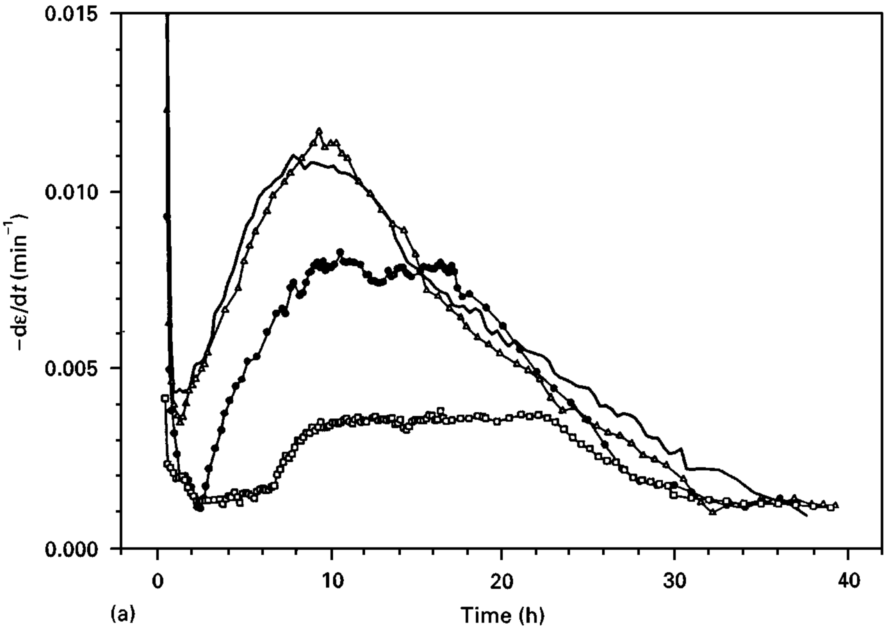
The retardation of the early hydration of OPC/PFA blend because of the slow reactivity of the PFA is associated with the reduction in some engineering properties such as early strength, which greatly limits the utilization of the PFA. Thus, activators are needed for accelerating the pozzolanic hydration of the PFA. Two commonly used activators, $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$, have been investigated [3, 7, 8]. However, the investigation of other activators is still inadequate. In order to investigate the effects of the various activators on the early hydration of OPC/PFA blends, we studied the effect of $Ca(OH)_2$, NaOH and $Na_2SO_4$ on the early hydration of OPC/PFA blends.

#### *3.2.1. The effect of $Ca(OH)_2$ on the early hydration of OPC/PFA blends*

It is found that the addition of 2% $Ca(OH)_2$ reduces the initial $\varepsilon$ value of the 20 and 40% PFA/OPC blends, but increases the initial $\varepsilon$ value of the 70% PFA/OPC blend. The final $\varepsilon$ values at the end of the 40 h hydration are reduced by the addition of 2% $Ca(OH)_2$ for the blend with 40% PFA, but almost not affected for the blends with 20 and 70% PFA (Fig. 3a).

For the 20% PFA/OPC blend, after about 10 h the $\varepsilon$ values of the blend with 2% $Ca(OH)_2$ are more or less the same as that of the blend without $Ca(OH)_2$ (Fig. 3a). It is found that within the first 16 h of hydration, value of the $-\mathrm{d}\varepsilon/\mathrm{d}t$ of the blend with 2% $Ca(OH)_2$ is lower than that without $Ca(OH)_2$. After 16 h there is no significant difference in the value of $-\mathrm{d}\varepsilon/\mathrm{d}t$ for these two samples (Fig. 3b). It appears that the addition of 2% $Ca(OH)_2$ does not accelerate the early hydration of the 20% PFA/OPC blend.

For the 40% PFA/OPC blend, the addition of 2% $Ca(OH)_2$ results in the overall $\varepsilon$ decrease increasing by only 0.3 and the maximum value of $-\mathrm{d}\varepsilon/\mathrm{d}t$ increasing a little. It seems that the addition of 2% $Ca(OH)_2$ has a little effect on the hydration of the 40% PFA/OPC blend. For the 70% PFA/OPC blend, the addition of 2% $Ca(OH)_2$ plays an obvious acceleration role in the early hydration. The overall $\varepsilon$ decrease increases by 1.7; the slow change stage in $\varepsilon$ is shortened by 4.6 h; and the value of $-\mathrm{d}\varepsilon/\mathrm{d}t$ also significantly increases.



