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QUANTIFICATION OF BOUND CO₂ IN VARIOUS CARBONATED CEMENTITIOUS MATRICES

M. Saillio¹, V. Baroghel-Bouny², M. Bertin², J. Vincent¹, J.B. de Lacaillerie³

ABSTRACT

For economic and ecological reasons, supplementary cementitious materials (SCM) are increasingly used in concrete. Although having a lot of advantages, these concretes have different cement matrices and do not have the same evolution as they are carbonated.

In this paper, comparison between various carbonated cement pastes with/without SCM (slag, fly ash and metakaolin), has been investigated. Samples are carbonated in accelerated conditions (1.5 % CO₂, RH 65% and T=20°C) until constant mass but in order to be relatively close to the natural conditions and to simulate a carbonation process in the long term. The microstructure was characterized not only by usual techniques such as XRD and TGA-DTA, but also by ²⁹Si and ²⁷Al NMR spectroscopy. The use of a combination of techniques for microstructural characterization allows to quantify the proportion of each cementitious phase and to determine how much there are carbonated in comparison to reference cement pastes.

This quantification shows the evolution of the carbonated cementitious matrix as a function of the binder content. In addition, the results show that the quantity of bound CO₂ is not just dependent of portlandite amount. All phases with calcium participate to the fixation of CO₂. However, all these phases are not completely carbonated. Bound CO₂ is almost only CaCO₃. Four CaCO₃ polymorphs are detected : calcite, vaterite, aragonite and amorphous.

1. INTRODUCTION

Corrosion of reinforcement is one of the main causes of reinforced concrete degradation. This corrosion is due to carbonation or chloride ingress [1-5]. In CO₂-free environment, the hydrated Portland cement consists of hydrated phases in equilibrium with a pore solution whose pH is around 13.5. Under natural conditions of temperature and pressure, the atmospheric CO₂ is dissolved into the pore solution to form H₂CO₃ which, by dissociation, decreases the pH of the pore solution [1-8]. Portlandite (Ca(OH)₂) plays the role of buffer and maintains the pH of the pore solution at pH=12.5 by releasing adequately OH⁻ ions. During the carbonation process, the dissolution can affect not only Ca(OH)₂ but also C-S-H, AFm, AFt... [8-10].

The changes in cementitious materials induced by carbonation are particularly significant when the mixture contains supplementary cementitious materials (SCM) [8][11-17]. Binders which contain ground granulated blast furnace slag (GGBS) for example are used in marine

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environment since the chloride diffusion coefficient of GGBS-mixtures is significantly reduced. But these binders form less portlandite than OPC binders [8,12]. Consequently, for a same exposure environment and time, carbonation ingress in these materials is higher than in OPC binders [11] as also expected for binders with fly ash or metakaolin.

The aim of this research is to investigate the effect of carbonation on cementitious matrixes with SCM or not and, finally, to quantify how much each phase can bind CO₂.

2. EXPERIMENTAL

2.1 Materials studied

Various cement pastes were designed with the same clinker. The main constituents of the clinker are given in tables 1 and 2. The water to binder ratio (w/b) is equal to 0.50 for all the mixtures. The studied binders are CEM I (OPC with 97% clinker), CEM III/A (with 62% GGBS) denoted CEM III GGBS(62%), CEM III/C (with 82% GGBS) denoted CEM III GGBS(82%), CEM I + 20% FA denoted CEM I FA(20%), CEM I + 30% FA denoted CEM I FA(30%), CEM I + 40% FA denoted CEM I FA(40%), CEM I + 10% MK denoted CEM I MK(10%) and CEM I + 25% MK denoted CEM I MK(25%).

