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Complementary use of thermogravimetric analysis and oven to assess the composition and bound CO₂ content of recycled concrete aggregates

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Abstract

The carbonation of recycled concrete aggregates (RCA) has emerged as a possible significant carbon sink to mitigate the increase of CO₂ concentration in atmosphere and global warming. A reliable determination of bound CO₂ content is thus needed to optimize carbonation processes but there is no real consensus on the existing quantification methods, mainly based on thermal decomposition of calcium carbonate. With the aim of developing a relevant quantification method of bound CO₂ during the carbonation of RCA, an experimental study based on the combination of two main techniques – thermogravimetric analysis (TGA) and high-temperature oven – was performed at different scales: paste, mortar, and concrete. XRD analyses allowed highlighting the overlaps between the decomposition of portlandite and calcium carbonate polymorphs during linearly increasing temperatures. Oven and TGA with isothermal steps were found to provide consistent and complementary data on RCA composition and their bound CO₂ content from initially dried specimens.

Keywords: Recycled Concrete Aggregates, TGA, XRD, CO₂, Portlandite, Calcite

1 Introduction

The acceleration of industrialization and urbanization, especially in developing countries, results in huge production of cement-based materials and create serious ecological and social issues [1] [2]. Some regions also suffer from a serious shortage of natural aggregates for the production of new concrete [1]. For example, in 2019 in France, only 326 million tons of aggregates were produced, while the needs were 453 million tons [3]. The difference between production and needs was compensated by recycled aggregates (127 million tons). Therefore, the reuse of construction and demolition waste is imperative to save natural resources, reduce demolition waste and achieve sustainable development in the construction industry [4]-[5].

Compared to the typical natural aggregates (NA), recycled concrete aggregates (RCA) have a lower quality [1] [6]. In recent years, accelerated carbonation has been suggested to improve several properties of RCA [7] [8]. In practice, under atmospheric conditions, concrete carbonation occurs but it could take more than 100 years to achieve a complete carbonation [9]. Cement industry is one of the main sources of carbon dioxide emissions [10]. The CO₂ concentration of cement plant fumes is approximately 15% (*i.e.* 370 times the percentage of CO₂ in the atmosphere). It is therefore suggested to use these fumes to ensure accelerated carbonation of RCA in order to improve rapidly their properties (National French Project FastCarb [11]).

The carbonation of RCA improves not only their physical and mechanical properties and those of new concrete but it also reduces the greenhouse effect caused by the emission of carbon dioxide [4]. RCA (before and after carbonation) show significant variability. This variability comes from several sources: the nature of the crushed concrete (possible mixture of different concretes), the heterogeneity of the distribution of the adherent cement paste in the different granular classes, and the unavoidable presence of bricks, glass or wood incorporated in the RCA

as demolition waste [12]. In order to characterize RCA and to study the effect of carbonation on their properties, it is necessary to determine their initial composition and to monitor its evolution during carbonation. Thermogravimetric analysis (TGA) allows combining temperature variations and mass measurements, thus this technique is often used to provide quantitative composition of cement-based materials from the known decomposition temperatures of several phases such as portlandite. The TG analyzer includes one crucible held in a furnace within a controlled environment [13]. The sample undergoes a user-defined thermal cycle, and the loss of mass is measured and recorded using an automatic acquisition system. The limitation of this test is the low mass of the analyzed sample. In the case of homogeneous materials such as cement paste, this limitation is not an issue. But in the case of RCA, and due to their intrinsic variability as well as their heterogeneity, questions arise about the representativeness and reliability of TGA results. Thus in the case of heterogeneous materials such as RCA, a high-temperature oven is useful as it allows characterizing a more representative sample [14]. Even in the case of the oven, limitations appear: the environment in the oven is not controlled and the mass measurements can only be performed at some chosen temperatures on an external scale, which is likely to affect their accuracy. As the mass of the sample is not continuously monitored, the limit temperatures for the dehydration of portlandite and the decarbonation of the three polymorphs of calcium carbonate should be preset before starting the test. For portlandite, numerous studies have assessed the limit temperatures of dehydration between 400 and 600 ° C [15] [16] [17]. For the polymorphs of calcium carbonate, only a very limited number of studies distinguish them. Calcite is the best known and most studied polymorph, whereas vaterite and aragonite remain very poorly characterized. In most studies [15] [16], vaterite and aragonite are grouped together as unstable polymorphs of calcium carbonate. However, they should be considered in the characterization of RCA as they have been identified as the products of the accelerated carbonation of cement-based materials [18].

Almost all previous studies have focused either on the physical and mechanical properties of carbonated RCA themselves [7] [19], or on the mechanical performance and durability of concrete prepared with carbonated RCA [1] [4]. A large number of studies have also focused on developing new methods to increase the efficiency of carbon dioxide sequestration [20] [2]. To our knowledge, no study has yet evaluated the reliability and accuracy of the current characterization methods used to estimate the CO₂ content of recycled aggregates and monitor its evolution during carbonation, nor has any attempt been made to develop a new method for characterizing RCA that takes into account their variability. Therefore, this study aims at investigating the thermogravimetric methods considering the limit temperatures of the decomposition of portlandite and calcium carbonates, and improving the reliability of the measures based on combined TGA and oven tests. This combination of thermogravimetric analysis (TGA) and oven has never been considered to quantify the bound CO₂ content and the composition of cement based material (especially RCA), so it constitutes the originality of the method developed in this study. The use of the oven to characterize RCA is interesting due to the heterogeneity of studied materials. Once the reliability of both tests has been checked, the objective of the second part of the study is to develop a new method of characterization of RCA based on the complementary use of TGA and oven.

2 Materials and methods

2.1 Materials and mixtures

2.1.1 Cement Paste

Portland cement CEM I 52.5 from Villiers-au-Bouin, France was used in this study (Table 1). Its density was 3.13 g/cm³ and its specific surface area was 3900 cm²/g. Cement paste was prepared with a water-to-cement ratio (W/C) of 0.4 to avoid segregation.

Oxide constituents (%)									
CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	SO ₃	TiO ₂	K ₂ O	Na ₂	P ₂ O ₃
63.70	19.60	4.50	3.90	2.30	2.60	0.20	0.70	0.13	0.20

Table 1: Chemical composition of the used cement.

2.1.2 Mortar

The same cement was used to prepare mortar samples. Natural siliceous sand (0-2 mm) with a specific gravity of 2.61 was used as aggregates. Cement mortar was prepared with mixture mass proportions of cement: sand: water of 1: 2.6: 0.6.

Two forms of samples are prepared, cylindrical samples ($\varnothing = 2$ cm and $h = 16$ cm) and spherical samples ($\varnothing = 4$ cm). Spherical mortar samples were used as model materials to reproduce the behavior of RCA and more particularly the mortar around the natural aggregates in the recycled aggregates. The spherical shape was used because it is the closest to the morphology of the recycled aggregates. Mortar spheres of 40 mm diameter (Figure 1) were obtained using spherical silicone molds placed in parallelepiped PVC molds confectioned using a 3D printer.



Figure 1: Mortar spheres of 40 mm diameter (model materials)

2.1.3 Concrete

In addition to the paste and mortar, the verification tests of the complementarity method (TGA and oven) were also performed on concrete cylinders ($\varnothing = 110$ mm and $H = 220$ mm)

manufactured in 2006 [21] [22] (Table 2) and stored in an air-conditioned room for 16 years ($T = 20 \pm 2^\circ\text{C}$ and $\text{RH} = 55\% \pm 5\%$). For that purpose, the edges of the cylinders were removed first. As the samples were stored for 16 years in an air-conditioned room, the outer layer was actually affected by natural carbonation. The concrete samples were taken from the inside inner part of the sample that have not been subjected to environmental actions. They were sawn into 3 cm cubes. Each test was carried out on about ten cubes.

	Gravel		Sand		Cement	Water
	kg/m ³	Type	kg/m ³	Type	kg/m ³	kg/m ³
					Type	
Conc-lab1	1070	Quartzite Siliceous	760	Quartzite Siliceous	352 CEM I 52.5 PM	174
Conc-lab2	978	Silico- calcareous sea gravel	880	Silico- calcareous sea gravel	260 CEM I 52.5 N	164
Conc-lab3	957	Crushed dense limestone	980	Crushed dense limestone	280 CEM I 52.5 N	162

Table 2 : Composition of concrete mixtures.

2.1.4 Recycled concrete aggregates

Recycled aggregates of 4-22.4 granular class were used. These recycled coarse aggregates produced by Lafarge company in Nantes had a water absorption of 4.3% and an actual density of 2.3 g/cm³.

