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Accelerated carbonation of Friedel's salt in calcium aluminate cement paste

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Abstract

The stability of Friedel's salt with respect to carbonation has been studied in calcium aluminate cement (CAC) pastes containing NaCl (3% of Cl^- by weight of cement). Carbonation was carried out on a powdered sample in flowing 5% CO_2 gas at 65% relative humidity to accelerate the process. At an intermediate carbonation step, a part of the sample was washed and dried up to 10 cycles to simulate a dynamic leaching attack. The two processes were followed by means of X-ray diffraction (XRD), pH and Cl^- analyses in the simulated pore solution.

Keywords: Carbonation; Kinetics; Friedel's salt; Katoite; Calcium aluminate cement; Soluble chloride; Leaching

1. Introduction

Knowledge of the stability of Friedel's salt ($Ca_4Al_2O_6Cl_2{\cdot}10H_2O$) is of great significance due to its capacity for binding chloride. Free chloride is one of the more aggressive ions for steel embedded in concrete and, in this sense, many corrosion studies have been carried out by Spanish researchers on hydrated calcium aluminate cement (CAC) [1–4].

Friedel's salt can be formed from many materials and in various circumstances, and its stability is strongly related to all of them. Nevertheless, a global mechanism of destabilisation appears to be pH-dependent: Friedel's salt dissolves at 20 °C generating a pH value of 12. Among the factors, which can decrease the pH of the concrete pore solution, are carbonation and pozzolanic mineral additions. In this sense, Kobayashi et al. [5] and Suryavanshi and Swamy [6] noted that carbonation of Portland concrete resulted in dissolution of Friedel's salt. Page and Venneland [7] stated that the solubility of Friedel's salt increased in Portland cements blended with silica fume, as the alkalinity of the pore solution dropped strongly as free chloride increased, due to the pozzolanic reaction of silica fume.

Important basic studies have been carried out in the $CaO-Al_2O_3-CaCl_2-H_2O$ system [8,9] to determine the stability of Friedel's salt. Birnin-Yauri and Glasser [9] studied the solubility relationships between Friedel's salt and hydroxy AF_m and discussed the implications of the buffering capacity of the OH/Cl exchange in the AF_m structural family. The formation of Friedel's salt by OH/Cl exchange was also described by Goñi et al. [10] in the interaction between simulated radioactive liquid wastes very rich in NaCl and mortars fabricated with pozzolanic fly ash cement.

Nevertheless, few studies have been carried out on the stability of Friedel's salt in CAC compositions and the amount of free chloride in the pore solution. In a previous study, Goñi et al. [11] examined a hydrated CAC, which contained 3% (by weight of cement) of chloride as NaCl at 20 °C; Friedel's salt partially dissolved during a period of 1 month, as revealed by the expressed pore solution and XRD analyses.

In the title study, the authors have extended the time and the temperature range of the experiments. The effect of accelerated carbonation on the stability of Friedel's salt and the amount of soluble chloride liberated to the pore solution were also determined. To accelerate carbonation, powdered samples (grain size <0.05 mm) and 5% CO_2 flowing gas were used. In addition, at an intermediate carbonation step, a part of the sample was washed and dried exhaustively (up to 10 cycles) to simulate dynamic leaching attack: the evolution of pH, chloride concentration and solid phase were

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Table 1
Chemical composition of the CAC (wt.%)

SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	$S^=$	Na_2O	K_2O
2.74	14.2	43.5	38.5	0.44	0.03	0.046	0.082

determined. The two processes, carbonation and leaching were followed by means of X-ray diffraction (XRD), pH and Cl analyses of the simulated pore solution.

2. Experimental

A commercial Spanish CAC was used in the studies; its chemical composition is given in Table 1. A paste of water/cement ratio 0.5, containing 3% of Cl^- by weight of cement, was made by dissolving the required quantities of AR Grade NaCl in the (de-ionized) mix water and the cast cement stored in sealed plastic cylinders at 100% RH. During the first 15 h after mixing, the sample was cooled in ice for 9 h to avoid self-heating from the strongly exothermic hydration reaction. After 1 day, the external disks of the hardened sample were removed in order to obtain better precision and the rest of the sample was stored at 40 °C in a sealed plastic cylinder throughout the experiment, lasting up to 215 days and resulting in formation of Friedel's salt and katoite syn (C_3AH_6).

Thereafter carbonation was carried out in powdered samples (grain size <0.05 mm) at 65% relative humidity and atmosphere of 5% CO_2 at 20 °C for 300 days by which time katoite was fully carbonated. The external surface of the powder submitted to CO_2 exposure was 9.4 cm^2 and the thickness of the powder layer was about 2 mm. The evolution of solid phase was followed by XRD by means of a Philips PW 1730 diffractometer using a graphite monochromator and Cu $K_{\alpha 1}$ radiation.

