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Petrographical analysis of calcium aluminate cement mortars Scanning electron microscopy and transmitted light microscopy

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Abstract

The samples studied for this paper were obtained from experimentally induced carbonation and alkaline hydrolysis of calcium aluminate cement (CAC) mortars. The mineralogical composition of phases present was studied from X-ray diffraction (XRD) spectra. Scanning electron microscopy (SEM) and transmitted light microscopy (TLM) were used to obtain some morphological (size and shape) and fabric data of mineralogical phases to improve the interpretation of damage processes. SEM is a useful tool to examine the evolution of mineral phases in cavities and discontinuity zones. The interpretation of the degree of carbonation and the distribution of carbonated phases in the samples, the presence of C_3AH_6 and CAH_{10}, as well as possible alterations of aggregates are well differentiated and defined using TLM method. The main objective of the present paper is to validate the use of both microscopic techniques (TLM and SEM) for the study of phase evolution in the CAC mortar during curing and degenerative processes.

Keywords: Petrography; Calcium aluminate cement; SEM; X-ray diffraction

1. Introduction

Calcium aluminate cement (CAC) is very suitable for some concretes; the strength gain is very fast. After setting, the cement develops most of its strength within hours. Unfortunately, the use of CAC in structural concrete is restricted due to loss of strength of the concrete over time. This reduction is due to a chemical reaction in which a cubic calcium aluminate hydrate is produced at the expense of the hexagonal hydrates formed initially [1–5].

The wide variety of damage processes observed in CAC concretes is not correctly interpreted using only mineralogical data from X-ray diffraction spectra (XRD) and chemical data. As a consequence, it is necessary to use some morphological (size and shape) and fabric data of mineralogical phases from scanning electron microscopy (SEM) and transmitted light microscopy (TLM) to improve damage process interpretation. TLM provides data on the presence of certain minerals with a detection level well below that of X-ray diffraction, since the presence of a single grain of a specific mineral can be detected through TLM. TLM gives data on the distribution of mineral phases, their mutual relationship, and even their potential weathering and other alterations.

The petrographical analysis using TLM of thin section is a widely used technique for the characterisation of minerals and rocks. The applicability of this technique to the study of phase evolution in Portland cement concretes is limited by the high percentage of amorphous phases. A different case is found in CAC concretes, where in the hydrated phases at any one stage the level of crystallinity is much higher. Few reviews on this subject are cited in the references [6,7]. The authors are not aware of the existence of any specific study relating to the optical microscopy of CAC concretes.

The main objective of the present paper is to validate the use of both microscopic techniques (TLM and SEM) for the study of phase evolution in the CAC mortar during the curing and degenerative processes.

2. Methods

2.1. Materials and specimen preparation

VI/55 electroland CAC meeting the Spanish standard [8] requirements was used. Silica sand was always employed as the aggregate. Different types of mortar were prepared using water/cement ratio of 0.7. The main variables for the curing process were temperature and time. Prisms (40 × 40 × 160

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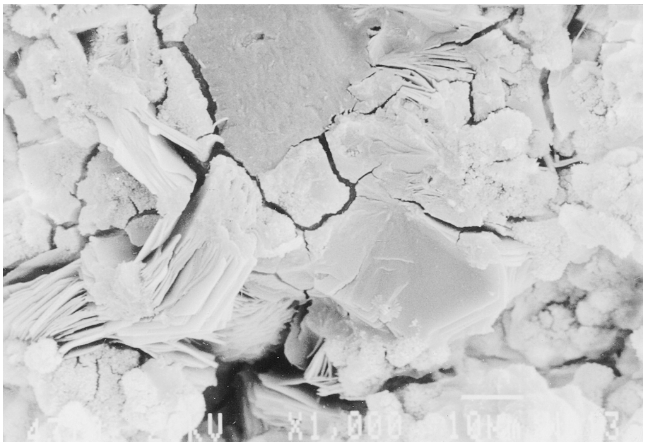

Fig. 1. SEM (SE) microphotograph of CAH_{10} being newly formed inside the paste. Specimen 3.

mm) of a cement/sand ratio of 1:3 mortars were prepared using CAC. Distilled water was used for samples 1, 2, 3, 4, 5, and 6. A solution of 1 M of NaOH was used for samples 7 and 8. The mortar specimens were prepared in the laboratory at 5 and 60°C and 90% relative humidity with mechanical compaction in two layers. Immediately after casting and surface finishing, the test specimens in the mould were covered with a polyethylene film 0.2-mm thick in prevailing weather. After demoulding 24 h later, the samples were placed in water for curing at the various temperatures mentioned above.