Diameter (mm)	Cumulative passing on sieve (%)
4	5.5
6.3	14.2
11.2	51.6

16	74.8
20	89.4
22.4	94.3

Table 3: Particle size distribution of recycled concrete aggregates.

2.2 Experimental program

The different stages of the study presented in this paper are summed up in Figure 2. The aim of the study carried out during Stage 1 is to check the dehydration temperature of portlandite and the decarbonation temperatures of the three polymorphs of calcium carbonates (calcite, aragonite and vaterite).

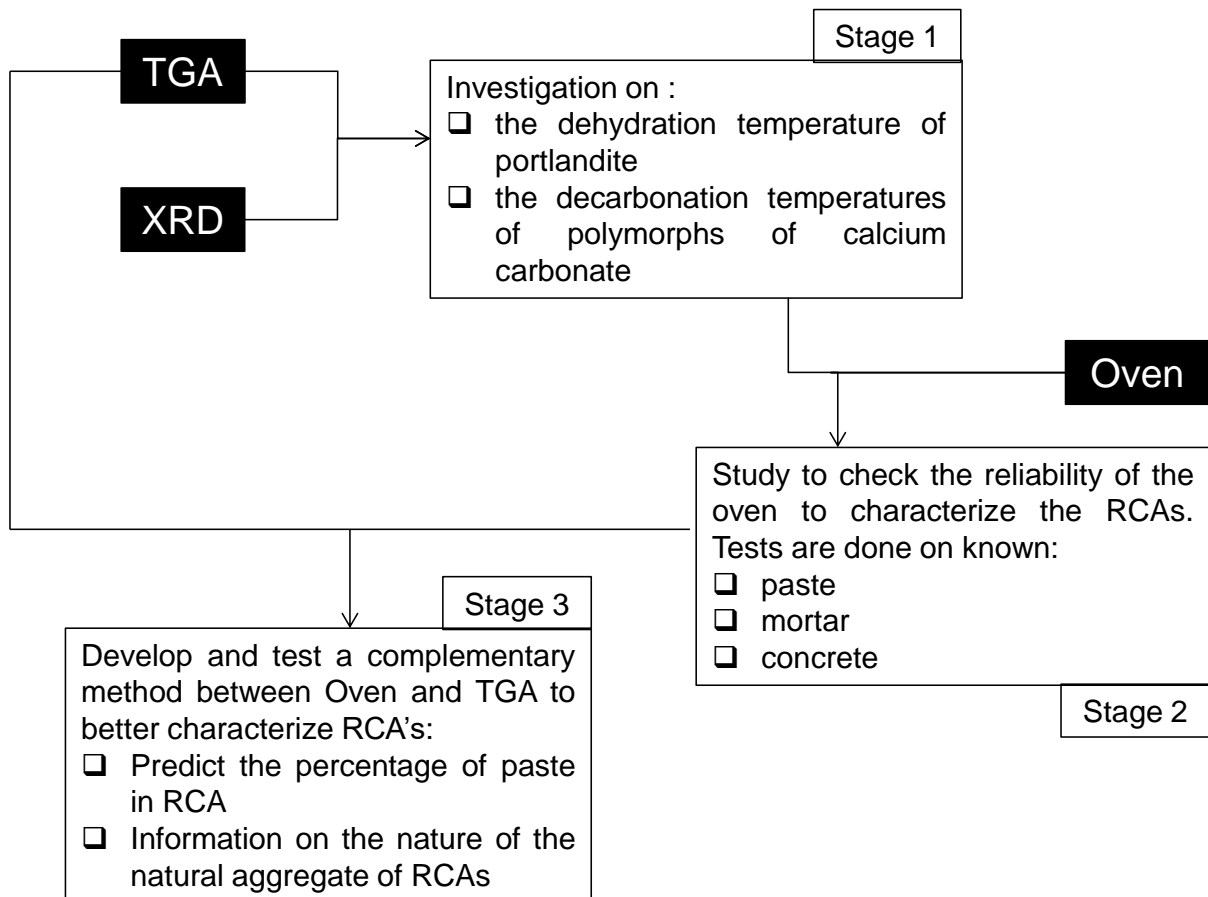


Figure 2: Main stages of the experimental program

In order to check the temperatures the following procedure (detailed in Figure 3) was adopted. A sample of paste was sawn into 10mm thick cylinders. Then they were subjected to a two-dimensional diffusion of CO₂ in a climatic chamber connected to a CO₂ tank at 20°C, 65% relative humidity and 15% of CO₂. This humidity value was chosen from the literature as it would correspond to the optimum humidity for carbonation at 20°C [15] [16]. The concentration of CO₂ in the chamber was controlled by an automatic CO₂ regulator at 15%, which is the typical CO₂ content of exhaust gases from cement manufacturing process. After accelerated carbonation (CO₂=15 %, HR=65% and T=20°C) of these cylinders for 4 days, a TGA test was carried out on one of these samples. From the DTG curve obtained, the temperatures of dehydration of portlandite and decarbonation of polymorphs of calcium carbonate were estimated. These temperatures were used to control the oven and heat the samples. All paste samples were first placed into the oven. The first temperature determined by DTG (lower peak of portlandite dehydration) was maintained for 4h after being reached by the oven. Then, a sample of paste was removed from the oven to be characterized by XRD and TGA. After that, the oven temperature increased until the second temperature (upper peak of portlandite dehydration) determined by DTG was reached, and maintained again for 4 hours before removing another sample from the oven to be characterized. These steps were repeated until the last temperature corresponding to the upper limit of the calcite peak in the DTG curve was reached.

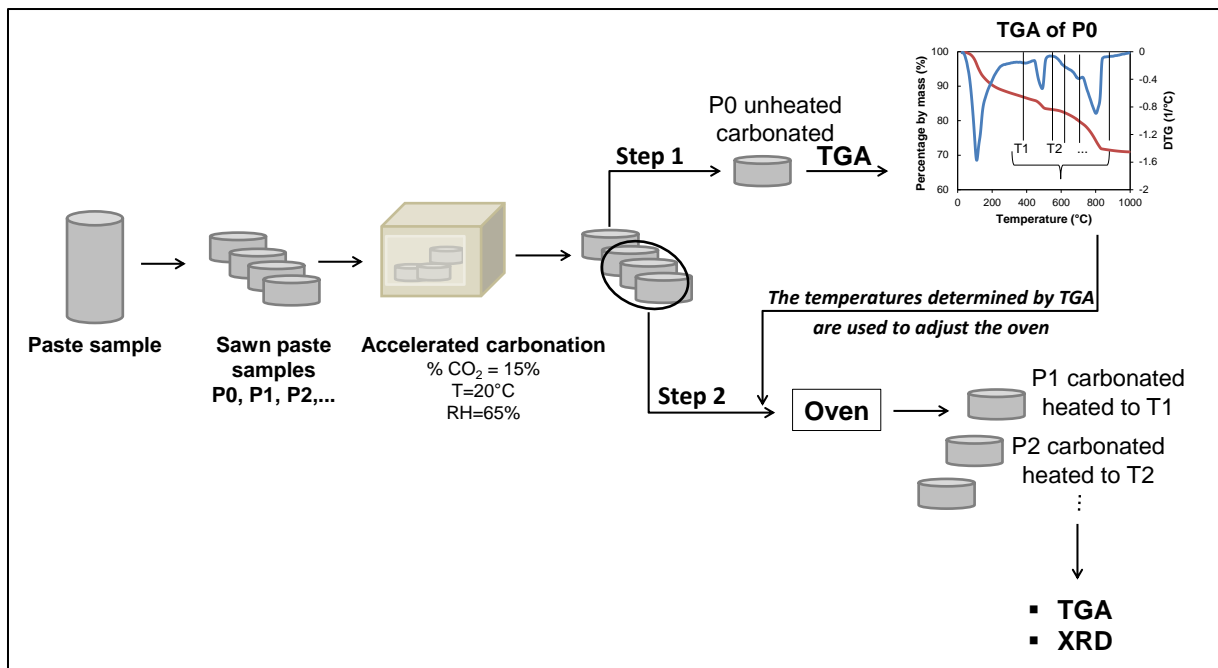


Figure 3: Experimental procedure of stage 1.

Once the study of the decomposition temperatures had been carried out, the second step was launched. This step consists of checking the reliability of the oven test. The verification method consists of comparing the results obtained by the oven test with those obtained by TGA on homogeneous material. The tests were carried out on homogeneous samples of paste, mortar and concrete. The compositions of those materials were completely controlled in order to achieve a comparison of the results but also a validation of the reliability of the test.

