JOURNAL OF MATERIALS SCIENCE 31 (1996) 2819–2827

Influence of KOH solution on the hydration and carbonation of high alumina cement mortars

F. PUERTAS, L. FERNÁNDEZ-CARRASCO, M. T. BLANCO-VARELA, T. VÁZQUEZ
Instituto Eduardo Torroja de Ciencias de la Construcción (CSIC), c/Serrano Galvache, s.n. Apdo. 19002 Madrid, Spain

A. DE LA FUENTE
Laboratorio de Barcelona de la Direcció General d'Arquitectura i Habitatge, Generalitat de Catalunya, Barcelona, Spain

The influence of KOH presence on the evolution of hydration and carbonation of high alumina cement mortars at two different curing temperatures (4 and 40 °C) has been studied. It has been confirmed that hydration reactions at both temperatures are accelerated with KOH presence and it has a great influence on hydrated and carbonated species. The massive deposition of carbonation products leads, in all cases to a decrease in mortar porosity which leads to an increase of mechanical strengths.

1. Introduction

Hydration processes of high alumina cement have been thoroughly studied by different authors [1–4]. However, there are still contradictory interpretations of the stabilization and evolution of certain phases such as C_2AH_8 [5].

A phenomenon that occurs simultaneously with hydration and conversion of high alumina cement is the carbonation of calcium aluminate hydrates. This carbonation has a great influence in the later mechanical strength behaviour of the concrete with high alumina cement. Vázquez *et al.* [6] in 1976 made a first approach to the problem, establishing differences in the processes of carbonation in high alumina cement pastes, depending on whether these processes happened in hexagonal or cubic hydrates.

Recently, Damidot *et al.* [7] determined the phase diagram of the $CaO–Al_2O_3–CaCO_3–H_2O$ closed system at 25 °C. They found that hemicarboaluminate, monocarboaluminate and calcite are the stable phases which form as carbonate concentration increases. They also determined that tricarboaluminate phase is not thermodynamically stable at 25 °C.

The literature says that carbonation in presence of soluble alkaline ions, Na^+ or K^+, has a highly destructive character in the concretes with high alumina cements, and it is known by the name of "alkaline hydrolysis" [8]. This is a very little studied phenomenon, recognized on many occasions by the presence of bayerite in the altered cement, which is a widely debated aspect.

Damidot *et al.* [7] studied the influence of Na_2O on the $CaO–Al_2O_3–CaCO_3–H_2O$ system. They came to the conclusion that the presence of alkalis significantly increases the carbonate concentration in the solution.

The goal of this work has been to study the carbonation processes of the hydrated high alumina cement as a function of the curing temperature and the presence of alkalis. Likewise, the authors have tried to determine the influence of this carbonation process on the strength behaviour of the material.

2. Experimental procedure

The molten high alumina cement from the Spanish cement factory Molins, S.A. was used. Its analysis is shown in Table I.

In order to determine the influence of the KOH solution on the hydration process of the high alumina cement, a calorimetric study was carried out using conduction calorimetry. To this purpose, mixtures with water/cement ratio of 0.4 were prepared. Two mixing liquids were used: distilled/deionized water and a 0.1 N KOH solution.

Cubic specimens of high alumina cement mortar were prepared with side length of 3.5 cm. The aggregate was quartz–sand with 99.9% of SiO_2. The ratios were: cement/aggregate 0.33 and water/cement 0.4.

Two series of specimens were made parallely differing in the nature of the mixing water. One series of high alumina cement specimens was mixed with distilled/deionized water and the other series was mixed with a 0.1 N KOH solution. Each series of specimens was divided into two groups: in one of them the mixing liquid (water or KOH solution) was at 4 °C and in the other at 40 °C. Fig. 1 presents a clarifying scheme of the mixtures prepared.

0022–2461 © *1996 Chapman & Hall*

TABLE I Chemical Analysis of high alumina cement

	LOI[a]	IR[b]	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	CaO Free
Weight (%)	0.00	0.46	2.85	42.47	15.31	40.49	0.00	0.00	0.11

[a] Loss of ignition at 1000 °C.
[b] Insoluble residue.