Table 1: Chemical compositions of the cements and SCM tested (in %)

	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	MgO	Na ₂ O	K ₂ O	MnO	SO ₃
CEM I	62.53	19.54	2.90	4.98	0.30	0.84	0.30	0.82	0.09	2.97
CEM III/A	49.77	29.86	1.28	8.10	0.46	4.61	0.40	0.56	0.16	2.29
CEM III/C	45.70	32.00	1.00	9.90	0.50	5.80	0.63	0.54	0.20	2.00
MK	2.00	66.29	4.29	21.30	1.12	0.25	0.84	0.49	0.00	0.08
FA	4.30	51.59	6.58	23.78	1.03	0.49	1.09	3.05	0.11	3.05

Table 2: Mineralogical composition of the CEM I from BOGUE calculation (in %)

	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
CEM I	51.2	28.3	9.9	8.8

Sound samples (i.e. non-carbonated) will be denoted “Ref sample” in the paper.

2.2 Carbonation process

Accelerated carbonation tests are often used to carbonate samples in lab as an alternative technique to the natural carbonation process which is much longer [9,18]. Tests consist in, after drying, leaving samples in an environment enriched in CO₂ at an optimal relative humidity (40-65%) [18]. Different CO₂ concentrations can be applied in accelerated tests. According to [9], a too high concentration can change the microstructure more than a natural carbonation process would. A drying process increases carbonation ingress but a too high temperature alters cementitious phases such as ettringite. In this study, samples were carbonated in accelerated conditions.

The following carbonation protocols have been chosen: after water curing (365 days), slices of concretes or pastes are dried during 3 days at 60°C. Then the slices are crushed. A part of the crushed samples is preserved in CO₂-free environment (as “Reference samples”). The other part is carbonated in chamber (1.5% CO₂ and 65% RH), until constant mass (as “Totally Carbonated” sample).

2.3 Microstructural characterization

Combination of usual technics (XRD, TGA/DTA and NMR ²⁹Si and ²⁷Al) [18-35] are used in order to obtain the phase assemblage of the various cementitious matrices carbonated or not. These calculations notably take into account the dilution effect provided by contribution of CO₂ in order to calculate adequately each phase proportion. It was not possible to make the characterizations on all samples. We focus on 6 type of binder : CEM I, CEM I MK(10%), CEM I MK(25%), CEM I FA(30%), CEM III GGBS(62%) and CEM III GGBS(82%).

3. RESULTS AND DISCUSSION

CaCO₃ becomes the main phase in terms of weight for all TC samples (see figure 1). The mass proportion of CaCO₃ in the OPC sample is over 60%. It was expected that this sample contains more CaCO₃, since it had the highest amount of calcium (the CaO amount of the clinker was 62%). There is a linear relationship between the amount of CaCO₃ produced and the quantity of CaO in the anhydrous binders (see figure 2) depending of the SCM type. The difference between MK, FA and GGBS cement paste is probably because calcium is almost only in hydrated phase for the Ref samples with FA or MK in the opposite case of cement paste with GGBS, where calcium can be also in anhydrous phases (slag). Hydrated and anhydrous phases do not have the same reactivity to the carbonation (see figure 3). Nevertheless, carbonation of anhydrous phases (C₂S and C₃S) obviously can occur. In addition, accessibility can be an another explanation because there are differences between porous network as a function of SCM binders. According to the results, CaCO₃ forms at the expense of portlandite and other hydrated phases. Portlandite has disappeared in all TC sample (DTA results do not show any peak) nevertheless it continues to appear on the diffractograms (small peak) except for CEM III GGBS(62%) and CEM III GGBS(82%) (see figure 4). Therefore, in the other samples, the carbonation process has not completely consumed portlandite. In this case, the formation of calcium carbonate on the surface of portlandite crystals probably limits calcium dissolution from portlandite as reported [18,35]. In addition, figure 1 show decreasing of all phases (excepted CaCO₃). Nevertheless, there is a mass contribution by the CO₂ arrival that causes a dilution phenomenon in carbonated materials for all the phase containing no CO₂. Figure 3 takes into account this dilution effect by reporting the amounts of each phase to the initial amount of clinker. The results confirm indeed that almost all phases decrease by degradation under carbonation and not only by dilution effect.

