Pergamon

Cement and Concrete Research 30 (2000) 1231–1238

CEMENT AND CONCRETE RESEARCH

Durability of new fly ash–belite cement mortars in sulfated and chloride medium

A. Guerrero*, S. Goñi, A. Macías

Institute of Construction Science "Eduardo Torroja" CSIC, Serrano Galvache, s/n 28033 Madrid, Spain

Received 2 May 1999; accepted 12 May 2000

Abstract

The durability of mortars fabricated with two kinds of low-energy cements containing hydrothermally activated Spanish fly ashes is presented. The study has been carried out by means of the Köch–Steinegger test at 21 ± 2°C for 180 days. The durability was evaluated from the changes of flexural strength of the mortars after immersion in the potential aggressive solution (0.5 M NaCl+0.5 M Na_2SO_4) compared with those obtained in similar samples immersed in demineralized water. The changes in microstructure were followed by mercury intrusion porosimetry (MIP) and mineralogy by X-ray diffraction (XRD). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Durability; Sulfated and chloride aggressive; Fly ash–belite cement

1. Introduction

Durability studies of a new type of low-energy cement, designated fly ash–belite cement (FABC) related to sulfate and chloride attack are presented. According to previous studies on hydration reaction and mechanical properties [1–5], FABC showed a better behavior than traditional belite cements. Nevertheless, no durability investigations have been found in the literature on these new cementitious materials.

Sulfate attack on ordinary Portland cement (OPC) leads to formation of ettringite and gypsum: Portlandite (CH) disappears and the Ca/Si ratio of the CSH decreases. The physical expansion has generally been attributed to ettringite formation, in which the $Al(OH)_4^-$, OH^-, and Ca^{2+} are mainly supplied by the AF_m phase, as well as by unreacted aluminate or ferrite phase [6].

In the case of FABC, its high alumina content (15–16%), together with the low sulfate content, in comparison with OPC and the absence of portlandite (CH), are the main factors that play an important role related to potential sulfate attack.

The aggressiveness of sulfate depends to a great extent on the other accompanying ions, as in sea water, where it is inhibited by the presence of chloride. In this sense, durability studies carried out in our laboratory, in NaCl+Na_2SO_4 solutions, with hydrated OPC mixed with fly ash and pozzolanic copper slag [7,8], determined both the preferred diffusion of chloride vs. sulfate and the formation of chloroaluminate (Friedel's salt).

The dramatic increase of the ionic strength of the pore solution caused by the ingress of NaCl and different reactions of Na and Cl with cement components, activated the pozzolanic behavior, leading to the formation of hydrated aluminates (AF_m type), which were subsequently transformed into non-expansive Friedel's salt, via OH^-–Cl^- ion exchange.

These aspects are approached in the present paper, in which the durability of different FABC mortars in a 0.5 M NaCl+0.5 M Na_2SO_4 solution has been studied by means of the Köch–Steinegger test [9] at a temperature of 21±2°C for 180 days. The durability was evaluated from the changes of flexural strength of mortars after immersion in the potential aggressive solution, compared with similar samples immersed in demineralized water. Changes of the microstructure were followed by mercury intrusion porosi-

---

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

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

0008-8846/00/$ – see front matter
PII: S0008-8846(00)00313-6

Table 1
Chemical composition of the two fly ashes (wt.%)

(%)	LOI	IR	CaO (total)	SiO_2	CaO (free)	Fe_2O_3	Al_2O_3	MgO	SO_3	Na_2O	K_2O
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

LOI = loss on ignition, IR = insoluble residue.

metry (MIP) and mineralogy by X-ray diffraction (XRD). The influence of fly ash characteristics on the durability behavior is also discussed.

2. Experimental

The cement fabrication was based on the Jiang and Roy methodology [10]. Two kinds of Spanish fly ashes (ASTM class F) and CaO (analytical reagent grade) were mixed at a Ca/Si molar ratio of 2 and demineralized water to a solid ratio of 5. The mixture was hydrothermally heated at 200°C, 1.24 MPa pressure for 4 h. Thereafter, the dried solid was heated at a rate of 10°C/min up to 600°C and at 5°C/min from 600°C to 800°C. The chemical and XRD analyses of the two FABCs (called FABC-A and FABC-B) are given in Table 1 and Fig. 1, respectively. The mortars were prepared at a (α-quartz) sand to a FABC ratio of 3 and demineralized water to a FABC ratio of 0.75.

After mixing, prisms were molded into 1 × 1 × 6 cm specimens and compacted by vibration. The samples were demolded after 2 days at >90% relative humidity (rh) and cured in demineralized water at 21 ± 2°C for 28 days. After curing, groups of six samples of each cement were immersed in the aggressive solution and stored in sealed plastic bottles at 21 ± 2°C for 180 days. The volume of solution was 800 ml per six samples. Similar groups of six samples were stored in demineralized water as reference.