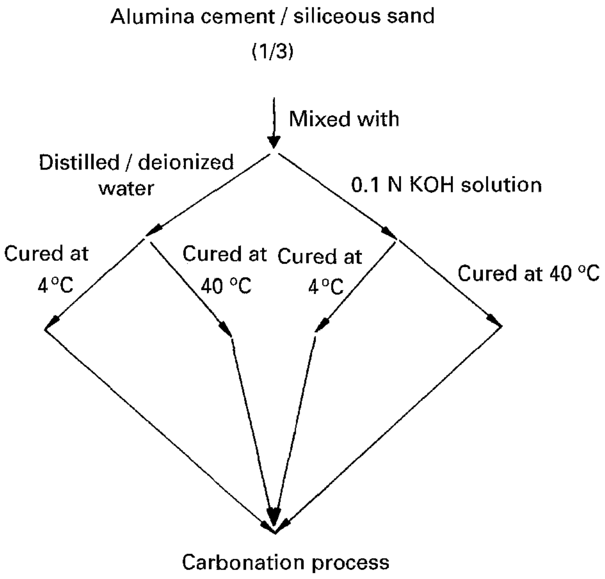


Figure 1 Scheme of the mixtures prepared.

2.1. Curing of the specimens

The specimens cured with cold water were kept in the refrigerator (≈ 4 °C) during the first 24 hours of hydration. After this time, they were demoulded and kept in the frigorific chamber for an additional seven days.

The specimens mixed with hot water were demoulded after 24 hours and were then kept in an oven at 40 °C for seven days.

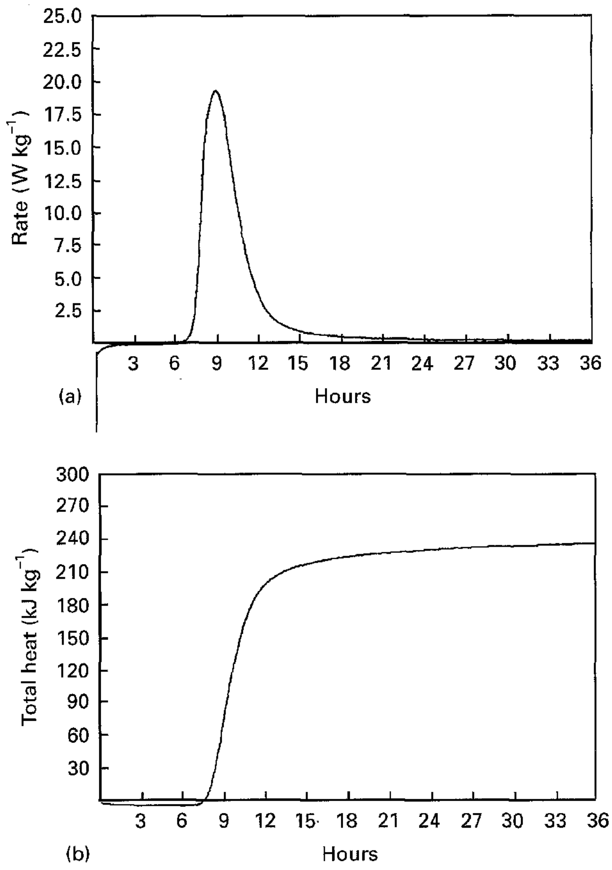


Figure 2 Calorimetric curves of high alumina cement mixed with water. (a) Maximum rate and (b) total heat.

2.2. Carbonation of the specimens

The specimens were subjected (after the first seven days) to an accelerated carbonation process. Closed prismatic containers of 25 × 30 × 35 cm were used as carbonation chambers in which, twice a day, CO_2 was insufflated. A vessel with a K_2CO_3 saturated solution was introduced into these chambers, which assured a relative ambient humidity of 43.2% [9].

The following tests and analyses were conducted on the non-carbonated specimens and those subjected to accelerated carbonation during 7, 28 and 90 days: compressive mechanical strength and porosity accessible to water.

The following analyses were conducted on the portions enriched with binding material: X-ray diffraction and infrared spectroscopy.

3. Results and discussion

3.1. Calorimetric studies

The maximum rate and the total heat given off by the high alumina cement pastes mixed with water and with the 0.1 N KOH solution are shown, respectively, in Figs 2 and 3.

The sample mixed with the KOH solution shows a maximum rate and a total heat after 36 h of testing, much superior to that shown by the high alumina cement hydrated with water. Table II contains the values obtained for both determinations.

In the sample mixed with KOH solution, the maximum rate of heat evolution is produced 3 h before it is produced in the sample mixed with water.

All these results point to the fact that the 0.1 N KOH solution used in the mixing water has an accelerating effect in the hydration reactions of the high alumina cement, since these reactions happen at a higher rate and with greater heat emission.

This increase in the hydration reaction rate can be justified by the greater disolution of anhydrous species, basically CA, as a consequence of the increase in the concentration of the OH^- ions in the mixing water by the alkaline presence of the 0.1 N KOH solution.