TGA allows to have the total amount of CaCO₃ produced (orange lines in figure 10). This amount can also be calculated by accounting the lost calcium for each of the sample phases that have been degraded between the Ref and TC sample (taking account the dilution effect) (see figure 5). When comparing the both results on the same figure, the overall amount obtained directly by TGA is higher for some samples than that calculated for each degraded phase. This means that the decalcification of certain phases such as aluminate phases is minimized and also some phases which contain calcium (TAH, C₃A, C₄AF ...) are not taking into account. In addition, some of these phases may remain their structure even they are

decalcified and therefore they still appear in NMR spectroscopy in the form of AFm and AFt phases.

In XRD pattern of carbonated samples (see figure 4), vaterite (peak at 3.28Å), calcite (peak at 3.08Å) and aragonite (peak at 3.39Å) are recorded as the main crystalline phases as already observed by previous studies [4,6,9]. The polymorphism of CaCO₃ crystal depends on the cementitious phase from which it was formed, the pH of the pore solution and on the temperature [36,37]. Portlandite generally induces the formation of calcite while the other phases (C-S-H and aluminates phases) form vaterite and aragonite which evolve to calcite with time [37]. This is in agreement with the present study. In fact, the Rietveld analysis applied to the TC CEM I paste shows that there are 38% of crystallized CaCO₃ in the form of vaterite, 41% as aragonite and 21% as calcite, while the proportions for the CEM III GGBS(82%) sample are 94% as vaterite, 1% as aragonite and 5% as calcite. According to figure 5, calcium present in CaCO₃ comes mainly from C-S-H for CEM III GGBS (only 2% of portlandite in Ref CEM III GGBS(82%) vs 18% in Ref CEM I), while the source of calcium is shared between C-S-H and portlandite in the case of the CEM I sample. This confirms that vaterite is formed from the C-S-H and that its presence is an indicator of the degradation (decalcification) of the C-S-H. However, aragonite amount is high in almost TC sample (except CEM III with GGBS) and it can not be explain only by the origin of the phases. Carbonation conditions (RH, T, level of CO₂, the duration,...) of cement paste can also influence the phase assemblage [36,37]. Finally, XRD and specially TGA results seem to indicate there is amount of amorphous CaCO₃ (in addition to crystallized forms) which can not be quantified, consequently it is not possible to determinate precisely each phase of CaCO₃ and the values of Rietveld analysis given below are at best semi-quantitative.

Other informations on cementitious matrices can be obtain with these results (see figure 6, 12). As said previously, the significant presence of vaterite and aragonite shows that there is degradation of the C-S-H and probably of the aluminate phases, since the amounts of ettringite and AFm decrease according to ²⁷Al NMR results (see figure 6). Aluminium from AFm and AFt phases moves to tetrahedral configuration phases. For example, the CEM III GGBS(82%) TC sample has 80% of its aluminum in tetrahedral configuration instead of 42% in the case of Ref sample. It seems that aluminum from decalcified AFm and AFt phases is incorporated into the C-S-H probably decalcified as silica gel.

The average lengths of the C-S-H chains increase for all TC samples (see figure 7). Furthermore, the degradation products C-S-H (Q³+Q⁴) also increase at the expense of the amount of C-S-H (Q¹+Q²) (see example in figure 7). The C-S-H chains polymerize to form a substantial silica gel. The deconvolution of the ²⁹Si NMR spectra of carbonated samples also shows the possible presence of Q⁴(1Al) or even Q³(1Al), in addition to the Q⁴ and Q³ species. Q⁴(1Al) represents silicon surrounded by four neighbours where one is aluminum, confirming thereby the ²⁷Al NMR results. The hydration rate of TC samples (obtained by ²⁹Si NMR) increases but no C-S-H is formed. Despite a weak accessibility, C₃S and C₂S phases seem to be partially decalcified. As expected, calcium amount of the C-S-H decreases in all TC samples (see figure 3) confirming thereby the massive decalcification of the C-S-H (over 60% of calcium moved).