XRD patterns were recorded with a diffractometer (Model PW-1730 Philips Research Laboratories, Eindhoven, The Netherlands) using a graphite monochromator and Cu Kα_1 radiation. Porosity and pore-size distribution were investigated by mercury intrusion porosimetry (model 9320 pore Sizer Micromeritics Instrument, Norcross, GA). Small cubic pieces of about 1 cm^3 were previously degasified in vacuum for 15 min prior to intrusion.

3. Results and discussion

3.1. XRD analysis

3.1.1. FABC-A

In spite of removing the sand from mortars prior to analyses, fine particles remained. In the case of samples immersed in demineralized water (Fig. 2), after 1 day,

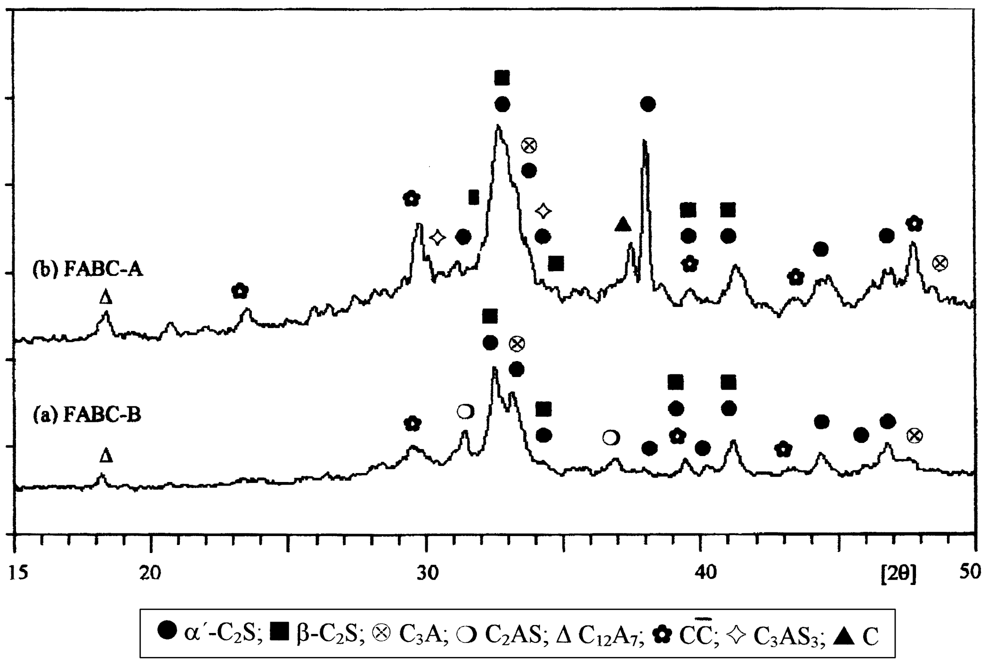

Fig. 1. XRD patterns of anhydrous cement.

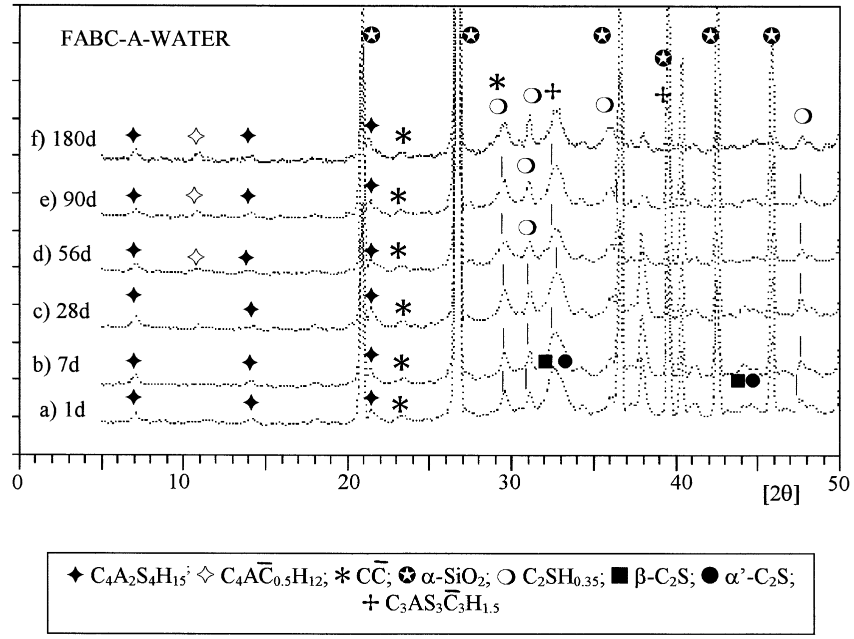

Fig. 2. XRD patterns of FABC-A mortar samples immersed in demineralized water.