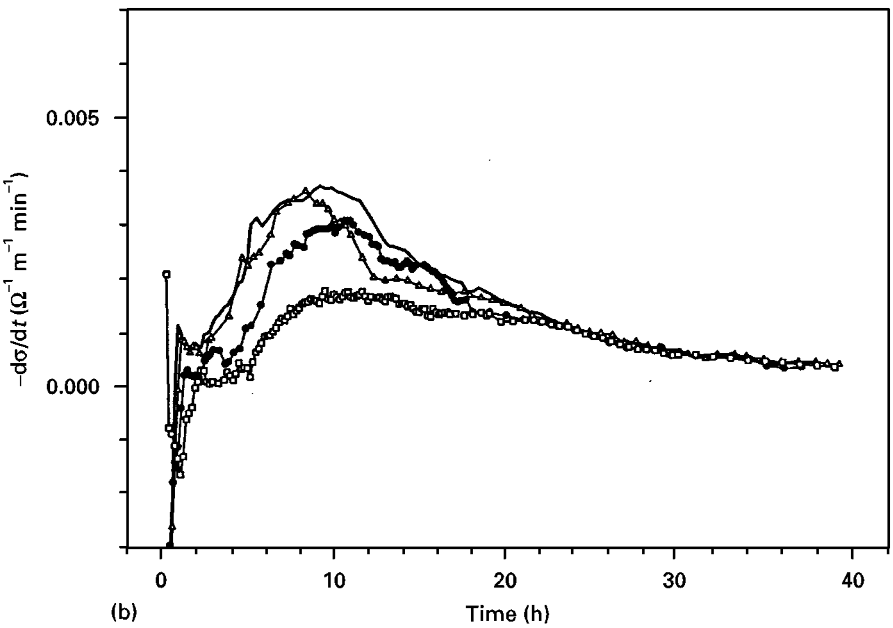


*Figure 2* Rate of change (a) in dielectric constant ε and (b) in electrical conductivity σ of OPC/PFA blends with various PFA proportions. —, OPC; △, PFA 20%; ●, PFA 40%; □, PFA 70%.

### 3.2.2. The effect of NaOH on the early hydration of OPC/PFA blend

It is found that the addition of 2% NaOH reduces the initial ε value for all the blends but raises the final ε value at the 40 h of hydration for the OPC/PFA blends with 20 and 40% PFA (Fig. 4a). For the 40 and 70% PFA/OPC blends, the $-d\varepsilon/dt$ curve of the blend with 2% NaOH is different from that without 2% NaOH in both the number of the peaks and the maximum value of the $-d\varepsilon/dt$ (Fig. 4b). In addition, the occurrence of the peak of $-d\varepsilon/dt$ curve is shifted to the earlier time and the duration of the slow change stage in the $-d\varepsilon/dt$ curve is shortened by the addition of 2% NaOH. The overall ε decrease $\varepsilon_{ini} - \varepsilon_{fin}$ and the percentage overall ε decrease $(\varepsilon_{ini} - \varepsilon_{fin})/\varepsilon_{fin}$ at the 40-h hydration are reduced by the addition of 2% NaOH for all the blends (Table II). This result indicates that the early hydration of the OPC/PFA blend is actually retarded by the addition of 2% NaOH.

Although the addition of 2% NaOH retards the early hydration, it does significantly accelerate the hydration of $C_3S$, thus shortens the slow change stage and advances the appearance of the maximum decreasing rate. The reduction in overall ε decrease for the blend with 2% NaOH is probably a result of the greatly accelerated hydration of $C_3S$ which results in the accumulation of the hydrates and thus impedes the further hydration. Thus, NaOH seems not to be suitable for the activation of the pozzolanic reactivity of PFA.

