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Mechanical properties, pore size distribution, and pore solution of fly ash-belite cement mortars

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

Instituto de Ciencias de la Construccion Eduardo Torroja, Serrano Galvache s/n, 28033 Madrid, Spain

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Abstract

The mechanical properties, pore size distribution, and extracted pore solution of fly ash-belite cement (FABC) mortars were studied for a period of 200 days. The influence of the calcination temperature, which ranged from 700 to 900°C, of the fly ash-belite cement was discussed. The evolution with hydration time of the pore size distribution was followed by mercury intrusion porosimetry, and the results correlated with those of flexural and compressive strength. The pore solution was expressed and analyzed at different times of hydration.

Keywords: Pore size distribution; Mechanical properties; Alkalis; Mortar

1. Introduction

In the 1990s new possibilities for extending the reuse of fly ash opened when the strong activation that hydrothermal treatment causes on the fly ash pozzolanic reaction and the potential applications of the hydrated products thus formed were realized [1–7]. Jiang and Roy in 1992 [1] synthesized for the first time a new reactive belite cement, called "reactive fly ash cement." On the basis of that work, we are developing an extensive investigation project in which different Spanish fly ashes (ASTM class F) are used as raw materials.

When the calcination temperature of the hydrated precursors (obtained after the hydrothermal treatment) was 900°C, gehlenite (C_2AS, of slow hydraulicity) together with a mixture of the α'- and β-C_2S polymorphs were formed. The microstructure and mechanical properties of that fly ash-belite cement (FABC) were studied first for a period of 90 days from mixing [5]. To avoid the presence of gehlenite, the calcination temperature was decreased to 700°C, where, in addition to the absence of gehlenite, an amorphous material of α'- and β-C_2S polymorphs was also produced. Previous studies carried out on paste determined that at the calcination temperature of 800°C, the cement developed the best hydraulicity [6,7].

According to those investigations, the mechanical strength, pore size distribution, and pore solution of FABC mortars are presented in the present paper. The study was carried out for 200 days from mixing. The porosity and pore size distribution were evaluated by mercury intrusion porosimetry. The pore solution was extracted and analyzed during the hydration time.

2. Methods

Mortars were prepared according to the European and Spanish standard (EN-UNE 196-1) at siliceous (α'-quartz) sand to FABC ratio of 3, and demineralized water to FABC ratio of 0.75. The chemical composition of the starting fly ash and X-ray diffraction (XRD) analyses of the three cements synthesized at 700, 800, and 900°C are given in Table 1 and Fig. 1, respectively.

After mixing, different amounts were molded into prism-shaped specimens ($1 \times 1 \times 6$ cm) and compacted by vibration. The specimens were demolded after 2 days at >90% relative humidity (rh) for cements synthesized at 800 and 900°C, and after 7 days for cement synthesized at 700°C. Groups of six specimens for each cement were stored at the temperature of 21 ± 2°C and >90% rh for 200 days.

XRD patterns were recorded using Cu $K\alpha_1$ radiation on a Philips PW-1730 diffractometer (Phillips Research Laboratories, Eindhoven, The Netherlands) equipped with a graphite monochromator. Porosity and pore size distribution were investigated by mercury intrusion porosimetry carried out with a Micromeritics Pore Sizer 9310 (Micromeritics, Norcross, GA, USA). The pore solution was extracted by apply-

* Corresponding author. Tel.: +34-91-302-0440; fax: +34-91-302-0700.
E-mail address: pesgb35@fresno.csic.es (A. Guerrero)

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Table 1
Chemical composition of the starting fly ash (%)

LOI	IR	CaO (total)	SiO_2	CaO (free)	Fe_2O_3	Al_2O_3	MgO	SO_3	Na_2O	K_2O	SiO_2 (reactive)
5.6	0.3	4.6	48.8	0.25	7.4	26.8	1.9	0	0.7	3.6	35.8

LOI = loss on ignition; IR = insoluble residue.

ing high mechanical pressure (500 MPa) [8]. The sodium, potassium, calcium, and aluminum concentrations of the pore solution were determined by atomic absorption spectroscopy (using Model 1100B, Perkin Elmer Corp., Eden Prairie, MN, USA). pH was measured with a combined electrode for range 0 to 14.