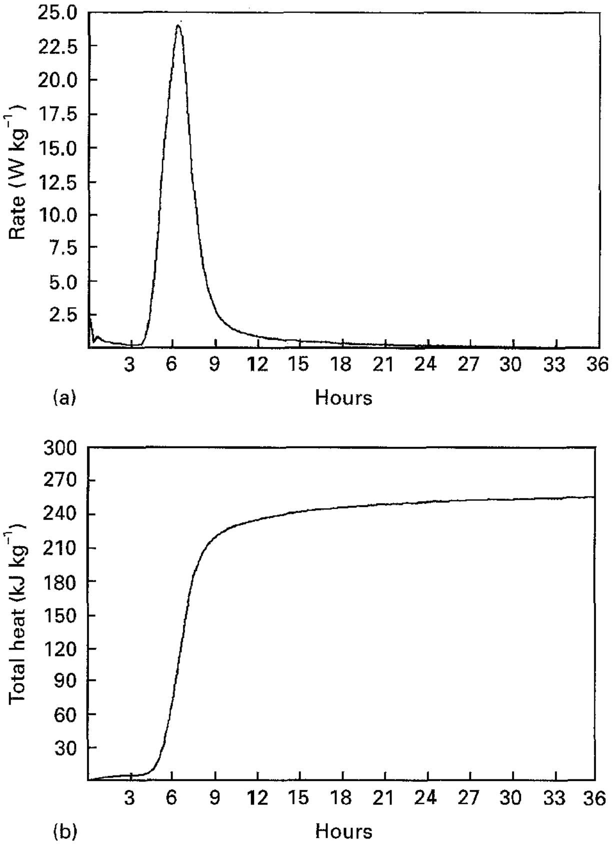


Figure 3 Calorimetric curves of high alumina cement mixed with 0.1 N KOH solution. (a) Maximum rate and (b) total heat.

TABLE II Calorimetric data

	Water	0.1 N KOH
Total heat (kJ kg^{-1})	237.92	269.99
Maximum rate (W kg^{-1})	19.34	23.92

3.2. X-ray diffraction

3.2.1. Samples mixed and cured at 4 °C

Tables III and IV contain the crystalline phases identified by X-ray diffraction (XRD) of the samples mixed with distilled deionized water and the KOH solution, respectively. Likewise, the relative proportion of the said phases in the samples are given. In all of them the predominant phase is the α-SiO_2 (quartz), since this was the material used as aggregate in the preparation of the mortars.

Analysing both tables, it can be deduced that samples mixed with the KOH solution have an evolution of the hydrated and carbonated phases different from that shown by the samples mixed with water. In the initial samples, those hydrated during seven days, the hydration reactions of high alumina cement happen at a greater rate in the presence of the KOH solution. When the diffractograms of the initial samples are compared, it can be found that the sample mixed with KOH has a greater amount of hydrated calcium aluminates of hexagonal nature ($CaAH_{10}$) and C_2AH_8), and practically all the anhydrous cement has reacted. On the contrary, the sample mixed with water shows a low proportion of CAH_{10} (the only hydrate formed) and there is still a great amount of anhydrous

TABLE III Mineralogical composition of pastes by XRD

Sample (20) water cured at 4 °C	Quartz 26.64	C_3AH_6 39.22	CAH_{10} 12.35	C_2AH_8 8.25	C_4AcH_{11} 11.68	AH_3 gibbsite 18.27	$CaCO_3$ calcite 29.40	$CaCO_3$ vaterite 27.03	$CaCO_3$ aragonite 26.22	CA 30.06	C_4AF 33.87
Without carbonation	+ + +	–	+	–	+	○	–	○	–	+ + +	+ +
7 days carbonation	+ + +	–	+	–	–	○	○	+	+	+ +	+ +
28 days carbonation	+ + +	–	○	–	–	○	+	+	+	+ +	+ +
90 days carbonation	+ + +	–	–	–	–	○	○	+	+ +	+ +	+ +

+ + + Abundant; + + moderate; + little; ○ traces.

cement without reacting. These results confirm those already presented on the conduction calorimetry.

In the pastes mixed with the KOH solution, hexagonal hydrates CAH_{10} and C_2AH_8 co-exist, while in those mixed with water, only CAH_{10} is found. The heat developed during the hydration with KOH solution allows the formation of the C_2AH_8 hydrate.

In hydrated samples, in water and KOH, monocarboaluminates are formed. These carboaluminates are formed basically from CO_2 dissolved in mixing water. According to Damidot *et al.* [7], in the presence of sodium, Ca^{2+} concentration in equilibrium solution with monocarboaluminate decreases, and Al^{3+} and CO_3^{2-} concentration increases, modifying and enlarging the CO_3^{2-} concentration range in which that phase is stable.

Suppose a similar system evolution, when K is the alkaline element instead of Na, this could justify the great monocarboaluminate proportion found in the sample mixed with KOH solution.

