Pergamon

Cement and Concrete Research 30 (2000) 553–559

CEMENT AND CONCRETE RESEARCH

Effect of the starting fly ash on the microstructure and mechanical properties of fly ash–belite cement mortars

A. Guerrero*, S. Goñi, A. Macías, M.P. Luxán

Institute of Construction Science Eduardo Torroja (CSIC), Aptdo. 19002, C/ Serrano Galvache s/n 28033 Madrid, Spain

Received 2 May 1999; accepted 23 December 1999

Abstract

The effect of two kinds of Spanish fly ashes ASTM (class F) on the mechanical and microstructure parameters of fly ash–belite cement (FABC) mortars was studied for up to 200 days from mixing. Pore-size distribution analyses were carried out by mercury intrusion porosimetry, and microstructure was investigated by scanning electron microscopy (SEM). The pore solution was expressed and analyzed at different periods of hydration. The results showed that the alkali and iron content of the starting fly ash strongly influenced the kinetics of hydration of the FABC cements. If the time factor is deleted, general correlation is obtained between the mechanical and microstructure parameters studied, irrespective of both the starting fly ash characteristics and the calcination temperature. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure; Mechanical properties; Fly ash; Mortar

1. Introduction

This paper is the continuation of an extensive investigation on the use of fly ash as raw material for synthesizing reactive belite cements according to Jiang and Roy's method [1]. The process involves two sequential steps. The first step consists of the hydrothermal treatment of fly ash (ASTM class F), CaO, and de-mineralized water to form calcium silicate and aluminate hydrates. After the hydrothermal treatment, the hydrates are calcined between 700°C and 900°C.

Two Spanish fly ashes (ASTM class F) called FA-A and FA-B in this paper, of different alkali content and granulometry, are being used in our laboratory as raw materials. During the first step of the cement synthesis, the fly ash pozzolanic reaction is strongly activated mainly in the case of the fly ash of higher alkali content, FA-A [2]. Besides, some differences were found for the hydrated phases formed as a function of the kind of fly ash.

In the case of the FA-A, the main hydrated compounds were: α-C_2SH, CSH gel, katoite (C_3ASH_4) and Fe-substituted katoite ($C_3A_{0.5}F_{0.5}SH_4$); calcite ($CaCO_3$) and portlandite ($Ca(OH)_2$). The two latter compounds indicate that the pozzolanic reaction was not completed during the first step of the synthesis process. The iron from the FA-B is combined as a mixed oxide: $CaFe_2O_4$.

During the second step of the fly ash–belite cement (FABC) synthesis, the hydrated materials produced in the first step were calcined at temperatures ranging from 700°C to 900°C. The main crystalline phases formed for the starting FA-A were: α'- and β-C_2S polymorphs (whose crystallinities increased progressively with the temperature); gehlenite (C_2AS), which was only formed at 900°C; calcite ($CaCO_3$); and C_3AS_3 and mayenite ($C_{12}A_7$), which appeared at 700°C, decreasing at higher temperature. A decrease of the BET–N_2 surface areas with temperature was noted. Measured surface areas were: 6.85, 4.37, and 4.06 m^2/g for 700°C, 800°C, and 900°C, respectively. Studies of hydraulicity, microstructure, and mechanical properties carried out on the FABC synthesized from the FA-A [3,4] revealed that the optimum FABC was obtained at a calcination temperature of 800°C.

In the case of the FABC synthesized from FA-B, preliminary investigations made in paste [2] (combined water, IR, and X-ray diffraction (XRD) analyses) showed that the best hydraulicity among the three calcination

---

* Corresponding author. Tel.: +34-91-302-04-40; fax: +34-91-302-07-00.

E-mail address: aguezzezo@ietcc.csic.es (A. Guerrero).

