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Carbonation of ternary building cementing materials

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ABSTRACT

The carbonation processes of ettringite and calcium aluminate hydrates phases developed by hydration of calcium aluminate cement, fly ash and calcium sulphate ternary mixtures have been studied. The hydrated samples were submitted to 4% of CO_2 in a carbonation chamber, and were analysed, previous carbonation and after 14 and 90 days of carbonation time, by infrared spectroscopy and X-ray diffraction; the developed morphology was performed with the 14 days carbonated samples. The results evidenced that ettringite reacts with CO_2 after 14 days of exposition time and evolves totally at 90 days; the developed hydrated phases C_3AH_6 in samples with major CAC content, also reacts with CO_2. Due to carbonation, calcium carbonate – mainly vaterite but also aragonite-, depending on the initial formulation, aluminium hydroxide and gypsum were detected.

1. Introduction

The Portland cements-based materials have been widely used in building and civil construction. In the modern architecture these materials often act as the principal constituent in the building, within the structural system or elements of the building envelope – facade, roofing, flooring. Considering the manufacturing process of cement, the average CO_2 emission for the production of each cubic metre of concrete is about 0.2 t [1]; the CO_2 emission from cement manufacture is about 5–8% of the global total attributed to anthropogenic activities [2]. The cement industry and research community are making efforts to improve not only manufacturing processes but also the understanding of cement chemistry to develop sustainable construction materials. At present, energy use, CO_2 emissions and other factors related to sustainability are the main drivers for innovation in cementing materials research. The range of supplementary cementing materials is broadening but also new clinker types are being developed to lower environmental impacts [2]. In this context, Damineli et al. propose indicators for measuring cement use efficiency, present a benchmark based on literature data, and discuss potential gains in cement use efficiency [3].

The supplementary cementing materials, i.e., fly ash, slag, etc., are one of the actual alternatives to reduce consume of large amounts of natural raw materials – clay and calcareous rocks- giving up to a huge spectrum of blended cements that have been noted not only for their properties of reducing energy consumption and CO_2 emission (RECCOE) but also for their well known durability properties [4]. Together with mentioned use of wastes, a recent strategy is the reduction of the clinker factor [5] and then allowing the use millions of tonnes of by-products by reducing the consumption of Portland cement per unit volume of concrete.

Currently, the blend of ordinary Portland cement (OPC), calcium aluminate cement (CAC) and a type of calcium sulphate is of much research interest [6–9]. These products based on ettringite have a broad range of uses: formulations with water contents near the minimum requirement to ensure plasticity are widely used in proprietary floor screeds and repair materials. The strength properties depend on formulation but it is comparable with those achieved by sulphate-free CAC cements. In the context of using wastes, new attempts to obtain ettringite-rich materials by the incorporation of fly ash (FA) as an alternative high sustainable ternary systems was investigated obtaining clearly good products [10,11].

The first approach on durability of "traditional" ternary systems preformed by Lamberet [12]; however, there exist very little published data on the behaviour of these materials over time; the most work to date on the carbonation of cementitious materials has concentrated on the study of OPC [13]. In OPC, the main developed phases are portlandite and the gel C–S–H. However, it has been reported [14] that under dry conditions, ettringite remained essentially stable, with fine gypsum and vaterite crystals forming rapidly on the surface but an excess of humidity lead to complete dissolution of ettringite to gypsum, vaterite and alumina gel [14,15]. But, a crane column exposed to air for 16 years show that ettringite persisted even in very near surface layers; it was

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suggested that it was a partially carbonate-substituted ettringite and $CaCO_3$ is only formed towards the final stages of carbonation [15].

The goal of this work is to study the evolution of developed AFt phases due to the action of CO_2 developed in the $CAC/FA/C\bar{S}H_x$ systems. Six selected formulations of the system were submitted to an accelerated carbonation treatment. The CO_2 incorporation to the ettringite or aluminates structures or decomposition are investigated by infrared spectroscopy, X-ray diffraction and scanning electron microscopy.

2. Materials, methods and instrumental set-up

An Electroland CAC, a fly ash (Type F according to the ASTM classification), and calcium sulphate 2-hydrate (Panreac PRS-CODEX) were used in this research as raw materials. A PHILIPS PW 2400 X-ray fluorescence spectrometer with a PW 2540 VTC sample changer was used to determine the chemical composition of the materials (see Table 1).

