Cement and Concrete Research 38 (2008) 1033–1037

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Supercritical carbonation of calcium aluminate cement

L. Fernández-Carrasco [a,*], J. Rius [b], Carles Miravitlles [b]

[a] Department of Construction Materials, Universitat Politècnica de Catalunya, ETSECCPB, c/ Jordi Girona 1-3, E-08034 Barcelona, Spain
[b] Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, 08193 Bellatera, Catalunya, Spain

ARTICLE INFO

Article history:
Received 23 May 2006
Accepted 25 February 2008

Keywords:
D. Calcium aluminate cement
C. Carbonation
B. Characterisation
C. Mechanical properties

ABSTRACT

The microstructural changes occurring during supercritical carbonation ($scCO_2$) of calcium aluminate cement (CAC) and changes to its strength have been investigated. Cylindrical specimens of CAC cured at different temperatures were prepared and then subjected to $scCO_2$. It is shown that CAC carbonation in supercritical conditions is accelerated with a positive effect on the compressive strength. Due to the $scCO_2$ treatment, both conversion and alkaline hydrolysis are avoided. The best behaviour of the studied specimens was attained for samples cured at 25 °C. The residual compounds after the $scCO_2$ process, i.e. monocalcium aluminate, calcium carbonate and aluminium hydroxide are durable in normal ambient conditions. Complete carbonation of CAC is particularly important for the reinforcement of CAC with polymer fibres to improve its mechanical strength.

1. Introduction

Supercritical carbon dioxide ($scCO_2$) is used as a benign solvent for a wide variety of industrial uses [1–3]. $ScCO_2$ has liquid-like density and activity but gas-like transport properties, allowing penetration into very fine pores. The action of $scCO_2$ on cements was studied in a limited manner by the oil industry [4] and the process of $scCO_2$ treatment of cement is patented in the USA [5].

In cement chemistry, major attention has been paid to weathering processes of PC (Portland Cement). Due to the action of CO_2 on the mineralogical compounds of PC, transformation of portlandite into calcium carbonate occurs. This causes the modification of the material microstructure and, consequently, of the mechanical and durability properties [6]. Since CO_2 concentration in air is relatively low, environmental carbonation of cement proceeds rather slowly; hence complete carbonation of the material is only achieved after years. The use of high pressure techniques like supercritical fluids, favours carbonation. It has been shown that cements prepared under high CO_2 pressure are significantly denser than similar cements lacking this treatment. Some benefits observed are the reduction in permeability, and increase in compressive strength [7].

The properties of CAC include rapid strength development, good resistance to sulfate attack as well as other forms of chemical attack and, when used with refractory aggregates, effectiveness in refractory concretes. Due to their rapid hydration, heat evolution during the first day can be high, rendering them useful for low temperature concreting [6]. In CAC the principal cementing component is CA. The reactions of the anhydrous phases with water mainly produce the hydrates CAH_{10} and C_2AH_8. These hydrates are metastable platy hexagonal phases that transform with time, the so-called "conversion" reaction, to the more stable and denser cubic hydrogarnet, C_3AH_6 and AH_3 [8]. Conversion increases the porosity of the paste, causing a decrease in compressive strength.

During CAC carbonation, CAH_{10}, C_2AH_8 and C_3AH_6 react to give calcium carbonate and aluminium hydroxide. Carbonation in the absence of alkalis normally increases the compressive strength of CAC concrete [6]. Some CAC hydration studies at temperatures higher than 30 °C – to avoid the presence of the above mentioned hexagonal calcium aluminate hydrates – and carbonated through conventional carbonation methods, e.g. in CO_2 gas, have shown a beneficial effect on the mechanical properties [10]. Unfortunately, such traditional carbonation methods are slow. In contrast, some degradation processes are related to the presence of alkalis contained in aggregates or other external sources. Alkaline hydrolysis, i.e. carbonation in the presence of alkalis, is a catalytic-like process leading to the destruction of the affected concrete [9].

The objective of the present research is the suppression of the conversion and alkaline hydrolysis processes by applying supercritical carbonation to CAC in order to obtain more stable and durable materials. This study is complemented with the measurement of the mechanical properties. In addition, possible technological applications of CAC supercritically carbonated materials are outlined.