0008-8846/00/$ – see front matter

PII: S0008-8846(00)00198-8

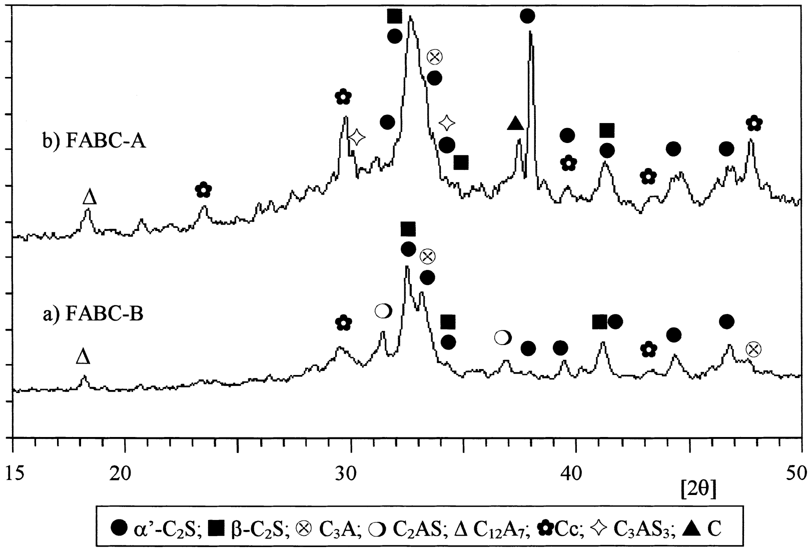

Fig. 1. XRD patterns of the starting FABCs.

temperatures was also obtained at 800°C. At 700°C, the cement only combined 3.6% of water; and at 900°C, it needed an induction period of about 60 days. In all cases, the hydraulicity of FABC synthesized from FA-B was considerably lower than that of FABC synthesized from FA-A.

On the basis of those preliminary results, we decide to extend the microstructure and mechanical investigations only for the FABC synthesized at 800°C, which are presented in the present paper.

The mechanical properties, pore-size distribution, and extracted pore solution were analyzed in mortar specimens during a period of 200 days from mixing. The microstructure study was carried out in paste specimens at the age of 200 days from mixing. All the results were compared with those obtained from equivalent FABC made with FA-A.

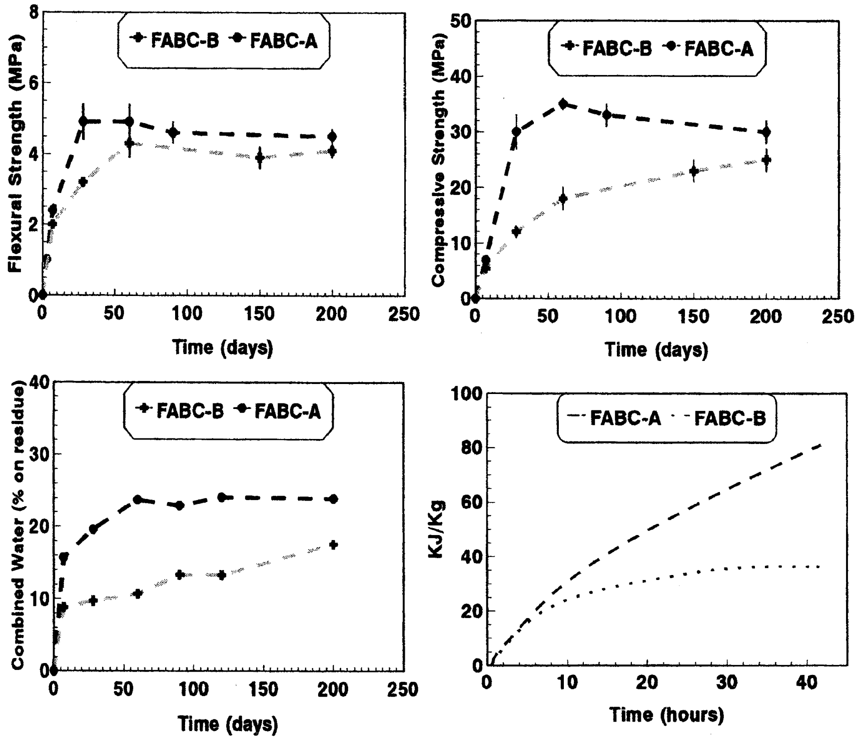

Fig. 2. Mechanical strength, combined water, and heat evolution of FABC.