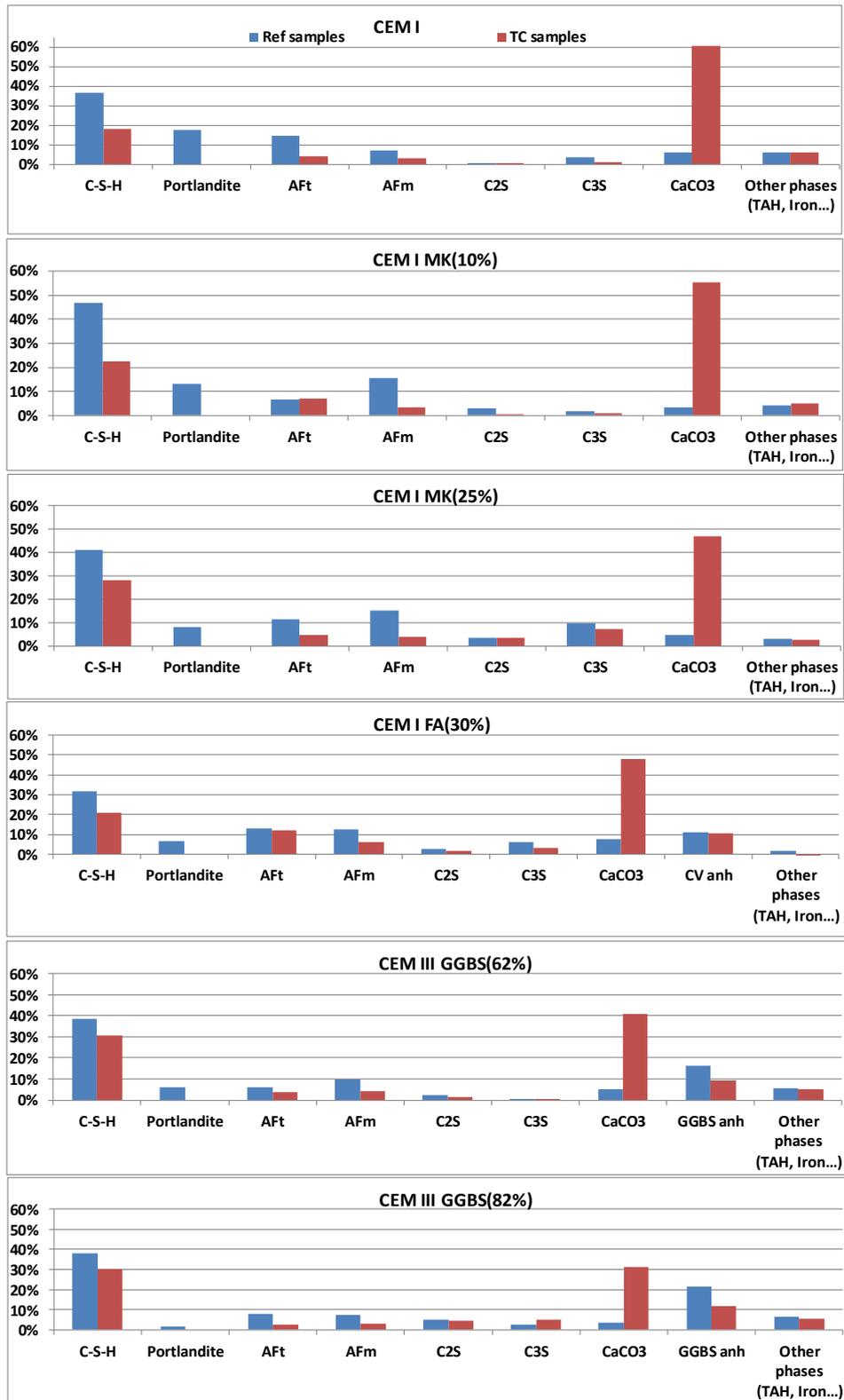


Figure 1: Comparisons of mass proportion between Ref and TC samples. TC samples were carbonated until constant mass in chamber at 1.5% CO₂ and 65% RH, after 365-day water curing. Here C-S-H= C-S-H+silica gel.