In carbonated samples (up to 90 days), both monocarboaluminate and hexagonal hydrate turn unstable when CO_3^{2-} concentration in the aqueous solution in contact exceeds its stability range. Thus, the cited minerals evolve to the formation of more stable phases when submitted to accelerated carbonation processes. When carbonation process progresses, the amount of hexagonal hydrates present in the samples decreases and disappears at 90 days carbonation.

At the same time, carboaluminates react with CO_2 excess and they are destroyed at the early stages of accelerated carbonation. This is the reason why they are not detected in any of the samples submitted to carbonation.

As a consequence of the carbonation of hexagonal hydrates, different calcium carbonates are formed. The sample mixed with water at 90 days carbonation presents predominantly $CaCO_3$ in the form of aragonite, together with vaterite and, in a smaller proportion, calcite. Nevertheless, in the sample mixed with the KOH solution the predominant carbonate is calcite although there is also vaterite and aragonite. The amount of calcium carbonates in this last sample is greater than that mixed with water, since the amount of hexagonal hydrates is also greater, due to the higher degree of reaction at all ages.

In the samples mixed with water, traces of AH_3 (gibbsite) can be detected at all ages of carbonation studied. Nevertheless, in those mixed with KOH only aluminium hydroxides can be detected at advanced ages of carbonation (see Table IV). In this case, a mixture of gibbsite, bayerite and probably some nordstrandite is obtained.

Finally, it is worth mentioning that the sample mixed with water has anhydrous phases (CA and C_4AF) at 90 days treatment. Although there are no thermodynamic data on the $CaO–Al_2O_3–CaCO_3–H_2O$ system at 4 °C, it is known that at 25 °C, no hydrated or carbonated species reach oversaturation and precipitate when CO_3^{2-} concentration is greater than 1.32×10^{-4} mol kg^{-1}. It seems that hydration process, in these samples, is retarded or stopped due to the high CO_2 concentration.

TABLE IV Mineralogical composition of pastes by XRD.

Sample (2θ) 0.1 N KOH cured at 4 °C	Quartz 26.64	C_3AH_6 39.22	CAH_{10} 12.35	C_2AH_8 8.25	C_4AcH_{11} 11.68	AH_3 gibbsite 18.27	$CaCO_3$ calcite 29.40	$CaCO_3$ vaterite 27.03	$CaCO_3$ aragonite 26.22	CA 30.06	C_4AF 33.87
Without carbonation	+ + +	–	+ +	+ +	+ +	–	○	–	–	+	+
7 days carbonation	+ + +	–	+ +	○	○	–	+	+	○	+	+
28 days carbonation	+ + +	–	+	–	○	○	+ +	+	+	○	+
90 days carbonation	+ + +	–	○	–	–	+	+ + +	+ +	+ +	○	○

+ + + Abundant; + + moderate; + little; ○ traces.

3.2.2. Samples mixed and cured at 40 °C

Tables V and VI show the results obtained by XRD of the samples cured at 40 °C and mixed with water and 0.1 N KOH solution, respectively; and, later, submitted to carbonation.

In the initial samples, those hydrated during seven days, in these curing conditions, it is also confirmed that cement hydration reactions occur faster in the sample mixed with KOH solution than in the sample mixed with water. In the samples mixed with KOH there is always a greater amount of C_3AH_6.

In the sample mixed with KOH solution the only hydrated calcium aluminate is cubic hydrate, while in those mixed with water hexagonal hydrate, C_2AH_8, is also detected as well as a large amount of anhydrous cement. In both samples the presence of hydrated calcium carboaluminate, C_4AcH_{11}, is detected, although in relatively small proportions.

In samples submitted to carbonation (maximum 90 days), the intensity of diffraction lines of C_3AH_6 decreases during the carbonation process. This phenomenon is already shown at seven days of carbonation in the sample mixed with water, while in the one mixed with KOH solution, this is not observed until 28 days of carbonation. At 90 days of carbonation, this hydrate does not appear in the sample mixed with water, nevertheless, it does stay in the sample mixed with alkaline hydroxide. This may be due to the greater amount of cubic hydrate in the sample or also to the fact that one part of CO_2 was used to react with the alkalis present in the aqueous phase of cement paste.

At 7 days of carbonation, in the sample mixed with water, there appears a large amount of carboaluminate, C_4AcH_{11}. This carboaluminate disappears in the presence of larger amounts of CO_2 and at 90 days of carbonation it cannot be detected any longer.