vertumnite ($Ca_4Al_4Si_4O_6(OH)_{24}\cdot 3H_2O$)($C_4A_2S_4H_{15}$)) reflections appeared whose intensities remained constant throughout the experiment. Vertumnite was named in 1977 by Passaglia and Galli [11]. Its JCPDS card no. 29-291 is very close to that of stratlingite (JCPDS card no. 29-285) and according to Dana's New Mineralogy [12], vertumnite may be regarded as a polytype of stratlingite, whose formation could take place from hydration of gehlenite (C_2AS). The main difference between the two phases is the X-ray reflection of intensity 100, which appears at 7.066, 2θ angular zone, for stratlingite ($Ca_2Al_2SiO_7\cdot 8H_2O$)C_2ASH_8, and at 21.2, 2θ angular zone, for vertumnite. This phase was more clearly detected in the study carried out with paste (see Fig. 2 in Ref. [3]). $C_2SH_{0.35}$($Ca_2SiO_4\cdot 0.35H_2O$) and $C_3AS_3\bar{C}_3H_{1.5}$($Ca_3Al_2(SiO_4,CO_3,OH)_3$) (JCPDS card no. 3-801) (cubic variety of garnet group, garnet subgroups) reflections increase over hydration time (compare Fig. 2(a) and (f)). The corresponding reflections of hydrated carboaluminate ($Ca_4Al_2O_6(CO_3)_{0.5}(OH)\cdot 11.5H_2O$)($C_4A\bar{C}_{0.5}H_{12}$) begin to appear after 28 days, increasing over time. Calcite

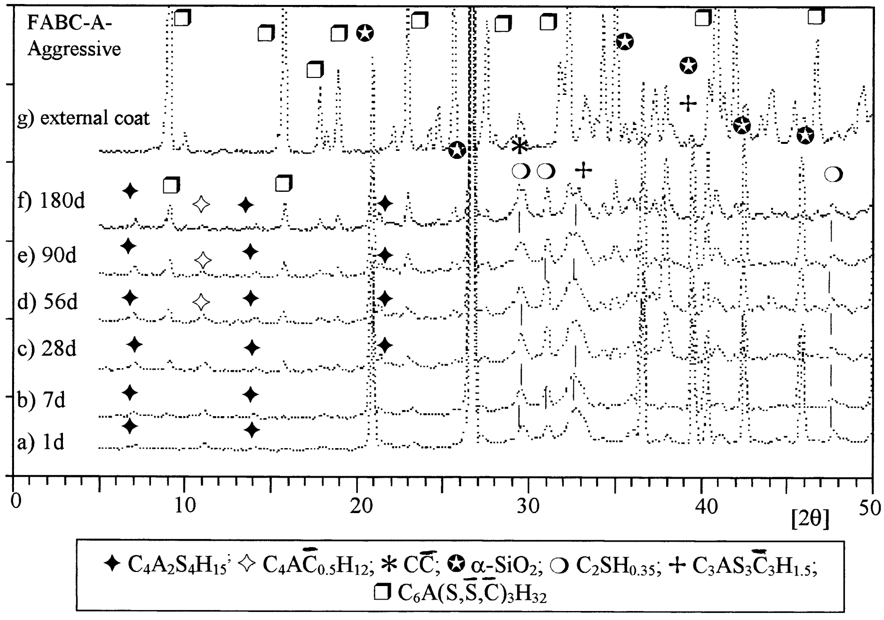

Fig. 3. XRD patterns of FABC-A mortar samples immersed in aggressive solution and external coat formed after 180 days of mortar immersion.

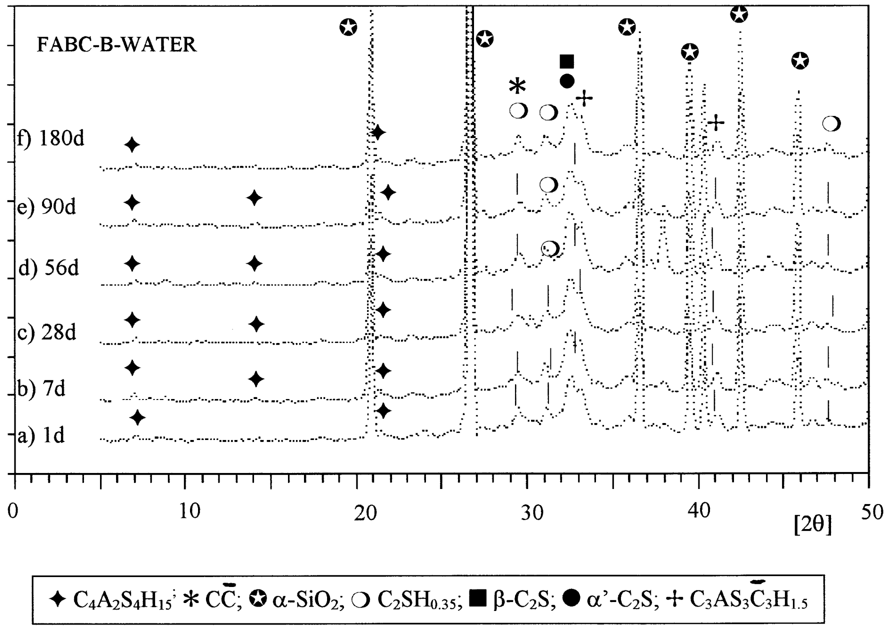

Fig. 4. XRD patterns of FABC-B mortar samples immersed in demineralized water.