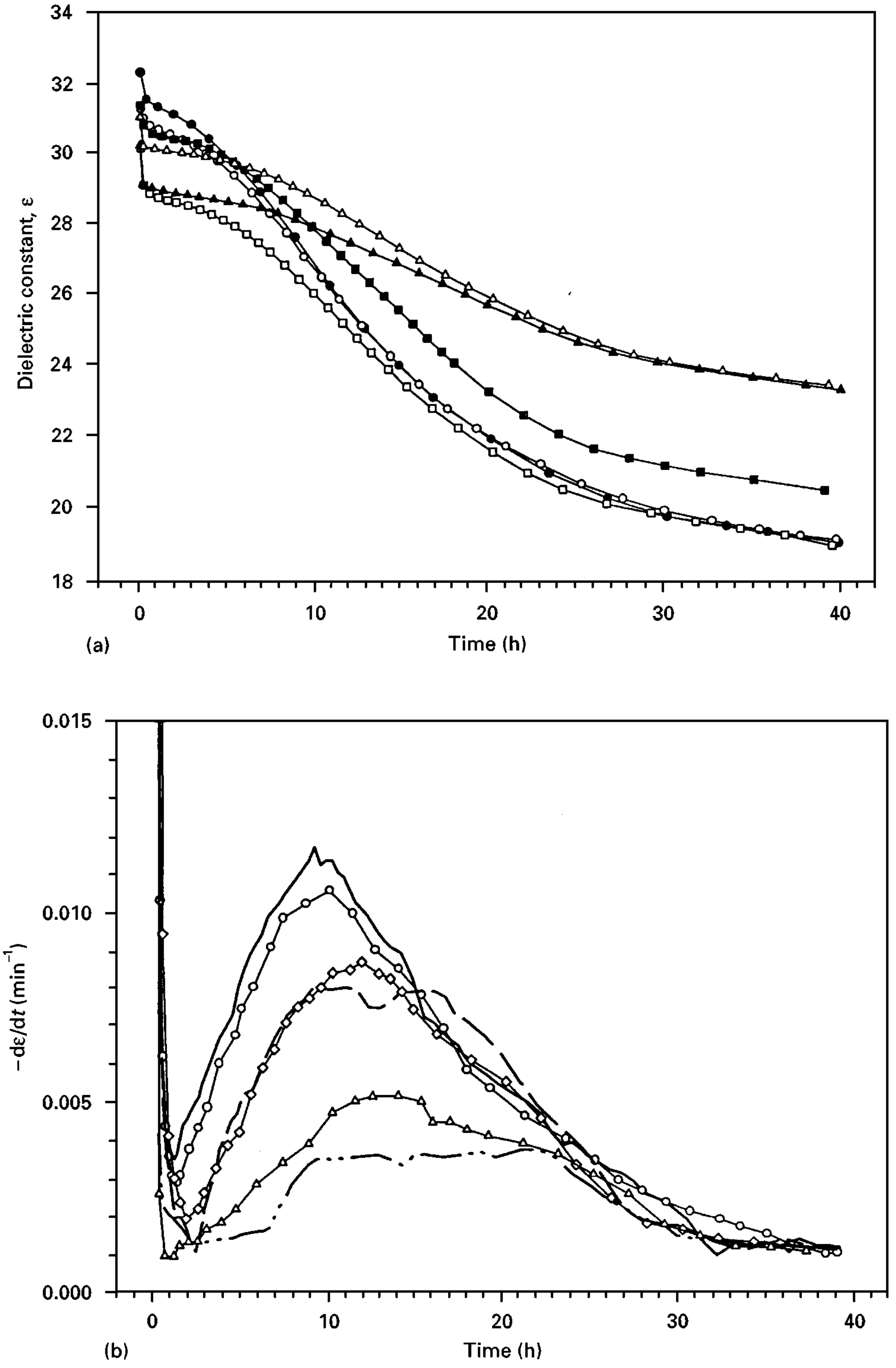


*Figure 3* The effect of 2% $Ca(OH)_2$ on (a) dielectric constant ε and (b) rate of change in dielectric constant for OPC/PFA blends with various PFA proportions (a): ●, 20% PFA; ○, 20% PFA + 2% $Ca(OH)_2$; ■, 40% PFA; □, 40% PFA + 2% $Ca(OH)_2$; ▲, 70% PFA; △, 70% PFA + 2% $Ca(OH)_2$. (b) :—, 20% PFA; ○, 20% PFA + 2% $Ca(OH)_2$; – –, 40% PFA; ◇, 40% PFA + 2% $Ca(OH)_2$; —-·, 70% PFA; △, 70% PFA + 2% $Ca(OH)_2$.