For the study, the formulations used are given in Table 2 and were prepared in a mixer by blending the raw materials during 1 h at a speed of 9 rpm. The Fig. 1 shows the studied compositions in the ternary system $CAC/FA/CSH_x$ and as the total $CaO/SiO_2/Al_2O_3$ content in the mixtures. The "water/binder" ratio used was 0.6 and the samples were prepared as described in a previous work [11].

2.1. Carbonation procedure

After curing, the hydrated pastes were submitted to a carbonation process in a chamber of $50 \times 30 \times 20\ cm^3$ dimensions. The gas -4% of CO_2 in air – was insufflating during 5 min twice each 24 h; the climatic conditions were maintained at 20 °C of temperature and 75% of relative humidity. The samples were taken after 14 and 90 days of carbonation time and analysed through the different techniques.

The mineralogical composition of the hydrated and carbonated materials was performed by an X-ray diffractometer (XRD) with a Siemens D500 instrument and a Bomem MB-120 Fourier transform infrared spectrophotometer (FTIR) with a frequency range of 4000–450 cm^{-1} was used. Potassium bromide pellets procedure was used for FTIR analysis. A JEOL JSM-6300 scanning electron microscopy (SEM) and attached a LINK ISIS-200 Energy Dispersive X-ray analysis (EDX) was used to determine the morphology of samples.

3. Results and discussion

3.1. Infrared spectroscopy

Raw materials characterisation has been done in a previous work, for more detailed information see [11]. In the identification of these materials is useful to consider the infrared spectrum of ettringite [16] which presents a very strong anti-symmetrical stretching frequency of the sulphate ion ($\nu_3\ SO_4$) centred towards 1120 cm^{-1}; this band is indicative of relative isolation of this ion in the hexagonal prism structure. The water absorption bands appear in the region 1600–1700 cm^{-1} (1640 and 1675 cm^{-1} $\nu_2\ H_2O$) and above 3000 cm^{-1} (3420 due to $\nu_1\ H_2O$ and 3635 cm^{-1} of $\nu\ OH_{free}$). The presence of $\nu\ AlO_6$ and Al–O–H bending bands are sited near to 550 cm^{-1} and 855 cm^{-1}, respectively.

Table 1
Chemical composition of raw materials.

	LOI[a]	Al_2O_3	CaO	SiO_2	Fe_2O_3	MgO	K_2O	Na_2O
CAC	0.36	40.52	34.89	2.94	12.91	0.5	0.06	0.14
Fly ash	1.27	25.84	5.93	41.49	20.76	1.22	1.37	–

[a] LOI: loss on ignition.

Table 2
Portioning of raw materials.

System	CAC	FA	C$
S1	20	70	10
S2	30	60	10
S3	40	40	20
S4	40	20	40
S5	80	10	10
S6	90	5	5

In the studied systems, the formation of ettringite is explained by the chemical reactions of the sulphates in presence of the aluminates [17,18] as described in the following equations:

$$CA + 3C\bar{S}Hx + 2C + (32 - 3x)H \rightarrow C_3A3C\bar{S}H_{32} \tag{1}$$

$$CA + C\bar{S}Hx + H \rightarrow C_3A3C\bar{S}H_{32} + AH_3 \tag{2}$$

Lamberet [2] in relation with the "traditional" ternary blend $CAC - PC - C\bar{S}H_x$ studies of hydration and durability established that the hydration mechanisms depend on PC/CAC and $CAC/C\bar{S}H_x$ ratios. The portion of ettringite should be explained in terms of $CAC/C\bar{S}H_x$ portions and then it will be directed related to the ratio $CAC/C\bar{S}H_x$ added as has been reported [11]. In this research, depending on the formulation the ettringite portion is different; then, also an increase of fly ash on formulations provokes a lower ettringite formation in the hydrated systems. By this reason, not only the presence of ettringite can be explained through the CA/CSH_x ratio.

By the other hand, the CAC rich formulations are on CAC hydrated dominance and calcium aluminates hydrates are formed but also AFm phases due to a deficiency of sulphates. Systems on fly ash formulation dominance would present major ettringite as fly ash content decrease (S4 > S3 > S2 > S1) due mainly to the increase in CA and sulphates available to reacts.