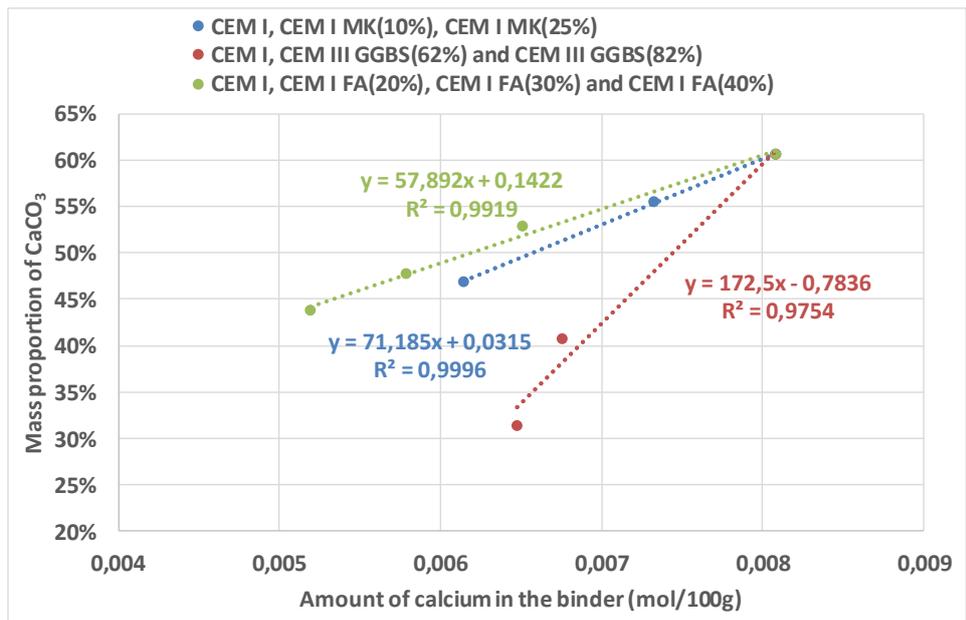


Figure 2: Comparison between the proportion of calcium in the binder and the mass proportion of CaCO₃ of the samples. TC samples were carbonated until constant mass in chamber at 1.5% CO₂ and 65% RH, after 365-day water curing.