After 7 days, curing specimens 1 and 2 were analysed. Specimens 3, 4, 5, 6, 7, and 8 were carbonated at room temperature in a CO_2 atmosphere chamber with a relative humidity in the air of $\cong$ 47% [9]. The duration of the carbonation process was 72 days. After the carbonation process all the specimens were analysed.

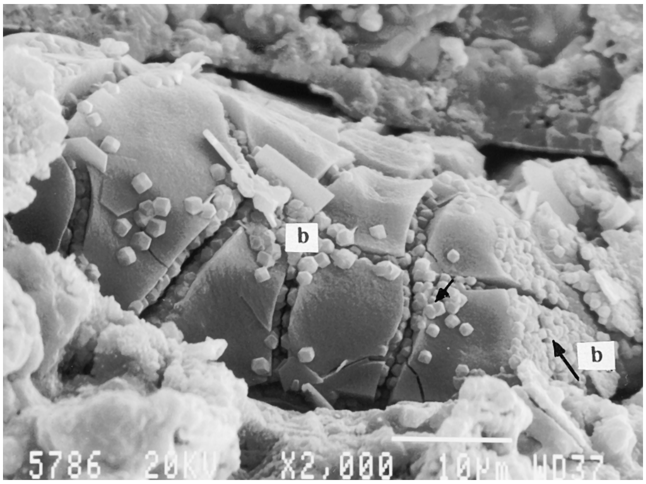

Fig. 2. SEM (SE) microphotograph of C_3AH_6 (b) concentrated in the retraction cracks of the gel paste. Specimen 5.

Table 1
Samples mixed with water at different temperatures

	Specimen 1 (5°C)	Specimen 2 (60°C)
Mineralogical phases present	Quartz CAH_{10} CA	Quartz C_3AH_6 Gibbsite

2.2. Testing

The types of test for the determination of various properties are described below.

2.2.1. X-ray diffraction

The X-ray diffraction (XRD) experiments were carried out in a Scheifer powder diffractometer (Scheifer, Ahrensburg, Germany) with a graphite monochromator and an NaI (Tl) scintillation detector using Cu Kα radiation. An aperture slit of 3° and detector slit of 0.15° were used. After being crushed in an agate mortar to a size of 40 μm, the samples were preserved in acetone at 5°C. The XRD spectra were taken at a speed of 1° min^{-1} and the intensities were calculated from the diffraction maxima after discounting the background.

2.2.2. TLM

An optical microscope (Axioscop, Zeiss, Jena, Germany) was used for the petrographical analysis of thin sections of specimens of CAC mortar samples obtained under different environmental conditions.

The specimens were trimmed with a large radius blade lubricated with water. The samples obtained ($30 \times 20 \times 15$ mm) were impregnated in a vacuum chamber (Struers Epovac, Rodrovre, Denmark) with epofix hardener (trietylenetetramine) containing fluoresceine. One face was lapped smooth by an automatic lapping machine (Struers PdM, Rodrovre, Denmark) using carborundum 320 F grade after 600 F grade and 1000 F grade. Afterward, its polished side was stuck on to a larger piece of glass and was cut down to 5 mm. Later it was placed back on the machine and cut down to 30 μm, polished with 1000 F grade carborundum, and covered with a thin piece of glass.

2.2.3. SEM

The scanning electron microphotographs were taken with a JEOL JSM-840 SEM (Tokyo, Japan) equipped with an energy dispersive X-ray analyser. High vacuum evaporation (SCD 004 from BALZERS UNION LIECHTENSTEIN) was the method used to form a thin gold film to make the surface of the specimens electrically conductive. Secondary electrons (SE) images of broken surfaces were studied.