Although it was not possible to express pore solution from the paste, due to the small amount of sample, an attempt was made to regenerate it by dissolving 0.5 g of powdered sample in 2 ml of de-ionized water; the mixture was maintained during 1 day at ambient temperature, after which the solid was filtered and the liquid analyzed. Chloride concentration was measured by titration against $AgNO_3$ with potentiometric determination of the end point by employing an automatic MemoTitrator Mettler DL40RC. The pH was measured with a combined electrode for the pH range 0–14. The sample carbonated for 115 days was exhaustively washed with de-ionized water and dried (up to 10 cycles) through the aforementioned experimental procedure. After each cycle, the sample was characterized by XRD and the aqueous pH and Cl^- concentration analyzed.

3. Results and discussion

3.1. Paste maintained at 40 °C

The evolution with time of the more representative XRD patterns of CAC paste and the semiquantitative evolution of the crystalline compounds, calculated from the intensity of reflections at 11.2 (2θ) for Friedel's salt, 12.35 (2θ) for CAH_{10} and 17.27 (2θ) for katoite (C_3AH_6), are presented in Figs. 1 and 2, respectively. After 1 day cured (Fig. 1(b)), the reflections of hexagonal Friedel's salt ($Ca_4Al_2O_6Cl_2 \cdot 10H_2O$)

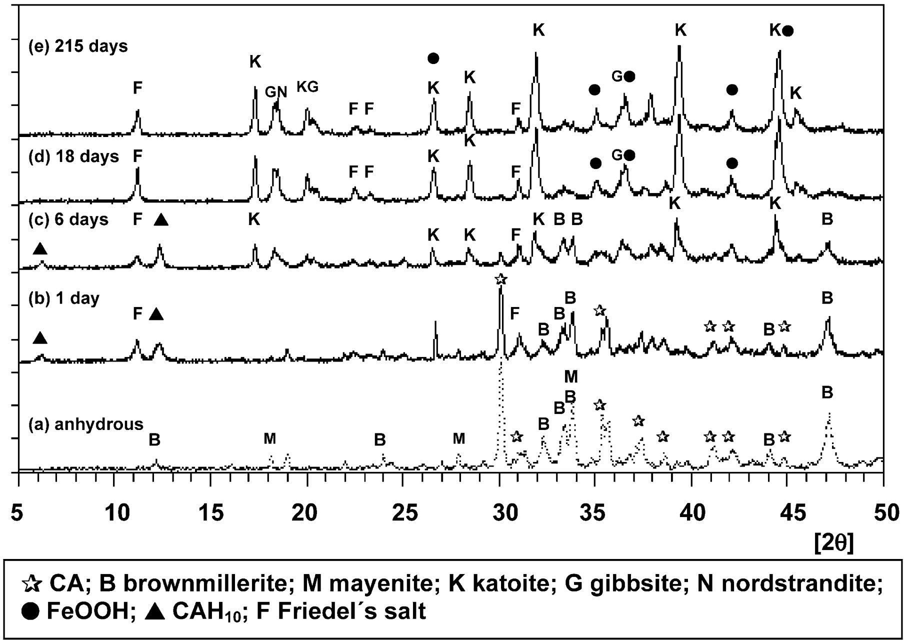

Fig. 1. Evolution with hydration time of the CAC paste at 40 °C.

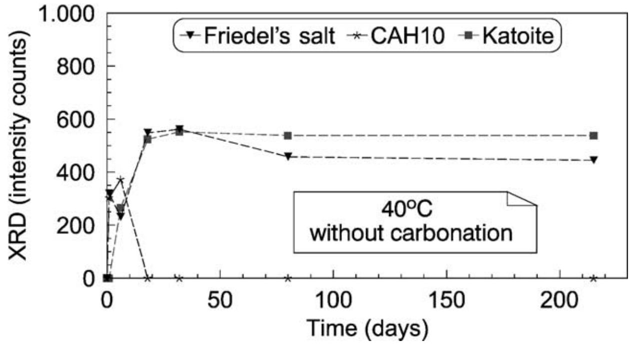

Fig. 2. Semiquantitative evolution with hydration time at 40 °C of Friedel's salt, katoite and CAH_{10}.

and CAH_{10} ($CaAl_2O_4 \cdot 10H_2O$) appeared: cubic katoite ($Ca_3Al_2(OH)_{12}$) and gibbsite γ-$Al(OH)_3$ are detected after 6 days at 40 °C (Fig. 1(c)). The intensity of their reflections increase with time while those corresponding to hexagonal CAH_{10} disappeared after 18 days (Fig. 1(d)); reflections due to nordstrandite and iron oxyhydroxide (FeOOH), the latter from hydration of brownmillerite, can be seen.