The inspection of the IR spectra of noncarbonated S1–S4 samples show clearly the ettringite presence throughout the bands at 3638, and 3430 cm^{-1} and near to 1665, 1110, 988 and 855 cm^{-1}; other absorption bands near to 600 and 536 cm^{-1} are assigned also to ettringite. The IR spectrum of S1 and S3 samples presented a very slight absorption bands near to 1025 and 990 cm^{-1} indicating AH_3 presence. Moreover, the IR spectrum of S4 sample presented absorption bands due to gypsum, at 1690, 1620 and 670 cm^{-1} and the absorption band towards to 600 cm^{-1} is also due to the contribution of gypsum.

With major CAC content, the IR spectra of systems S5 and S6 are almost identical; but a weak band near to 3665 cm^{-1} characteristic of OH_{free} from cubic calcium aluminate hydrates, C_3AH_6 is observed in the S6 spectrum. Both IR spectrums presented absorption bands towards 3620, 3525 and 3465 cm^{-1} due to aluminium hydroxide as gibbsite. An absorption band towards 3684 cm^{-1} (ν-OH_{free}) could indicate presence of C_4AH_{13} [19] and also an absorption band near 3640 cm^{-1} would indicate ettringite; and a band around 3673 cm^{-1} could be due to calcium monocarboaluminate. Most important difference between S5 and S6 spectrums are the relative intensity of the absorption band sited near 1110 cm^{-1} – of major relative intensity in S5 sample spectrum; an anti-symmetrical stretching frequency of the sulphate ion (ν_3-SO_4) indicates the relative isolation of this ion in the hexagonal prism, although a greater degeneracy of the symmetry would result in more bands in this area of the spectrum of ettringite. The absorption bands near to 1025 and 970 cm^{-1} are assigned to AH_3. At lower frequencies, the aluminate bands towards 790 cm^{-1} (Al–O–H bending) and 530 cm^{-1} (ν-AlO_6) are not suitable for identification because

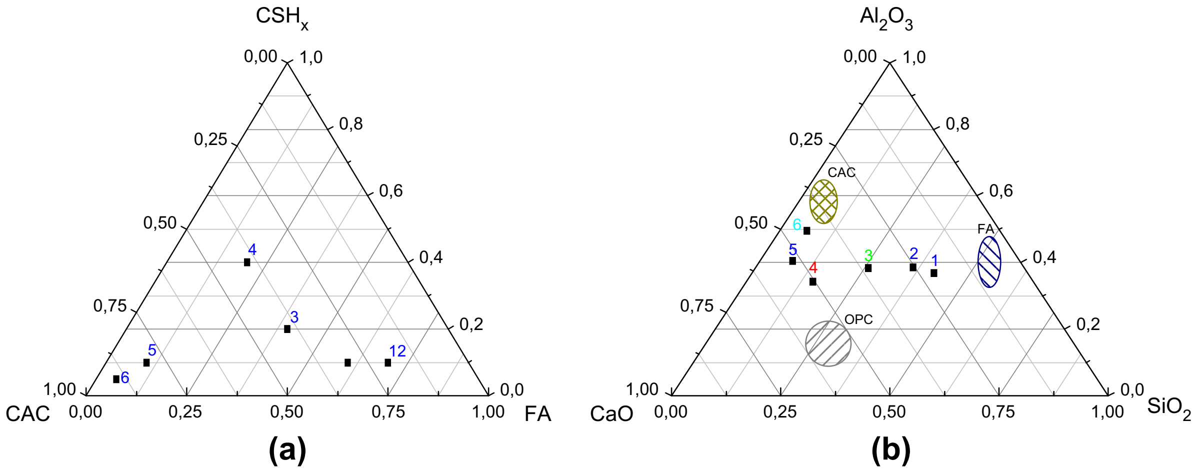

Fig. 1. (a) Formulations of the ternary system studied, (b) ternary system of the total CaO/SiO$_2$/Al$_2$O$_3$ content.