2. Experimental

The chemical composition of the starting fly ash FA-B and the XRD analyses of the cement synthesized at 800°C (called FABC-B) are given in Table 1 and Fig. 1, respectively. The chemical composition of the FA-A and the XRD pattern of the equivalent cement (called FABC-A) are included for comparison in Table 1 and Fig. 1.

Several series of six mortar specimens were prepared using (α-quartz) sand. The sand-to-FABC ratio was 3.0; the de-mineralized water-to-FABC ratio was 0.75. After mixing, different portions were molded into 1 × 1 × 6 cm prism specimens and compacted by vibration. The specimens were demolded after 2 days at >90% relative humidity (rh). Groups of six mortar specimens for each age studied were stored at the temperature of 21 ± 2°C and >90% rh for 200 days. Equivalent pastes were prepared at a de-mineralized water-to-cement ratio of 0.75 and were kept at >90% rh and 21 ± 2°C during 200 days.

The XRD patterns were recorded using Cu $K\alpha_1$ radiation on a Philips PW-1730 diffractometer, equipped with a graphite monochromator. Porosity and pore-size distribution of pastes were investigated by mercury intrusion porosimetry carried out with a Micromeritics Pore Size 9310. The pore solution was expressed by applying high mechanical pressure (500 MPa) [5]. The sodium, potassium, calcium, and aluminum concentrations of the pore solution were determined by atomic absorption spectroscopy, using a Model 1100B A.A.S., Perkin Elmer, Eden Prairie, MN. The pH was measured with a combined electrode designed for measurement over the pH range 0 to 14. SEM analyses were made with a JEOL 5400 scanning electron microscope with an Oxford EDS microanalysis ISIS model. The samples were coated with gold by sputtering.

3. Results and discussion

3.1. Mechanical properties and pore-size distribution analysis

The changes of the flexural and compressive mechanical strength of mortars with hydration time are presented in Fig. 2. Each value represents the average of six measurements, and the bars represent the standard deviation of the mean value. After the flexural strength of specimens was determined, the compressive was carried out on the two halves of each specimen, according to the Spanish standard UNE EN 196-1 or UNE 80-101. In Fig. 2, we have included the previously published [4] strength data obtained from equivalent FABC calcined at 800°C from the starting fly ash FABC-A.

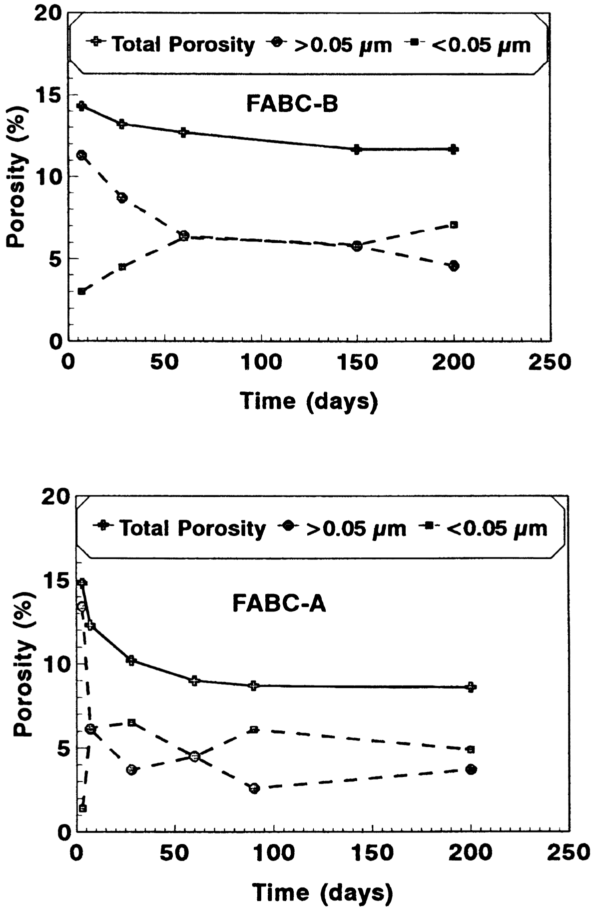

Fig. 3. Porosity and pore-size distribution changes of mortars with hydration time.