2. Experimental

A series of cylindrical cement samples were prepared with "Electroland" Calcium Aluminate Cement manufactured by "Ciments Molins Industrial S.A.". The cement pastes were prepared mixing the CAC with distilled water at three different temperatures: 5, 25 and

---

* Corresponding author. Tel.: +34 93 405 4247; fax: +34 93 401 7262.
E-mail address: lucia.fernandez@upc.edu (L. Fernández-Carrasco).

0008-8846/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2008.02.013

Table 1
Mineralogical composition of the hydrated and carbonated CAC5, CAC25 and CAC40 samples studied by XRD

Sample	CA	C_4AF	CAH_{10}	C_2AH_8	C_3AH_6	AH_3	Calcite	Aragonite	Vaterite
Hydrated CAC5	5	4	4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
$ScCO_2$ CAC5	4	4	2	n.d.	n.d.	3	2	3	2
Hydrated CAC25	3	3	3	2	2	1	n.d.	n.d.	n.d.
$ScCO_2$ CAC25	2	3	1	n.d.	n.d.	2	2	2	2
Hydrated CAC40	1	1	n.d.	n.d.	6	3	n.d.	n.d.	n.d.
$ScCO_2$ CAC40	1	1	n.d.	n.d.	4	3	3	n.d.	1

(Semi-quantitative analysis: 6: abundant to 1: traces; n.d.: no detected).

40 °C. These pastes are denoted CAC5, CAC25 and CAC40, respectively. The water to cement ratio was 0.4. The treatments were conducted on cylindrical cement samples 20 mm diameter × 40 mm length. Before the $scCO_2$ treatment, the specimens were cured for 48 h in a climatic chamber with the relative humidity maintained at 99.9% and the temperature held at the hydration temperature, i.e. 5, 25 and 40 °C.

The Supercritical Fluids Facility Equipment is a fully-automated, closed-loop supercritical CO_2 treatment system. The liquid CO_2 storage vessel has a capacity of 2 l. The treatment vessel operated during 4 h at pressure of 100 bar and 40 °C of temperature with a flow rate of 1.5 kg/h. The pressurization and the depressurization time were 1/2 h and 1 h, respectively.

After each $scCO_2$ treatment the specimens were mechanically tested to determine the compressive strengths. For comparative purposes, non $scCO_2$ treated specimens were also tested after the curing period. The mineralogical composition of the samples was analysed by X-ray diffraction (XRD) and Infrared Spectroscopy (IR). The XRD patterns were collected on a BRUKER D5000 powder diffractometer (Bragg–Brentano geometry) equipped with a secondary graphite monochromator ($CuK\alpha_{12}$ radiation, flat sample). Angular range: 5–60° (2θ); step size: 0.02° (2θ); counting time: 1 s. A Shimadzu Fourier Transform Infrared Spectrophotometer model FTIR-8300 was used; the spectrum resolution was 2 cm^{-1} and the frequency range 4000–400 cm^{-1}, the pellet was prepared by adding 2.0 mg of the synthesised sample to 300 mg of BrK. The quantification of the carbonation reactions was made through differential thermal analysis and thermogravimetry (TG/DTG). The TG equipment used was a thermo-gravimetric analytical system model sensitive to 10^{-7} g and the analysis was carried out under argon, between 30 and 900 °C at a heating rate of 5 °C min^{-1}. The microstructural development of the samples was verified by Scanning Electron Microscopy (SEM). A JEOL JSM-6300 scanning electron microscopy and attached a LINK ISIS-200 Energy Dispersive X-Ray Analysis (EDX) was used. The porosity accessible to water was also determined.

3. Results and discussion

3.1. X-ray diffraction

Table 1 lists the crystalline phases identified by XRD in the hydrated and carbonated samples together with their approximate relative proportions. From these results, it follows that the initial phases CAH_{10}, C_2AH_8 and C_3AH_6 produced during hydration were strongly carbonated during the supercritical treatment yielding calcium carbonate and aluminium hydroxide.

In the carbonation of the hexagonal hydrates three calcium carbonate polymorphs were formed while carbonation of the cubic hydrate produced mainly calcite. It should be noted that $CaCO_3$ formed can be not only crystalline but also as amorphous carbonates which are not easily detected by XRD.