3. Results and discussion

3.1. Mechanical properties

The changes with hydration time of the flexural and compressive mechanical strength of mortars are shown in Fig. 2. Each value represents the average of six measurements, and the bars represent the standard deviation of the mean values. After the flexural strength of specimens was determined, the compressive strength measurement was carried out on the two halves of each specimen according to the Spanish standard UNE EN 196-1 or UNE 80-101.

For the FABC calcined at 700°C (FABC-700°C), the first data could be measured after 14 days from mixing, due to its slow hydration rate at early ages; for FABC-800°C data was measured after 3 days; and for FABC-900°C data was measured after 7 days from mixing.

As seen in Fig. 2, the main differences among the three calcination temperatures occurred during the first 28 days, where the strength values for the FABC-800°C practically duplicated those of the FABC-900°C. For the FABC-700°C, the values were the lowest during that period. The strength of FABC-900°C progressively increased for 60 days, remaining thereafter more or less constant (23 and 4 MPa for compressive and flexural, respectively).

The FABC-700°C began to gain strength after the initial induction period, reaching practically the same rate and values as those of FABC-900°C. The flexural strength began decreasing after 60 days, resulting in a value of 3 MPa at the end of the experiment. This decrease did not happen in compressive strength (28 MPa after 200 days).

As detected by scanning electron microscopy (SEM) analyses of the FABC-700°C paste (Figs. 9a and 9b of our previous work [7]), microcracks appeared that could be produced via conversion of hexagonal hydrated carboaluminate ($C_4Ac_{0.5}H_{12}$) to cubic katoite ($C_3AS_3c_3H_{1.5}$) (corroborated by XRD data). This conversion released a great amount of water molecules, which could provoke shrinkage and therefore microcracks when the samples are dried or during the microscopy examination. It is possible that those microcracks affected flexural strength but not compressive strength.

The FABC-800°C showed the best mechanical properties among the three calcination temperatures studied, principally at earlier ages of hydration. This is in a good agreement with the combined water and hydration degree results previously reported [7]. This is due to its compact micro-