3. Results and discussion

3.1. XRD results

As pointed out earlier, 5 and 60°C were selected as temperatures of fabrication of the specimen mortars to repro-

Table 2
Samples mixed with water at different temperatures and carbonated in absence of alkalis

	Specimen 3 (5°C)	Specimen 4 (5°C)	Specimen 5 (60°C)	Specimen 6 (60°C)
Mineralogical phases present	Quartz CAH_{10} Aragonite Nordstrandite	Quartz CAH_{10} Vaterite Nordstrandite Aragonite	Quartz Calcite C_3AH_6 Gibbsite Vaterite Nordstrandite	Quartz Calcite C_3AH_6 Gibbsite Vaterite Aragonite

duce the behaviour of hexagonal phases, which remain stable indefinitely at 5°C (see Fig. 1), and the cubic stable phase C_3AH_6, which is the main phase found at 60°C in the early ages (see Fig. 2). Table 1 shows the mineralogical composition of samples mixed with water at different temperatures.

For sample 1 (5°C, after a curing time of 7 days) the CAH_{10} appears to be the only product of the hydration process, along with significant amounts of anhydrous CA. In sample 2 (60°C, after a curing time of 7 days) the main phases formed were cubic hydrate(C_3AH_6) and crystalline gibbsite (AH_3). Furthermore, part of the AH_3 produced took the form of amorphous gel.

Table 2 shows the mineralogical composition of samples mixed with water at different temperatures and carbonated in the absence of alkalis.

Samples cured at 5°C and studied 90 days after the beginning of the carbonation process show a very small amount of CAH_{10}. No C_3AH_6 is observed. The AH_3 is identified as nordstrandite. $CaCO_3$ was present in large amounts. It was found both as aragonite and vaterite, but the latter polymorph appears in the larger proportion.

The mineralogical phases in mortars mixed at 60°C are also shown in Table 2. After 90 days all three $CaCO_3$ polymorphs coexist. The formation of aragonite as a stable carbonated phase from calcite suggests a more complete carbonation. After undergoing the carbonation process, samples show a gradual decrease in C_3AH_6 and AH_3 appears as gibbsite.

An attempt has been made to reproduce the phenomenon of alkaline hydrolysis in CAC mortars as an accelerated process in the laboratory. In other work we had made a general study of alkaline hydrolysis in calcium aluminate cement mortars under a broad range of experimental conditions [10]. Table 3 shows the mineralogical composition of samples mixed with 1 M of NaOH at different temperatures and subsequently carbonated.

Table 3
Samples mixed with 1 M of NaOH solution at different temperatures and carbonated

	Specimen 7 (5°C)	Specimen 8 (60°C)
Mineralogical phases present	Quartz CAH_{10} C_3AH_6 Gibbsite Vaterite Aragonite Calcite	Quartz C_3AH_6 Calcite Gibbsite Nordstrandite Bayerite Vaterite Aragonite

Samples cured at 5°C contained amounts of CAH_{10} similar to those found in previously described experiments. After 90 days the presence of calcite became predominant when compared to vaterite and aragonite, but a small amount of calcium monocarboaluminate was also detected in these samples. This phase is mainly formed from CO_2 dissolved in the mixing liquid. AH_3 appears in a small quantity as bayerite. Finally, we must emphasize the presence of significant quantities of C_3AH_6.

In the mortars at 60°C (Table 3), results indicate that the hydration reaction was more widespread due to increased temperature and the presence of alkalis. We detected a small amount of carboaluminate, which is not detected when the mixing is made with water. The appearance of AH_3 takes place in the form of gibbsite and norstrandite in considerable amounts. We also detected the formation of a great quantity of $CaCO_3$, mostly as calcite.