$(CaCO_3)(C\bar{C})$ is also detected. The α′ and β-C_2S reflections from the anhydrous cement remained.

When the samples were immersed in the aggressive solution, an external white coat was produced whose XRD pattern (Fig. 3(g)) revealed the presence of ettringite $(Ca_6Al_2(SO_4, SiO_4,CO_3)_3(OH)_{12}\cdot 26H_2O)(C_6A(\bar{S},S,\bar{C})_3H_{32})$, called $AF_t{}'$ to differentiate it from pure ettringite $(Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O)((C_6A\bar{S}_3H_{32})$, AF_t. In the bulk of samples, the reflections of the $AF_t{}'$ phase begin to appear after 7 days of immersion, increasing thereafter progressively: compare Fig. 3(b) and (f).

The mechanism of the $AF_t{}'$ formation could include reaction with carbonated katoite $(C_3AS_3\bar{C}_3H_{1.5})$ due to their similar compositions. This mechanism has been

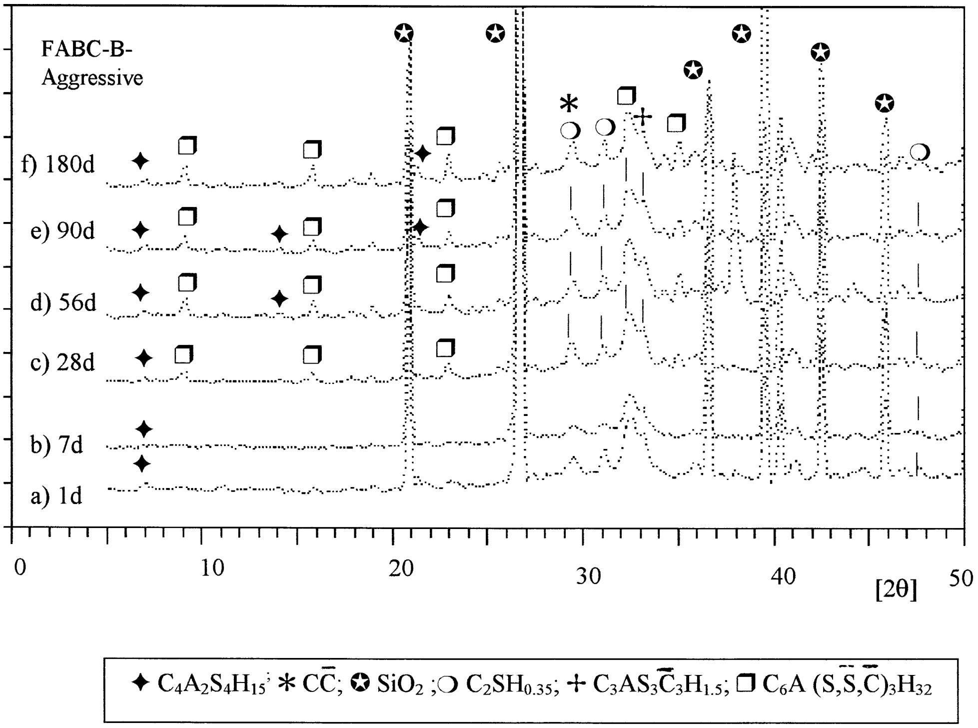

Fig. 5. XRD patterns of FABC-B mortar samples immersed in aggressive solution.

corroborated from EDS microanalyses [13]. In addition, SEM and EDS microanalysis data revealed the presence of cubic crystals with Na^+ and SO_4^{2-} concentration ratio equal to Na_2SO_4.

After 1 day of immersion, the vertumnite ($C_4A_2S_4H_{15}$) reflections are considerably lower than those obtained in water (compare Fig. 2(a) and Fig. 3(a)), increasing over time. Nevertheless, the $C_4A\bar{C}_{0.5}H_{12}$ reflections are more intense than those obtained in water, practically disappearing after 180 days of immersion in the aggressive solution. There is no evidence of the formation of crystalline chloride compounds such as Friedel's salt, although chloride was detected by EDS microanalysis [13]. The XRD results of samples immersed in the aggressive solution suggest that sulfate ions are preferentially combined with solid phase compared to chloride.

3.1.2. FABC-B

The main difference with respect to the XRD results obtained for samples immersed in demineralized water (Fig. 4) compared with those of FABC-A (Fig. 2) are: (i) the reflections of all the new hydrated compounds are much less intense and (ii) the reflections of α' and β-C_2S from the anhydrous cement are considerably higher with almost no change over immersion times up to 180 days.