After 215 days (Fig. 1(e)), Friedel's salt decreases to 21% with respect to the value obtained after 32 days, as the semiquantitative XRD analysis of Fig. 2 showed. Crystalline $CaCO_3$ does not appear in any of its varieties: calcite, aragonite or vaterite.

3.2. Accelerated carbonation

The changes caused by carbonation (Fig. 3) showed that katoite, as expected, is more resistant than Friedel's salt to carbonation: Friedel's salt practically disappeared after 6 days of carbonation (Fig. 3(b)), whereas katoite disappeared after 300 days of carbonation (Fig. 3(e)). Aragonite, together with traces of calcite, are the calcium carbonates formed. Crystalline carboaluminates were not detected during the carbonation process.

The pH of the simulated pore solution (obtained by leaching 0.5 g of powdered sample with 2 ml of de-ionised water), after 300 days of carbonation, decreased to 6.3, compared with the value of uncarbonated sample (11.97). Nevertheless, the concentration of Cl (0.098 M) does not increase much in comparison with that obtained in the uncarbonated sample (0.09 M). These values correspond to percentages of dissolved chloride of 43% and 47% assuming all the chloride added (3% by weight of cement) to be dissolved in the 2 ml. The small increase of dissolved chloride suggested that chlorides released by carbonation of Friedel's salt are trapped by the solid.

The behavior of katoite and aragonite differ, as can be seen in Fig. 4(a), where the semiquantitative evolution of the crystalline compounds is depicted as a function of carbonation time; carbonation of katoite produces aragonite, according to the following chemical equation where $c = CO_2$:

$$C_3AH_6 + 3c \rightarrow 3Cc + AH_3 + 3H$$

This can be clearly seen when the carbonation degree of katoite and aragonite formation are represented vs. the carbonation time (Fig. 4(b)) (the points corresponding to aragonite formation are equal to those of katoite carbonation degree); in other words, the rate of decrease of

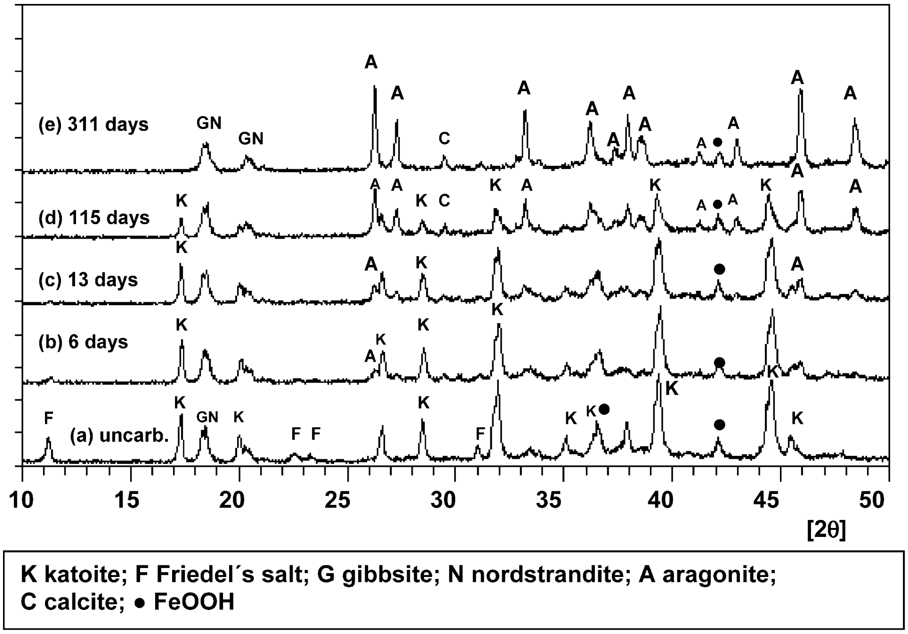

Fig. 3. Effect of accelerated carbonation at 20 °C on the CAC paste 215 days old.