The formation of the cited carboaluminate has not been observed in carbonated samples mixed with KOH solution (although the presence of alkali increases CO_3^{2-} level providing monocarboaluminate stability). This could point out that monocarboaluminate found at seven days treatment in samples without alkali is from the carbonation of C_2AH_8 hexagonal hydrate in the original sample and not from the cubic hydrate. However, its presence has not been detected in any of the samples cured at 4 °C. The carbonation of cubic hydrate in equilibrium conditions goes through intermediate phases as monocarboaluminate or hemicarboaluminate, to produce $CaCO_3$ and AH_3 in alkali presence or absence. The results suggest that monocarboaluminate experimentally found as an intermediate species in the carbonation process of high alumina cement hydrates (hexagonal or cubic), in other words depends on their rate of formation and later destruction and, then, depends on the time at which the sample is examined and not on the carbonated species.

Similar to the samples cured at low temperatures, the presence of KOH seems to favour the formation of $CaCO_3$ in the form of calcite, although vaterite and, in a smaller proportion, aragonite co-exist. In the samples mixed with water and in equal conditions, this

TABLE V Mineralogical composition of pastes by XRD

Sample (2θ) water cured at 40 °C	Quartz 26.64	C_3AH_6 39.22	CAH_{10} 12.35	C_2AH_8 8.25	C_4AcH_{11} 11.68	AH_3 gibbsite 18.27	$CaCO_3$ calcite 29.40	$CaCO_3$ vaterite 27.03	$CaCO_3$ aragonite 26.22	CA 30.06	C_4AF 33.87
Without carbonation	+ + +	+ +	–	+	+	○	○	–	–	+ +	+ +
7 days carbonation	+ + +	+	–	○	+ + +	+	+	○	○	+ +	+ +
28 days carbonation	+ + +	○	–	–	+	+	○	○	+ +	+	+ +
90 days carbonation	+ + +	–	–	–	–	+	+	+	+ +	+	+ +

+ + + Abundant; + + moderate; + little; ○ traces.

last phase, aragonite, is the carbonate that is mainly formed.

As the carbonation progresses the content of AH_3 increases slightly. In the sample mixed with water the AH_3 appears almost exclusively in the form of gibbsite; in the sample elaborated with KOH the joint presence of gibbsite, bayerite, and most probably, nordstrandite is detected.

TABLE VI Mineralogical composition of pastes by XRD

Sample (2θ) 0.1 N KOH cured at 40 °C	Quartz 26.64	C_3AH_6 39.22	CAH_{10} 12.35	C_2AH_8 8.25	C_4AcH_{11} 11.68	AH_3 gibbsite 18.27	$CaCO_3$ calcite 29.40	$CaCO_3$ vaterite 27.03	$CaCO_3$ aragonite 26.22	CA 30.06	C_4AF 33.87
Without carbonation	+ + +	+ + +	–	–	+	+	O	–	–	O	–
7 days carbonation	+ + +	+ + +	–	–	O	+	+	O	–	O	–
28 days carbonation	+ + +	+	–	–	–	+	+ + +	+	O	–	–
90 days carbonation	+ + +	+	–	–	–	+	+ + +	+ +	+	–	–

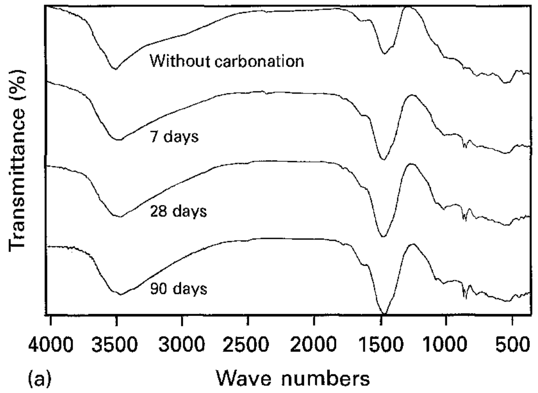
+ + + Abundant; + + moderate; + little; O traces.

3.3. Infrared spectroscopy

Figs 4 and 5 show i.r. spectra of the samples mixed with water and with KOH solution, respectively. The analysis of these i.r. spectra confirms completely the results already described by X-ray diffraction.

3.3.1. Samples mixed and cured at 4 °C

It is confirmed, as with XRD, that reaction rate of samples mixed with KOH solution is higher than the corresponding samples mixed with water. Thus, for example, in their spectra, characteristic absorption bands for anhydrous high alumina cement could be observed (600–700 cm^{-1} range and mostly over 800 cm^{-1}) while in KOH solution ones these bands are practically absent. The intense and broad band appearing in 3400–3600 cm^{-1} region in all the spectra is caused by valence OH of water molecule vibrations, associated with the hexagonal hydrates. The position of this band informs about bonding strength of OH groups to the rest of the molecule; in general if this band is stronger, its frequency is less and vice versa. As it is shown in Table VII, as carbonation progresses