3.2. Optical and electronic microscope data

SEM and TLM have been applied to CAC mortars that have been subjected to experimentally accelerated alkaline hydrolysis to validate the usefulness of the methods in the diagnosis of alkaline hydrolysis pathologies. While well-developed minerals are observed by SEM, TLM provides data about the concentration of certain mineral phases, hence its great utility in assessing the carbonation state of a paste (See Figs. 3, 4, and 5).

SEM with secondary electron images (SE) offers three-dimensional images of surface cracks in which we could observe the new formation of CAH_{10} and C_3AH_6 directly from the paste in a gel state, with retraction cracks (sineresis cracks) generated by volume decrease because of gel phase dehydration (Figs. 1 and 2). Carbonation in cavities is also well observed with SEM (Fig. 6).

C_3AH_6 is clearly distinguished by TLM because of its cubic crystal structure (Figs. 5, 7, and 8). Because it is anisotropic the hexagonal phase, CAH_{10}, can be observed

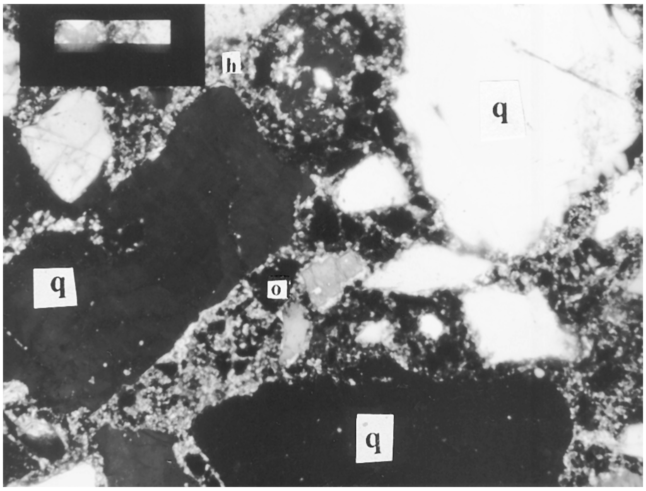

Fig. 3. TLM microphotograph of quartz (q) (aggregates), CAH_{10} (h) (nonbirefringent crystals), aragonite (a) (birefringent needle crystals), and nordstrandite (o). Aragonite is concentrated around aggregates. Specimen 3. Scale bar = 0.3 mm. Crossed polarizers.

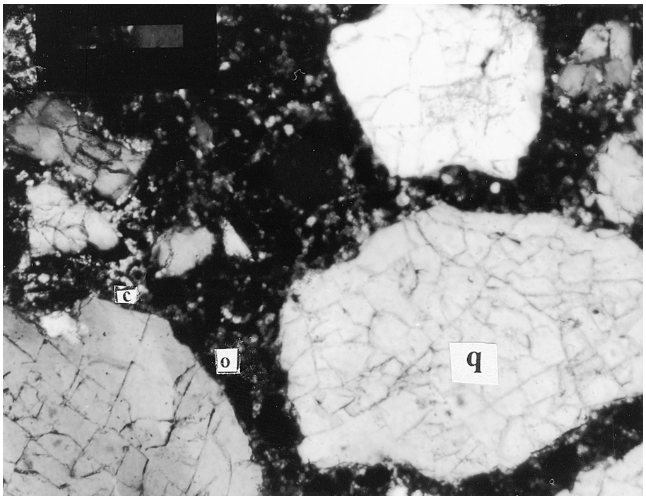

Fig. 5. TLM microphotograph of quartz (q) (aggregates), C_3AH_6 (isotropic crystals, identified by comparison with parallel polarizers image), calcite, and vaterite (c) gibbsite and nordstrandite (o). Microcracks into aggregates. Specimen 5. Scale bar = 0.3 mm. Crossed polarizers.

with crossed polarizers (Figs. 3, 4, and 9). These crystals are only stable if the sample is kept at low temperatures and the preparation process of thin sections is made quickly and without reaching high temperatures.

The different hydroxide phases of aluminium cannot be differentiated using TLM. These phases show a variable degree of opacity depending on their composition (substitutions of iron or titanium).