### 3.2.3. The effect of $Na_2SO_4$ on the early hydration of OPC/PFA blends

The addition of 2% $Na_2SO_4$ reduces the ε value significantly for all OPC/PFA blends during the 40-h hydration (Fig. 5a). The overall ε decrease and the percentage overall ε decrease after 40 h of hydration are greater for the 40 and 70% PFA/OPC blends with 2% $Na_2SO_4$ than that without $Na_2SO_4$ (Table III), indicating the early hydration of these two blends are accelerated by the addition of 2% $Na_2SO_4$. However, the addition of 2% $Na_2SO_4$ seems not to accelerate the early hydration of the 20% PFA/OPC blend, as the overall ε decrease of the blend with 2% $Na_2SO_4$ is less than that without $Na_2SO_4$, although the corresponding percentage overall ε decrease increases.

It is found that by the addition of 2% $Na_2SO_4$, value of the $-d\varepsilon/dt$ increases for the 40 and 70% PFA/OPC blends but decreases for the 20 % PFA/OPC blend, the peak of the $-d\varepsilon/dt$ curve also appears earlier for all OPC/PFA blends. It is also found

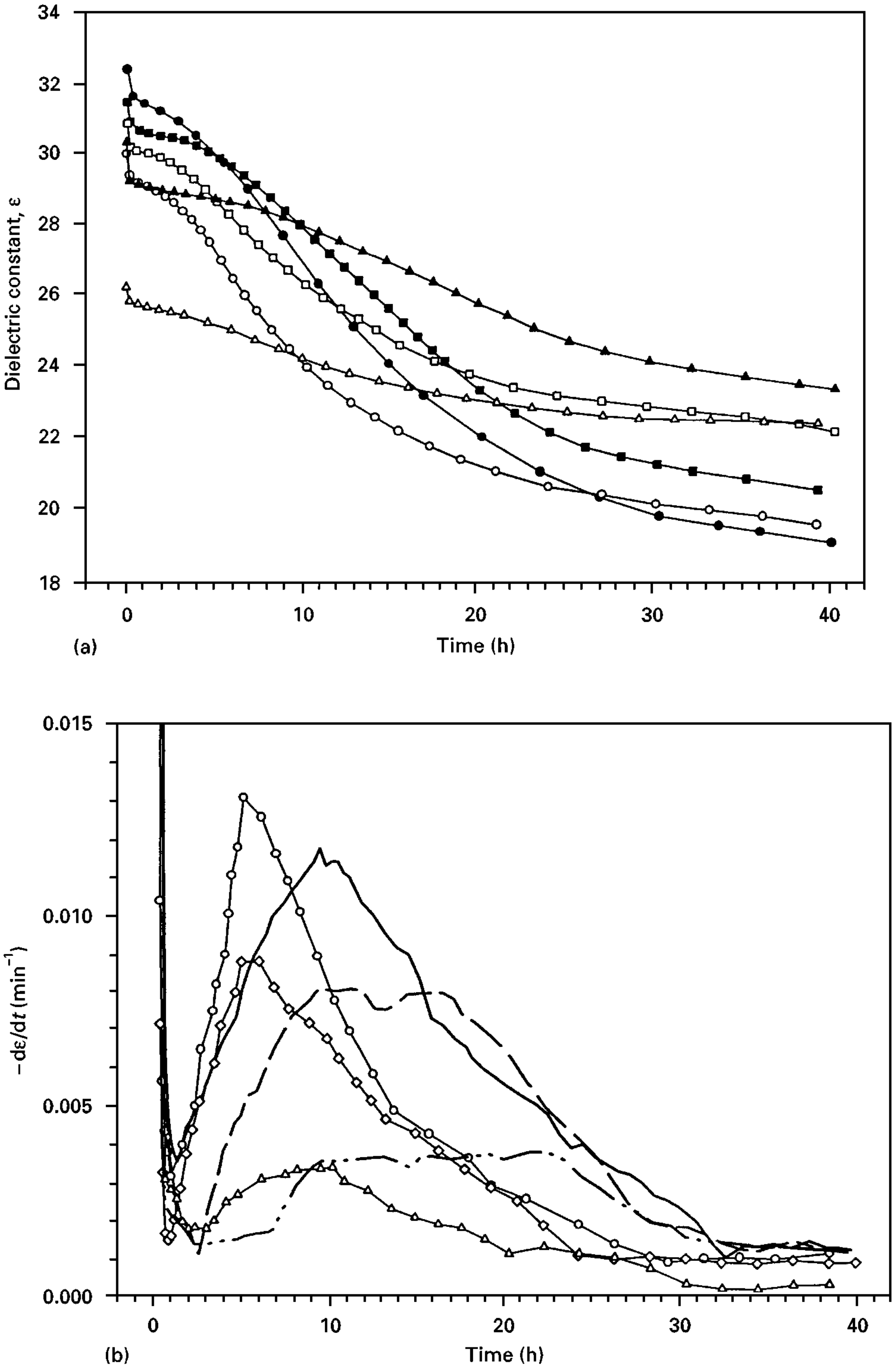


*Figure 4* The effect of 2% NaOH on (a) dielectric constant ε and (b) rate of change in dielectric constant − dε/d$t$ for OPC/PFA blends with various PFA proportions. (a): ●, 20% PFA; ○, 20% PFA + 2% $Ca(OH)_2$; ■, 40% PFA; □, 40% PFA + 2% $Ca(OH)_2$; ▲, 70% PFA; △, 70% PFA + 2% Ca(OH) $_2$. (b): —, 20% PFA; ○, 20% PFA + 2% $Ca(OH)_2$; – –, 40% PFA; ◇, 40% PFA + 2% $Ca(OH)_2$; —·—, 70% PFA; △, 70% PFA + 2% $Ca(OH)_2$.

TABLE II The decrease in the dielectric constant ε of OPC/PFA blends hydrating with or without 2 % NaOH

| | OPC/PFA blend | $\varepsilon_{ini}$ | $\varepsilon_{fin}$ ($t$ = 40 h) | $\varepsilon_{ini} - \varepsilon_{fin}$ | $(\varepsilon_{ini} - \varepsilon_{fin})/\varepsilon_{fin}$ (%) |
|---|---|---|---|---|---|
| Hydrating | PFA 20% | 32.3 | 18.9 | 13.4 | 41.5 |
| without | PFA 40% | 31.3 | 20.4 | 10.9 | 34.8 |
| 2% NaOH | PFA 70% | 30.1 | 23.2 | 6.9 | 22.4 |
| Hydrating | PFA 20% | 29.8 | 19.4 | 10.4 | 34.9 |
| with | PFA 40% | 30.7 | 22.1 | 8.6 | 27.0 |
| 2% NaOH | PFA 70% | 26.2 | 22.3 | 3.9 | 14.8 |