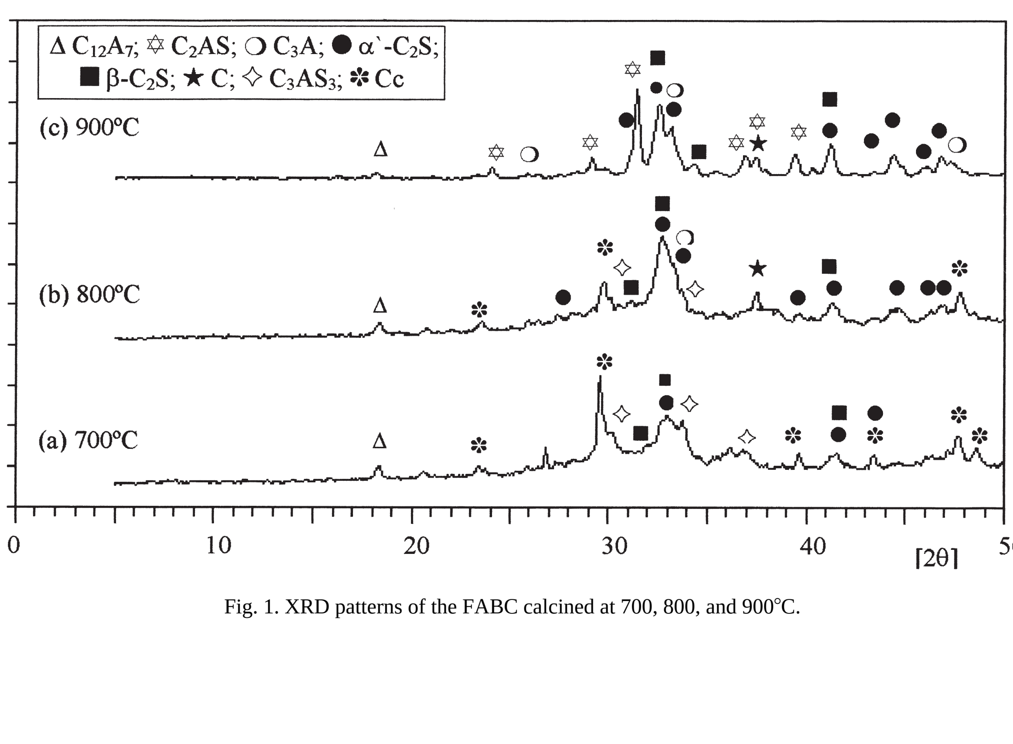

Fig. 1. XRD patterns of the FABC calcined at 700, 800, and 900°C.

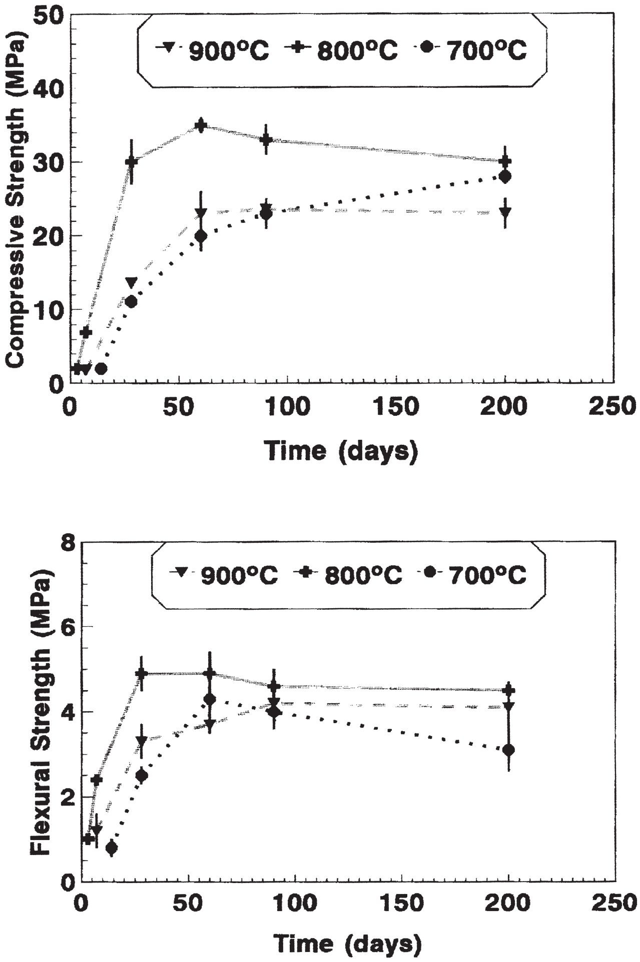

Fig. 2. Flexural and compressive strength evolution as a function of the hydration time.

structure, as the SEM analyses evidenced (see Figs. 10a through 10c of our previous work [7]). The vertumnite phase ($C_4A_2S_4H_{15}$) (see Fig. 2 in our previous work [7]) combined a great amount of water molecules and perhaps that could explain its best mechanical behavior.

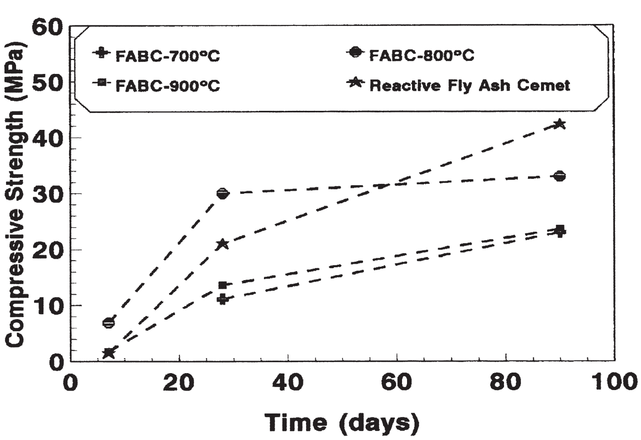

Fig. 3. Comparison of the compressive and strength data from Jiang and Roy [1] and results obtained in the present study.

