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General study of alkaline hydrolysis in calcium aluminate cement mortars under a broad range of experimental conditions

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Abstract

In the present paper the phenomenon of alkaline hydrolysis of calcium aluminate cement (CAC) mortars has been studied. It has been reproduced from different conditions, in specimens manufactured at temperatures of 5°C and 60°C. Phase evolution was studied from X-ray diffraction (XRD) spectra. An evaluation of the compressive and flexural strengths obtained from different curing conditions is also described. The carbonation process in the absence of alkalis can be considered beneficial when it takes place on totally converted CAC mortars. The degradation process through alkaline hydrolysis, and hence the loss of resistance characteristics, takes place only when CAC conglomerates contain hydrated CAC. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Calcium aluminate cement (CAC) is very suitable for fast concrete because the strength gain is very rapid. After setting, the cement develops most of its strength within hours. Unfortunately, the use of CAC in structural concrete is not allowed due to the loss of strength of the concrete with time. This reduction is due to a chemical reaction whereby cubic calcium aluminate hydrate is produced at the expense of the hexagonal hydrates initially formed [1–7].

From 1950 to 1970 CAC was extensively used in different countries, mainly UK, France, Germany and Spain. One of its applications was the manufacture of prestressed concrete beams. In Spain the zones where CAC was most commonly used were Catalunya, Valencia, the Balearic and Canary Islands. In 1990 two prestressed concrete beams of a building roof in Barcelona collapsed. X-ray diffraction (XRD) methods [8] were used to study the causes of the failure and to identify the cement type and the changes in the aluminate hydrates.

Among the processes involved in CAC concrete durability, carbonation in presence of alkaline solutions requires further research because its effect on corrosion is not very clear. Several authors had already reported the hazardous effects that the attack by alkali was causing on the hydrated phases [9,10]; many more have studied it later [11–14]. Puertas et al. [15] conclude that the massive deposition of carbonation products leads, in all cases, to a decrease in mortar porosity which produces an increase in mechanical strengths. Goñi et al. [16] suggest that: “an alkaline hydrated aluminate could be identified by XRD linked to the cases where loss of strength is sometimes detected. Its presence in a sample may suggest the occurrence of this process.” In this context the goal of this work was to study, by XRD, the process of development of phases in the carbonation of mortars in the presence and absence of alkaline solutions and specially the characterization of the $CaCO_3$ and AH_3 polymorphs. An evaluation of the compressive and flexural strengths of mortars obtained from different curing conditions is also described. The main aim of this paper is to study the alkaline hydrolysis phenomenon in CAC mortars under a broad

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range of experimental conditions in order to characterize their durability.

2. Experimental program

2.1. Materials and specimen preparation

The VI/55 Electroland CAC was used. Mortars were prepared according to Spanish standard requirements [17]. Silica sand was always employed as the aggregate, and distilled water was always used. Mortars were prepared under different conditions. The w/c ratio was always 0.7 in order to obtain high porosity that facilitates the phenomenon of alkaline hydrolysis. Prismatic mortars ($4 \times 4 \times 16$ cm) were prepared using CAC with a ratio c/s of 1:3. The mortar specimens were prepared in laboratory at 5°C and 60°C, and 90% RH, with mechanical compaction in two layers. Immediately after casting and surface finishing, the test specimens in the mold were covered with a polyethylene film (0.2 mm thick) in order to prevent water loss. The specimens were kept also at 5°C and 60°C. After demolding 24 h later test specimens were cured in water for 7 days at the same two temperatures mentioned above. After the curing period the test specimens were carbonated. In the preliminary experiments (see Table 1) test specimens were carbonated by bubbling CO_2 into attacking solutions for 100 days at 20°C. In the following experiments (see Table 2) test specimens were carbonated in a chamber holding a CO_2 atmosphere for 7, 28 and 90 days at 20°C. A vessel containing a glycerin (58%) solution was introduced into this chamber, which assured a relative ambient humidity of about 75%.

2.2. Testing

The types of specimens and tests for the determination of various properties are described below.

2.2.1. Flexural strength

All control specimens were tested under laboratory conditions, directly taken from the storage container. Three prismatic specimens of $4 \times 4 \times 16$ cm prepared at each specified carbonation age and temperature were broken by bending with one middle loading point.

2.2.2. Compressive strength

Six prismatic specimens of $4 \times 4 \times 8$ cm, taken from broken samples in flexural tests, were tested (at their respective moisture conditions) under the same laboratory conditions as those applied in the other strength test. The method used to determine the compressive strength of prismatic mortar was according to Spanish standards [18]. The crushing load was determined using a 10 000 kN capacity automatic compression machine.

2.2.3. XRD spectra

The XRD experiments were carried out with a Scheifer powder diffractometer provided with a graphite monochromator and a NaI (T1) scintillation detector using Cu Kα radiation. The aperture slit of 3° and the detector slit of 0.15° were used. After being crushed in an agate mortar to 40 μm size, the samples were preserved in acetone at 5°C. XRD spectra were taken at a speed of $1° \text{ min}^{-1}$.

2.2.4. Scanning electron microscope (SEM)

The scanning electron microphotographs were taken with a JEOL JSM-840 SEM equipped with an energy dispersive X-ray detector (EDX, QX200 from LINK) and with 20 kV accelerating voltage. The method used for producing a thin gold film to make the surface of specimens electrically conductive was a high vacuum evaporation (SCD 004 from BALZERS UNION).