As shown, FABC-B gains strength at a slower rate compared with FABC-A. FABC-A cement mortars practically reach the maximum value after 28 days, whereas FABC-B mortars keep gaining strength progressively. After 60 days of hydration, the differences decreased. These

Table 1
Chemical composition of the two starting fly ashes and cements (% by weight)
LOI = Loss on ignition, IR = insoluble residue.

(%)	LOI	IR	CaO (total)	SiO_2	CaO (free)	Fe_2O_3	Al_2O_3	MgO	SO_3	Na_2O	K_2O	SiO_2 (reactive)
FA-A	5.6	0.3	4.6	48.8	0.25	7.4	26.8	1.9	0	0.67	3.6	35.8
FA-B	8	0.2	6.7	45.2	0.14	9.1	25.3	1.7	0	0.48	3.2	35.3
FABC-A	1.6	2.3	49.3	26.8	1.2	3.6	14.7	1.3	0.6	0.3	1.1	
FABC-B	2	2.5	47.4	26.7	1.0	4.6	16.4	1.3	0.6	0.2	0.98	

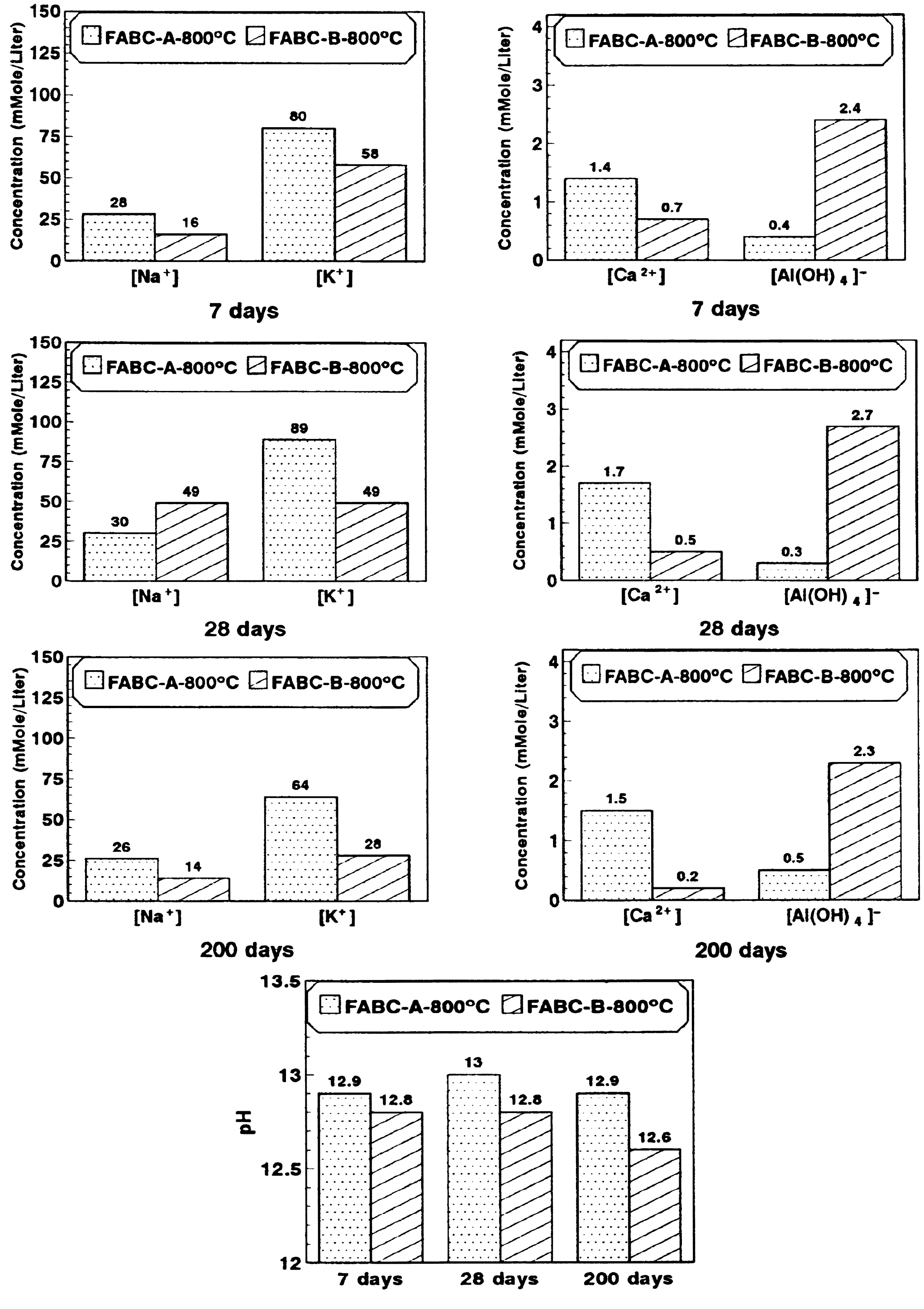

Fig. 4. Mortar pore solution analyses.

mechanical behaviors are in acceptable accordance with the gain of combined water content (determined from TG analyses carried out in equivalent paste samples). The heat evolution of the FABC-B paste stabilizes after 27 h at about 35 kJ/kg, whereas that of FABC-A paste increases progressively, reaching after 40 h with a value of 80 kJ/kg (2.3 times higher).

As a result of the gain of combined water, the porosity of both mortar samples decreased (see Fig. 3). For the FABC-B, the total porosity decreased from 14.3% (by weight) to 11.7% between 7 and 200 days, respectively, which represent a relative decrease of 18%. However, for comparison for FABC-A, at the end of the experiment, the porosity decreased 42% from the initial value.

The pore-size distribution of FABC-B mortar experimented major changes; the pores of the diameter range >0.05 μm decreased 59% and those <0.05 μm increased 58%. This pore-size distribution change toward smallest pores produces a microstructure that is denser, and consequently, an increase of the mechanical strength.