These results seem to indicate that the hydration of this kind of cement is less compared with that of FABC-A, or in other words, the α' and β-C_2S polymorphs are more persistent for FABC-B. Previous studies carried out in paste [2,3] confirmed their different hydraulicity, which was attributed to both a lower alkali content and higher iron content of FABC-B.

When the samples were immersed in the aggressive solution, AF_t' reflections began to appear after 28 days, increasing thereafter with immersion time (see Fig. 5(c) and (f)). After 180 days, the AF_t' reflections were less intense than those of FABC-A (compare Fig. 3(f) and Fig. 5(f)). The vertumnite ($C_4A_2S_4H_{15}$) and $C_4A\bar{C}_{0.5}H_{12}$ reflections are insignificant.

These XRD results suggest that FABC-B is less sensitive than FABC-A to all the reactions in which sulfate are involved and, consequently, exposure will have different effects on the pore solution, porosity and flexural strength of mortars. The analyses of extracted pore solution (previously published in Ref. [14]) (Table 2) showed that chloride ions easily diffuse through the porous microstructure. Therefore, the concentration of chloride in the pore solution is equal to that of aggressive (0.5 M), after 1 day of immersion in the case of FABC-B and after 7 days of immersion, for FABC-A. This suggests that chloride ion does not combine with solid phase, as XRD of Figs. 3 and 5 evidenced.

Table 2
Chloride and sulfate concentrations of the extracted mortar pore solution [14]

	FABC-A		FABC-B	
Immersion time (days)	$[Cl^-]$ (mol/l)	$[SO_4^{2-}]$ (mol/l)	$[Cl^-]$ (mol/l)	$[SO_4^{2-}]$ (mol/l)
1	0.30	0.25	0.46	0.29
7	0.47	0.28	0.46	0.40
28	0.55	0.33	0.41	0.38
56	0.48	0.25	0.42	0.41
90	0.48	0.30	0.48	0.40
180	0.45	0.19	0.50	0.39

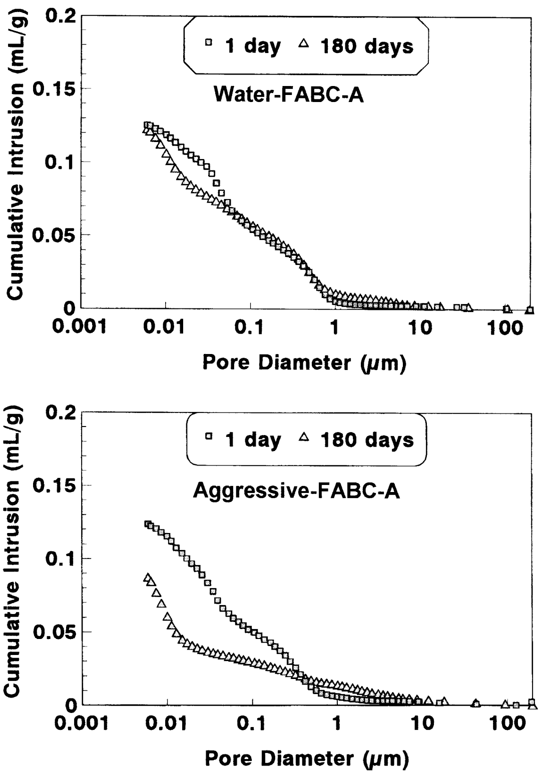

Fig. 6. Pore-size distribution curves of FABC-A mortar samples immersed in demineralized water and in aggressive solution.

Nevertheless, sulfate concentration in the pore solution is always lower than that of aggressive (0.5 M). This behavior is marked in the case of FABC-A and can be attributed to the formation of sulfated phases, as shown by XRD, together with a slower diffusion of sulfate vs. chloride.

3.2. Pore-size distribution analysis

3.2.1. FABC-A

When the samples were immersed in the aggressive solution (Fig. 6), the main pore-size distribution change compared with samples immersed in water is the refinement of pores whose diameters shifted to lower values.

In Fig. 7, the total porosity (wt.%) and the percentage of pores of diameter >0.1 and <.0.1 μm are represented vs. the square root of time. Data at 0 day correspond to those obtained before immersion of mortar in the aggressive solution. Between 1 and 7 days immersion in the aggressive solution, the changes mentioned above were produced. Thereafter, the values remain more or less constant. The