3. Description of experiments

The experimental conditions used in the preliminary work are summarized in Table 1. These preliminary experiments suggested further lines of study with different attacking conditions, each of them was carried out at two different working temperatures, 5°C and 60°C. The intention, in all cases, was to reproduce the behavior of the different stable hydrated calcium aluminates at each working temperature, in order to study the changes in the mineral phases and to determine their influence in the

Table 1
Summary of experimental conditions used during the preliminary experiments

Cement	w/c	Mixing liquid	Temperature condition (°C)	Curing age	Attacking solutions (20°C)	Time test (days)
CAC VI/55	0.7	H_2O distilled	5	7 days	NaOH 1 M + CO_2 NaOH 0.01 M + CO_2 KOH 1 M + CO_2 KOH 0.01 M+ CO_2	100
			60		NaOH 1 M + CO_2 NaOH 0.01 M + CO_2 KOH 1 M + CO_2 KOH 0.01 M + CO_2	100

Table 2
Summary of experimental conditions used during the following experiments

w/c	Mixing liquid	Temperature (°C)	Curing age (days)	Carbonation days (20°C)	Attacking solution (20°C)	Time (days)
0.7	H_2O distilled	5	7	0, 7, 28, 90		
	H_2O distilled			72	NaOH 1 M	0, 7, 28, 90
	NaOH 1 M			0, 7, 28, 90		
	Na_2CO_3 2 M			0, 7, 28, 90		
	H_2O distilled	60		0, 7, 28, 90		
	H_2O distilled			72	NaOH 1 M	0, 7, 28, 90
	NaOH 1 M			0, 7, 28, 90		
	Na_2CO_3 2 M			0, 7, 28, 90		

evolution of mechanical resistances. The experiments proposed and the working conditions in these later studies are summarized in Table 2.

4. Results and discussion

4.1. Preliminary experiments. Influence of alkaline solutions on the hydration and carbonation of CAC mortars

In these experiments (see Table 1) attempts have been made to reproduce the phenomenon of the alkaline hydrolysis as an accelerated process in the laboratory.

The temperatures of fabrication of the specimen mortars (5°C and 60°C) were selected to reproduce the behavior of hexagonal and cubic phases. CAH_{10} phase remains indefinitely stable at 5°C (see Fig. 1) and the cubic stable phase C_3AH_6, which is the main phase during the early ages cured at 60°C, is shown in Fig. 2. C_2AH_8 phase has not been detected in mortars fabricated with water at these temperatures. The influence of the "alkaline hydrolysis" process on the phase and strength evolution in the mortar specimens has been investigated.

4.1.1. Mortars at 5°C

Table 3 shows the phase composition under different attacking solutions. Quartz is not included because it may be considered as an inert component.

Before carbonation CAH_{10} appears as a product of the hydration process. It seems that the degradation process in these specimens has not been completed at this time. At laboratory temperature, the conversion to cubic phase C_3AH_6 is also not observed after 100 days. So, the attack is effected directly on CAH_{10}. Different polymorphs of AH_3 and $CaCO_3$ are identified for high carbonation age, 100 days.

It has been published that the conversion from hexagonal hydrates to cubic hydrates is accelerated as a result of the alkalis [19]. However, this tendency has not been observed in Table 3.

From Table 3 it can be deduced that specimens in 0.01 M alkali solutions do not show significant differences in their phases composition with the nature of cation. In both (Na and K) it appears a large quantity of CAH_{10} and small quantities of $CaCO_3$ in the form of calcite appears. Polymorphic phases of AH_3 appear in small quantities. On the other hand, for specimens placed in 1 M alkaline solutions, the following results are noted: in NaOH solution the hexagonal phase CAH_{10} appears in a smaller proportion and different AH_3 phases and $CaCO_3$ appear in a greater amount than in KOH solution. This result suggests that the extension of the process depend on the cation nature. So, in KOH solution the specimens degrade on a smaller scale [20].

AH_3 in the form of bayerite can be detected after 100 days of carbonation. No significant differences among NaOH and KOH solutions were observed. The amounts of

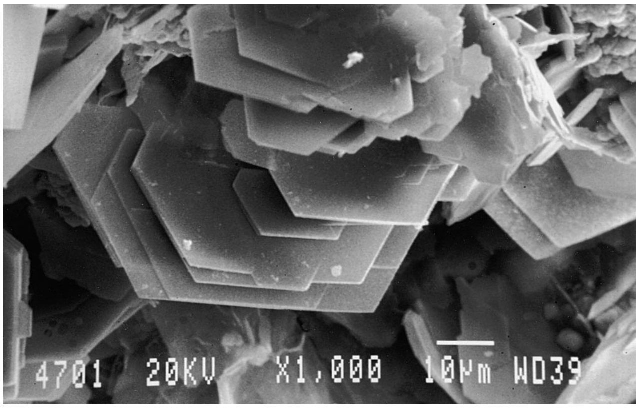

Fig. 1. SEM photo of hexagonal phase.

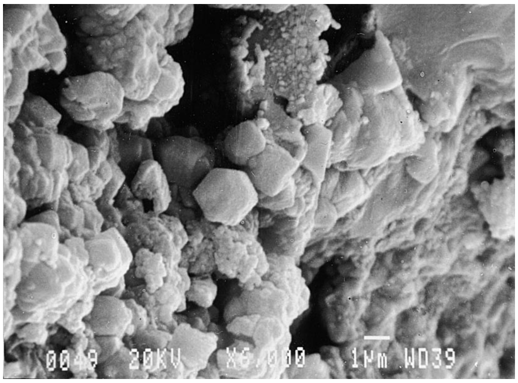

Fig. 2. SEM photo of cubic phase.