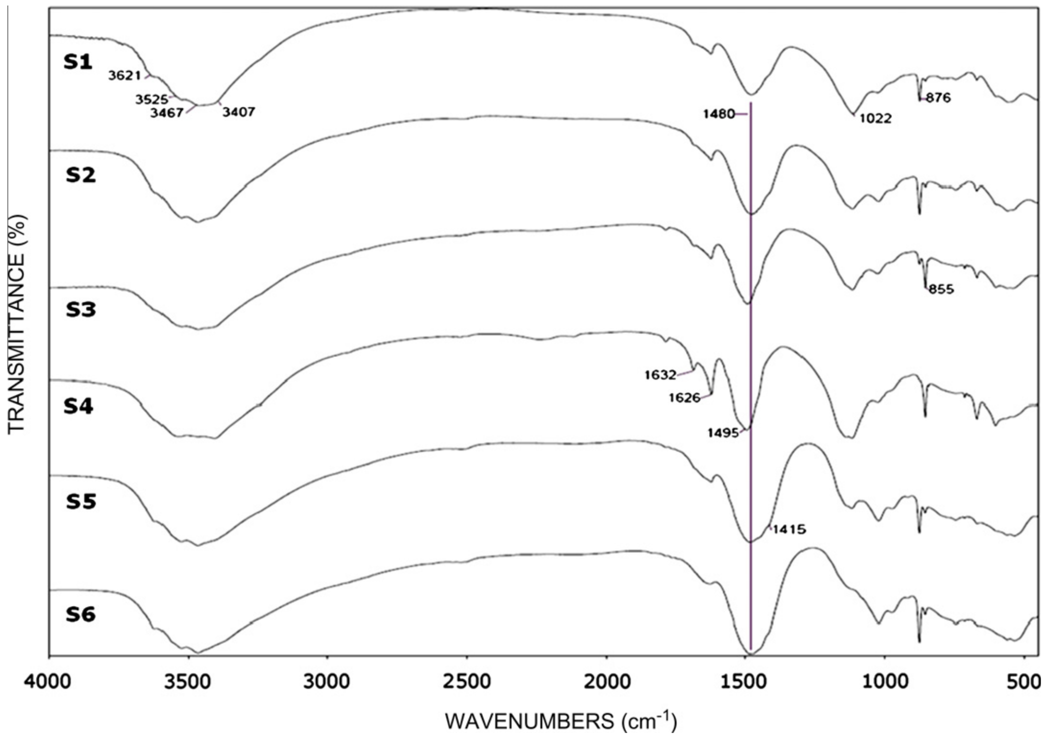

Fig. 2. IR spectras of samples at 14 carbonation days.

C_3AH_6, monosulfoaluminate, C_4AH_{13} and ettringite present very close absorption bands.

Due to carbonation, the analysis of IR spectra of 14 days carbonated samples show a very broad absorption area between 3650 towards 3350 cm^{-1} with maximums near to 3621, 3525 and 3467 cm^{-1} due mainly to aluminium hydroxide as gibbsite (Fig. 2). The spectra show a broad strong ν_3 carbonate bands between 1600 and 1300 cm^{-1} – centred near 1480 cm^{-1} in S1, S2, S5 and S6 spectra but towards to 1495 cm^{-1} in S3 and S4 spectra, respectively. The ν_1 $-CO_3^{2-}$ bands appear near 876 cm^{-1} in the spectra of S1, S2, S5 and S6 samples but close to 855 cm^{-1} in the S3 and S4 spectra. The developed calcium carbonate polymorph was vaterite and aragonite, respectively. In the spectra was also observed the ν_4 carbonate bands at 713 and 700 cm^{-1}, clearly in the S3, S4, S5 and S6 spectra and as a shoulder for S1 and S2 spectra. These results indicate that the main calcium carbonate polymorph formed is vaterite in samples S1, S2; aragonite is developed through carbonation of S3 and S4 samples and both polymorphs in S5 and S6.

At 90 days of carbonation, S1–S4 spectra also show a very broad absorption area between 3650 towards 3350 cm^{-1} but some modifications can be observed in the absorption band position of maximums with respect to the spectra at 14 carbonation days: 3540, 3470, 3410 and 3245 cm^{-1} (Fig. 3). However, the absorption bands due to AH_3 increase in spectra of S5 and S6 samples, with maximums at 3624, 3525 and 3468 cm^{-1}. The absorption bands due to carbonate compounds do not experiment an important modification – S1, S2, S5 and S6 present absorption bands at 1480 and 875 cm^{-1} while samples S3 and S4 at 1500 and 855 cm^{-1}, indicating the presence of same carbonate compounds –vaterite and ara-