Characteristics of the starting cement, such as the absence of the crystalline gehlenite (C_2AS) (of slow hydraulicity) together with the amorphization of the α'- and β-C_2S polymorphs, can contribute to the higher and fastest hydraulicity at early ages, and consequently, to their higher and fastest strength gain rate. In fact, the heat evolution of the FABC-900°C stabilized at a value of ≈30 KJ/Kg, whereas the heat of FABC-800°C increased progressively, reaching a value about 2.6 times higher after 40 h [7].

In Fig. 3 the compressive strength of FABC mortars is compared with values previously reported by Jiang and Roy [1]. As shown, the values of the mortars fabricated with the

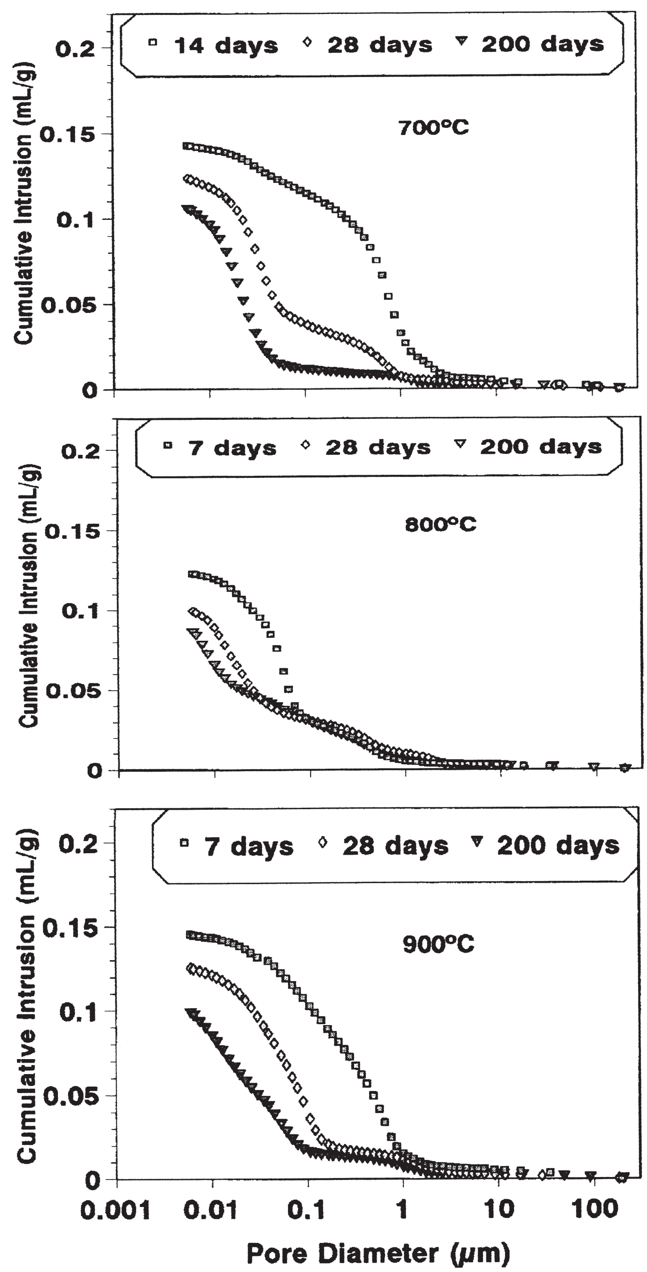

Fig. 4. Evolution with hydration time of pore size distribution curves of the FABC calcined at 700, 800, and 900°C.

FABC calcined at 800°C were the highest during the first 28 days of hydration. Nevertheless, after 90 days, the cement synthesized by Jiang and Roy reached the highest strength. Although the global synthesis process of the FABC is very similar to that used by Jiang and Roy, there are differences in the mineralogical composition of the final product, such as the formation of gehlenite (C_2AS) and α'-C_2S polymorph at the calcination temperature of 900°C. No XRD data for lower calcination temperature were published by those authors.