Once the reliability of the oven had been checked, the study focused on the complementary use of the oven and the TGA for a better characterization of RCA and bound CO₂. This complementarity makes possible the determination of the average percentage of paste in recycled aggregates and the type of natural aggregate from their possible decomposition at high temperature.

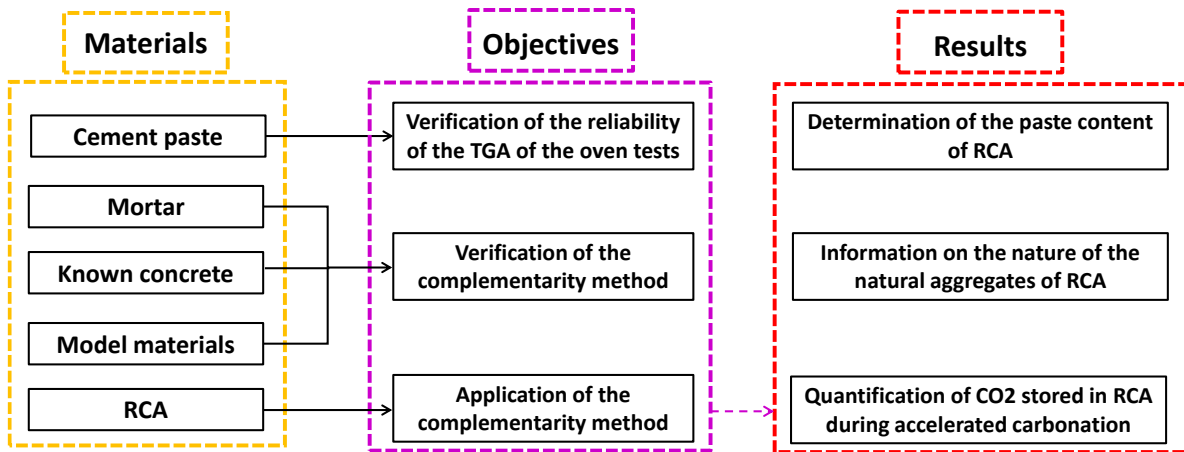


Figure 4: Diagram showing the stages of the comparative study between the oven and the TGA.

2.3 Testing procedures

2.3.1 X-ray diffraction analysis (XRD)

This technique was used during stage 1 (**Erreur ! Source du renvoi introuvable.**) on the carbonated paste samples heated up to different temperatures. Each sample was crushed and sieved through an 80 μ m sieve. The powder was then subjected to XRD. A Malvern Panalytical Aeris instrument (XRD) was used. This later provides full material characterization by adding information about elemental composition. Scanning program consisted in rotating between 7 and 70 $^{\circ}2\theta$ with a step size of 0.01 $^{\circ}2\theta$ and a time per step of 480.165 ms.

2.3.2 Thermogravimetric analysis (TGA) and oven

The TGA-FTIR analyses were performed using a thermal analyzer system (Netzsch microbalance) coupled with a Fourier transform infrared spectrometer (FTIR, Vector 22type, Bruker Optics Inc., Germany) equipped with an IR gas cell. FTIR measurements were conducted with a DTGS detector in a specifically developed low-volume gas cell. The tests were performed under a nitrogen stream.

The TGA was performed during stage 1 (**Erreur ! Source du renvoi introuvable.**), stage 2 (**Erreur ! Source du renvoi introuvable.**) and stage 3 (**Erreur ! Source du renvoi introuvable.**)

introuvable.) For stage 1, an usual temperature program without isothermal sequences was used, the sample taken from the oven after being heated up to a temperature T was then tested by TGA. This sample was crushed and sieved using a 80 μm sieve. An intensive and manual grinding was carried out on samples of approximate mass 2g for 2 min. Intensive, manual grinding was performed on samples of approximately 2 g mass for 2 minutes. Intensive grinding is performed in an attempt to get all the cement paste in the test sample through the sieve. Manual grinding with moderate energy was chosen so that no abrasion of the sand was induced. The resulting powder, with a mass of around 100-120 mg, was collected in an alumina crucible and placed in the thermal balance. The temperature increased continuously from 20°C to 1000°C with a heating rate of 10°C/min.

During stage 2 and stage 3, which allow checking the reliability of the oven and the TGA, two temperature programs were imposed for the TGA test, *i.e.* with and without isothermal sequences. For the tests carried out without isothermal sequences, the temperature increased continuously from 20 to 1000°C with a heating rate of 10°C/min (solid line in Figure 5), whereas for the TGA tests carried out with isothermal sequences, the temperature rose from 20 to 1000°C with a programmed stabilization for one hour at each specific temperature (double solid line in Figure 5). The temperature values chosen for the isothermal steps were the critical values often used to reach the dry mass (80, 105 and 200°C respectively), to dehydrate the portlandite (400, 475, 500, 550, and 600°C respectively) and decarbonate polymorphs of calcium carbonates (675, 730, 800 and 875°C respectively). These temperatures were determined from the preliminary TGA test performed on the non-heated carbonated sample (Figure 3). The mass loss of the sample was recorded. The gaseous products were directly introduced into the gas cell and analyzed by the FTIR spectrometry which was carried out to provide confirmation of the identity of released gases. The FTIR generated a Gram-Schmidt profile of absorbance versus temperature.

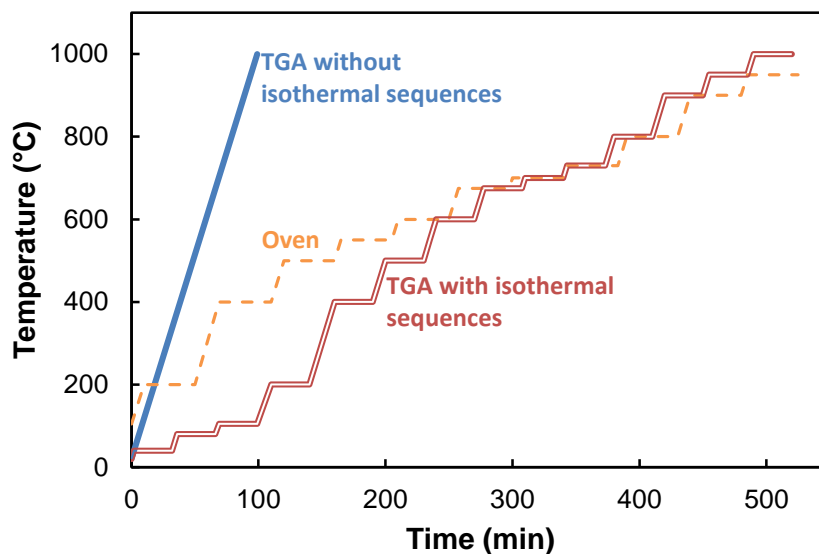


Figure 5: Temperature setpoint program for oven and TGA tests.

In addition to the TGA, experimental campaign carried out in **stage 2 and 3** also included oven tests. The KITTEC oven used in this study heats up to 1300°C with an adjustable heating rate and possible temperature stabilization (isothermal sequences). The mass of the sample was 150-200g. Prior to oven tests, the samples were successively stored in other ovens regulated at three selected temperatures: 40, 80 and 105°C respectively until mass stabilization. The procedure adopted for oven test is described in Figure 5. The samples were heated up to 1000°C with a heating rate of 10°C per minute. The stabilization temperatures were chosen from the first stage. The temperature of the oven was maintained constant for at least 30 min before weighing the samples for periods of 10 min. Weighing was performed with a scale outside the oven and directly without waiting for the samples to cool. The rise in temperature was applied again when the difference between two consecutive mass measurements was lower than 0.5% (dash line in Figure 5).

In order to check the reliability of the different estimation methods of the water and CO₂ losses associated to the main decompositions, the same paste sample was tested according to the three

methods mentioned above: 1- TGA without isothermal sequences, 2- TGA with isothermal sequences, 3- Oven test with isothermal approach.

2.3.3 Data analysis and complementary use of TGA and oven

Once the consistency of oven and TGA methods is verified (stage 2), the complementary use of both methods can be defined and analyzed. This method consists of the comparison between the results of TGA carried out on a crushed and sieved sample and those of the oven carried out on an uncrushed sample of the same heterogeneous cementitious material (mortar, concrete, RCA). This comparison makes possible to check the reliability of the testing procedure, to estimate the bound CO₂ content, and the identification of the presence of carbonates in the natural aggregates of RCA. The methodologies and calculations used to achieve these objectives are detailed in the following three sections.

2.3.3.1 Determination of the paste content of cement-based material

Sample preparation for the TGA, oven tests and details of the masses cited in this section are presented in Figure 6.