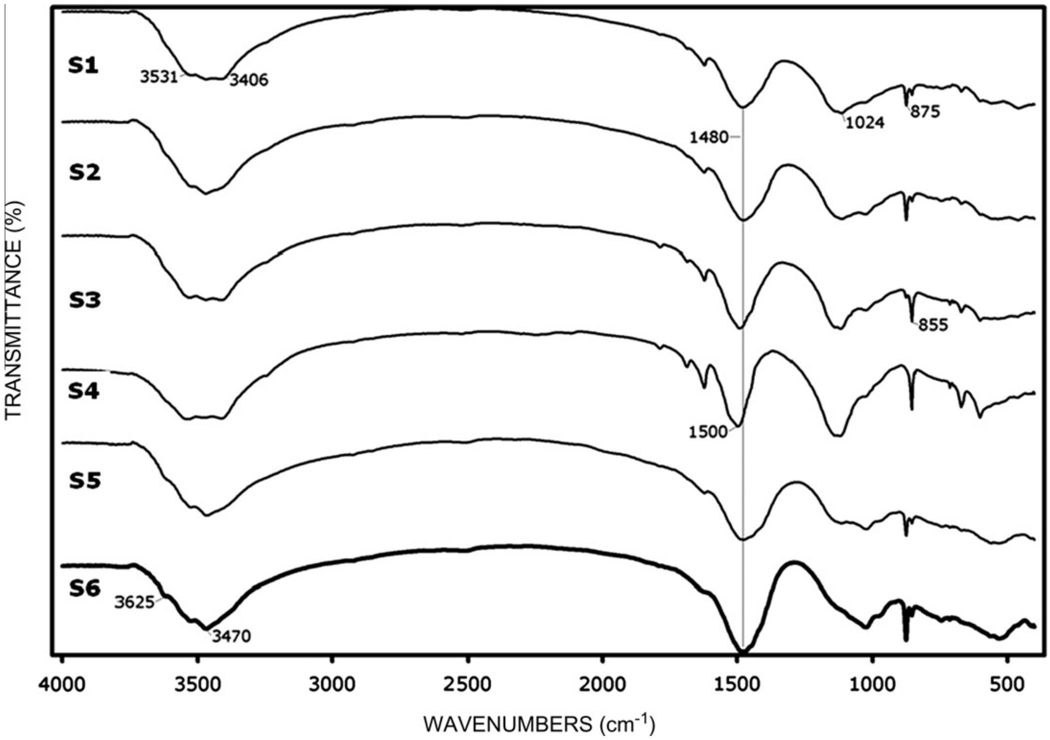

Fig. 3. IR spectras of samples at 90 carbonation days.

Table 3
Major identified compounds by XRD.

Sample	Curing time	Ettringite	Gypsum	Calcite	Aragonite	Vaterite	AH_3
S1	Hydrated	1.3	0	0	0	0	0
	14 days	1	0.7	0	0	1.3	0.5
	90 days	0	10	0	12	13	0
S2	Hydrated	1	0	0	0	0	0
	14 days	0.5	0.7	0	0	1.6	0.5
	90 days	0	9	0	12	15	0
S3	Hydrated	3	0	0	0	0	0
	14 days	2	2	0	2	0	1
	90 days	0	16	0	12	0	0
S4	Hydrated	4	2	0	0	0	0
	14 days	1	6	0	1.4	0	0.5
	90 days	0	50	0	11	0	0
S5	Hydrated	0.5	0	0	0	0	0.4
	14 days	0.2	0.3	1	0.8	2	1
	90 days	0	7	14	0	20	9
S6	Hydrated	0.3	4	0	0	0	0.4
	14 days	0	0	0	0	1.7	1
	90 days	0	0	0	0	12	10

The number relates to number of measured counts (1–100 counts).

gonite, respectively; but they are higher in intensity at 90 days carbonation time showing a major portion of them (Fig. 3).

The position of the absorption bands sited near to 3540, 3470, 3410, 3245, 1685, 1623, 1143, 1115, 670 and 600 cm^{-1} indicate the presence of a sulphate compound similar to gypsum. The intensity of the mentioned bands indicate major portion in S4 sample and then S3, minor in S1, S2 and S5, respectively (Fig. 3). Moreover, the presence of 1025 cm^{-1} absorption band, indicating the aluminium hydroxide compounds presence, is specially noted in the spectrums of S6 and then S5 samples; but they are present in all spectra.