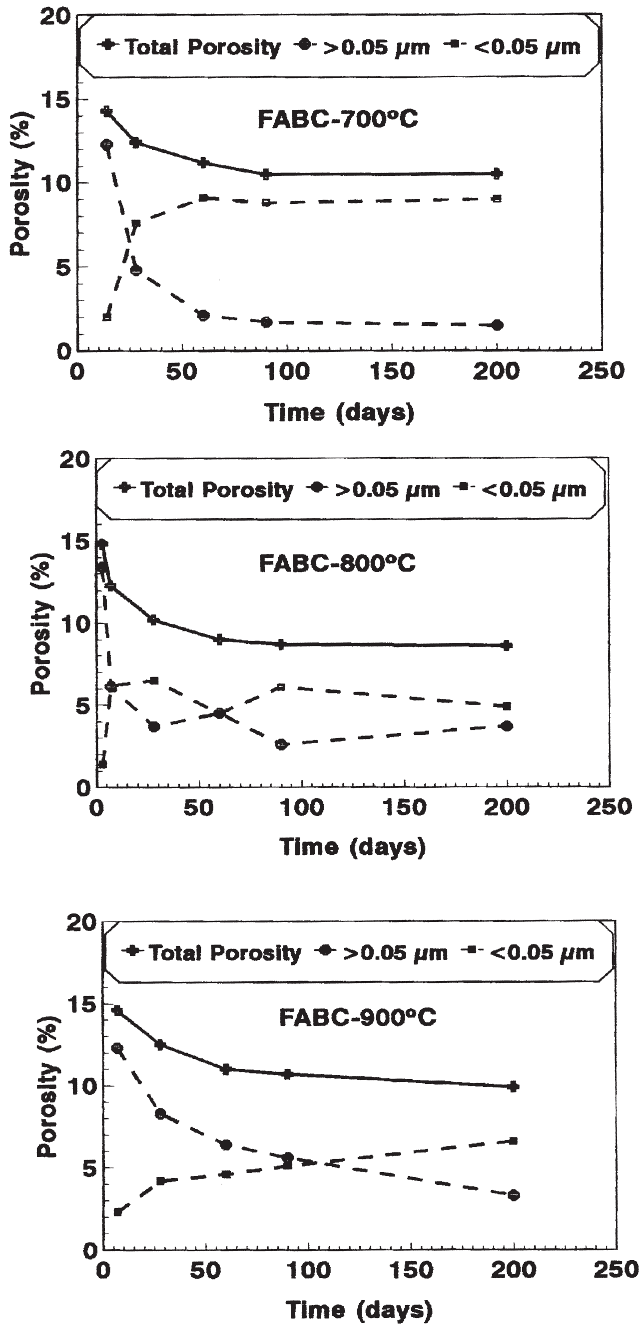

Fig. 5. Percentage of pores of diameter >0.05 and <0.05 μm and total porosity vs. time.

3.2. Porosity and pore size distribution analysis

The pore size distribution curves of mortar specimens made with the three FABC calcined at 700, 800, and 900°C, are presented in Fig. 4. Cubes about 1 cm^3 were previously degasified under vacuum.

As shown, the majority of pores had a diameter smaller than 1 μm for FABC-900°C and FABC-700°C at the ages of 7 and 14 days, respectively. Nevertheless, for FABC-800°C after 7 days of hydration, the majority of pores had a diameter less than 0.1 μm. In addition, the total porosity of that cement was the lowest (12.3% by weight vs. 14.3% at 700°C and 14.6% at 900°C). The curves shifted over time to lower pore diameter sizes, and the total porosity decreased.

The main pore size distribution change as a result of hydration was produced in the range of pores of diameter >0.05 μm, which strongly decreased during the 28 days, as the percentage of pores of <0.05 μm increased almost symmetrically (see Fig. 5). After 7 days, the number of smaller pores (<0.05 μm) was higher than those of diameter >0.05 μm, in the case of FABC-800°C. This occurred after 28 days for the FABC-700°C, and after 90 days for FABC-900°C (see Fig. 5).