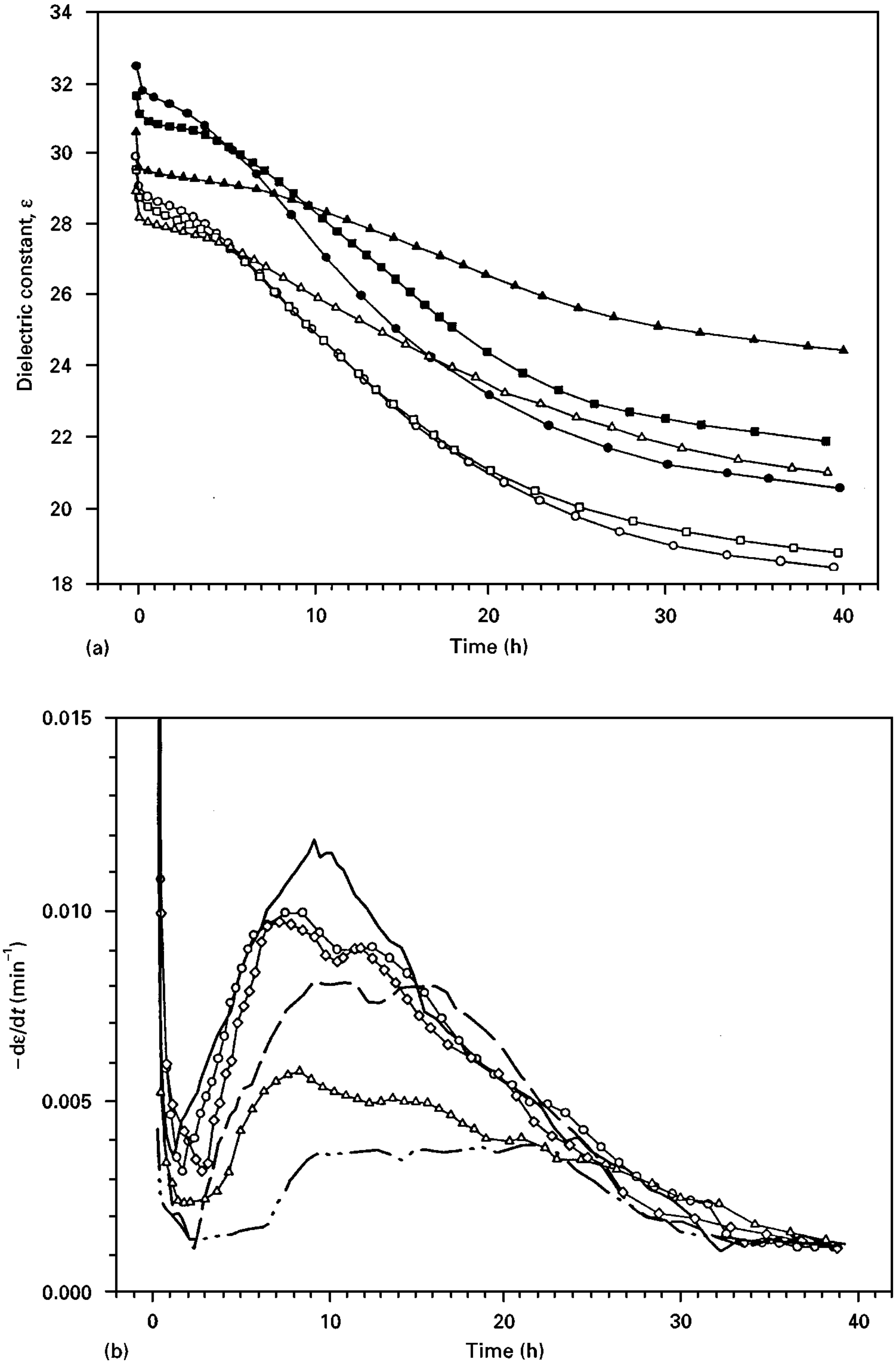


*Figure 5* The effect of 2% $Na_2SO_4$ on (a) dielectric constant ε and (b) rate of change in dielectric constant − dε/d*t* for OPC/PFA blends with various PFA proportions. (a): ●, 20% PFA; ○, 20% PFA + 2% $Ca(OH)_2$; ■, 40% PFA; □, 40% PFA + 2% $Ca(OH)_2$; ▲, 70% PFA; △, 70% PFA + 2% $Ca(OH)_2$. (b):—, 20% PFA; ○, 20% PFA + 2% $Ca(OH)_2$;– –, 40% PFA; ◇, 40% PFA + 2% $Ca(OH)_2$; —-·-, 70% PFA; △, 70% PFA + 2% $Ca(OH)_2$.

TABLE III The decrease in the dielectric constant ε of OPC/PFA blends hydrating with or without 2% $Na_2SO_4$ additive

| | OPC/PFA blend | $\varepsilon_{ini}$ | $\varepsilon_{fin}$ ($t = 40$ h) | $\varepsilon_{ini} - \varepsilon_{fin}$ | $(\varepsilon_{ini} - \varepsilon_{fin})/\varepsilon_{fin}$ (%) |
|---|---|---|---|---|---|
| Hydrating without 2% $Na_2SO_4$ | PFA 20% | 32.3 | 18.9 | 13.4 | 41.5 |
| | PFA 40% | 31.3 | 20.4 | 10.9 | 34.8 |
| | PFA 70% | 30.1 | 23.2 | 6.9 | 22.4 |
| Hydrating with 2% $Na_2SO_4$ | PFA 20% | 29.3 | 16.4 | 12.9 | 44.0 |
| | PFA 40% | 28.9 | 16.8 | 12.1 | 41.9 |
| | PFA 70% | 28.3 | 19.0 | 9.3 | 32.9 |