Regarding air voids and discontinuous aggregate-paste surfaces, we have observed new formation of mineral phases associated with them (Figs. 3, 7, and 8). Because the surface of the aggregates is a special/preferential concentration point for newly formed mineral phases, it has important implications in the aggregates/paste adherence. TLM has enabled us to observe the presence of microcracks.

Carbonation is more developed along cracks. For this reason, the authors believe that all the cracks detected in the aggregates in the mortar specimens are due to changes in volume related to the setting and/or alteration processes (Figs. 4 and 5).

4. Conclusions

1. The XRD technique has been shown to be a most useful tool for a reliable and fast analysis of the composition of phases present in specimens of CAC

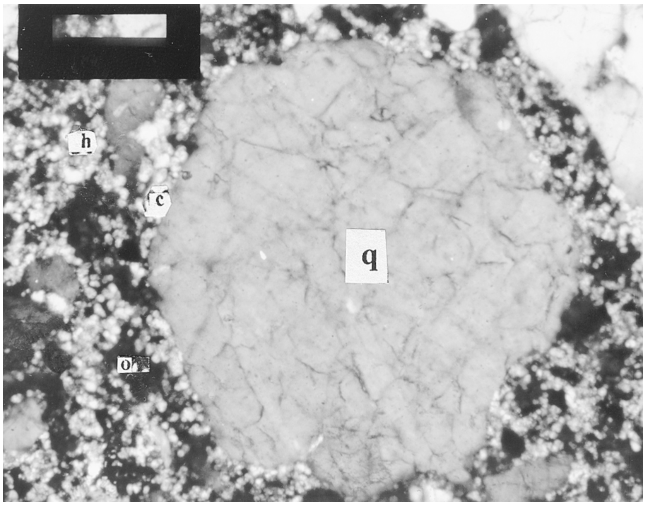

Fig. 4. TLM microphotograph of quartz (q) (aggregates), CAH_{10} (h) (nonbirefringent crystals), vaterite (c) (birefringent nonneedle crystals), aragonite (c) (birefringent needle crystals), and nordstrandite (o). Microcracks into aggregates. Specimen 4. Scale bar = 0.6 mm.

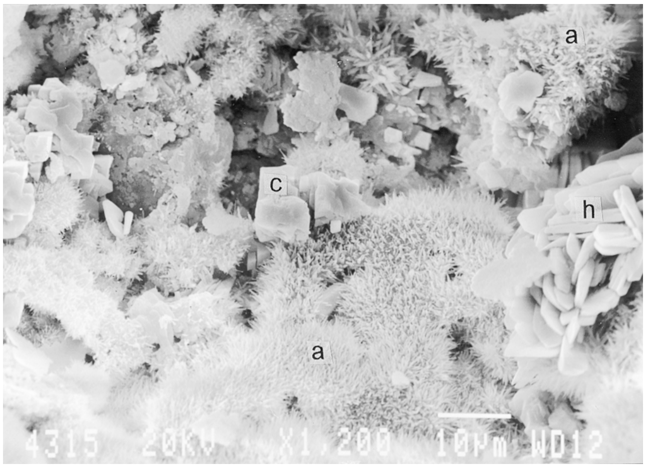

Fig. 6. SEM (SE) microphotograph of carbonate phases: aragonite (a), calcite (c), and CAH_{10} (h). Specimen 11.

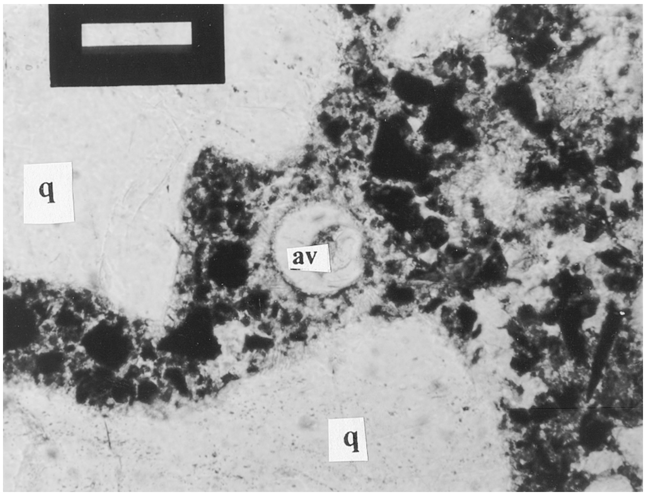

Fig. 7. TLM microphotographs of air void (av), C_3AH_6 (b) (isotropic crystals), quartz (q) (aggregates), and gibbsite (o) (opaque minerals). Specimen 2. Scale bar = 0.3 mm. Parallel polarizers.