Although the decrease of the total porosity carried over time is not relevant (27, 42, and 32% for FABC-700°C, FABC-800°C, FABC-900°C, respectively), the shift toward smaller pores produced in the case of the FABC-700°C, is significant (the percentage of pores of diameter <0.05 μm after 200 days is six times higher than that of pores >0.05 μm).

An apparent contradiction between the flexural strength evolution at late ages and the porosity of FABC-700°C appeared. As mentioned previously, the flexural strength began to decrease after 60 days (see Fig. 2) and consequently the total porosity, or at least the bigger pores, should have increased. A possible explanation for this contradiction could be that part of the water released during the conversion produced an additional hydration, and consequently an additional microstructure densification, which counteracted the effect of conversion.

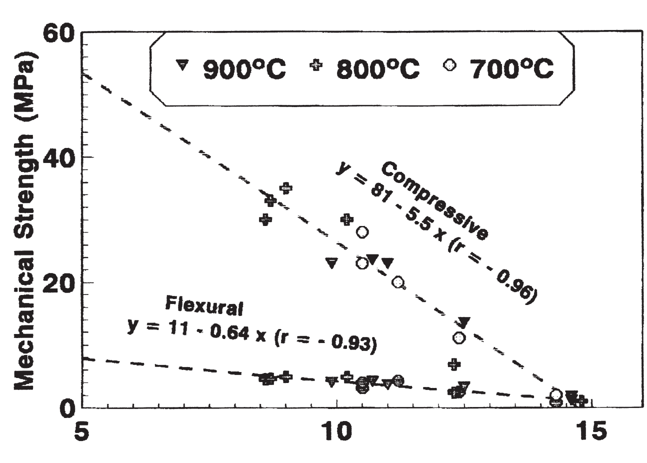

Fig. 6. Correlation between mechanical strength and porosity.

In Fig. 6, the compressive and flexural strength values are correlated to the total porosities of the three cements: FABC-700°C, FABC-800°C, and FABC-900°C studied. As shown, an acceptable inverse linear correlation is found.

3.3. Pore solutions analyses

The analytical study of the extracted pore solution was carried out for the calcination temperatures of 800 and 900°C. Results are presented in Fig. 7.