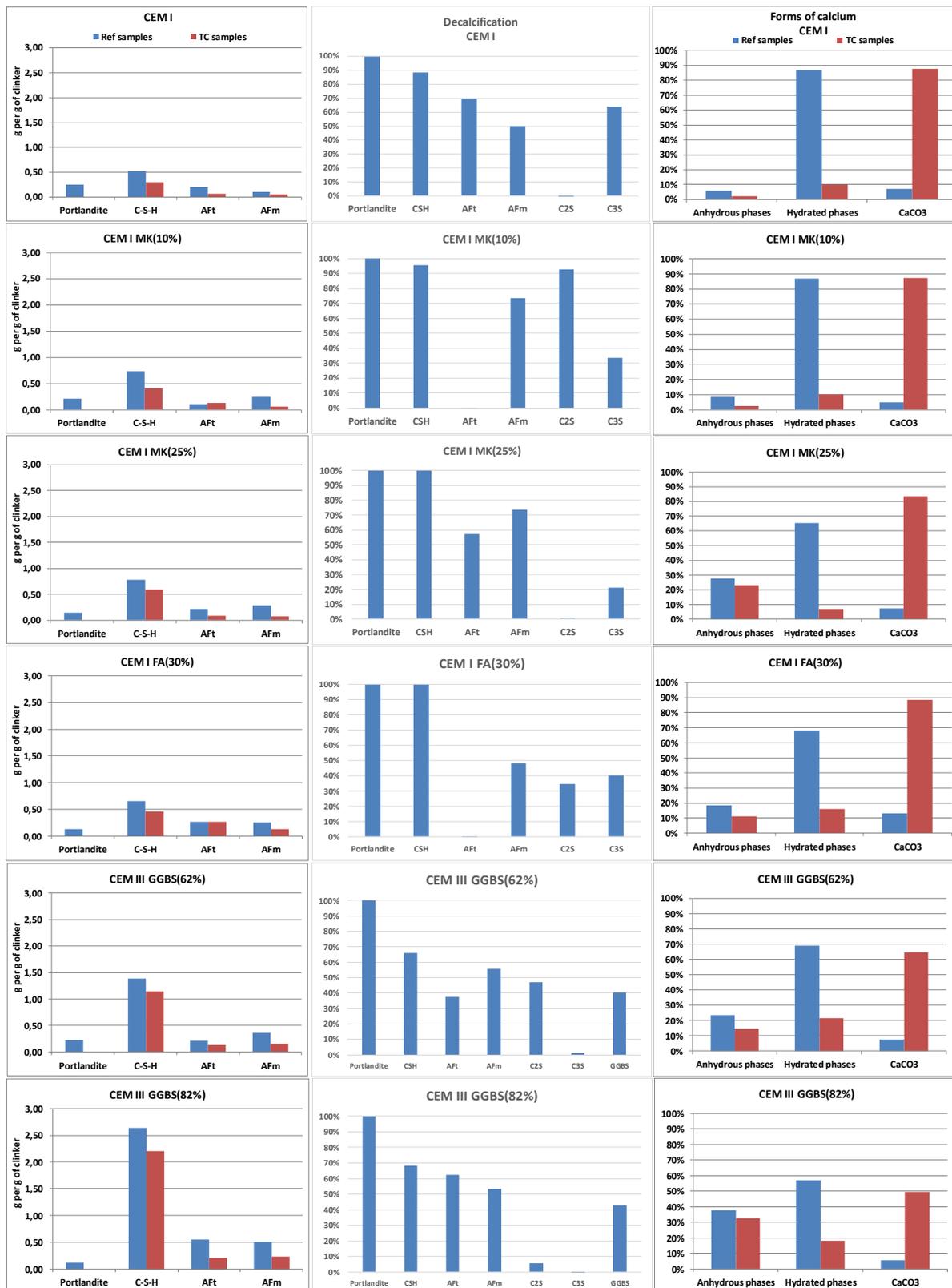


Figure 3: Mass proportion reported to clinker (in left), decalcification of each phase (in middle) and forms of calcium in cement pastes.