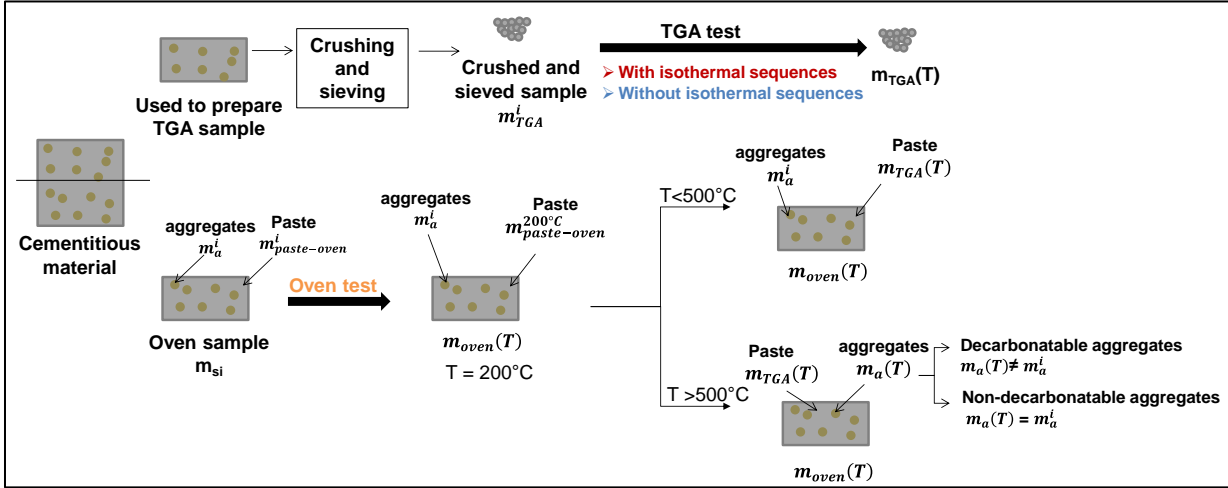


Figure 6: Schematic definition of the process and masses used in the complementarity method

The mass percentages in the equations presented hereafter are calculated by reference to the dry mass at 200°C to avoid the effect of the initial saturation state of the sample. The mass variations

obtained by thermogravimetric analysis $M_{TGA}(T)$ and by oven $M_{oven}(T)$ are plotted as a function of temperature T , as defined in Equation 1 and Equation 2. In the case of a heterogeneous material, $m_{TGA}^{200^{\circ}C}$ and $m_{TGA}(T)$ are the masses of the sample crushed, sieved, and heated by TGA to $200^{\circ}C$ and temperature T , respectively. $m_{oven}^{200^{\circ}C}$ and $m_{oven}(T)$ are the mass of the intact sample (without crushing or sieving) after heating in the oven to $200^{\circ}C$ and temperature T , respectively.

$$M_{TGA}(T) = \frac{m_{TGA}(T)}{m_{TGA}^{200^{\circ}C}} * 100 \quad \text{Equation 1}$$

$$M_{oven}(T) = \frac{m_{oven}(T)}{m_{oven}^{200^{\circ}C}} * 100 \quad \text{Equation 2}$$

The heterogeneous cementitious material consists of cement paste and natural aggregates. The mass percentages obtained by the oven test $M_{oven}(T)$ can then be written as follows:

$$M_{oven}(T) = \frac{m_{oven}(T)}{m_{oven}^{200^{\circ}C}} * 100 = \frac{m_{paste-oven}(T) + m_a(T)}{m_{paste-oven}^{200^{\circ}C} + m_a^{200^{\circ}C}} * 100 \quad \text{Equation 3}$$

$m_a^{200^{\circ}C}$ and $m_a(T)$ are the mass of natural aggregates in the cementitious material after heating to $200^{\circ}C$ and T respectively. The mass of natural aggregates at $200^{\circ}C$ is equal to the mass of initial natural aggregates m_a^i .

At temperatures below $500^{\circ}C$, the mass of natural aggregates is considered constant. Even if decarbonatable products are potentially present, they do not decarbonate in these temperature ranges. $M_{oven}(T)$ can then be written as follows:

$$\begin{aligned} M_{oven}(t) &= \frac{m_{paste-oven}(T) + m_a^{200^{\circ}C}}{m_{paste-oven}^{200^{\circ}C} + m_a^{200^{\circ}C}} * 100 \\ &= \frac{m_{paste-oven}(T) + m_a^i}{m_{paste-oven}^{200^{\circ}C} + m_a^i} * 100 \end{aligned} \quad \text{Equation 4}$$

Therefore, for two temperatures $T1$ and $T2$ lower than $500^{\circ}C$, we obtain :

$$\begin{aligned} \frac{M_{\text{oven}}(T1) - M_{\text{oven}}(T2)}{M_{\text{TGA}}(T1) - M_{\text{TGA}}(T2)} &= \frac{\frac{m_{\text{oven}}(T1)}{m_{\text{oven}}^{200^\circ\text{C}}} - \frac{m_{\text{oven}}(T2)}{m_{\text{oven}}^{200^\circ\text{C}}}}{\frac{m_{\text{TGA}}(T1)}{m_{\text{TGA}}^{200^\circ\text{C}}} - \frac{m_{\text{TGA}}(T2)}{m_{\text{TGA}}^{200^\circ\text{C}}}} \\ &= \frac{\frac{m_{\text{oven}}(T1) - m_{\text{oven}}(T2)}{m_{\text{paste-oven}}^{200^\circ\text{C}} + m_a^i}}{\frac{m_{\text{TGA}}(T1) - m_{\text{TGA}}(T2)}{m_{\text{TGA}}^{200^\circ\text{C}}}} \end{aligned} \quad \text{Equation 5}$$

In the range of these two temperatures, the mass of the natural aggregate is considered constant and the loss of mass is strictly associated with the cementitious matrix of the material. In the following calculation, it will be assumed that after grinding and sieving, only and entirely the cement paste is collected. Therefore, the relative mass loss of a ground and sieved sample (TGA) is equal to the relative mass loss of the same sample before grinding and sieving in the oven between these two temperatures, *i.e.*, $\frac{m_{\text{oven}}(T1) - m_{\text{oven}}(T2)}{m_{\text{paste-oven}}^{200^\circ\text{C}}} = \frac{m_{\text{TGA}}(T1) - m_{\text{TGA}}(T2)}{m_{\text{TGA}}^{200^\circ\text{C}}}$.

Therefore, Equation 5 can then be expressed as follows:

$$\frac{M_{\text{oven}}(T1) - M_{\text{oven}}(T2)}{M_{\text{TGA}}(T1) - M_{\text{TGA}}(T2)} = \frac{m_{\text{paste-oven}}^{200^\circ\text{C}}}{m_{\text{paste-oven}}^{200^\circ\text{C}} + m_a^i} \quad \text{Equation 6}$$

This ratio represents the proportion of paste in the heterogeneous cementitious material tested

$$\text{Paste Proportion (PP)} = \frac{M_{\text{oven}}(T1) - M_{\text{oven}}(T2)}{M_{\text{TGA}}(T1) - M_{\text{TGA}}(T2)} \quad \text{Equation 7}$$

2.3.3.2 Nature of RCA natural aggregates

At temperatures higher than 500°C, natural aggregates containing carbonated products undergo mass losses. Thus, the mass loss of a TGA sample (obtained from crushing and sieving the original sample) between two temperatures above 500°C will not be equal to that of an oven sample (original sample). In this case, a natural aggregate factor noted as (NAF) is defined as the ratio between the mass lost by the paste of RCA and the mass lost by the whole RCA

$$NAF = \frac{M_{oven}(T3) - M_{oven}(T4)}{(M_{TGA}(T3) - M_{TGA}(T4)) * PP} \quad \text{Equation 8}$$

At least one of these two temperatures (T3 and T4) must be above 500°C. If this parameter is equal to one, the mass loss of the entire heterogeneous material corresponds then to the mass loss of the paste. Thus, the natural aggregate contained in the heterogeneous material does not undergo mass loss at high temperature. In the opposite case ($NAF > 1$), the mass loss of the heterogeneous material is greater than that of the paste so that the natural aggregate undergoes mass loss and contains carbonated products.

2.3.3.3 CO₂ stored in RCA during accelerated carbonation

It is noteworthy that all mass percentages used below are calculated by reference to the mass of the sample heated at 950°C. The amount of calcium carbonate obtained by TGA or by oven of a sample of heterogeneous cementitious material (RCA) subjected to accelerated carbonation is the sum of three distinct quantities: initial carbonate due to natural carbonation, carbonate corresponding to the decarbonatable products in the natural aggregates, and carbonate resulting from accelerated carbonation.