Table 3
Semiquantitative phase composition (analyzed by XRD) of mortars prepared and cured at 5°C; and 100 days carbonation, at 20°C, into the different alkaline solutions

Solution	CAH_{10}	AH_3 bayerite	AH_3 nordstrandite	$CaCO_3$ calcite	$CaCO_3$ aragonite	$CaCO_3$ vaterite
Before carbonation	++++					
KOH 0.01 M	+++	o	o	+		
KOH 1 M	++	++	++	+++	o	o
NaOH 0.01 M	+++	o	o	+		
NaOH 1 M	+	+++		++++	+	+

++++ Very abundant; +++ abundant; ++ moderate; + little; o traces.

calcium carbonate are similar in both solutions. Calcite is the predominant $CaCO_3$ polymorph although there are also in a smaller proportion vaterite and aragonite.

In accordance with these results the degradation process of mortars occurs on a greater scale in concentrated solutions, independently of the cation nature.

4.1.2. Mortars at 60°C

The phase composition is shown in Table 4. During the hydration of CAC mortar at 60°C the phase composition comprises cubic hydrate C_3AH_6 and gibbsite as a crystalline phase of AH_3. The extent of the process is higher in NaOH solutions. Also, for a given cation the more concentrated the solution the more intense is the process. However, bearing in mind that the amount of C_3AH_6 detected after 100 days of attack is still significant, it can be considered that the reaction has not been completed after the time of treatment. The value of mechanical resistance in this case should not be considered in civil engineering calculations.

It may be pointed out that in this study the formation of carboaluminate-type compounds has not been checked. This result is common for all the samples studied, regardless of the nature and concentration of the solution. Hemicarboaluminate, monocarboaluminate and calcite are the stable phases that are formed as the concentration of the carbonate anion increases [21]. These species can be considered as intermediate compounds and for this reason these species are not detected. These compounds could react with excess CO_2 and could be destroyed in the first stages of carbonation, giving the different polymorphs of $CaCO_3$ as the final product.

Table 4
Semiquantitative phase composition (analyzed by XRD) of mortars prepared and cured at 60°C; 100 days carbonation, 20°C in the different alkaline solutions

Solution	C_3AH_6	AH_3 gibbsite	AH_3 nordstrandite	$CaCO_3$ calcite	$CaCO_3$ vaterite
Before carbonation	++++	+			
KOH 0.01 M	+++	+		+	
KOH 1 M	+	+	+	++	o
NaOH 0.01 M	+++	+		++	
NaOH 1M	+	+	++	++++	+

++++ Very abundant; +++ abundant; ++ moderate; + little; o traces.

Table 5 shows the results of mechanical strengths of specimens of CAC prepared at 5°C and 60°C after 100 days of carbonation. Mineralogical results shown in Tables 3 and 4 could explain the results obtained from the study of mechanical strengths. The greater the amount of hexagonal hydrates (specimens at 5°C) and of cubic hydrates (specimens at 60°C), the smaller the extent of the degradation reaction through alkaline hydrolysis. Therefore, the mechanical behavior of the sample is better. On the other hand, hexagonal hydrates develop higher intrinsic strengths than those developed by the cubic phases on their own [22]. Thus, the mechanical strength values of samples manufactured at 60°C that have gone through the process of carbonation in the presence of alkalis are logically inferior to those produced at 5°C (see Table 5).

In general, massive deposition of products by carbonation (for long periods in carbonation treatments) reduces porosity of mortars. This leads to a progressive increase of mechanical strengths [15]. This fact justifies that at 60°C specimens in more concentrated NaOH solutions have higher mechanical strengths.

4.2. Study of the effects of carbonation in the absence of alkalis in CAC mortars

Table 2 shows the experimental process.

4.2.1. Mortars at 5°C

The phase composition is represented in Table 6 for different carbonation times. Before carbonation CAC mortar specimens show a high content of CAH_{10}, a small amount of AH_3 in the form of nordstrandite and significant amounts of calcium aluminate anhydride (CA).

Table 5
Values of flexural strength (S_f) and compressive strength (S_c) of specimens prepared and cured at 5°C and 60°C, after 100 days of carbonation into different alkaline solutions studied

	S_f (N/mm^2)		S_c (N/mm^2)	
Solution	5°C	60°C	5°C	60°C
KOH 0.01 M	9.61	2.94	74.41	11.06
KOH 1 M	7.64	5.09	64.11	20.29
NaOH 0.01 M	8.92	3.04	74.04	13.64
NaOH 1 M	6.86	5.47	62.76	24.88

Table 6
Semiquantitative phase composition (analyzed by XRD) of mortars prepared and cured at 5°C and then carbonated at 20°, in the absence of alkalis

Carbonation time (days)	CAH_{10}	C_3AH_6	AH_3 gibbsite	AH_3 nordstrandite	$CaCO_3$ calcite	$CaCO_3$ vaterite	$CaCO_3$ aragonite	CA
0	+++			+				++
7	++++			+				
28	+++	+	+			++		
90	+			++	+	+++	++	

++++ Very abundant; +++ abundant; ++ moderate; + little; o traces.