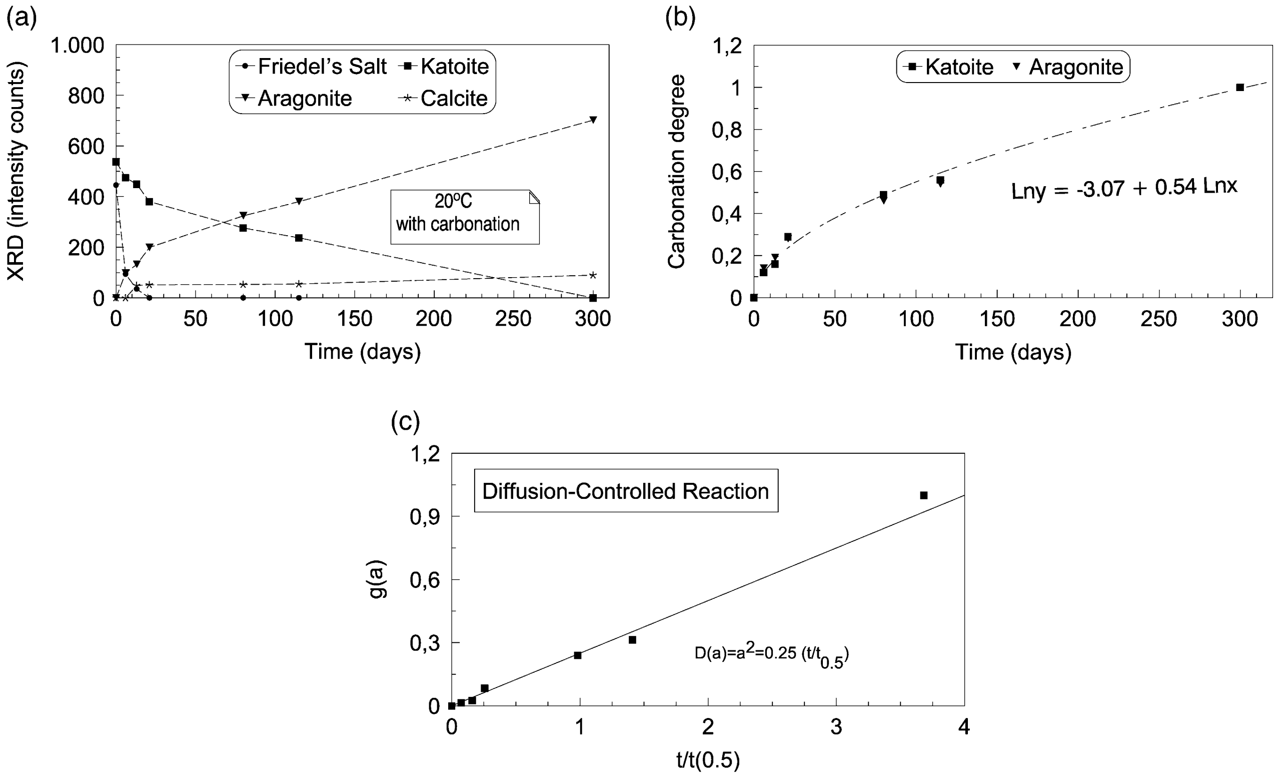

Fig. 4. Semiquantitative evolution with carbonation time of Friedel's salt, katoite, aragonite and calcite, and kinetic of katoite carbonation reaction.

katoite is equal to the rate of increase of aragonite. Time zero in Fig. 4(b) corresponds to the start of carbonation. For calculating the carbonation degree of katoite, the X-ray reflection intensity of uncarbonated katoite at 17.3° (2θ) was taken as reference; in the case of aragonite formation, the intensity of X-ray reflection at 26.2° (2θ), after 300 days of carbonation, was taken as a reference. The value of the slope of the potential regression (0.54) indicates that