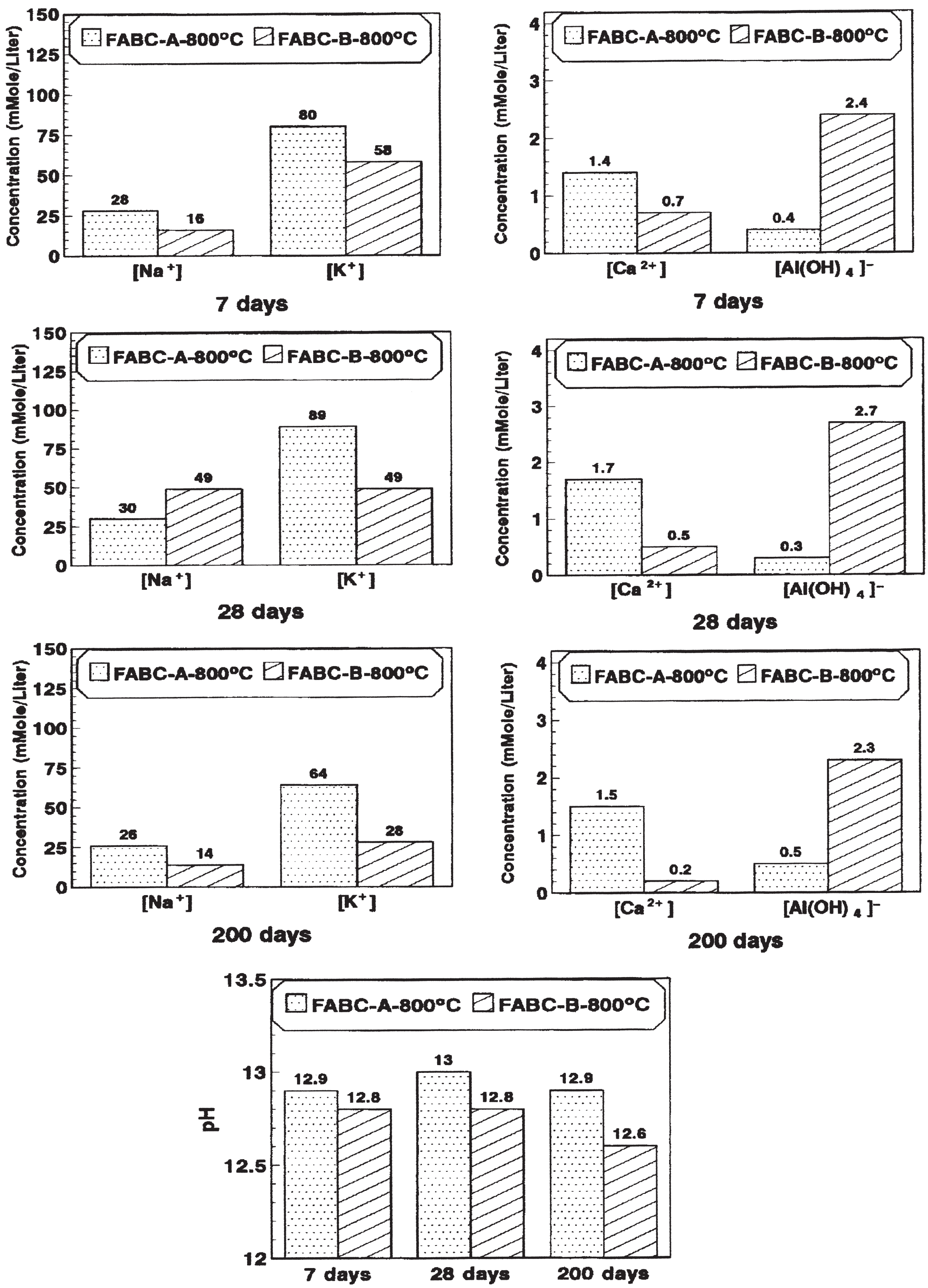

Fig. 7. Concentration of Na^+, K^+, Ca^{2+}, $Al[(OH)_4]^-$, and pH of the FABC-800°C and FABC-900°C mortar pore solution at different hydration times.

The alkalinity of these materials is comparable to that of ordinary Portland cements with low alkali content. As shown in Fig. 7, the pH values were about 13 and did not present significant changes during the 200 days of hydration. In the case of the FABC calcined at 800°C, the pH was always slightly lower than that of FABC calcined at 900°C. As explained in a previous paper [7], crystalline portlandite ($Ca(OH)_2$) was not detected from XRD analysis in any of the cases. The relatively high pH values were due to the alkaline ions (sodium and potassium) of the starting fly ash (see Table 1). With respect to these ions, the concentration of potassium was about three times higher than that of sodium for the FABC-800°C and nine times higher for the FABC-900°C. Calcium and aluminate concentrations were much lower compared to those of alkaline ions.

4. Conclusions

The FABC calcined at 800°C showed the best mechanical properties. The strength gain rate was the fastest at early ages and strength values remained the highest thereafter. This mechanical behavior is in accordance with combined water and hydration degree results previously reported [7].

The FABC calcined at 700°C had a very slow mechanical hydraulicity at early ages, but after the induction period (about 14 days), the strength reached similar values to FABC calcined at 800°C.

The pore size distribution changes mainly occurred in the range of pores of diameter >0.05 μm, which decreased at the same rate that pores of <0.05 μm diameter increased. Thus, total porosity was not affected to a great degree.

The alkalinity of the extracted pore solution of these materials is comparable to that of ordinary Portland cements of low alkali content and this is attributable to the alkalis present in the starting fly ash.

Acknowledgments

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