Several factors could influence the different FABC-A and FABC-B hydration behaviors. From the XRD results of Fig. 1, two significant differences can be observed in FABC-A as compared to FABC-B: (i) the virtual absence of gehlenite (C_2AS) reflections (of low hydraulicity), and (ii) more amorphous character of XRD patterns. For example, in the 32–34 2θ angular zone, where the more intense reflections of the two α'- and β-C_2S polymorphs appear, the reflections located at 32.5 and 33.2 are not well-resolved for FABC-A. All of these suggest that the potential reactivity will be higher in the case of FABC-A, as the mechanical properties and microstructure parameters confirmed (see Figs. 2 and 3). In addition, the lower reactivity of FABC-B could be attributed to the lower alkali content and the higher iron content of starting FA-B fly ash (see Table 1). It is well-established that the alkali-substituted-C_2S [6] promotes a higher reactivity, mainly for potassium, whereas Fe-substitution stabilizes the crystal lattice, as in the case of brownmillerite in Portland cements.

3.2. Pore solution analysis

Results of the mortar pore solution analyses from FABC-A and FABC-B appear in Fig. 4. The concentration of alkali ions (Na^+ and K^+) and the pH of the FABC-B pore solution are lower than those of FABC-A, especially after 200 days of hydration. Calcium and aluminate concentrations are markedly lower than those of alkalis.

As was mentioned previously [4], the alkalinity of this kind of cements is comparable to that of ordinary Portland cements (OPC) of low alkali content. Portlandite ($Ca(OH)_2$) is not formed during hydration of FABC, and therefore, the alkalinity is attributable entirely to sodium and potassium from the starting fly ashes. In accordance, the lower alkalinity of the FABC-B mortar pore solution is consistent with the lower alkali content of the FA-B fly ash (3.1% and 2.6% Na_2O equivalent for FA-A and FA-B, respectively).

3.3. Scanning electron microscopy (SEM) analyses

SEM analyses were carried out in paste samples after 200 days of hydration. The composition of the more representative area is represented in Fig. 5 as a plot of Al/Ca atom ratio against Si/Ca atom ratio. The lines on the graph are the theoretical composition of the main crystalline hydrated compounds determined from XRD: vertumnite ($C_4A_2S_4H_{15}$), carbonated-katoite ($C_3AS_3C_3H_{1.5}$), and $C_2SH_{0.35}$.