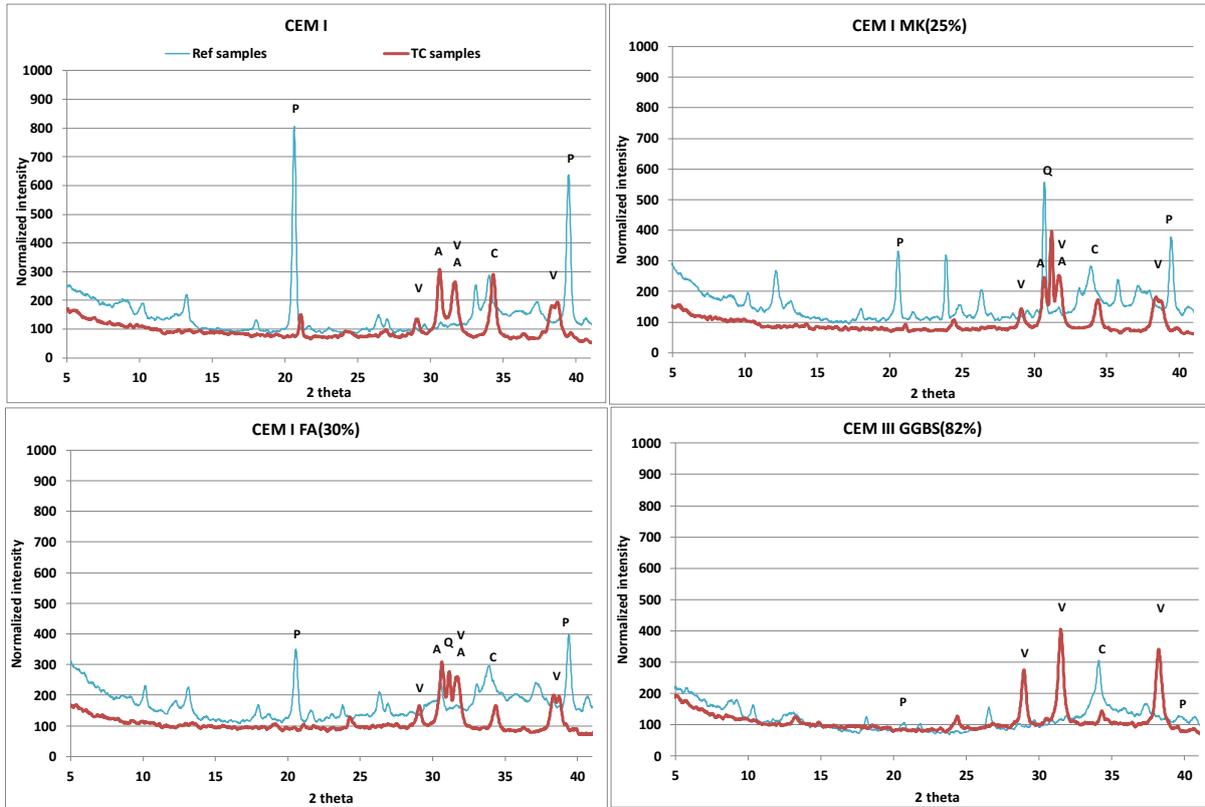


Figure 4: Partial XRD patterns of cement pastes for Ref and TC samples. TC samples were carbonated until constant mass in chamber at 1.5% CO₂ and 65% RH after 365-day water curing. Portlandite (P), calcite (C), vaterite (V), aragonite (A), quartz (Q).

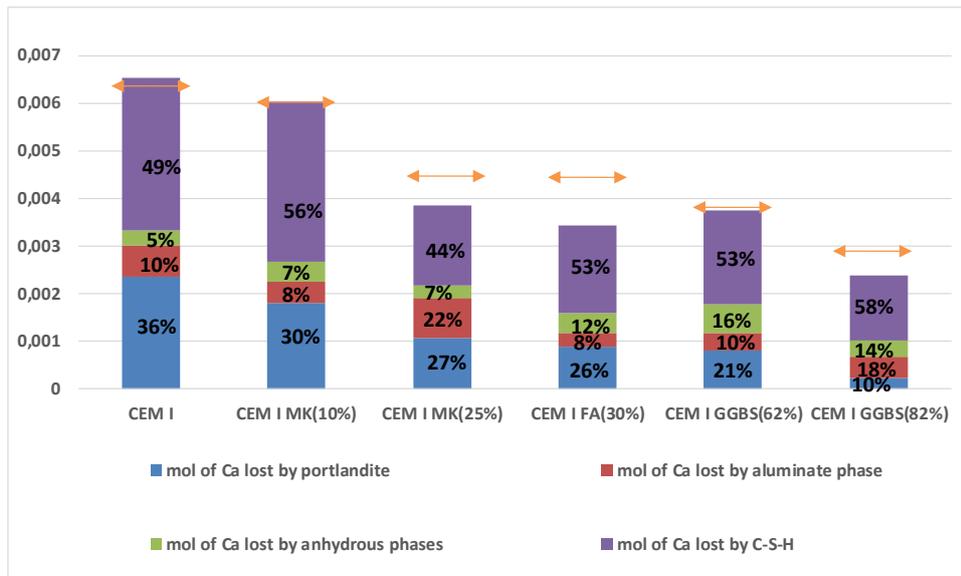


Figure 5: Amount of calcium in CaCO₃ produced as a function of each phases for TC samples compared to the total amount of CaCO₃ produced during carbonation.