It is interesting to remark that there were not observed intense bands of ettringite both in 14 but also in the 90 days carbonated spectrum, this will be discussed after the X-ray diffraction analysis of these samples.

3.2. X-ray diffraction

The main crystalline hydration product of the reactions in the S1–S4 studied systems was ettringite. Apart from ettringite, the sample S4 presented a high portion of nonreacted gypsum. The samples S5 and S6 – with major portion of CAC- presented minor ettringite content but in addition also presented C_3AH_6; and the broad diffraction lines between $2\theta = 6–16°$ indicated calcium monosulfoaluminate and hemicarboaluminate. The diffraction lines for aluminium hydroxide polymorphs are observed only in the diffraction patterns of samples with high CAC content (S5 and S6). Moreover, the samples S5 and S6 presented a very low portion of the compound C_2ASH_8.

Due to the chemical reactions of them with CO_2, an evolution of hydrated phases towards the formation of calcium carbonate, gypsum and aluminium hydroxide is observed. The Table 3 presents a semiquantitative interpretation made of the analysis of the major developed hydrated and carbonated compounds detected in the diffraction patterns. The Figs. 4–6 presented diffraction patterns of hydrated and carbonated samples – 14 and 90 days, respectively.

At 14 carbonation days, the relative intensity of diffraction lines of ettringite decrease and no signals of it were shown at 90 carbonation days. Other minor hydration products, i.e., $C_3AH_{6,}$ calcium monosulfoaluminate, hemicarboaluminate and C_2ASH_8, also reacted totally with CO_2.

The crystalline detected products were calcium carbonate, aluminium hydroxide and gypsum. At 14 carbonation days, the main detected calcium carbonate polymorph was vaterite; but the samples S3 and S4 presented aragonite in major portion than vaterite. In the pattern of sample S5 were observed less intense diffraction lines due to calcite and aragonite (Fig. 5). At 90 days, an important increase in the presence of vaterite was observed for samples S1, S2, S5 and S6. Samples S1 and S2 also increased in aragonite. By the other hand, the main calcium carbonate polymorph detected at 90 days carbonation time for samples S3 and S4 was aragonite (Fig. 6).

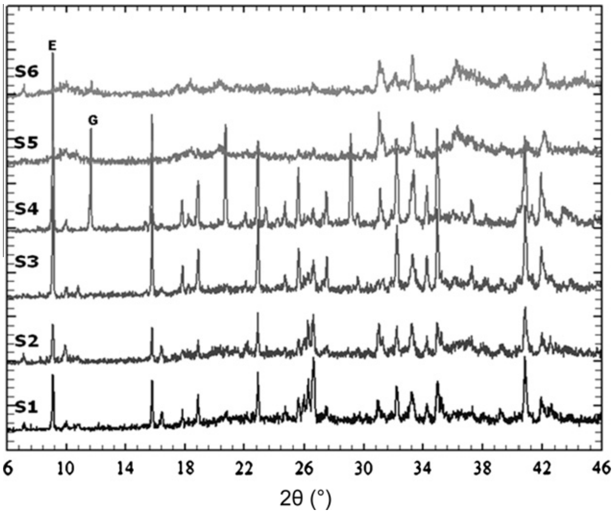

Fig. 4. X-ray diffraction patterns of hydrated samples.

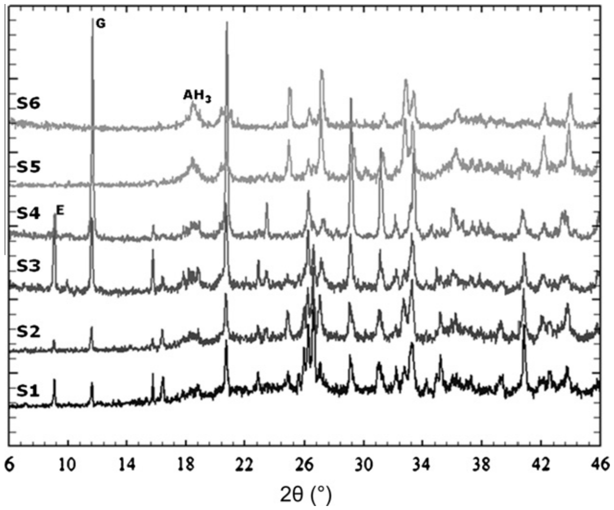

Fig. 5. X-ray diffraction patterns of samples at 14 days of carbonation.