When carbonation was started 7 days after curing the samples showed an increase in CAH_{10}, along with a considerable decrease in CA, which is no longer detected through XRD. The amount of AH_3 in the form of nordstrandite remains practically constant with time. No appearance of $CaCO_3$ is detected. Therefore, it can be concluded that nothing occurs, except that the hydration process progresses. The consequences of the carbonation process cannot be detected through XRD, as the presence of amorphous calcium carbonate has been proved in hydrated mortars at low temperatures, or in the initial stages of those hydrated mortars at medium temperatures, in the presence of CO_2 [23].

After 28 days of curing the consequences of carbonation are noticeable and could be visually detected. The formation of vaterite is observed. AH_3, which again remains practically constant, is detected in the form of gibbsite. The amount of CAH_{10} decreases slightly. It is relevant to mention the appearance of considerable amounts of C_3AH_6 from the conversion of CAH_{10}. This fact can be due to the process of carbonation that takes place at room temperature, and can be checked by mechanical strength studies.

Finally, the samples studied after 90 days show a very small amount of CAH_{10}. C_3AH_6 is not observed. The amount of AH_3 in the form of nordstrandite increases slightly. There is a noticeable increase in the amount of $CaCO_3$ due to the decrease in CAH_{10} and C_3AH_6. $CaCO_3$ is simultaneously found as calcite, aragonite and vaterite, the latter being the polymorph, which appears in the highest proportion.

4.2.2. Mortars at 60°C

The phase composition is shown in Table 7 for different carbonation times. Before the carbonation process CAC mortar specimens show a high content of C_3AH_6. Considerable amounts of AH_3 is detected as gibbsite and the presence of CA is not detected. These results indicate an increase in the hydration rate due to the effect of temperature for samples mixed at 60°C in contrast with those mixed at 5°C.

Table 7
Phase evolution, analyzed by XRD, of mortars prepared and cured at 60°C and then carbonated at 20°, in the absence of alkalis

Carbonation time (days)	C_3AH_6	AH_3 gibbsite	$CaCO_3$ calcite	$CaCO_3$ vaterite	CaCO3 aragonite
0	+++	++			
7	++	+++	+		
28	+	+++	+++	+	
90	o	++	+++	++	o

++++ Very abundant; +++ abundant; ++ moderate; + little; o traces.

After undergoing the process of carbonation the samples show a gradual decrease in the amount of C_3AH_6 with time.

From the early stages the formation of $CaCO_3$ is detected. After 7 days calcite is the only polymorph of $CaCO_3$ detected. After 28 days, calcite and vaterite coexist. Finally, after 90 days all three polymorphs coexist. The formation of aragonite as a stable carbonated phase suggests a more complete carbonation. However, calcite prevails for all stages.

On the other hand, AH_3 appears in the form of gibbsite after all the times studied. The amount of this phase increases with the carbonation time. Besides, this increase agrees with the decrease in C_3AH_6.

Formation of gibbsite takes place through the stages of alumina gel and bayerite, which become gibbsite on aging [23]. Aging rate increases with (increased) temperature. Hence, the result obtained seems logical.

Finally, it must be emphasized that neither under the different stages nor under the working temperatures has the formation of carboaluminates been observed as an intermediate species in the process of carbonation. This could be due to the short period of life of these species in the system, and 7 days could be a very long period of time to detect them. On the other hand, it could be due to the fact that the XRD technique is not suitable for their detection since their amount could be under the limit of detection of this technique.

Fig. 3 shows the effect of accelerated carbonation on the evolution of compressive strength (Y_1-axis) and flexural strength (Y_2-axis) vs. time (axis X) in CAC specimens of mortars manufactured at 5°C and 60°C, and then carbonated at 20°C. It can be observed that the evolution of mineralogical phases studied by XRD (see Tables 6 and 7) can explain the results on mechanical strengths.

From early ages of the carbonation process the compressive and flexural strength of specimens manufactured at 5°C increase due to the development of the hydration process that yields large amounts of CAH_{10}. This phase is progressively carbonated or converted to C_3AH_6. In agreement with this a clear decrease appears in the strength in compression

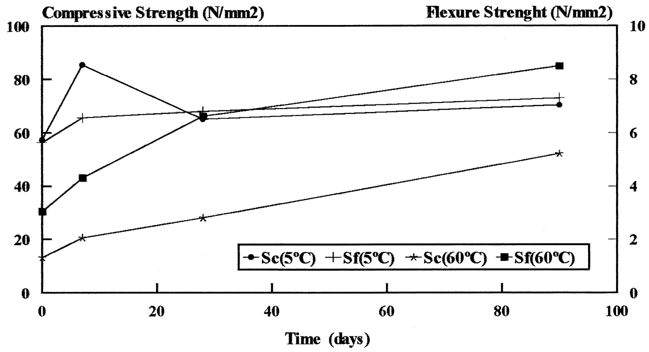

Fig. 3. Evolution of compressive strength (S_c) and flexural strength (S_f) with time for CAC mortars prepared and cured at 5°C and 60°C and then carbonated at 20°C, in the absence of alkalis.

after 28 days. Later, and as the carbonation process proceeds, the strength recovers slightly due to the precipitation of significant amounts of $CaCO_3$. However, flexural strength remains almost constant during the whole carbonation process without being affected by the formation of C_3AH_6 or later by the formation of $CaCO_3$ later.

From the early ages of the carbonation process of specimens manufactured at 60°C a positive evolution of both compressive and flexural strengths is detected with time. This is due to the total disappearance of C_3AH_6 along with the massive precipitation of $CaCO_3$.