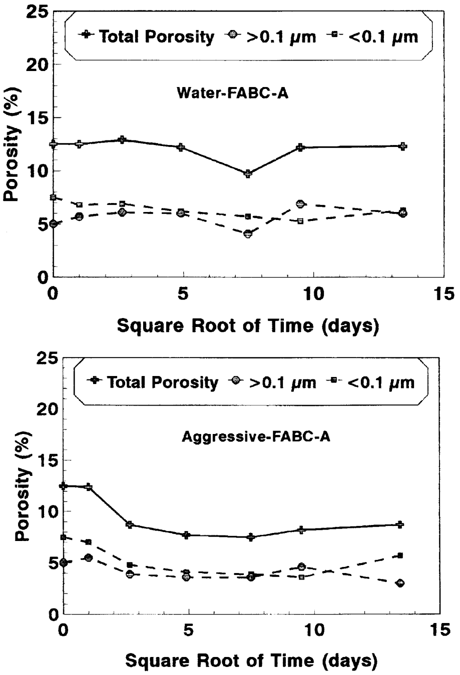

Fig. 7. Percentage of pores of diameter >0.1 and <0.1 μm and total porosity of FABC-A mortar samples.

total porosity decreased from 12.5% at 0 day to 8.7% (after 180 days of immersion) in the aggressive solution; nevertheless, for samples immersed in demineralized water, the total porosity almost does not vary (from 12.5% after 0 day to 12.3% after 180 days).

The cause of the dramatic decrease of total porosity and shift of the pore-size distribution towards smaller pores, is due first to the diffusion of sulfate, chloride and sodium ions from the aggressive (as the pore-solution analyses corroborated) and, second, to the formation of new sulfate compounds. The ettringite, AF_t', phase formed does not produce expansion over time, perhaps due to the space available for it to grow inside pores or perhaps due to ettringite formed from katoite ($C_3AS_3\bar{C}_3H_{1.5}$).

3.2.2. FABC-B

The FABC-B mortar samples do not undergo significant pore-size distribution changes when immersed in demineralized water (see Fig. 8). However, after 180 days of immersion in the aggressive solution, the pore-size distribution curve strongly shifted to lower values of pore diameter.

The changes of the total porosity, and pores of diameter >0.1 and <0.1 μm (Fig. 9) with the square root of time showed a progressive decrease in the aggressive solution, mainly of pores of diameter >0.1 μm, while the percentage of pores <0.1 μm practically is constant over time.

If the FABC-A and FABC-B behavior in the aggressive solution is compared, the following differences can be established: (i) the porosity of FABC-A mortars decreased at a faster rate than FABC-B and (ii) both large and small

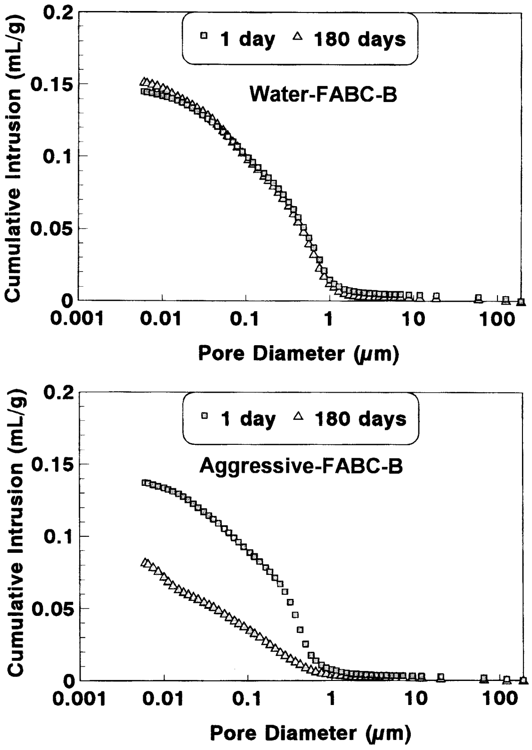

Fig. 8. Pore-size distribution curves of FABC-B mortar samples immersed in demineralized water and in aggressive solution.

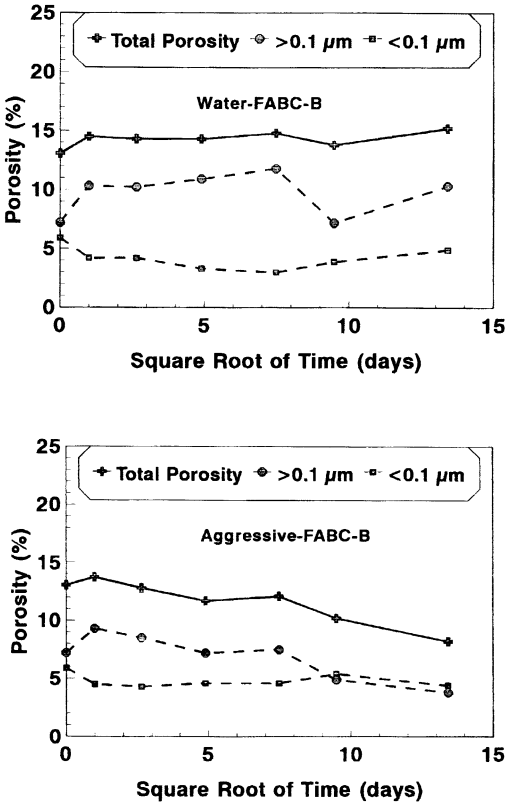

Fig. 9. Percentage of pores of diameter >0.1 and <0.1 μm and total porosity of FABC-B mortar samples.

pores decreased for FABC-A, whereas only the larger pores decreased in the case of FABC-B.