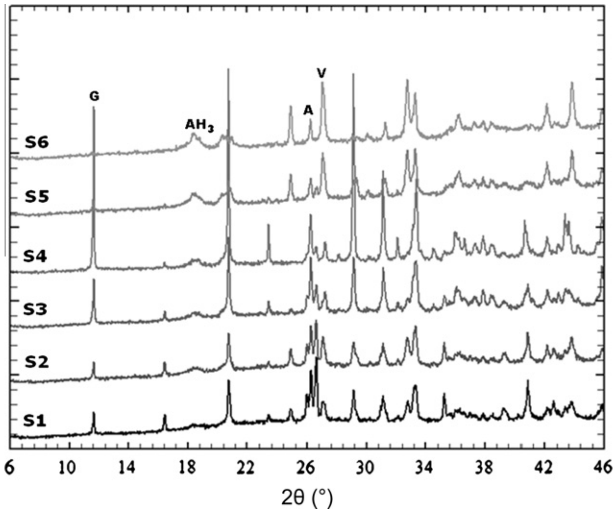

Fig. 6. X-ray diffraction patterns of samples at 90 days of carbonation.

Zhou and Glasser [15] studied ettringite stability under controlled relative humidity at 68 and 88% in different solid forms, as powder and in pellets. Ettringite completely transformed to gypsum and vaterite, when it was in powder form, while only the exposed surface presented complete dissolution in pellets. In the exposed pellets, the layers beneath revealed partial dissolution and transformation to monophase, while in the deepest layer, ettringite remained intact. In the present study – carbonation of solids as powder and at 75% of RH – a different developed calcium carbonate was analysed depending on the formulation: samples S1, S2, S5 and S6 presented mainly vaterite; but samples S3 and S4 presented important amounts of aragonite. The carbonation of samples also produced the formation of aluminium hydroxide and gypsum – the formation of that sulphate type compound, probably gypsum was also detected by XRD in carbonated samples S1–S5 but mainly in S3 and S4; however more research needs to be done on this aspect in order to determine possible modifications on its crystal structure. In such context, it has been reported about the existence of a carbonate analogue of SO_4-AFt as CO_3-AFt, but the synthesis of this compound was presented with some difficulties. Poellman et al. [20] and Barnett et al. [21] indicated the existence of possible solid solutions formed between SO_4-AFt and CO_3-AFt. Moreover, Peng et al. [22] explained that the ettringite itself undergoes union exchanges in which part of its sulphate is replaced by carbonate; they suggest that ettringite undergoes significant ion exchange, of CO_3 for SO_4, prior to its decomposition and thus also buffers the paste against carbonate penetration. In the studied samples and with the analytical used techniques is not possible to confirm these ion exchanges but only a suspicious can be mentioned due to the modification of the position of certain absorption bands in the infrared or in the diffraction lines in the XRD patterns.

Respecting the aluminium hydroxide, at 14 carbonation days, its diffraction lines were observed in the all pattern of samples – S1 to S6. However, at 90 carbonation days, aluminium hydroxide was only detected as a crystalline phase in pattern of S5 and S6

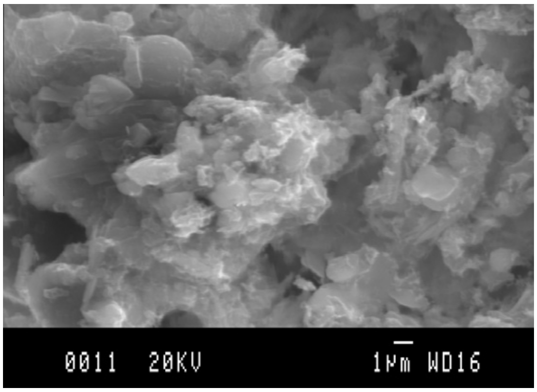

Fig. 7. Dense morphology of carbonates.