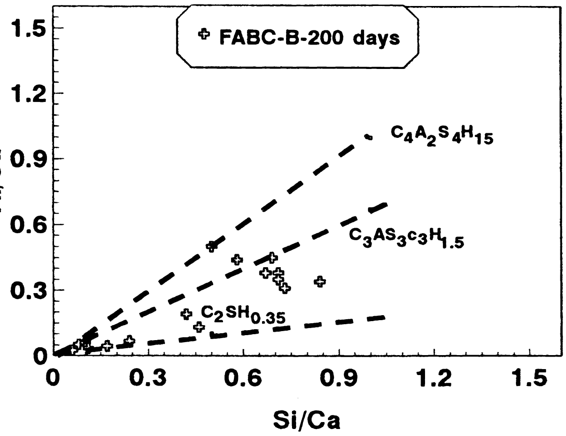

Fig. 5. Al/Ca atom ratio against Si/Ca atom ratio of the more representative crystals.

In the microstructure of the FABC-B paste (Fig. 6a–e), numerous thin plates appeared (Fig. 6a–c), which could be consistent with the vertumnite ($C_4A_2S_4H_{15}$) composition; the Al/Ca, Si/Ca values are located in the vertumnite line of Fig. 5. The more compact plaques have a composition consistent with $C_2SH_{0.35}$, and the smallest and rounded particles could correspond to the cubic carbonated-katoite ($C_3AS_3C_3H_{1.5}$), since their Al/Ca and Si/Ca ratios are located near the theoretical $C_3AS_3C_3H_{1.5}$ line. Zones of Fig. 6d–e are very rich in Ca, perhaps due to calcite ($CaCO_3$), because no portlandite ($Ca(OH)_2$) is detected in the sample. The very low Al/Ca and Si/Ca ratios are located in the $C_2SH_{0.35}$ line.

3.4. Mechanical strength, porosity, and combined water correlation

It appears that for the different microstructure parameters studied for these cements, the main variations are related to the kinetics of hydration. Nevertheless, if the time factor is deleted, a general tendency can be established among them, as observed in Fig. 7. A correlation among porosity, mechanical strength, and combined water is drawn in this figure.

When total porosity and combined water results are compared, an inverse linear correlation is obtained. The small value of the slope (−0.27) is due to the fact that during hydration the bigger pores become smaller, almost symmetrically, as shown in Fig. 3. When the compressive strength is compared with combined water, these results suggest that a minimum of about 7% of combined water is necessary for the specimens to start to gain strength. The dispersion of data is considerable and no regression equation is given.

Porosity and the mechanical strength parameters have an inverse linear correlation with a slope value about nine times higher for the compressive strength. This indicates that the compressive strength is nine times more sensitive to the porosity changes than is the flexural strength.