As the XRD results show, much ettringite (AF_t') formed in the case of FABC-A filling space, and perhaps that was one reason explaining its porosity behavior in the aggressive solution.

3.3. Flexural strength

The flexural strength changes observed in Fig. 10 are consistent with those of porosity shown in Figs. 7 and 9.

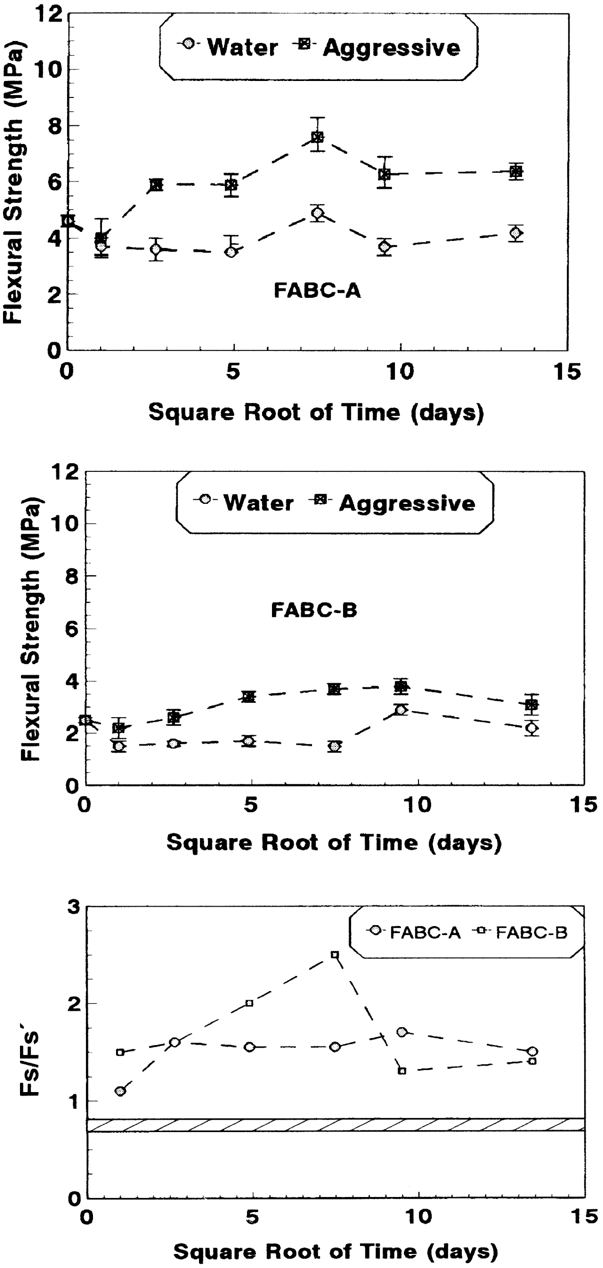

Fig. 10. Flexural strength and corrosion index (F_s/F_s') of mortar samples vs. time, F_s=strength after immersion in the aggressive solution; F_s'=strength after immersion in demineralized water.

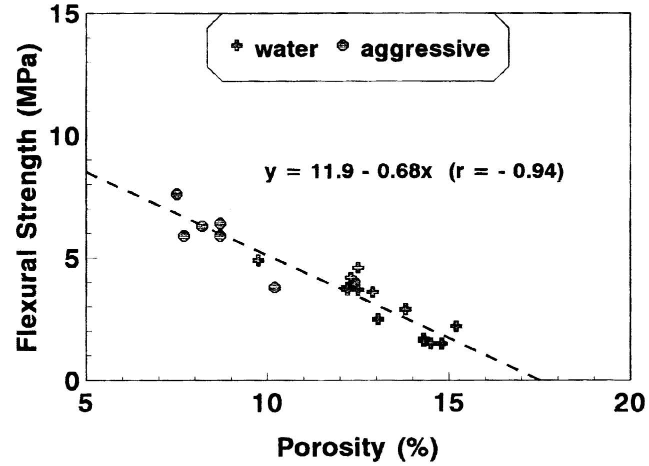

Fig. 11. Flexural strength vs. total porosity.

Each value in Fig. 10 represents the average of six measurements; bars show standard deviations of the mean values. The data at "0 day" correspond to samples after 28 days curing and are taken as reference.

As shown in Fig. 10, no significant changes are observed when both FABC-A and FABC-B mortars were immersed in demineralized water. Nevertheless, the values for FABC-B are considerably lower compared with those of FABC-A. This is in accordance with the more dense FABC-A microstructure (see Figs. 7 and 9). The percentage of pores of diameter >0.1 μm for FABC-B is higher than that of FABC-A.