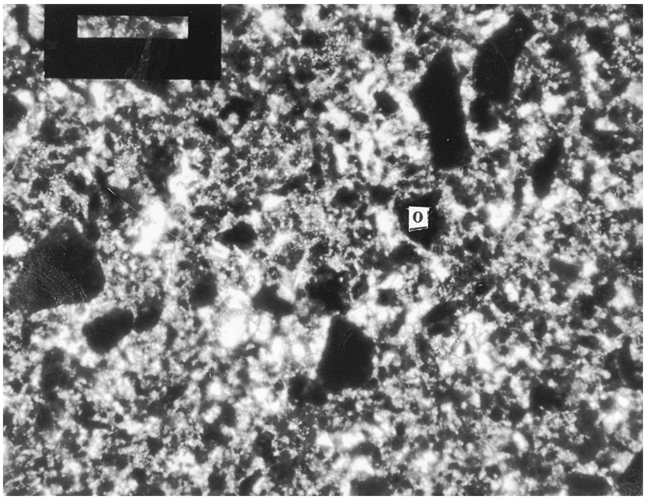

Fig. 9. TLM microphotograph of CAH_{10} (h) (the intermediate and smallest crystals), quartz (q) (the biggest crystals), and gibbsite (o) (opaque minerals). Specimen 1. Scale bar = 0.6 mm. Crossed polarizers.

mortars. Phase content smaller than 5% are not well detected.

2. SEM, mainly secondary electron images, is a useful tool to see the evolution of mineral phases in cavities and discontinuity zones. In the study of CAC mortars SEM permits one to see the relation of gels with CAH_{10} and C_3AH_6 and the coexistence of different phases of carbonates (calcite and aragonite).
3. TLM provides information about the presence of cracks, air voids, discontinuity of aggregate-paste surfaces, lithological (textural and mineralogical) composition of aggregates, and their chemical and physical alteration. The degree of hydration of cement paste and the extent of carbonation can be studied with TLM. TLM of CAC mortars produces data on the presence and distribution of different mineralogical phases: isotropic phases (C_3AH_6) and hexagonal phases (CAH_{10}) are well differentiated. It is not possible to differentiate amorphous phases of similar chemical composition with TLM.

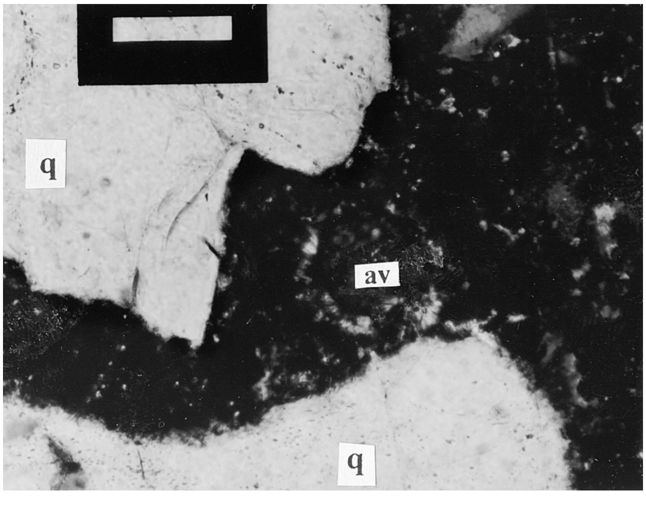

Fig. 8. Same as Fig. 5, with crossed polarizers. Isotropic crystals are evident.

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