4.3. Effects of the alkaline attack on carbonated CAC samples

Table 2 shows the experimental conditions.

4.3.1. Mortars at 5°C

Table 8 shows the phase composition of specimens prepared and cured at 5°C, carbonated at 20°C for 72 days and then introduced into a solution of 1 M NaOH, also at 20°C. Initially, the amount of CAH_{10} detected is small. AH_3 appears in the form of nordstrandite. All three polymorphs of $CaCO_3$ coexist, the presence of vaterite being predominant. After 28 days immersion in the alkaline solution, no CAH_{10} is detected, the amount of $CaCO_3$ has significantly increased, calcite being the prevailing polymorph, and bayerite is detected as the predominant phase among AH_3 polymorphs. No significant changes of the crystalline phases are observed later.

Table 9

Semiquantitative phase composition (analyzed by XRD) of mortars prepared and cured at 60°C, carbonated for 72 days and then introduced into a solution of 1 M NaOH at 20°C

Time (days)	C_3AH_6	AH_3 gibbsite	AH_3 bayerite	$CaCO_3$ calcite	$CaCO_3$ vaterite	$CaCO_3$ aragonite
0	++	++		+++	++	+
7	++	++		+++	++	+
28	+	++	+	++++	++	++
90	o	++	++	++++	++	++

++++ Very abundant; +++ abundant; ++ moderate; + little; o traces.

4.3.2. Mortars at 60°C

Table 9 shows XRD results of phase composition of the specimens prepared and cured at 60°C, carbonated for 72 days at 20°C, and then introduced into a solution of NaOH 1 M also at 20°C.

From early ages the amount of C_3AH_6 progressively diminishes, so that the amount found after 90 days is almost negligible. Simultaneously, the amount of $CaCO_3$ increases with time. All three polymorphs of $CaCO_3$ coexist at all stages, calcite always being the prevailing phase. A significant proportion of AH_3 appears as gibbsite at all ages.

Fig. 4 shows the effect of the aforementioned process on the evolution of compressive strength (Y_1-axis) and flexural strength (Y_2-axis) vs. time (into NaOH solution) in specimens of CAC mortars prepared and cured at 5°C and 60°C, carbonated at 20°C for 72 days and then introduced into a solution of 1 M NaOH also at 20°C.

Up to 28 days, strengths in compression and flexure gradually decrease with time. This might be caused by the progressive loss of C_3AH_6. Then strength in flexure experiences a slight recovery that could be attributed to the formation of significant amounts of $CaCO_3$. However, this fact does not seem to affect the evolution of strength in compression which, from the 28th day on, keeps decreasing slightly.

After 28 days, in specimens manufactured at 5°C, CAH_{10} is no longer detected by XRD. From that moment onwards the mechanical strength in compression remains almost constant. The behavior of the strength in flexure is similar. This result suggests that strongly alkaline solutions 1 M NaOH has no effect whatever on the mechanical behavior of completely carbonated mortars.

Table 8

Semiquantitative phase composition (analyzed by XRD) of mortars prepared and cured at 5°C, carbonated for 72 days and then introduced into a solution of 1 M NaOH at 20°C

Time (days)	CAH_{10}	AH_3 gibbsite	AH_3 nordstrandite	AH_3 bayerite	$CaCO_3$ calcite	$CaCO_3$ vaterite	$CaCO_3$ aragonite
0	++		++		+	+++	++
7	+		+	++	++	+++	++
28			+	++	++++	+++	+++
90		+	+	++	++++	+++	+++

++++ Very abundant; +++ abundant; ++ moderate; + little; o traces.

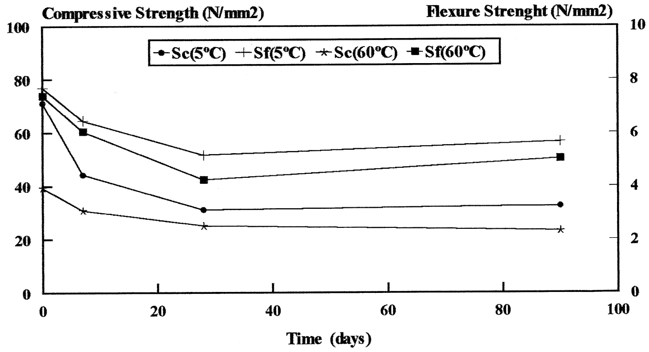

Fig. 4. Evolution of compressive strength (S_c) and flexural strength (S_f) with time for CAC mortars prepared and cured at 5°C and 60°C, carbonated for 72 days at 20°C and then introduced into a solution of 1 M NaOH also at 20°C.

4.4. Effect of NaOH on hydration and carbonation of CAC mortars

Table 2 shows the experimental process. In this part of the work samples were prepared using a solution of 1 M NaOH as mixing liquid instead of distilled water. This work is carried out following the hypothesis of an attack through an internal action.

4.4.1. Mortars at 5°C

Table 10 shows the XRD results of phase composition of specimens prepared with 1 M NaOH at 5°C that have then undergone a process of accelerated carbonation at 20°C.

Initially, specimens show similar amounts of CAH_{10} and C_2AH_8. The heat released during hydration of mortar in the presence of alkalis increases the temperature of the material and allows the formation of C_2AH_8 [15]. On the other hand, compared to samples mixed with water (Table 6), the amounts of hexagonal hydrates are, in this case, smaller. This result suggests that the extent of the hydration reaction in the presence of alkalis is lower. This fact is also supported by the presence of larger amounts of CA, about the same as those of hexagonal hydrates formed. Another factor that may have an influence and cause the amount of hexagonal hydrate to be smaller is the capacity of these compounds to dissolve in strongly alkaline solutions, migrating in the form of an aluminate anion to the aqueous phase of pores [16,24].