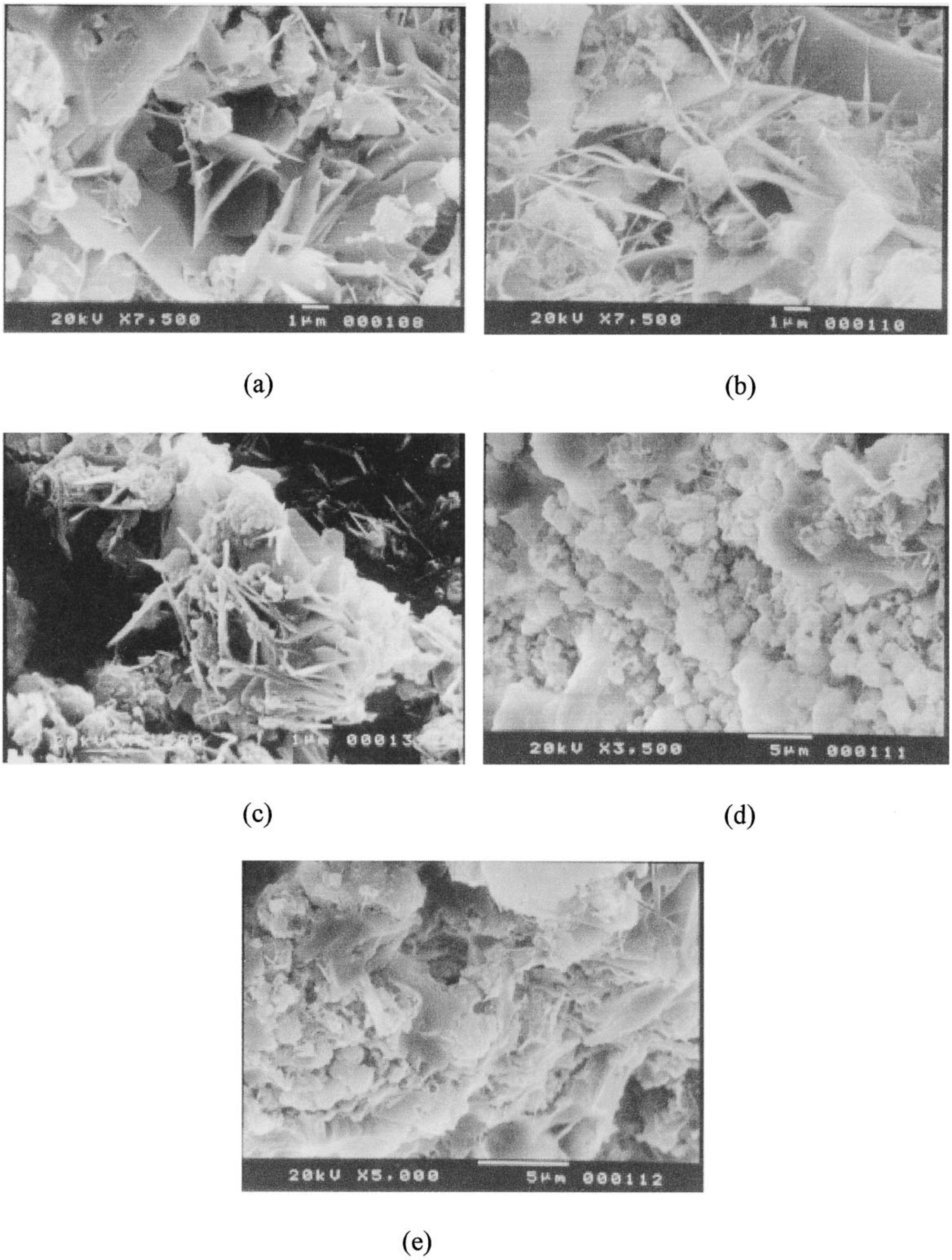

Fig. 6. SEM images of FABC paste after 200 days of hydration.

The results for FABC-B–800°C correlations are located on the linear regression obtained for FABC-A. This fact suggests that if the hydration time factor is deleted, the two cements have similar general behavior, irrespective of the starting fly ash characteristics and calcination temperature.

4. Conclusions

The characteristics of the starting fly ash strongly influence the kinetics of hydration, and, consequently, the rate of mechanical strength development.