In order to determine the amount of carbon dioxide captured and stored in the recycled aggregates during accelerated carbonation, noted as C_{AC} , two tests (oven or TGA) must be performed, *i.e.*, before and after accelerated carbonation. C_{AC} can be calculated using the following relationship:

$$C_{AC}(\text{g/kg RCA}) = (\%M_c - \%M_{c0}) * 10 \quad \text{Equation 9}$$

Where $\%M_c$, $\%M_{c0}$ represent the mass percentage of carbon dioxide present in the RCA before and after accelerated carbonation, respectively. The amounts of carbon dioxide are determined from the amount of calcium carbonate obtained from the oven or TGA results.

$$C_{AC}(g / kg RCA) = (\%M_c - \%M_{c0}) * 10 \quad \text{Equation 10}$$

$$= \frac{(\%M_{CaCO_3} - \%M_{CaCO_30}) * 44}{100} * 10$$

Where $\%M_{CaCO_3}$ and $\%M_{CaCO_30}$ represent the mass percentage of calcium carbonate in the RCA before and after accelerated carbonation calculated based on the dry mass at 950°C. This mass percentage of calcium carbonate is evaluated on the basis of the mass loss of the TGA curve between 600 and 900°C.

It should be noted that the oven and the TGA are destructive tests, thus the samples used to determine the amount of calcium carbonate before and after carbonation are different. Due to the heterogeneity and high variability of recycled aggregates, only results of the oven are considered regarding the representativeness of the sample,

Based on the complementarity method and on the knowledge of the percentage of paste in the recycled aggregate and of the type of natural aggregate present, it is possible to distinguish the amount of carbon dioxide captured and stored in the RCA cementitious matrix C_{paste} from the amount of carbon dioxide present in the natural aggregates C_{NA} .

$$C_{paste}(g / kg RCA) = \%MC_{TGA} * PP * 10 \quad \text{Equation 11}$$

$$C_{NA}(g / kg RCA) = \%MC_{oven} * 10 - C_{paste} \quad \text{Equation 12}$$

Where $\%MC_{TGA}$ and $\%MC_{oven}$ represent the percentage mass loss between 600°C and 900°C of the RCA by TGA (ground and screened RCA) and by the oven (RCA without grinding) respectively. It is important to underline again the assumption that only cement paste is collected after grinding.

3 Results and discussion

3.1 Decarbonation of the polymorphs of calcium carbonate

Figure 7 shows the results of Gram Schmidt and DTG analyses performed on carbonated paste samples before and after heating at different temperatures.

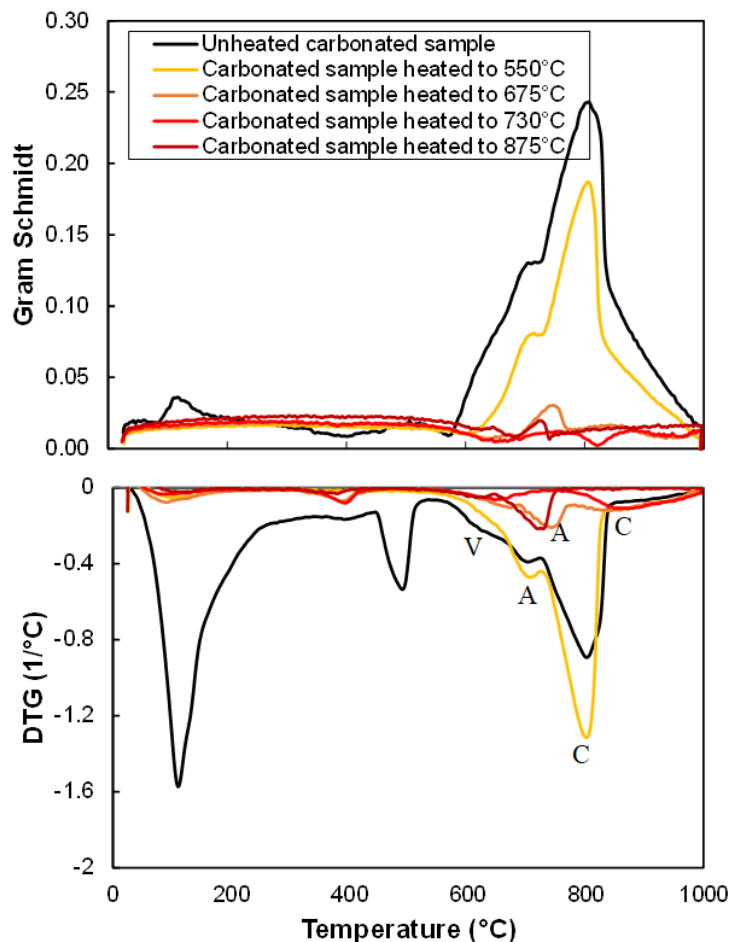


Figure 7: Gram Schmidt and DTG curves of the carbonated samples before and after heating to different temperatures. The calcium carbonate polymorphs are identified as “V” for vaterite, “A” for aragonite and “C” for calcite

For non-heated carbonated sample, negative peaks can be distinguished after 400°C on DTG curve. The first one is related to the dehydration of portlandite CH (around 450-550°C [23]) whereas the others correspond to the decarbonation of the three polymorphs of calcium

carbonate around 550-900°C [24]. Gram Schmidt's results confirm that these three peaks correspond to calcium carbonate polymorphs since it detects carbon dioxide emission at the same temperatures as DTG. According to Ghosh [25], aragonite is a calcium carbonate polymorph that dissociates at lower temperatures than calcite. Gaztanaga et al.[26] pointed out that the presence of other decarbonation peaks in the DTG curve is due to the decomposition of either aragonite and vaterite or even amorphous carbonate. According to literature, calcite is the most thermodynamically stable polymorph of calcium carbonate and vaterite the least stable in ambient conditions [27]. Consequently, the decarbonation of the less stable polymorph, vaterite, corresponds to the first peak of the three observed between 550 and 675°C, then aragonite between 675 and 720°C and finally calcite between 720 and 875°C, the most stable with the highest decarbonation temperature. In order to check the presence of the phases at these temperatures, XRD and TGA tests were carried out on heated samples.

Based on the Gram Schmidt and DTG curves and using the TGA mass loss curves, the remaining percentage of each of the oven detected components (portlandite, calcite, aragonite and vaterite) is calculated in the different samples tested (non-heated and heated at different temperatures). Figure 8 shows the evolution of this remaining percentage as a function of the heating temperature. The remaining percentage is calculated relatively to the dry mass at 950°C to ensure the same basis in all calculations performed at different temperatures and to avoid the effect of the initial state of the sample.

Figure 9 shows the XRD spectra of the carbonated samples before and after heating at 550, 675, 730 and 875°C. It should be noted that aragonite was not detected by the XRD test, which may be due to its poor crystallization. Thus for aragonite, the results will be limited to those of TGA.

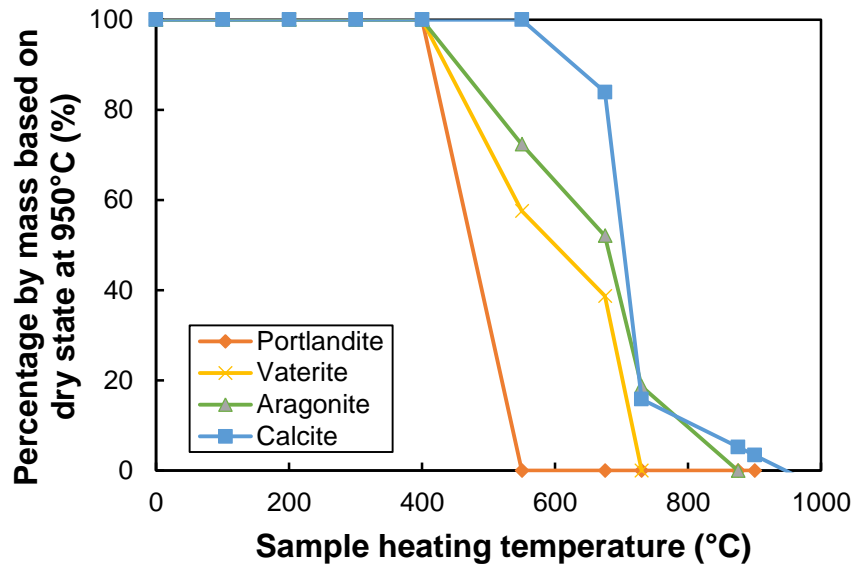


Figure 8: Remaining percentage of the main components of the cementitious matrix as a function of heating temperature.