Besides, a small amount of calcic monocarboaluminate, C_4Ac11H is also detected in these samples. This species is mainly formed from CO_2 dissolved in the mixing liquid. In the presence of Na ion, the concentration of Ca^{2+} in the solution in equilibrium with monocarboaluminate diminishes. Concentrations of aluminum and carbonate ions increase [21]. Therefore, the range of carbonate concentrations in which the monocarboaluminate phase remains stable is modified and widened. This explains why monocarboaluminate appears in these samples when mixed with a solution of 1 M NaOH.

In the carbonated samples one can observe that hexagonal hydrates show a different behavior. C_2AH_8 diminishes with time, not being detected after 28 days. On the other hand, CAH_{10} increases during the first days of the carbonation process, due to CA hydration with the water released from the conversion and carbonation of C_2AH_8. Thus, after 7 days one can observe an increase in CAH_{10}, a drastic decrease in C_2AH_8, the disappearance of CA and the appearance of small amounts of AH_3 and $CaCO_3$. As the carbonation process goes on CAH_{10} diminishes, eventually disappearing after 90 days. Simultaneously, the amount of $CaCO_3$ progressively increases. Initially, only vaterite and aragonite are detected. After 28 days calcite, vaterite and aragonite appear in similar amounts. However, after 90 days the presence of calcite becomes predominant if compared to that of vaterite and aragonite. Anyway, the amount of $CaCO_3$ in these samples are larger than in the samples mixed with water. This probably means that a part of the carbonate comes from the decomposition of other calcium aluminates that are present in the samples [20].

In these samples carboaluminates react with the excess CO_2, being destroyed in the first stages of the carbonation process. Thus, 28 days after the beginning of the process they are no longer detected.

Small amounts of AH_3 appear as bayerite after 7 days. However, after 28 days significant amounts of bayerite and gibbsite are detected.

Finally, the presence of important amounts of C_3AH_6 from the 28th day onwards must be noticed. This phase could appear from the conversion of hexagonal hydrates since the carbonation process takes place at 20°C and in the presence of humidity. This is particularly true for C_2AH_8 for which the process of conversion at temperatures over 20°C is faster than for CAH_{10} [4,25]. On the other hand, it must be taken into account that the conversion of hexagonal hydrates into cubic ones is accelerated by the presence of alkalis [11,19]. The formation of carboaluminates partially reduces or inhibits the transformation from hexagonal aluminate to cubic aluminate but does not prevent their

Table 10
Semiquantitative phase composition (analyzed by XRD) of mortars prepared with 1 M NaOH at 5°C and then carbonated at 20°C

	Carbonation time (days)			
Mineralogical phase	0	7	28	90
CAH_{10}	++	+++	++	
C_2AH_8	++	+		
C_3AH_6			++	+
AH_3 (gibbsite)	+		+	+
AH_3 (bayerite)		+		+
$CaCO_3$ (calcite)			+	+++
$CaCO_3$ (vaterite)		+	+	++
$CaCO_3$ (aragonite)		+	+	++
CA	+++			
C_4Ac11H	+	+	o	

++++ Very abundant; +++ abundant; ++ moderate; + little; o traces.

degradation by CO_2 in the presence of humidity [23]. The diffractograms show the simultaneous appearance of C_3AH_6 and the disappearance of monocarboaluminate.

4.4.2. Mortars at 60°C

Table 11 shows the results of phase composition identified by XRD of specimens manufactured with 1 M NaOH at 60°C, and then exposed to an accelerated carbonation process at 20°C.

Initially, after the carbonation process, one can notice the presence of C_3AH_6 in large amounts. Its abundance is greater than in samples mixed with water (Table 7). Unlike the situation found at 5°C, CA is not detected at 60°C. Both findings point out the higher extent of the hydration reaction due to increased temperature and the presence of alkalis. A small amount of carboaluminate, which is not detected when the mixing is made with water, is also present. AH_3 appears as gibbsite and nordstrandite in considerable amounts. Carboaluminate almost disappears after 7 days. As carbonation proceeds one can detect the formation of great amounts of $CaCO_3$, mostly as calcite.

Fig. 5 shows the evolution of mechanical strength in compression (Y_1-axis) and in flexure (Y_2-axis) of specimens manufactured and cured at 5°C and 60°C as mentioned above. For specimens at 5°C, it is interesting to mention the limited initial mechanical resistance shown by the samples, when they still have not undergone carbonation. This is probably due to the smaller quantity of hexagonal hydrates formed and to the great quantity of CA detected in samples manufactured with NaOH, if compared with those manufactured with distilled water under the same conditions. Alternatively, it may also be attributed to the dissolution of hydrated calcium aluminates. Thus, Fig. 5 shows that the values of mechanical resistance increase after 7 days, a fact that is in agreement with the increasing quantities of hexagonal hydrates detected together with that of $CaCO_3$. With the appearance of C_3AH_6 after 28 days, a slight decrease in these values takes place. Later, with the development of the carbonation process, the mechanical resistance recovers as the amount of precipitated $CaCO_3$ increases.