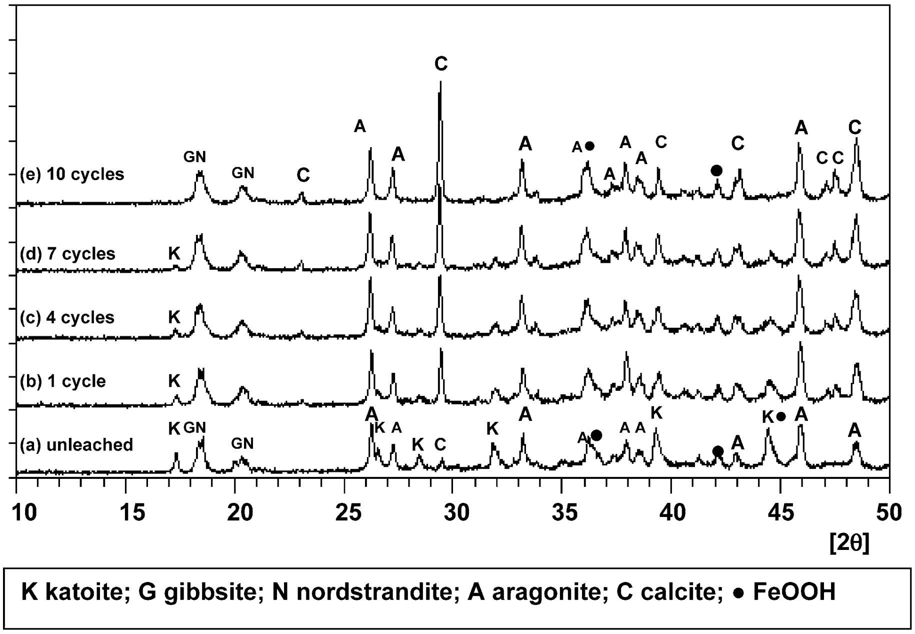

Fig. 5. Influence of simulated leaching cycles on the X-ray diffraction patterns of the sample carbonated during 115 days.

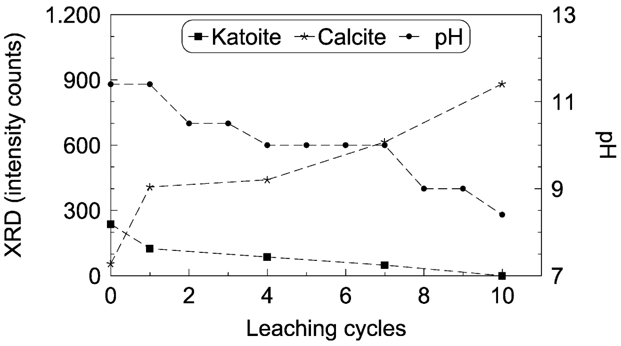

Fig. 6. Semiquantitative evolution with leaching cycles of katoite and calcite (calculated from the intensity of reflections at 17.27 and 29.46 (2θ) angular zones, respectively).

diffusion is the controlling mechanism of katoite carbonation. In fact, as can be seen in Fig. 4(c), the experimental points of katoite carbonation are fitted to the following equation:

$$D(\alpha) = \alpha^2 = 0.2500(t/t_{0.5})$$

where D is one-dimensional diffusion process with constant diffusion coefficient governed by a parabolic law [12]. The value of $t_{0.5}$ has been extrapolated from the regression equation of Fig. 4(b).

3.3. Leaching attack

The main objective of this study was to verify that chloride ions from carbonation of Friedel's salt are effectively liberated. For that, the sample carbonated for 115 days (Fig. 2(e)), when katoite was still present, was exhaustively washed and dried (up to 10 cycles). After each cycle, the sample was characterized by XRD and the pH and Cl^- concentrations were analyzed in the water.

As shown in Fig. 5, katoite reflections disappeared progressively while those of calcite strongly increased. Nevertheless, aragonite reflections remained essentially unchanged. This suggests that katoite is carbonated during leaching giving rise to calcite instead of aragonite (the CO_2 could be trapped during the leaching process from the deionized water together with that present in the starting carbonated sample).

Similarly to the case of accelerated carbonation, the opposite behavior of katoite and calcite can be better seen in Fig. 6, where the semiquantitative evolution of katoite and calcite is represented as a function of the number of leaching cycles: Time zero in Fig. 6 corresponds to the start of leaching.

The concentration of chloride dropped from 0.099 to 0.0039 M, which represents percentages of soluble chlorides of 47% and 2%, for the unleached sample and after 10 leaching cycles, respectively. It is known that the aragonite polymorph of $CaCO_3$ is preferentially formed in the presence of chloride, as occurs in sea water. So, as chloride concentration decreases in the sample, owing to leaching, calcite is formed in preference to aragonite.

The pH decreased from 11.4 to 8.4 for the unleached sample and after 10 leaching cycles (Fig. 6), respectively; a stabilization plateau at a pH value of 10 is attained between 4 and 7 cycles, which can be attributed to the buffering effect of dissolution of katoite; pH values lower than 10.8 cause the dissolution of katoite, according to its solubility constant (K_s=$10^{-22.3}$) [13].

4. Conclusions

- The carbonation of Friedel's salt does not produce a significant increase of soluble chloride. This indicate that chloride is trapped in another solid phase.
- Chloride is effectively eliminated from the carbonated sample after 10 cycles of simulated semidynamic leaching.
- The mechanism of katoite carbonation corresponds to a one dimensional diffusion-controlled reaction, giving aragonite as the $CaCO_3$ variety formed.
- Nevertheless, the carbonation of katoite produced during leaching gives rise to the calcite variety of $CaCO_3$.

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