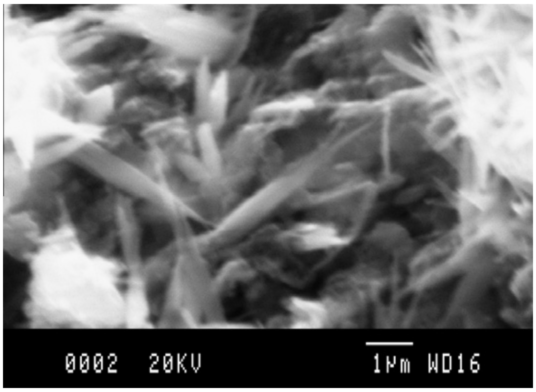

Fig. 8. Needle-like morphology of carbonates.

samples. The formation of a sulphate type compound, probably gypsum was also detected by XRD at 14 carbonation days in samples S1–S5; however more research need to be done on this aspect. Major portion of this sulphate was detected at 90 days, mainly in samples S4 and S3 (Figs. 5 and 6). Another aspect to be in present is that during the hydration process of cements if waste ions are mixed with, several types of waste ion interactions may occur in the cement microstructure: chemisorb, precipitate, form a surface compound to any of several cement phases surfaces, form inclusions or be chemically incorporated into the cement structures, or have simultaneous occurrence of several of these situations. Then, ettringite structure can withstand modest deviations in composition without a change in structure. This compositional change occurs on the crystal chemical level in the form of ionic substitution; the ions available for substitution in the ettringite structure are Ca^{+2}, Al^{3+}, SO_4^{2-} and OH^-. The examination of ettringite group structures provides information on some natural and, therefore, stable ionic substitutions possible in the structure [20]. The aluminium site accommodates a variety of trivalent and tetravalent cations and this can be a place of instability respecting the CO_2.

3.3. Scanning electron microscopy

Most important results from the morphological analysis developed of 14 days carbonated samples were the observed differentiate morphology of calcium carbonates. The calcium carbonate morphology of samples S1, S2, S5 and S6 was very poor and aggregate, with a very low particle size (Fig. 7). On the other hand, the microstructure of calcium carbonate developed in samples S3 and S4 was observed as needles of around 2 µm size (Fig. 8). No ettringite crystals were identified at this age but spheres of remained fly ash can also be observed intermixed and normally surrounded by films or crystals products growing from their surface.

The revised results indicated that samples S1, S2, S5 and S6 presented, at 14 days, only calcium carbonate as vaterite while samples S3 and S4 the calcium carbonate at the same age was developed as aragonite, then it can be justified the different morphologies of carbonates – the vaterite is developed as aggregates with very a poor morphology while aragonite is develop as needles in this systems.

Many researchers have expressed concern about the long term stability and indicated a rapid rate of carbonation of ettringite-based matrices [15,23]. Carbon dioxide would dissolve ettringite not only due to the inferior pH value due to absence of portlandite in these systems, but also through direct carbonation reactions. The morphology of pastes –and specially that of ettringite would have a notable importance on durability. The special properties of these systems differentiated kinetics and giving up to a rapid set and hard times. Obviously, the kinetics will affect the morphology of hydrated developed phases and a conexion could be found with the developed carbonated phases but more research need to be done in this aspect. In a recent work [24] formation of metastable phases of calcium carbonate has been correlated with inorganic substrates, i.e., aluminium oxide promote vaterite formation. Additionally particles size can also have effect in metastable calcium carbonate formation.

4. Conclusions

The following conclusions can be drawn from the present work:

Sample exposure to CO_2 affects the evolution of the hydrated phases, due to the chemical reactions of them with CO_2, towards the formation of calcium carbonate, gypsum and aluminium hydroxide. It has been reported that the carbonation of the "traditional" ettringite (i.e., without ionic substitutions in the structure due to wastes) evolves towards calcium carbonate and gypsum [14].

A different developed calcium carbonate was analysed depending on the initial CAC/fly ash/$C\bar{S}H_x$ formulation: samples S1, S2, S5 and S6 presented mainly vaterite; but samples S3 and S4 presented important amounts of aragonite. As has been reported in the bibliography the carbonation of ettringite has been associated to vaterite.

At early age carbonation, aluminium hydroxide was detected in the diffraction patterns of all the samples. However, at 90 carbonation days, aluminium hydroxide was only detected in samples S5 and S6. Then, secondary chemical reactions due to AH_3 presence take place: reaction due to carbonation develops new phases.

The morphology of calcium carbonate of samples S3 and S4 appeared as needle-like and is attributed to aragonite, while calcium carbonate from samples of S1, S2, S5 and S6 appeared as an aggregate dense morphology and attributed to vaterite.

Acknowledgements

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