Table 11
Semiquantitative phase composition (analyzed by XRD) of mortars prepared with NaOH 1 M at 60°C and then carbonated at 20°C

	Carbonation time (days)			
Mineralogical phase	0	7	28	90
C_3AH_6	++++	+++	++	+
AH_3 (gibbsite)	++	+++	++	+++
AH_3 (nordstrandite)	++	+++	+++	+++
AH_3 (bayerite)			++	
$CaCO_3$ (calcite)		+++	++++	++++
$CaCO_3$ (vaterite)		+	++	++
$CaCO_3$ (aragonite)		+	++	++
C_4Ac11H	+	o		

++++ Very abundant; +++ abundant; ++ moderate; + little; o traces.

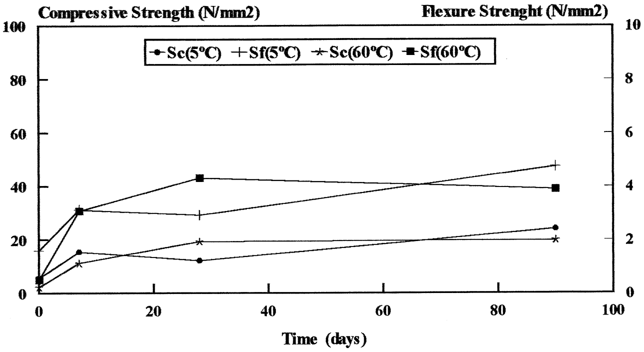

Fig. 5. Evolution of compressive strength (S_c) and flexural strength (S_f) with time for CAC mortars prepared with 1 M NaOH at 5°C and 60°C and then carbonated at 20°C.

For specimens at 60°C, the evolution of strength in compression and in flexure is similar, showing an increase during the first 28 days and then remaining constant. Again, the strength in compression shown by samples mixed with NaOH is very low, which is in agreement with XRD data that indicate the existence of a great amount of cubic aluminate hydrate. Furthermore, strengths developed are quite inferior to those corresponding to a sample mixed with water at the same temperature (Fig. 3). This fact is due to the dissolution of hydrated aluminates in strongly alkaline media, which negatively affects resistances as mentioned above. This fact cannot be compensated for the rapid formation of $CaCO_3$. Finally, it has been confirmed that the presence of alkalis does modify the rate of the carbonation process since, in the presence of alkalis, strengths after 28 and 90 days are similar, whereas in the absence of alkalis the value after 28 days is lower than after 90 days.

4.5. Effect of Na_2CO_3 on hydration and carbonation of CAC mortars

The experimental process is summarized in Table 2. In this part of the work the samples were manufactured using a solution of 2 M Na_2CO_3 as mixing liquid instead of distilled water. Again the work was conducted under the hypothesis of an attack through internal action. However, the content of alkalis is smaller in this case because the pH in the aqueous phase is significantly lower than in previous cases. This way, the extent of the dissolution of the calcium aluminates will be more limited and, hence, the effect will be less harmful for the mortar resistance.

4.5.1. Mortars at 5°C

Table 12 shows the XRD results of phase composition of specimens prepared with 2 M Na_2CO_3 at 5°C that was then carbonated at 20°C.

Initially, one observes the presence of a great proportion of CAH_{10}, small amounts of CA, AH_3 in the form of bayerite and $CaCO_3$ as calcite. No C_2AH_8 is detected.

Table 12
Semiquantitative phase composition (analyzed by XRD) of mortars prepared with 2 M Na_2CO_3 at 5°C and then carbonated at 20°C

	Carbonation time (days)			
Mineralogical phase	0	7	28	90
CAH_{10}	++++	+++	+++	++
AH_3 (gibbsite)			+	+
AH_3 (nordstrandite)				+
$CaCO_3$ (bayerite)	o	+	+	+
$CaCO_3$ (calcite)	+	+	++	+++
$CaCO_3$ (aragonite)				+
CA	+	+		
C_4Ac11H			+	+

++++ Very abundant; +++ abundant; ++moderate; + little; o traces.

Ninety days after the carbonation started, a gradual decrease in CAH_{10} is observed. Likewise, one must highlight the absence of detectable quantities of C_3AH_6. This proves that, due to its lower pH, the action of Na_2CO_3 is much weaker in favoring conversion process. All three polymorphs of AH_3 appear in small quantities. As for $CaCO_3$, the prevailing phase detected is calcite coexisting with aragonite. Finally, the presence of small amounts of monocarboaluminates from the 28th day on is noted. The monocarboaluminates behave as final stable phases [24] in this case.

4.5.2. Mortars at 60°C

Table 13 shows the XRD results of phase composition of specimens manufactured with Na_2CO_3 2 M at 60°C, and then carbonated at 20°C.

Initially, a great quantity of C_3AH_6 is noticed. The content is similar to that found in samples mixed with NaOH (Table 11) and much higher than in samples mixed with water (Table 7). The presence of non-hydrated aluminates enables one to consider that hydration has been practically complete. Carboaluminates, which were detected in samples mixed with 1 M NaOH, are not present here. AH_3 is detected showing similar proportions of gibbsite and nordstrandite. When water was used only gibbsite was detected, and in the case of 1 M NaOH mixed mortars all three polymorphs were found. $CaCO_3$ is detected as calcite in very large amounts due to the high concentration of carbonate during hydration.