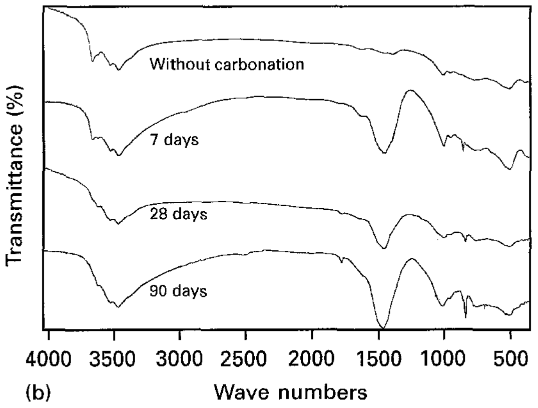


Figure 4 Infrared spectra of the pastes prepared with water. (a) 4 °C; (b) 40 °C.

(in samples mixed with water and KOH), the band frequency decreases, pointing out an increase in OH bonding strength to the molecular structure. The absorption bands in that region 3400–3600 cm^{-1} of samples without KOH are due specifically to CAH_{10}, except at 90 days where the OH absorption of the sample appears very broad and different from the former. Probably this sample contains $Al_2O_3 \cdot nH_2O$ type compounds in gel form.

Characteristic vibration bands of carbonates, inform us about CO_2 action in the samples studied. It is observed that "non-carbonated" samples are, however, affected by carbonic anhydride (environmental and re-dissolved in mixing water); an action that could not be avoided. Infrared spectra show very broad and badly-defined ν_3 carbonate bands in the region 1360 to 1500 cm^{-1} and the ν_1 sharp band (850 to 900 cm^{-1} region). This last band is very weak, which has been interpreted as being due to the presence of an almost amorphous calcium carbonate form [10].

At 423 cm^{-1}, a weak band appears and joined to the asymmetric shape of the 1370–1400 cm^{-1} band, it is interpreted as being due to the hydrated calcium monocarboaluminate.

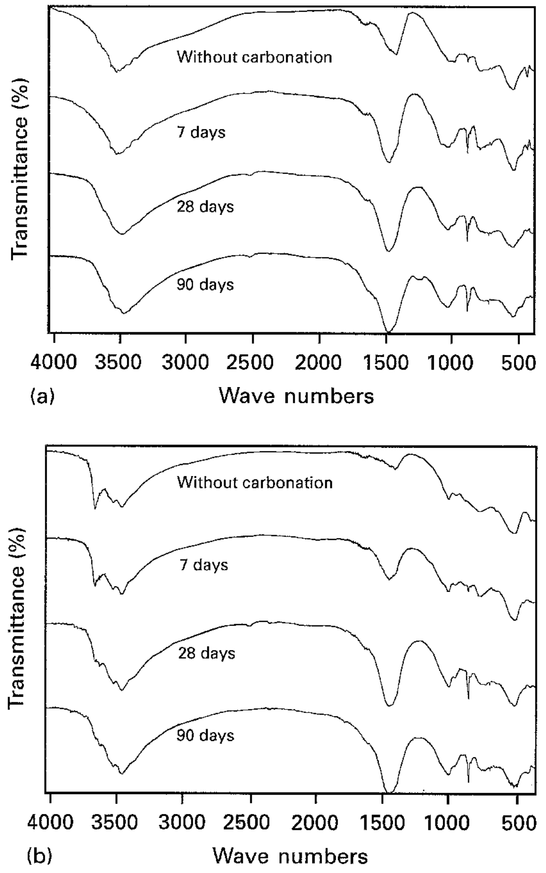


Figure 5 Infrared spectra of the pastes prepared with 0. 1 N KOH solution. (a) 4 °C; (b) 40 °C.

As the treatment of samples with CO_2 takes longer, it is proved in the i.r. spectra of both series that the $CaCO_3$ formation crystallizes in the form of calcite and aragonite; however, there is a greater proportion of aragonite in samples made without KOH and greater proportion of calcite in samples made with KOH solution. Carboaluminates decrease until they disappear at 90 days in the sample mixed in the absence of KOH and at 28 days in the sample mixed with KOH solution.

It is worth pointing out that in samples mixed with water, weak bands in 3460–3480–3520 and 3460 cm^{-1} are observed; these are characteristic of $Al(OH)_3$, probably gibbsite.

3.3.2. Samples mixed and cured at 40 °C

Infrared spectra of all samples hydrated during seven days show an acute absorption at 3661 cm^{-1} due to valence vibration of OH from C_3AH_6. This band is more intense in the sample mixed with KOH solution.

The bands in 3524–3468 cm^{-1} are caused by $Al(OH)_3$ (gibbsite) and they are already seen in the seven days hydration samples.