Regarding the aluminium hydroxide, carbonation of the sample hydrated at 5 °C (CAC5) gives rise to formation of nordstrandite and bayerite, both in similar proportions. When the 25 °C hydrated sample is carbonated only nordstrandite is produced. The aluminium hydroxide, gibbsite, detected in CAC40 was formed together with C_3AH_6 in the hydration process, but also in the carbonation process. Aluminium hydroxide formation can be explained by the solution alkalinity [11,12]. The pH would control the aluminium hydroxide

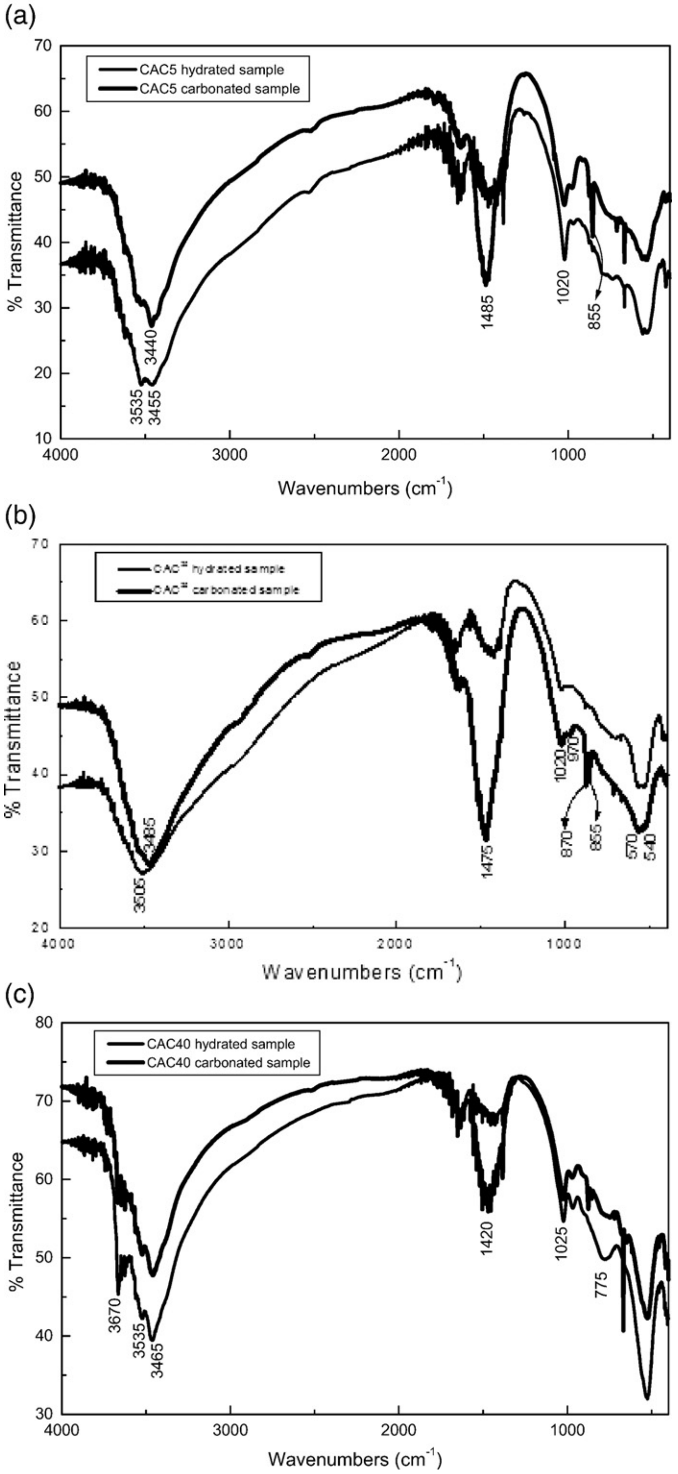

Fig. 1. Infrared spectra of hydrated and carbonated CAC samples (a) CAC5, (b) CAC25 and (c) CAC40.

polymorphous form developed. For low pH values formation of gibbsite is favoured while for high pH values formation of bayerite is promoted; nordstrandite would appear by bayerite aging at intermediate or high pH values.