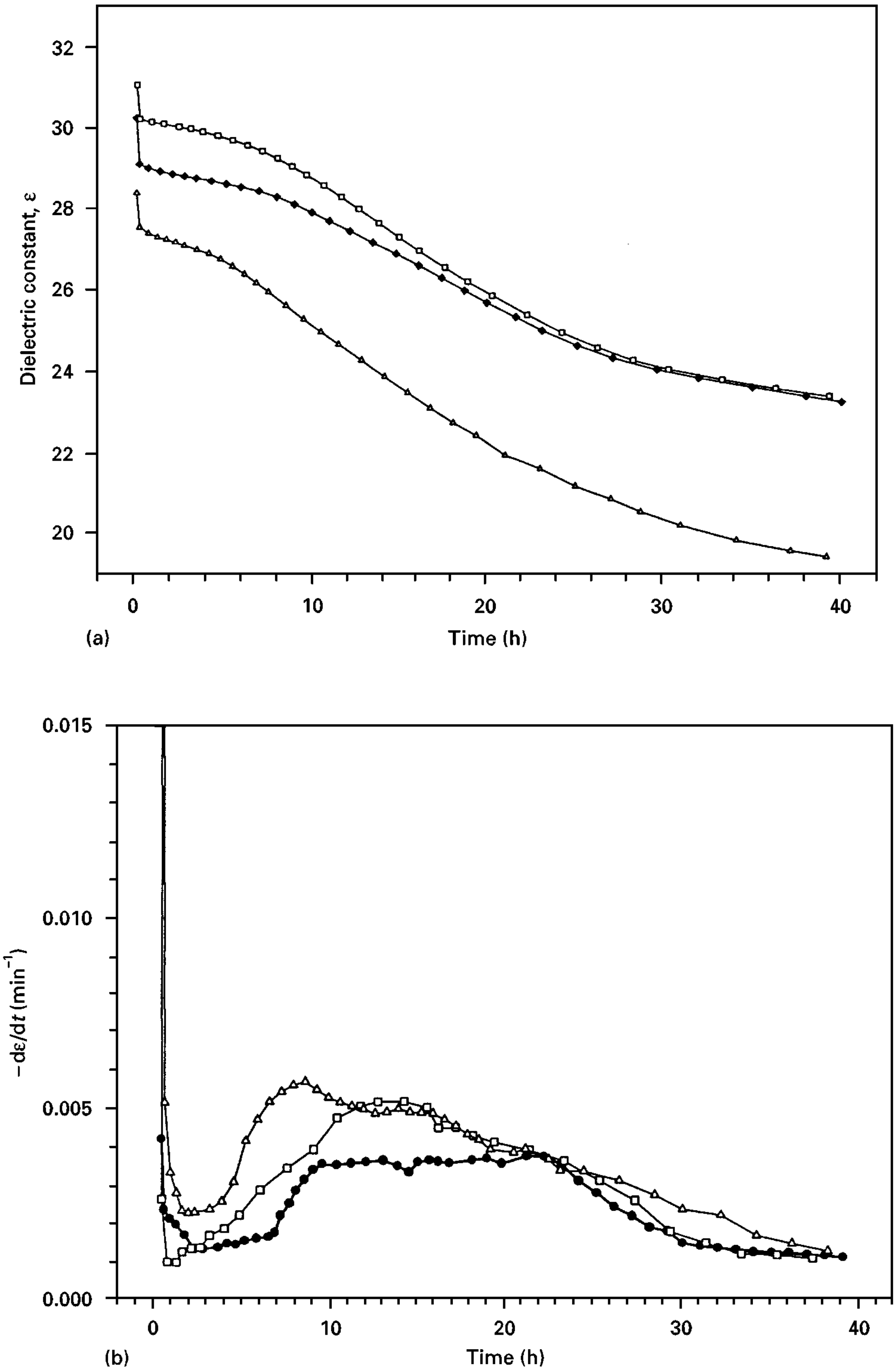


*Figure 6* The comparison of the effect of 2% $Ca(OH)_2$ and 2% $Na_2SO_4$ on (a) dielectric constant ε and (b) rate of change in dielectric constant − dε/d*t* for 70% OPC/PFA blends. (a): ♦, PFA 70%; □, PFA 70% + 2% $Ca(OH)_2$; △, PFA 70% + 2% $Na_2SO_4$. (b): ●, PFA 70%; □, PFA 70% + 2% $Ca(OH)_2$; △, PFA 70% + 2% $Na_2SO_4$.

that by the addition of 2 % $Na_2SO_4$, the slow change stage in the − dε/d*t* curve is slightly prolonged for the 20% PFA/OPC blend, not affected for the 40% PFA/OPC blend but obviously shortened for the 70% PFA/OPC blend. The shape of the − dε/d*t* curve is also found to be altered by the addition of 2% $Na_2SO_4$. It appears that the addition of 2% $Na_2SO_4$ does accelerate the early hydration of the 40 and 70% PFA/OPC blends, but not the early hydration of the 20% PFA/OPC blend.