As hydration and carbonation progress, in the spectra of all samples a progressive decrease of the 3661 cm^{-1} band and an increase in the carbonates bands (1400–1500 cm^{-1} region and sharp bands in 850–800 cm^{-1} region) can be seen. These processes are more intense in the KOH-treated samples.

3.4. Porosity accessible to water

Fig. 6 shows the evolution of the porosity accessible to water of the specimens mixed with water and KOH solution respectively, when they are subjected to the accelerated carbonation processes.

Under the initial conditions, i.e. at zero carbonation time, in both series the cold-cured specimens always have lower porosities than the heat-cured specimens. The reduction is of about 33% in those mixed with water and 25% in those mixed with KOH solution.

It is worth pointing out that at seven days hydration, samples (both cold- and heat-cured) mixed with KOH solution have lower porosities than those mixed with water. This is accounted for by the higher rate of the hydration reactions in the samples mixed with KOH solution, and therefore, by the greater precipitation of hydration products which lead to a porosity decrease. This phenomenon, as has been discussed before, occurs both at 4 and 40 °C cured specimens.

As carbonation times increase, the evolution of porosity is different in the two series of specimens. In those mixed with water, both in those cured at 4 and

TABLE VII Variation on the infrared frequencies of the valence OH of water molecules vibrations (cm^{-1})

	Without carbonation	Carbonation 7 days	Carbonation 28 days	Carbonation 90 days
Water	3520	3486	3479	3447
0.1 N KOH	3510	3500	3480	–

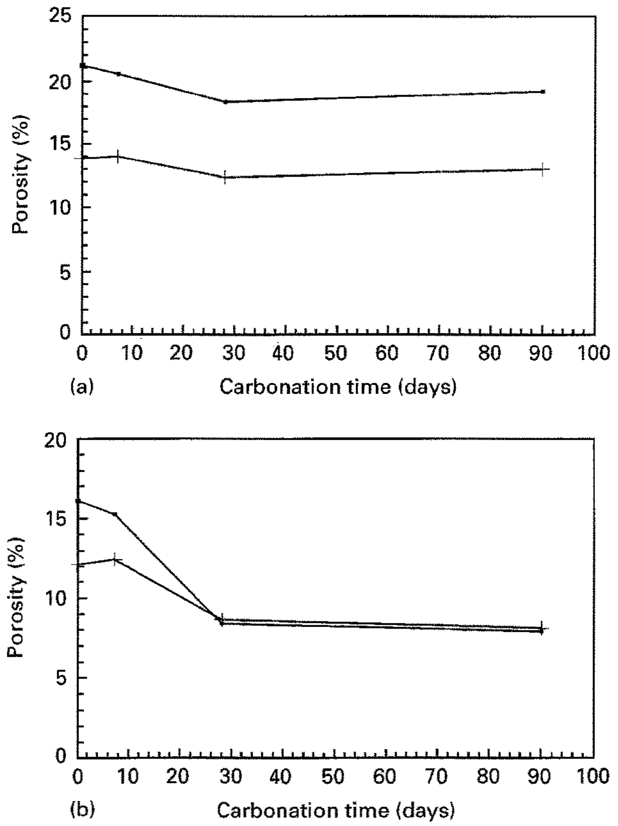


Figure 6 Mortar porosity accesible to water evolution as a function of carbonation time. (a) Mixed with water and (b) mixed with 0.1 N KOH solution. ■ 40 °C; + 4 °C.

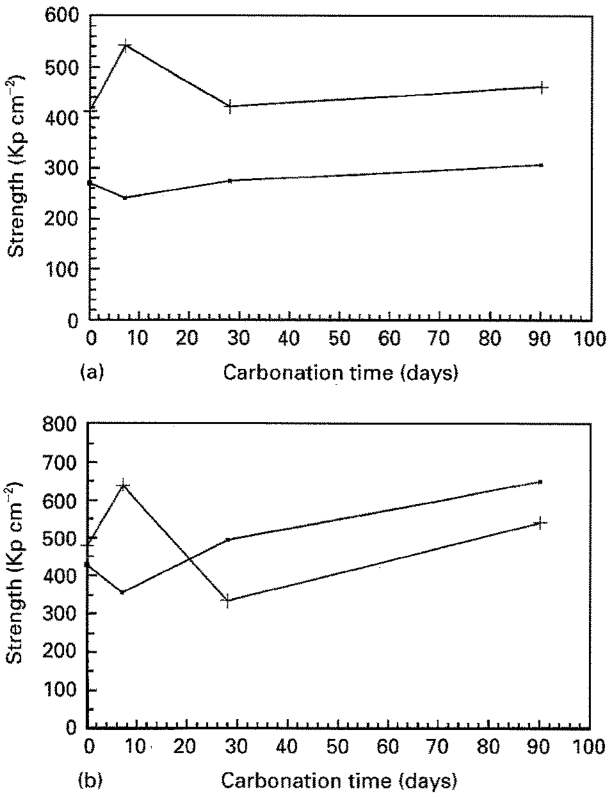


Figure 7 Compressive strength evolution as a function of carbonation time. (a) Mixed with water and (b) mixed with 0.1 N KOH solution. ■ 40 °C; + 4 °C.