3.2. Infrared spectroscopy

The IR spectra of the hydrated and carbonated samples are presented in Fig. 1. The strong broad bands appearing in the 3400–3600 cm^{-1} region are due to valence OH vibrations of the water molecules in the CAH_{10} and C_2AH_8 hexagonal and cubic C_3AH_6 hydrated phases present in CAC5, CAC25 and CAC40 samples. The valence OH vibrations of the water molecules from aluminium hydroxide also occur in this region of the spectrum. Through IR spectroscopy it can be seen that even non-carbonated samples were slightly affected by CO_2 (environmental and dissolved in mixed water); an effect that cannot be avoided.

Table 2
Thermoanalysis of the carbonated CAC5, CAC25 and CAC40 samples

	T at the maximum (°C)	*T* range (°C)	Lost weight (%)	Decomposition process
CAC5	102	30–150	3	CAH_{10}
	266	150–475	11.6	AH_3
	703	475–900	9.3	$CaCO_3$
CAC25	105	30–150	3	CAH_{10}
	270	150–475	13.4	AH_3
	710	475–900	9.4	$CaCO_3$
CAC40	92	30–150	1.3	AH_3 gel
	278	150–475	18.1	AH_3
	292			C_3AH_6
	700	475–900	5.7	$CaCO_3$

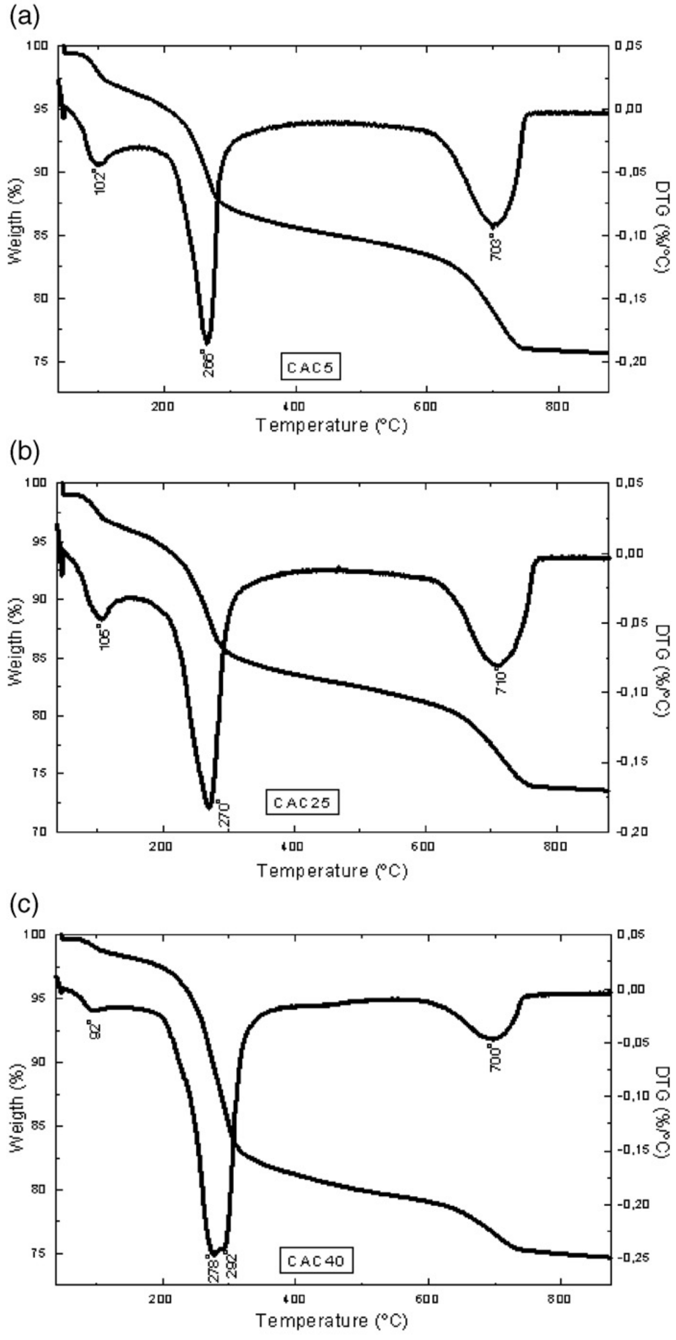

Fig. 2. DTG/TG curves of carbonated CAC5, CAC25 and CAC40 samples.