### 3.2.4. Comparison of the effect of $Ca(OH)_2$ and $Na_2SO_4$ on the early hydration of OPC/PFA blends with high PFA proportion

From previous section, it is clear that both $Ca(OH)_2$ and $Na_2SO_4$ additives have an obvious acceleration effect on the early hydration of the OPC/PFA blends with high PFA proportion. The acceleration effect of $Ca(OH)_2$ and $Na_2SO_4$ on the 70% PFA/OPC blend is compared in Fig. 6. It is found that the addition of 2%

$Ca(OH)_2$ and the addition of 2% $Na_2SO_4$ cause ε to drop rapidly, but the acceleration effects of the two activators are different. The addition of 2% $Na_2SO_4$ caused a larger overall ε decrease, a larger percentage overall ε decrease, and significant increase in the value of $-d\varepsilon/dt$ than the addition of $Ca(OH)_2$. The results indicate that $Na_2SO_4$ has a larger acceleration effect on the early hydration of the 70% PFA/OPC than $Ca(OH)_2$. The slow change stage in the $-d\varepsilon/dt$ curve of the blend is also considerably shortened by the addition of 2% $Ca(OH)_2$ or 2% $Na_2SO_4$. However, the occurrence of the first peak in the $-d\varepsilon/dt$ curve is only advanced by the addition of 2% $Na_2SO_4$, indicating again that $Na_2SO_4$ is a better activator than $Ca(OH)_2$ for early hydration of the 70% PFA/OPC blend.

## 4. Conclusions

PFA acts as almost inert filler in OPC/PFA blends during the first 40 h of hydration and it retards the early hydration of the blends. Both $Ca(OH)_2$ and $Na_2SO_4$ can accelerate the early hydration of the OPC/PFA blends, especially those blends with high PFA proportion, while NaOH is not suitable for the acceleration of the hydration of the OPC/PFA blend. For OPC/PFA blend with high PFA proportion, $Na_2SO_4$ is a better activator than $Ca(OH)_2$.

## Acknowledgements

We are most grateful to Dr. T. H. Wee for providing the PFA.

## References

1. G. M. IDORN and K. R. HENRIKSEN, *Cem. Concr. Res.* **14** (1980) 463.
2. S. Y. HUANG, "Hydration of fly ash cement and microstructure of fly ash cement pastes", CBI, 1981.
3. P. M. GIFFORD, B. W. LANGAN and M. A. WARD, *Cem. Conc. Aggregates* **15** (1993) 14.
4. K. TORII, K. TANIGUCHI and M. KAWAMURA, *Cem. Concr. Res.* **25** (1995) 759.
5. P. S. MAGAT and J. M. KHATIB, *ACI Mater. J.* **92** (1995) 542.
6. W. P. MA, D. SAMPLE, R. MARTIN and P. W. BROWN, *Cem. Concr. Aggregates* **16** (1994) 93–99.
7. A. L. A. FRAAY, J. M. BIJEN and Y. M. DE HANN, *Cem. Concr. Res.* **19** (1989) 235.
8. D. M. ROY and M. R. SILSBEE, *Mater. Res. Soc. Symp. Proc.* **245** (1992) 153.
9. M. I. SANCHEZ DE ROJAS and M. FRIAS, *Cem. Concr. Res.* **26** (1996) 203.
10. X. ZHANG, X. Z. DING, T. H. LIM, C. K. ONG, B. T. G. TAN and J. YANG, *Cem. Concr. Res.* **25** (1995) 1086.
11. *Idem*, *J. Mater. Sci.* **31** (1996) 1345.
12. X. Z. DING, X. ZHANG, C. K. ONG, B. T. G. TAN, and J. YANG, *ibid.* **31** (1996) 5339.
13. X. ZHANG, Y. YANG and C. K. ONG, *Cem. Concr. Res.* **27** (1997) 1419.
14. *Idem*, *J. Mater. Sci. Lett.* **16** (1997) 1885.

*Received 8 July 1997*
*and accepted 11 May 1998*