Table 13
Semiquantitative phase composition (analyzed by XRD) of mortars prepared with 2 M Na_2CO_3 at 60°C and then carbonated at 20°C

	Carbonation time (days)			
Mineralogical phase	0	7	28	90
C_3AH_6	++++	++++	+++	+
AH_3 (gibbsite)	++	++	++	++
AH_3 (nordstrandite)	++	++	+++	++
$CaCO_3$ (calcite)	+++	+++	++++	++++

++++ Very abundant; +++ abundant; ++ moderate; + little; o traces.

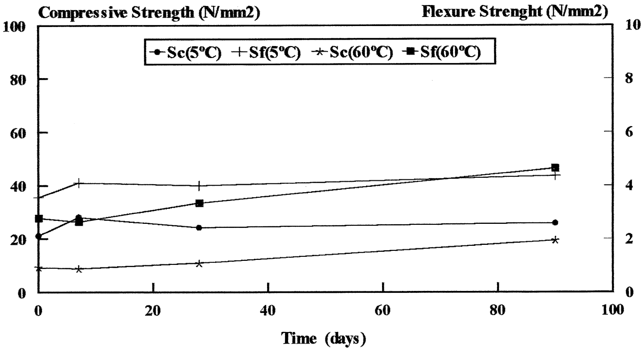

Fig. 6. Evolution of compressive strength (S_c) and flexural strength (S_f) with time for CAC mortars prepared with 2 M Na_2CO_3 at 5°C and 60°C and then carbonated at 20°C.

After 90 days a very small amount of C_3AH_6 is detected. Therefore, the carbonation process is, in this case, longer than in samples mixed with water or with 1 M NaOH. The amount of AH_3 remains practically constant during the whole carbonation process. Gibbsite and nordstrandite appear simultaneously. $CaCO_3$ is exclusively detected as calcite, its proportion increasing as carbonation proceeds.

Fig. 6 shows that, for mortars at 5°C, strength values slightly increase at the beginning and then remain practically constant; a behavior that can be due to the carbonation of the hexagonal hydrate with the subsequent appearance of $CaCO_3$. As carbonation proceeds strengths do not show a steep increase since this process is not very widespread, the amounts of $CaCO_3$ being significant but not very high. The initial strengths obtained by samples mixed with Na_2CO_3 are in an intermediate position between those mixed with water and those mixed with NaOH. The final strengths in samples prepared with Na_2CO_3 are greater than in samples prepared with NaOH, probably due to the appearance of monocarboaluminate in the former ones.

The evolution of strength in compression and in flexure for mortars at 60°C is different, showing an increase at all times. A behavior that can be due to the carbonation of the cubic hydrate, with the subsequent appearance of $CaCO_3$. The carbonation process is, in this case, longer than in samples mixed with water or with 1 M NaOH.

5. Conclusions

1. The carbonation process in the absence of alkalis can be considered beneficial when it takes place on totally converted CAC mortars. The formation of important amounts of carbonated phases improves the mechanical performance of these mortars. The loss of mechanical resistance during the conversion process is then largely recovered, although it does not reach the values corresponding to non-converted CAC mortars. However, this process

does not have a significant influence (i.e. neither positive nor negative) on the mechanical performance of non-converted CAC mortars.

2. Alkaline hydrolysis is a degradation process that can also take place in CAC conglomerates that show an excellent mechanical behavior due to the absence of the conversion process.

3. The presence of alkalis in CAC mortars has a detrimental effect on their resistance characteristics. Besides, the high pH value coming from the alkaline solution brings about the dissolution of both hexagonal and cubic hydrated calcium aluminates. On the other hand, their presence during hydration causes modifications on the mineral composition of pastes with respect to those hydrated in the absence of alkalis. These modifications give rise to a progressive loss of mechanical resistances. The presence of an intermediate hydrated alkaline aluminate, which could be responsible for this behavior, has not been detected in any of the samples studied.

4. In all the samples studied, the final products obtained through the carbonation processes, in the presence as well as in the absence of alkalis, are the same. However, it does not mean that final mechanical resistances should be similar since these processes follow different mechanisms. In addition, the existence of other compounds, either dissolved in the liquid that fill the pores, or in an amorphous gel state, both impossible to detect by XRD, could be responsible for the deterioration of mechanical characteristics of the material.

5. The degradation process through alkaline hydrolysis, and hence the loss of resistance characteristics, takes place only when CAC conglomerates contain hydrated calcium aluminates. The result of these attacks is more harmful when the process takes place in totally converted CAC mortars, where the cubic hydrate is the prevailing phase. Besides, strongly alkaline solutions have no effects on the mechanical behavior of totally carbonated CAC mortars.

6. Be the initial hydrate hexagonal or cubic (i.e. regardless of the working temperature), the spread of the degradation reaction depends on the alkaline ion used and on the concentration of the solution. The reaction extent is larger for Na than for K ion, and for concentrated solutions than for less concentrated ones, regardless of the ion used.

7. Regardless of working conditions, samples manufactured at 60°C give rise to higher amounts of carbonated products. This is due to the fact that the porosity of these samples is higher than in those manufactured at 5°C, so that the access of CO_2 is easier and the degradation process is more widespread.

8. The XRD technique is not suitable for the study of the intermediate reaction products (i.e. carboaluminates compounds), either because they are formed in small amounts or because in most cases they are found in an amorphous gel state.

9. As regards the formation of carbonated phases, which are responsible for the recovery of resistances observed in mortars exposed to the process of degradation through alkaline hydrolysis, regardless of working conditions, the prevailing polymorphic variety is calcite. The formation of aragonite and vaterite depends on manufacturing temperature and treatment conditions.

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