IR spectra of carbonated samples show a broad strong ν_3 carbonate band between 1300–1600 cm^{-1}. This band appears stronger for CAC5 and CAC25 carbonated samples than for CAC40, thus confirming the results obtained by XRD which show a major carbonation effect for CAC5 and CAC25 in comparison to CAC40 specimens. The ν_3-carbonate band is centred near 1475 cm^{-1}, 1485 cm^{-1} and 1420 cm^{-1} in CAC5, CAC25 and CAC40, respectively. This indicates the main calcium carbonate polymorph formed, i.e. aragonite and vaterite for higher frequencies and calcite for the ν_3 band at 1420 cm^{-1}. The ν_1 carbonate bands near 875 cm^{-1} and 855 cm^{-1} have different relative intensities depending on the calcium carbonate polymorph developed, calcite and/or aragonite and vaterite, respectively.

3.3. Scanning electron microscopy

The microstructural analysis of the CAC5 carbonated sample shows plates with hexagonal morphology growing in all directions and forming rosette-like crystals. Sometimes, these tabular hexagonal crystals have considerable width (1 μ). Occasionally, smooth microstructures of ferrite phases are observed by EDX microanalysis. EDX microanalysis confirms that the hexagonal plates are aluminium hydroxide. A few smooth morphologies with high calcium content are also detected. This would indicate the existence of some poorly crystallised calcium carbonate.

The microstructures of CAC5 and CAC25 carbonated samples are very similar. The size difference of the AH_3 hexagonal crystals in CAC5 (2–5 μ) and CAC25 (2–3 μ) is not significant and explains why both specimens have similar mechanical properties and compressive strength behaviours. Smooth morphologies of aluminoferrite phases can be also observed. However, it was very difficult to find calcium carbonate.

The morphology of CAC40 carbonated sample is quite different from those observed for low temperature cured specimens, CAC5 and CAC25. The observed mixed morphologies are: smooth large particles of ferrite phases similar to that already described for CAC5 and CAC25; a smooth Al-rich film, probably poorly crystallised AH_3, which where several crystals thereupon, namely; large hexagonal prisms of calcium carbonate, and particles of crystalline aluminium hydroxide, larger but less abundant than the calcium carbonate crystals.

3.4. Differential thermal analysis and thermogravimetry

The ATD/TG curves of the carbonated samples showing the effect of the $scCO_2$ treatment of the solid phases in the cement matrices are given in Fig. 2. In Table 2, the quantitative analysis derived from TG curves and the decomposition processes associated with the weight loss produced in a temperature range are summarised.

The thermograms of the CAC5 and CAC25 carbonated samples are similar. The ATD curves display three endothermic signals: the signal below 150 °C which was assigned to dehydration of the hexagonal hydrated phase, CAH_{10}; the two signals in the temperature range 150–475 °C were assigned to the dehydroxylation of AH_3. At higher temperatures (>600 °C) calcium carbonate decomposes. It is interesting to note that for both samples the total weight loss is similar which indicates a similar degree of supercritical carbonation. In contrast, the ATD curve of the CAC40 carbonated sample has four endothermic signals: One weak signal below 150 °C could indicate the presence of AH_3 gel [13]; a second signal at 278 °C due to crystalline AH_3; a third one at 292 °C showing the presence of C_3AH_6; and, finally, the fourth one at 700 °C corresponding to the decarboxylation of $CaCO_3$.

It is interesting to remark that the AH_3 dehydroxylation signals of CAC5, CAC25 and CAC40 appear at slightly different temperatures. This can be explained by the presence of three different AH_3 polymorphs, namely, bayerite at 266°, nordstrandite at 270° and gibbsite at 278 °C, respectively. The weight loss derived from the signal assigned to the carbonates was found to be significantly smaller for carbonated CAC40 than for carbonated CAC5 and CAC25; consequently, supercritical carbonation was less effective for CAC40.

3.5. Porosity accessible to water

Fig. 3 shows the evolution of the porosity accessible to water in hydrated and carbonated specimens. At the initial conditions, i.e. at zero carbonation time, CAC5 and CAC40 specimens had lower porosity than CAC25 specimens. As can be observed in the Fig. 3, the amount of porosity accessible to water after the $scCO_2$ action decreased for CAC5 to 8% and for CAC25 to 10% but increased for CAC40 to 12%. The porosity decrease can be explained by the mass precipitation of carbonates and aluminium hydroxide in the pore system of the specimens that leads to a reduction of the final accessible porosity. The opposite behaviour found in CAC40 specimens could be explained by the conversion of non-crystalline hexagonal hydrates. These cannot be detected by XRD and would evolve by conversion and/or carbonation processes towards cubic hydrates and/or calcium carbonate.