When the mortars were immersed in the aggressive solution, the flexural strength for FABC-A markedly increased between 1 and 7 days. Nevertheless, for FABC-B the increase is much less marked and progressive.

According to the Köch–Steinegger test [9], the criterion to classify a material as durable in a specific aggressive in that the relative strength of aggressive-solution-stored samples (F_s) to water-stored (F_s') ones should be higher than 0.7–0.8. In all the cases, the relative strength is above the aforementioned threshold (Fig. 10), and, consequently, it can be deduced that both FABC-A and FABC-B mortars are durable in the aggressive solution over the duration of the test.

The flexural strength behavior is related to porosity. As seen in Fig. 11, an inverse linear correlation is obtained when flexural strength and porosity data are compared. The regression equation is practically the same as that previously given for all the FABC studied during hydration (see Fig. 7 of Ref. [5]).

4. Conclusions

The crystalline non-expansive ettringite: $Ca_6Al_2(SiO_4,SO_4,CO_3)_3(OH)_{12}\cdot 26H_2O(C_6A(\bar{S},S,\bar{C})_3H_{32})$ is preferentially formed as a result of sulfate diffusion from the aggressive solution. No XRD evidence appears for chloroaluminate such as Friedel's salt, although chloride and sodium concentrations of the extracted pore solution reached practically the same values as those of the aggressive. Consequently, the porosity decreased and the pore-size distribution shifted to smaller pores, densifying the microstructure.

This densification causes an increase of the flexural strength values, which are maintained above those of the samples immersed in demineralized water throughout the experiment. Accordingly, the FABC mortars can be considered as durable materials in the solution studied, irrespective of the starting FABC characteristics.

From the results obtained here, it is not possible to know the role that chloride plays on the inhibition of sulfate aggressiveness. For that, more studies are needed in sulfated solution (without chloride).

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 supply of fly ash.

References

[1] S. Goñi, M.P. Luxán, A. Guerrero, M.S. Hernández, A. Macías, Microstructural study of hydration reactions of a fly ash–belite cement, in: V.M. Malhotra (Ed.), Proceedings of the Sixth CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, American Concrete Institute, Bangkok, 1998, pp. 207–224.

[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, 1998, pp. 93–108.

[3] A. Guerrero, S. Goñi, A. Macías, M.P. Luxán, Hydraulic activity and microstructural characterization of new fly ash–belite cement synthesized at different temperature, J Mater Res 14 (6) (1999) 2680–2687.

[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 (1999) 1753–1758.

[5] A. Guerrero, S. Goñi, A. Macías, M.P. Luxán, Effect of the starting fly ash on the microstructure and mechanical properties of fly ash–belite cement mortars, Cem Concr Res 30 (4) (2000) 553–559.

[6] H.F.W. Taylor, Cement Chemistry, Academic Press, Harcourt Brace Jovanovich, Publishers, London, 1990.

[7] S. Goñi, M.P. Lorenzo, J.L. Sagrera, Durability of hydrated portland cement with copper slag addition in $NaCl+Na_2SO_4$ medium, Cem Concr Res 24 (8) (1994) 1403–1412.

[8] M.P. Lorenzo, The Effect of Two Kinds of Spanish Fly Ashes on the Microstructure and Durability of the Hydrated Portland Cement Paste, PhD Thesis, University Complutense, Madrid, Spain, 1993.

[9] A. Köch, H. Steinegger, A rapid test for cements for their behaviour under sulphated attack, Zem-Kalk-Gips 13 (1960) 317.

[10] W. Jiang, D.M. Roy, Hydrothermal processing of new fly ash cement, Ceram Bull 71 (4) (1992) 642–647.

[11] E. Passaglia, E. Galli, TMPM, Tschermarks Mineral Petrogr Mitt JCPDS no. 29-291, (57) (1977) p. 24.

[12] Dana's New System of Mineralogy, eighth ed., pp. 1548.

[13] A. Guerrero, S. Goñi, A. Macías, E. Fernández, Microstructure of new fly ash–belite cement mortar: Changes provoked by sulphate, chloride and sodium ions, in: L. Jany, A. Nisperos (Eds.), Proceedings of 21st International Conference on Cement Microscopy, Las Vegas, NV, International Cement Microscopy Association, Duncanville, Texas, 1999, pp. 230–237.

[14] A. Guerrero, S. Goñi, A. Macías, Efecto de los Iones Sulfato, Cloruro y Sodio en la Fase Acuosa y la Microestructura de un Nuevo Mortero fabricado con Cemento Belítico de Cenizas Volantes, Proceedings of V Congreso Internacional de Química de la Anque: Solid, Liquid and Gaseous Wastes: Their Best Destination (III), Vol. 1, 1999, pp. 357–368 Ed. Asociación Nacional de Químicos, ISBN: 84-88233-191.