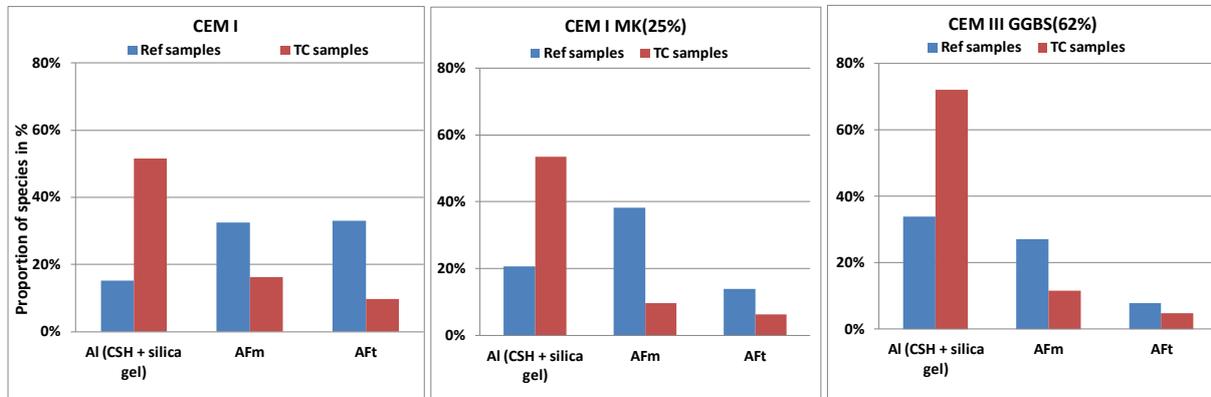


Figure 6: Proportion of Al species in cement pastes before and after total carbonation (carbonation until constant mass in chamber at 1.5% CO₂ and 65% RH, after 365-day water curing), obtained by ²⁷Al NMR.

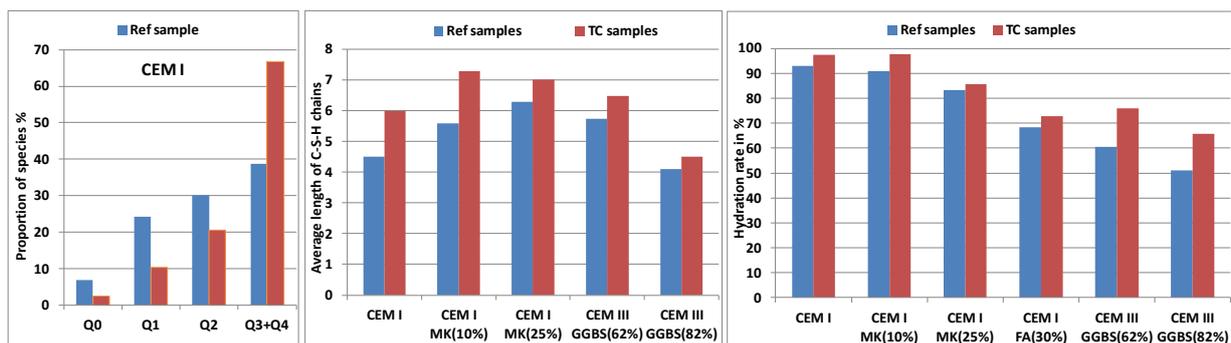


Figure 7: Hydration rate and average length of C-S-H chains obtained ²⁹Si by NMR for reference (Ref) samples and totally carbonated (TC) ones (carbonation until constant mass in chamber at 1.5% CO₂ and 65% RH) after 365-day water curing.

4. CONCLUSION

In this paper, quantification of each mineral phase has been obtained by combination of various techniques (XRD, DTG/TGA and ²⁹Si and ²⁷Al NMR MAS spectroscopy). The effect of total carbonation on the cement pastes was investigated for all cementitious phases. Consequently, bound CO₂ amount can be quantified.

Total carbonation modifies all the hydrated phases. In totally carbonated CEM III with GGBS, there is no more portlandite (or just few traces depending on cement type). There is a linear relationship between the amount of CaCO₃ produced and the percentage of CaO in the anhydrous binders but also depending of the SCM type. The crystalline type of CaCO₃ depend also of the initial binder. Nevertheless, the decalcification is not complete for the other phases than portlandite, probably as a result of a weak accessibility (in the case of anhydrous phases)

or maybe a lower reactivity to carbonation. C-S-H and aluminate phases tend to become an aluminosilicate gel in all carbonated materials.

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