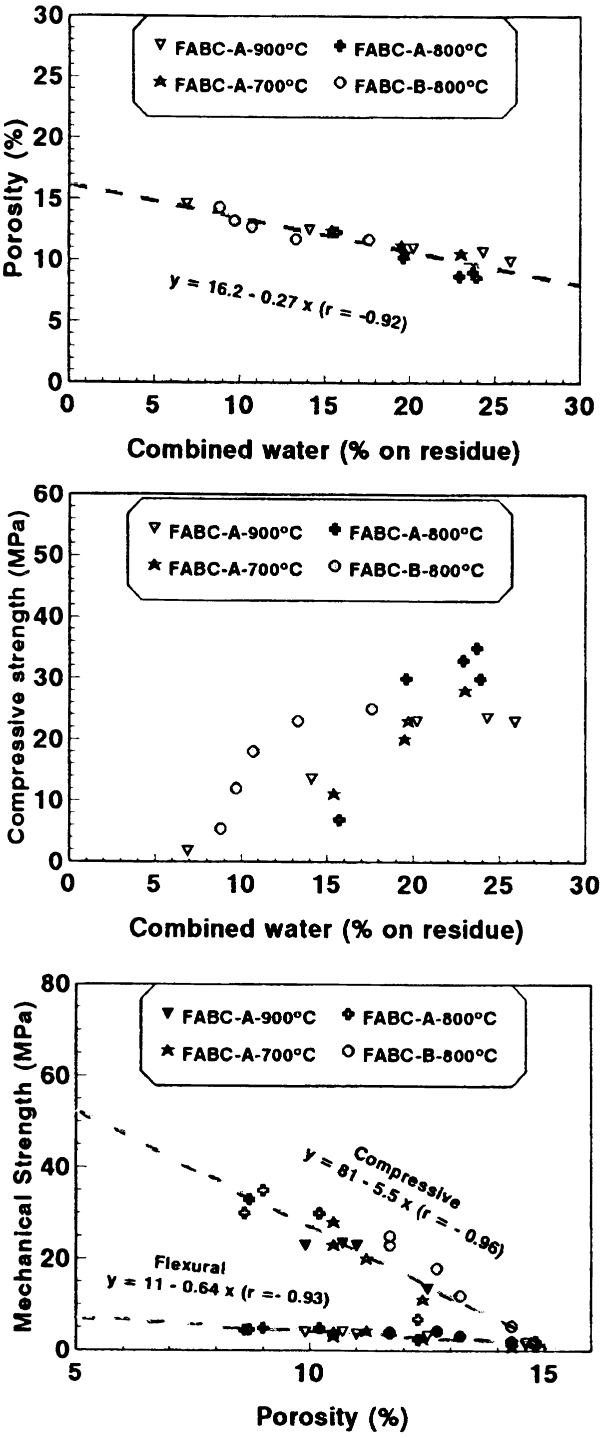

Fig. 7. General correlation obtained among the different microstructure parameters studied for all the FABC.

The mechanical properties of mortar prepared with FABC-B cement synthesized at 800°C, are markedly worse than those of equivalent FABC-A mortars. However, the differences tend to decrease after 200 days of hydration.

The difference in mechanical behavior is attributed to both the lower alkali content and higher iron content of FA-B starting fly ash, which promote formation of α' and β-C_2S polymorphs of lower reactivity. In addition, the formation of gehlenite (C_2AS) of low hydraulicity also influences the rate of development of mechanical properties of mortars made with FABC-B. As a result, the alkalinity of FABC-B mortar pore solution is lower than that of FABC-A mortar pore solution.

If the time factor is deleted, a general correlation is obtained among the microstructure and mechanical parameters for pastes and mortars for all the FABC cements synthesized, irrespective of the starting fly ash and calcination temperature.

Acknowledgments

The authors are thankful for the financial support of the CICYT (Project no. MAT 95-0054) and the Power Station of Soto and Ribera and Velilla de Río Carrión for the fly ash supplied.

References

[1] W. Jiang, D.M. Roy, Hydrothermal processing of new fly ash cement Ceram Bull 71 (4) (1992) 642.

[2] S. Goñi, A. Guerrero, A. Macías, M.P. Luxán, Effect of the synthesis temperature on the hydration reaction of fly ash–belite cement in: M. Mindess, S. Mindess, J. Skalny (Eds.), Materials Science of Concrete: The Sidney Diamond Symposium The American Ceramic Society, Westerville, OH, vol. 1, 1998, pp. 93–108.

[3] A. Guerrero, S. Goñi, A. Macías, M.P. Luxán, Hydraulic activity and microstructural characterization of new fly ash–belite cements synthesized at different temperature J Mater Res 14 (6) (1999).

[4] A. Guerrero, S. Goñi, A. Macías, M.P. Luxán, Mechanical properties, pore-size distribution and pore solution of fly ash–belite cement mortars, Cem Concr Res 29 (11) (1999) 1753–1758.

[5] R.S. Barneyback Jr., S. Diamond, Expression and analysis of pore fluids from hardened cement pastes Cem Concr Res 11 (2) (1981) 279–285.

[6] K. Suzuki, S. Ito, S. Shibata, Hydration and Strength of α–α' and β-Dicalcium Silicates Stabilized with Na–Al, K–Al, Na–Fe and K–Fe 7th Int Congr Chem Cem Paris Vol. II (1980) 47.