40 °C there is a slight decrease of porosities until 28 days of carbonation, after which they remain practically constant until the end of the test. This is interpreted as a consequence of the precipitation of calcium carbonates resulting from the hydrated calcium aluminate carbonation. Since hydrating reactions do not progress at all or very slowly during the carbonation process, hydrates are not formed, and therefore, the porosities are not modified until the end of the test. The behaviour at 4 and 40 °C cured specimens is parallel during carbonation. The specimens mixed with KOH solution have a different behaviour to that described in the water mixed ones. As can be observed in Fig. 6(b), as carbonation times increase, the porosity accessible to water abruptly decreases both in cold- and heat-cured specimens, until reaching the same values, in the order of 8% starting from 28 days of carbonation. This is due to the mass precipitation of carbonates as a consequence of the hydrates formed in the curing conditions. These hydrates exist in very large amounts due to the acceleration of the reactions as a consequence of the presence of KOH solution, as was discussed under XRD and i.r. spectroscopy. This greater proportion of hydrates leads to a large amount of carbonates which fill massively the porous system of the mortars and thus lead to the reduction in the final accessible porosity.

3.5. Mechanical strengths

Fig. 7 shows the evolution of the mechanical compressive strengths of the same specimens upon which the water accessible porosity was determined. It can be deduced that the presence of KOH, as a consequence of the acceleration of hydration reactions, increase mechanical strengths. Likewise, those mixed in cold water develop, as expected, greater strengths than those mixed in hot water.

Finally, the carbonation of all specimens does not seem to have a negative effect on the evolution of the compressive strengths.

4. Conclusions

The following conclusions can be drawn from the present work:

1. The presence of KOH dissolved in mixing water increases the rate of high alumina cement hydration reactions, in those cured both at 4 and 40 °C. Due to this higher rate of reaction an increase in the hydration heat is produced which provokes modifications in the mineralogical composition of the pastes, under the same conditions.
2. The presence of KOH does not seem to modify the carbonation rate of the pastes, although it does affect their mineralogical composition. Thus, while in those mixed with KOH, the final carbonation products are predominantly $CaCO_3$ in the form of calcite and a mixture of AH_3 in the form of gibbsite, bayerite and nordstrandite, in those mixed with water the most abundant carbonate is aragonite and in aluminium hydroxide it is gibbsite. These differences are produced both in the samples cured at 4 and 40 °C.
3. The mass deposition of carbonation products in all the cases studied leads to a reduction of porosity of the

pastes, which is manifested with a progressive increase of mechanical strength.

4. Hydration process of high alumina cement is retarded (or even stopped) when specimens are simultaneously submitted to accelerated carbonation processes.

Acknowledgements

The authors wish to thank to the Scientific and Technical Commission of the Spanish Education Ministry for support given through the general knowledge promoting programme (PB92-0100) necessary to carry out this research.

References

1. C. M. GEORGE, in "Structure and Performance of Cements", edited by P. Barnes (Applied Science, 1983) p. 415.
2. A. CAPMAS, D. SORRENTINO and D. DAMIDOT, in "Calcium Aluminate Cements", edited by R. J. Mangabhai (E. & F.N. Spon, 1990) p. 65.
3. J. BENSTED, G. J. AUDLEY and P. N. AUKETT, in Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, Vol. IV (1992) p. 220.
4. P. BARRET and D. BERTRANDIE, in "Advances in Cement and Concrete", edited by M. W. Grutzeck and S. L. Sarkar (American Society of Civil Engineers, 1994) p. 132.
5. S. RASHID, P. BARNES and X. TURRILLAS, *Adv. Cem. Res.* **4** (1991/92) 61.
6. T. VÁZQUEZ, F. TRIVIÑO and A. RUIZ DE GAUNA, *Monografía IET*, **334** (1976).
7. D. DAMIDOT, S. STRONACH, A. KINDNESS, M. ATKINS and F. P. GLASSER, *Cem. Concr. Res.* **24** (1994) 563.
8. P. STIGLITZ, *Revue des Matériaux de Construction*, **671–672** (1970) 219.
9. ASTM, E-104-71 (1971).
10. T. VÁZQUEZ, *Materiales de Construcción*, **163** (1976) 51.

Received 9 August
and accepted 21 December 1995