3.6. Compressive strength

As can be expected from the previously presented results, the compressive strengths of the hydrated CAC5 and CAC25 specimens were found to be quite similar (Fig. 4) both before and after supercritical carbonation. The main calcium aluminate hydrate formed was the hexagonal CAH_{10}, both for CAC5 and CAC25. The small quantities of C_2AH_8 and C_3AH_6 also present in CAC25 samples seem to have no significant effect on the compressive strength. A possible explanation could be that the C_2AH_8 and C_3AH_6 formation is compensated – in terms of compressive strength – by the higher hydration level of this sample compared to the hydration degree of CAC5.

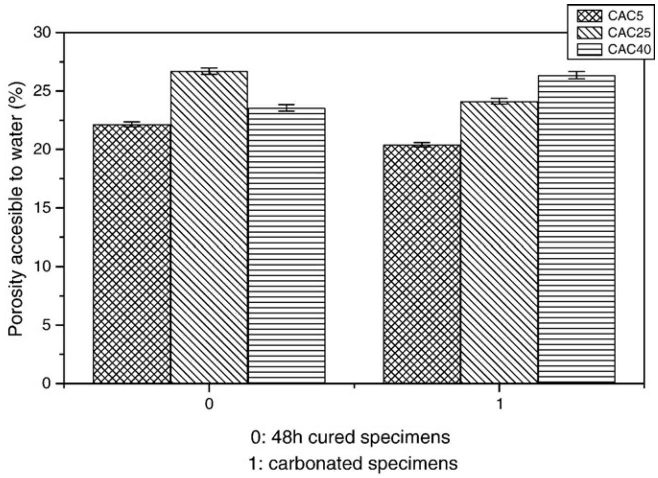

Fig. 3. Porosity accessible to water (%) of the hydrated and carbonated CAC5, CAC25 and CAC40 samples as a function of carbonation.

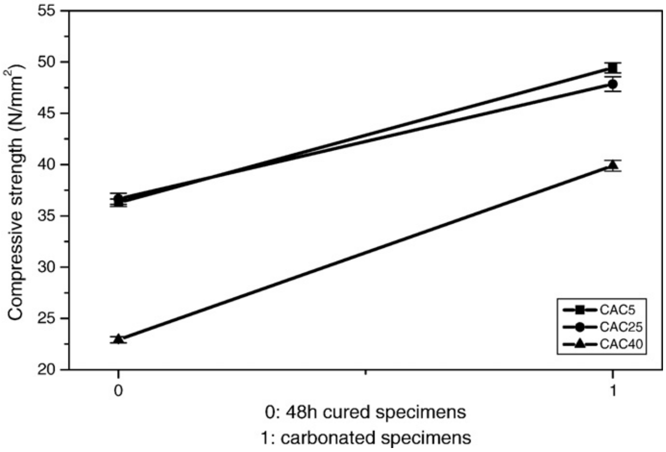

Fig. 4. Compressive strength (N/mm^2) of the hydrated and carbonated CAC5, CAC25 and CAC40 samples as a function of carbonation.

Supercritical carbonation has a significant positive effect on mechanical strength. The increase of compressive strength for carbonated CAC5 and CAC25 specimens was approximately 26% and 23%, respectively. The SEM study of some samples showed in both cases comparable microstructures thus justifying the similar experimental values of compressive strength.

In spite of the positive effect of carbonation on CAC40 specimens, the much lower starting values of compressive strength causes this samples to show the worst final compressive behaviour. The low initial values are due to the formation of the cubic hydrate, C_3AH_6, during the hydration and curing processes. The strength increase after carbonation was 57%. The different strength values observed in CAC40 compared to the CAC5 and CAC25 carbonated samples is surely related to the presence of a larger amount of intergrown particles in these.