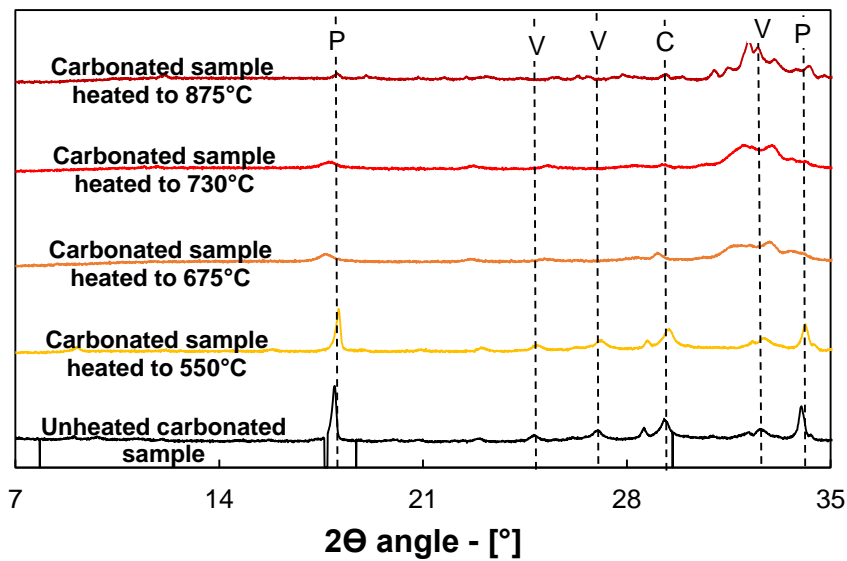


Figure 9: XRD analyses of the carbonated paste sample before and after heating to different temperatures. The portlandite is identified as “P” and the calcium carbonate polymorphs are identified as “V” for vaterite, “A” for aragonite and “C” for calcite

The DTG results (Figure 7) of the carbonated sample heated to 550°C show that the three peaks of the calcium carbonate polymorphs are still present, whereas the peak of portlandite has disappeared. This result is in agreement with the XRD curve for the calcium carbonate

polymorphs. The portlandite peak still appears in the XRD spectrum but its amplitude significantly decreases and disappears after heating the sample to 675°C. In addition to portlandite, vaterite peaks disappear from the XRD curves after heating to 675°C while they persist with aragonite and calcite peaks on the DTG curves of the sample heated to 675°C. Figure 8 quantifies the remaining amounts of the studied phases and shows that the amount of remaining vaterite decreases significantly after heating to 675°C, a possible reason for its non-detection by XRD. Poor crystallization caused by heating at high temperature for a long time may also be an explanation. This peak disappears after heating to 730°C and only the aragonite (Figure 8 and Figure 9) and calcite peaks persist (Figure 7, Figure 8 and Figure 9).

The aragonite peak on the Gram Schmidt and DTG curves disappears after heating the sample to 875°C, only the calcite peaks on the XRD (Figure 9) and DTG (Figure 7) curves persist in the sample but in small quantities as shown in the quantitative results in Figure 8.

3.2 Oven tests and new method to characterize RCA

3.2.1 Comparison of TGA and oven test on paste

This study allows investigating the effect of initial state and heating rate. In order to verify the reliability of the different techniques for estimating the water and CO₂ losses associated with the main decompositions of the cementitious material during its heating, the same paste sample was tested according to the three methods described in the previous section: 1- TGA without isothermal sequence 2- TGA with isothermal sequences 3- Oven with isothermal sequences. Figure 10 shows the curves obtained for the studied cement paste. A significant shift between them can be observed especially at relatively low temperatures ($T < 200^{\circ}\text{C}$). This difference highlights the significant effect of the initial state of the sample and the heating rate on the obtained results [28] [29] [30]. Different results on the effect of heating rate have been reported in literature. Khachani et al [28] confirmed that dehydroxylation of calcium hydroxyde

Ca(OH)₂ is extremely sensitive to the choice of heating rate. They observed that the TGA/DTG curves carried out on synthetic calcium hydroxyde exhibited an asymmetric character and moved towards higher temperatures with an increase in the heating rate. According to Galan et al [32], modifying the heating rate leads to a shift in the temperature range when the calcium carbonate decomposition occurs. Higher rates correspond to broader temperature decomposition ranges, *i.e.*, when increasing the rate; the decomposition is accelerated in terms of time and delayed in terms of temperature.

From 200°C, the three curves have the same trend. The oven curve is closer to that of TGA with isothermal sequences, which is expected as they follow approximately the same temperature program.

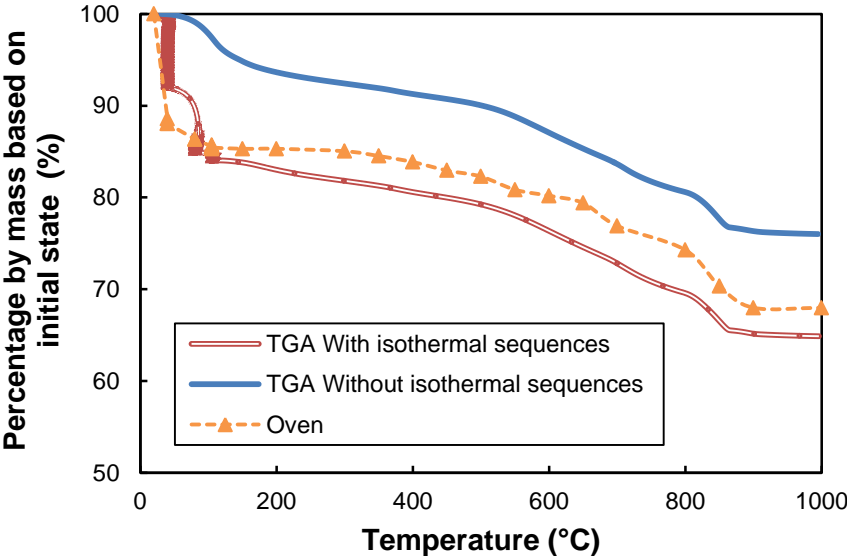


Figure 10: Evolution of the mass loss of cement paste versus temperature for different heating protocols.

To eliminate the impact of the initial state of the sample on the obtained results, the percentages of mass loss are calculated by reference to the dry state of the sample. Figure 11 shows the evolution of the mass loss calculated with respect to the dry state at 200°C (Equation 13).

$$M_{200^{\circ}\text{C}} = \frac{\text{mass at temperature } T}{\text{mass at } 200^{\circ}\text{C}} * 100$$

Equation 13

Figure 11 clearly shows that after excluding the effect of the initial state, the curves become very close and the gap between them has narrowed considerably. The effect of the isothermal sequences does not appear clearly in Figure 11. In order to analyse the effect of this parameter, the average of the difference between the mass loss obtained by the oven and TGA (equation 14) $\Delta\%(TGA - \text{oven})$ for the two TGA methods (with and without isothermal sequences) are presented in Figure 12 according to the reference temperatures used to calculate these percentages.

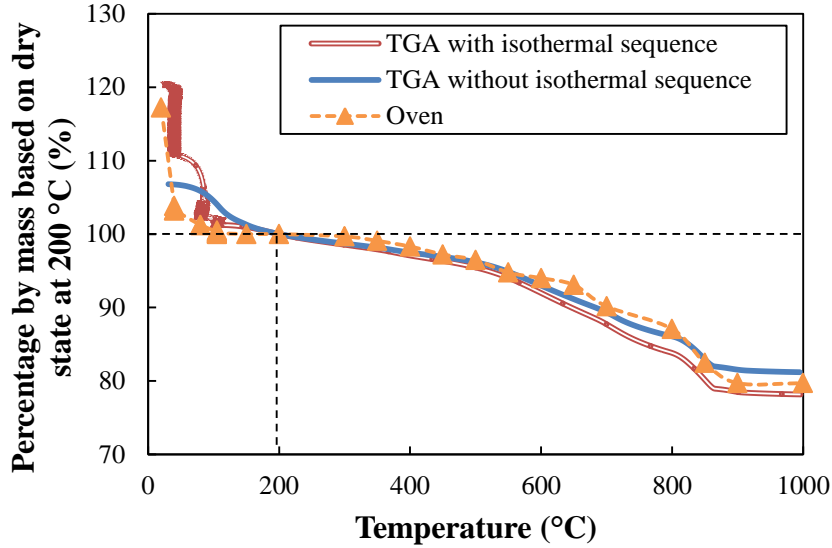


Figure 11: Mass variations of cement paste based on dry state at 200°C.

$$\Delta\%(TGA - \text{oven}) (T) = \frac{\sum_{T=T_1}^{T_n} \text{abs}(M_{\text{oven}}^{T_i} - M_{TGA}^{T_i})}{n}$$

Equation 14

$$\text{with } M_{\text{oven}}^{T_i} = \frac{m_{\text{oven}}(T_i)}{m_{\text{oven}}(T)} * 100$$

Equation 15

$$M_{TGA}^{T_i} = \frac{m_{TGA}(T_i)}{m_{TGA}(T)} * 100$$

Equation 16

Where n is the number of temperatures tested during oven drying (points on the orange curve).