4. Conclusions

CAC as an immobilisation matrix should have good mechanical properties, reduced porosity/leachability, good thermal stability and tolerance to a wide range of waste types in order to increase its shielding effect. In addition it must be inexpensive and easy to process and handle. It has been shown that carbonation of CAC with supercritical CO_2 significantly reduces its porosity and hence increases its density. According to the existing bibliography the pH of CAC in fully carbonated areas is lowered from a basic (~12) to a more neutral value (~8) [14]. This allows reinforcement of the cement with polymer fibres such as certain polyamides (e.g. nylon) to increase the mechanical strength. The reinforcement with fibres is incompatible with normal cements due to their basic pH values.

Finally, the following conclusions can be drawn from the present work:

1. Carbonation process of CAC is highly accelerated in supercritical conditions.
2. $ScCO_2$ has a positive effect over the compressive strength evolution of specimens of CAC, including carbonation over converted CAC samples.
3. $ScCO_2$ reduces the porosity of CAC5 and CAC25 specimens.
4. From a practical standpoint the supercritical carbonated CAC25 sample is the most important one. It is the sample which shows the highest degree of carbonation and shows very good mechanical strength behaviour. In this sample all calcium aluminate hydrates were carbonated during the supercritical treatment. Consequently: a) there are no calcium aluminate hydrates which could evolve to other more stable compound, and b) there is still some non-hydrated monocalcium aluminate. The possible hydration of the anhydrous

compounds will give rise to new hydration products that will fill the porous matrix and decrease the specimen permeability. Anyway, the residual compounds after the supercritical carbonation process, i.e., calcium carbonate and aluminium hydroxide, are stable enough in normal ambient conditions.

5. In the carbonated CAC5 sample some CAH_{10} is still present. This phase is susceptible to conversion and will produce a strength decrease, but hydration of residual CA could have increase the strength.
6. In the carbonated CAC40 sample, no anhydrous cement is left. Only the cubic hydrate evolves during carbonation thereby improving the mechanical properties.

Acknowledgements

The financial help of the "Ministerio de Ciencia y Tecnologia" (Project No.: MAT2002-02808) and of the CSIC-Fondo Social Europeo (contract I3P-PC2001-1) is gratefully acknowledged. The authors also thank Carburos Metalicos, S.A for allowing the use of the supercritical plant facility at ICMAB and Raúl Solanas for the technical support, the Materials Section of Departament d'Enginyeria de Construcció of the Universitat Politècnica de Catalunya for providing the mechanical testing facilities and, finally, Ciments Molins Industrial S.A. for providing the Electroland Cement.

References

[1] M.E. Paulaitis, et al., Chemical Engineering at Supercritical Fluids Conditions, Arbor Science, Ann Arbor, MI, 1983.
[2] M. McHugh, V. Krukonis, Supercritical Fluid Extraction, Principles and Practice, Butterworths, MA, USA, 1986.
[3] R. Noyori (Ed.), Chem. Rev., vol. 99(2), 1999, pp. 353–634.
[4] D.D. Onan, Effects of supercritical carbon dioxide on well cements, Proceedings of the Permian Basin Oil and Gas Recovery Conferences, Midland, TX, USA, Society of Petroleum Engineers, 1984, pp. 161–172, #SPE12593.
[5] R. H. Jones. Cements treated with high-pressure CO_2. US Patent 5,518,540, 21 May 1996.
[6] H.F.W. Taylor, Cement Chemistry, Thomas Telford, 1997.
[7] F.C. Knopf, M. Dooley. "Pressure-assisted Molding and Carbonation of Cementitious Materials" US 6264736, 2001.
[8] J. Bensted, P. Barnes, Structure & Performance of Cements, E & F N Spon, 2002.
[9] L. Fernández-Carrasco, M.T. Blanco-Varela, Puertas, T. Vázquez, F.P. Glasser, E. Lachowski, Hydration of high alumina cement in the presence of alkalis, Adv. Cem. Res. 12 (4) (2000) 143–152.
[10] M. Pérez, Tesis Doctoral, Universidad Complutense de Madrid, Sección de Químicas, 1981.
[11] R.I. Barnhisel, C.I. Rich, Proc. Soil Sci. Soc Am. 29 (1965) 531–534.
[12] R. Schoen, E. Roberson, Am. Miner. 35 (January/February, 1970).
[13] P. Galtier, B. Guilhot, M. Murat, A. Bachiorrini, A. Negro, 7th ICCC Paris, vol. 2 , 1980, pp. 214–218.
[14] A. Neville, High Alumina Cement Concrete, The Construction Press, Lancaster, 1975.