The first point of each curve shows the average of the difference between the TGA and the oven

curves when the percentages are calculated based on the initial mass of the sample. For the oven, the initial sample mass represents the mass of the sample before heating, whereas for the TGA test, the initial mass represents the mass of the crushed and sieved sample used for TGA test before being heated. Compared to the other ones, the values of these two points are the highest, which highlights the significant effect of the initial state on the percentages calculated as indicated in the previous paragraph. The curve showing the difference between the oven and the TGA with isothermal sequences is lower than the difference between the oven and the TGA without isothermal sequences, which shows the significant effect of isothermal sequences [31]. If isothermal sequences are not ensured, especially in the temperature ranges corresponding to the highest mass losses (critical temperatures), the temperature increase could be faster than the time needed for the release of water and CO₂ due to drying and phase decompositions possible at a given temperature T. Thus a mass loss at a temperature T+dT partly corresponds to the mass that should have been lost at the temperature T. In other words an overlap between the mass losses will occur [15] and therefore the use of TGA curves without isothermal sequences to quantify some phases could be less accurate.

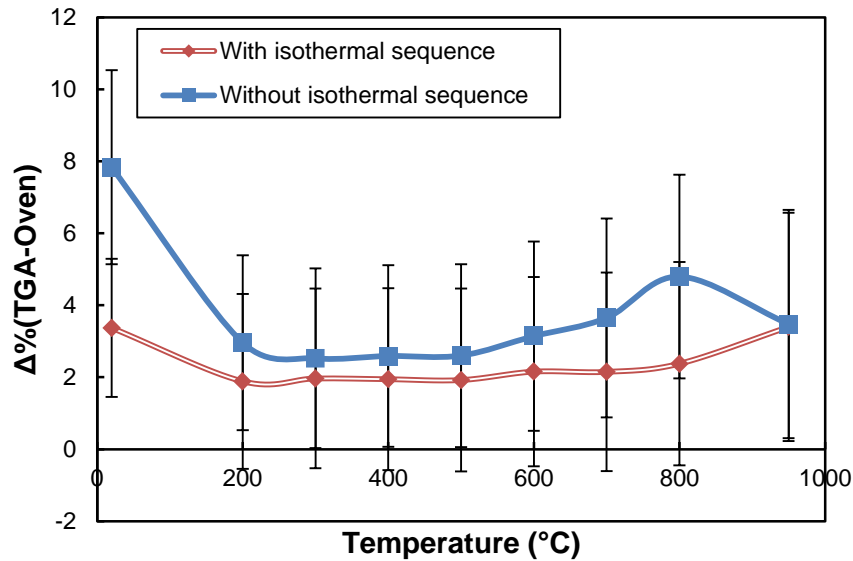


Figure 12: Average of the difference between the percentage of mass obtained by the oven and that obtained by TGA as a function of the reference temperatures.

Considering both oven and TGA tests, this study shows that several criteria (heating rate, reference temperature and isothermal sequences) should be taken into account to improve the obtained results.

3.2.2 Complementarity of oven tests and TGA tests on heterogeneous materials

3.2.2.1 Verification on materials of known composition

The complementary method based on the oven and the TGA tests aims to determine, on the one hand, the percentage of aggregate in a cementitious material and, on the other hand, the amount of bound CO₂ by taking into account the mineralogy of natural aggregates (§2.3.3). The new approach proposed in this study was first validated on samples of mortar and concrete of known compositions. Figure 13 shows the evolution of the mass percentage of the **sieved mortar** on the basis of the dry mass at 200°C (to avoid the effect of the initial state) carried out by two methods. The first curve "sieved mortar-oven (calculation)", is deduced from the mass loss of

the sample of **mortar** heated in the **oven**. Using the aggregates content of the mixture composition, the curve showing the evolution of the mass of the **paste of the tested mortar** is deduced from the mass loss of the **mortar** obtained by the **oven method**. The second curve "sieved mortar-TGA (experimental)" is directly obtained by TGA test carried out on sieved mortar. Good agreement of experimental results and calculations was obtained for different temperatures. This agreement for low temperatures (<500°C) validates the complementary method based on the oven and the TGA which assumes that the mass loss at low temperature is mainly due to the cement paste. Such agreement is also observed for high temperatures, indicating that the siliceous sand used in the mortar does not contain decarbonatable products.

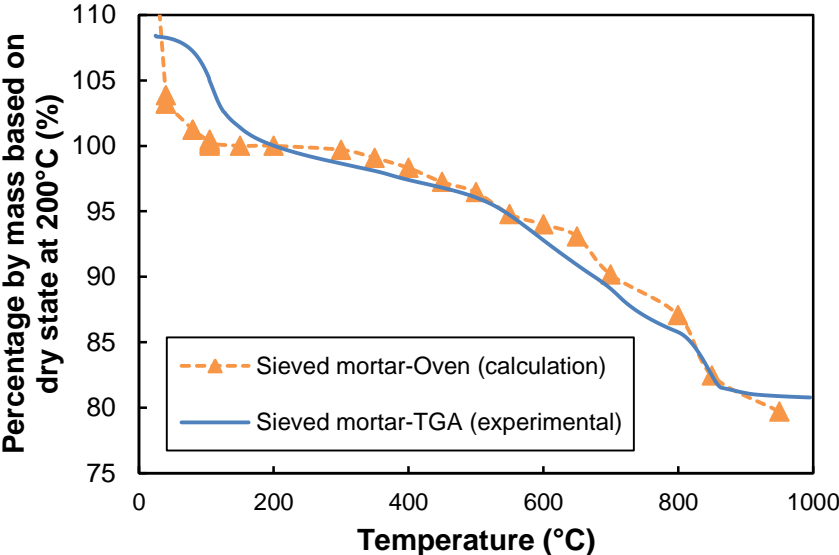


Figure 13: Evolution of the percentage by mass of sieved mortar based on dry state at 200° as a function of temperature increase.

The oven and TGA tests were also performed on the spherical model materials and on cubes from concrete mixtures recorded in Table 2. Figure 14 shows the paste content (Equation 7) calculated from two methods: complementarity method using the oven and the TGA on one hand and the direct calculation from the mixture composition on the other hand. The results show that both methods provide the same values for each material.

In addition, Table 4 shows the value of NAF (Natural Aggregate Factor) for the concrete mixtures given in table 2. As defined (§2.3.3.2), this factor indirectly characterizes the natural aggregates contained in the studied cement-based material. It is equal to 1 when the natural aggregate does not contain decarbonatable products and it increases proportionally with their percentage. For the first concrete mixture “Conc-lab1”, the NAF value is 1.2, *i.e.*, close to 1. This result is in agreement with the mineralogy of the siliceous aggregates used. The NAF values for “Conc-lab2” and “Conc-lab3” are higher and close to 2. This indicates that the mass loss of each considered concrete between two temperatures T1 and T2 (at least one these two temperatures is higher than 500°C) is twice the mass loss of the associated cement paste between these two temperatures.

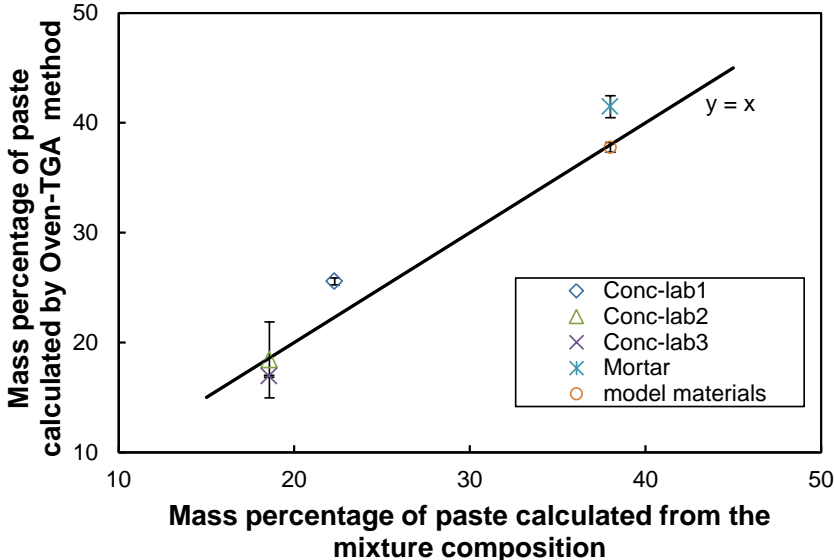


Figure 14: Correlation between percentage of paste calculated by the method of complementarity and percentage of paste of the mix design for known mortar and concrete

As a result, the aggregates of these concretes undergo mass losses between these two temperatures and thus contain decarbonatable products. Such result is consistent with the nature of the natural aggregates used in these two concretes indicated in the design mix (Table 2 and Table 4).

	Type of aggregates	NAF
Conc-lab1	Siliceous	1.2
Conc-lab2	Sea gravel	1.8
Conc-lab3	Limestone	2.2

Table 4: NAF values of the three known concretes and RCA during carbonation.

In addition, the value of NAF for concrete with limestone aggregates is higher than the value of NAF for concretes with silico-calcareous aggregates, showing that this parameter is sensitive to the amount of calcium carbonates present in natural aggregates.

3.2.2.2 Application on recycled concrete aggregates (RCA)

The objective of the complementarity method, based on the combination of the oven and TGA data, is to characterize recycled concrete aggregates, an unknown material in terms of composition and nature. For the oven, depending on the crucible used, the sample could be representative of the material tested, whereas this cannot be the case for the TGA test. For a better characterization of RCA in the TGA test, two methods can be used: the first one consists in crushing and sieving a representative sample and then homogenizing it to collect the TGA sample. The other one consists in performing several TGA tests on small samples in order to obtain an average value. In this study, the second method was applied on RCA and model materials. Using the results of the complementarity method developed, it becomes possible to estimate the overall amount of carbon dioxide bound by the RCA or model materials as well as the distribution of this amount between the paste (C_{paste} - Equation 11) and the natural aggregates (C_{NA} - Equation 12) as shown in Figure 15 and Figure 16.

The storage of CO_2 in the natural aggregates of RCA and model materials remains constant as carbonation proceeds. A significant increase in the bound CO_2 content is observed for the model materials (mortar): the amount of CO_2 stored increased from 3.1 to 51.6 g/kg after 4 days of

carbonation and then to 70.6 g/kg after 13 days. The increase was much smaller in the case of RCA: the amount of bound CO₂ stored in the paste varied from 6.5 to 8.6 g/kg after 4 days of carbonation and then to 12.2 g/kg after 20 days. The measured amounts of stored CO₂ are consistent with those reported in the literature [44]. Sereng [44] obtained values of stored CO₂ in the same range using a method based on increasing the dry mass of the sample after carbonation coupled with a TGA test to determine the amount of water released during carbonation. Such approach requires two TGA tests. Fang et al [156] also obtained values of the same order using only TGA results to determine the amount of carbon dioxide stored in RCA. However, the high variability and heterogeneity of RCA questions the reliability of the adopted methodology.

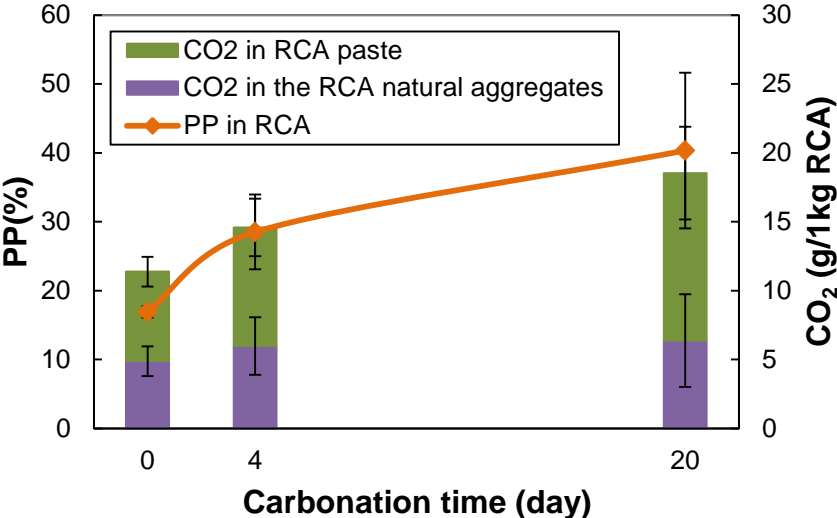


Figure 15: Evolution of the paste proportion (PP) and bound CO₂ content of recycled aggregates during accelerated carbonation

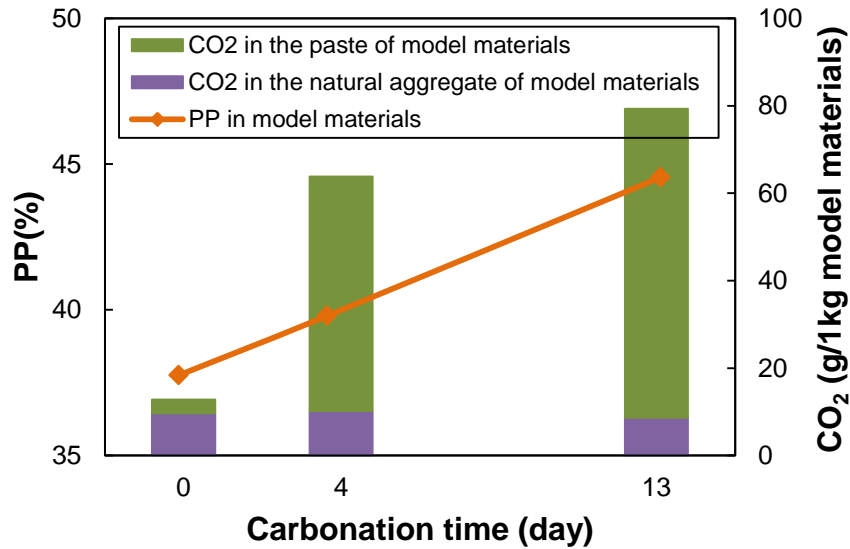


Figure 16: Evolution of the paste proportion and bound CO₂ content of model materials during accelerated carbonation

Another aspect worth discussing is the difference in storage capacity between RCA and model materials: 67.5 g of CO₂ were bound within 13 days of carbonation of the model materials while RCA only took 5.7 g in 20 days of accelerated carbonation. This difference is due, on the one hand, to the considerably higher percentage of paste in the model materials (37%) compared to RCA (17%), and on the other hand, to the significant natural carbonation of RCA prior to accelerated carbonation, as evidenced by the initial amount of CO₂ stored in GBRs. This initial natural carbonation decreases the potential of CO₂ binding since a large part of the carbonatable hydrates has already been carbonated, which could lead to the clogging of the outer layer and thus makes the diffusion of carbon dioxide more difficult.

4 Conclusions

Two thermogravimetric (TG) methods were combined in this study to design a new methodology to characterize recycled concrete aggregates (RCA). The tests were performed

using an automatic TG analyzer and an oven respectively and both series of data were combined. From the analysis of experimental results, the following conclusions can be drawn:

- Based on the TGA and XRD results, vaterite was the least stable calcium carbonate polymorph and first decomposed between 550 and 675°C followed by aragonite, which decomposed completely between 675 and 730°C. Finally, most of calcite decarbonated between 730 and 875°C.
- As RCA are heterogeneous material, they present very large disparities in terms of paste content for the same granular class, which is likely to induce a dispersion in the test results, in particular for tests using small samples such as thermogravimetric analysis (TGA). The oven can be used instead of the TGA to characterize a representative volume of RCA. The reliability of the use of the oven to assess the composition of cement-based materials and the consistency with TGA was checked on homogenous material. This closely depends on heating rate and procedure.
- The results of TGA test and oven test were found to depend significantly on the initial state of the sample used as a reference for the mass loss calculation. The dry state at 200°C made possible to minimize the error due to the initial state of the sample.
- Isothermal sequences should be added especially for the critical temperatures in order to avoid or reduce overlaps between mass losses due to consecutive decompositions.
- A new method of complementarity between TGA and oven was validated on concrete of known composition and then used to characterize recycled aggregates. Using this method, the paste content of RCA and the CO₂ bound during their accelerated carbonation can be estimated, as well as some information about natural aggregates.

This study was mainly focused on the composition of RCA. Accelerated carbonation has been reported to influence the properties of RCA. The evolution of mechanical properties during

carbonation depends on the nature of the precipitated calcium carbonate polymorphs, thus multiscale approach would be necessary to investigate the influence of carbonation on macroscopic properties of carbonated RCA.

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