CO_2 uptake by accelerated carbonation of recycled concrete aggregates: quantifying bound CO_2 by a defined protocol

Thomas PERNIN[1*], Laurent CASSAYRE[2], Séverine CAMY[2], Kilesh JAUNKEYPERSAD[3], Farah KADDAH[4], Gaël CORVEC[5,6], Jena JEONG[3], Emmanuel ROZIERE[4], Philippe TURCRY[5], Ouali AMIRI[4], and Riccardo ARTONI[6]

[1]CERIB, Epernon, France, t.pernin@cerib.com (corresponding author)*
[2]LGC, CNRS/UT3/INP, Université de Toulouse, Toulouse, France, laurent.cassayre@ensiacet.fr, severine.camy@ensiacet.fr
[3]IR – Communauté Université Paris-Est, ESTP, Cachan, France, kjaunkeypersad@estp.fr, jjeong@estp.fr
[4]GeM, UMR CNRS 6183, Nantes Université, Ecole Centrale de Nantes, France, farahchloe.kaddah@ku.ac.ae, emmanuel.roziere@ec-nantes.fr, ouali.amiri@univ-nantes.fr
[5]LaSIE, UMR 7356 CNRS, La Rochelle Université, France, gael.corvec@univ-lr.fr, philippe.turcry@univ-lr.fr,
[6]MAST-GPEM, Université Gustave Eiffel, Bouguenais, France, riccardo.artoni@univ-eiffel.fr

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Abstract

The ANR CO_2NCRETE project builds upon the FastCarb initiative, which demonstrated the industrial feasibility of accelerated carbonation of recycled concrete aggregates (RCA). CO_2NCRETE aims to refine carbonation mechanisms by optimizing key parameters (temperature, water content, CO_2 pressure…) to achieve enhanced carbonation levels. In this study, RCA was carbonated in a reactor with an increased CO_2 supply under pressure, leading to higher CO_2 storage capacity. To accurately quantify bound CO_2, thermogravimetric analysis (TGA) and loss-on-ignition (LOI) were compared. While LOI ensures better sample representativity, TGA offers higher precision and efficiency. Interlaboratory results demonstrated strong consistency between both methods.

1 Introduction

Carbon dioxide (CO_2) capture, utilization and storage are essential strategies nowadays in the fight against climate change. Recent research now considers carbonation of concrete as a means of CO_2 sequestration [1]. Especially, accelerated carbonation of recycled concrete aggregates (RCA) is a promising process [2]. This approach requirerepr precise quantification of the CO_2 trapped in RCA to optimize carbonation processes and certify the associated environmental benefits. However, existing quantification methods still present certain limitations in terms of sample representativeness and measurement accuracy.

Historically, concrete carbonation has been primarily studied in the context of reinforced concrete durability, particularly due to its potential impact on rebar corrosion. Traditional evaluation tools, such as the phenolphthalein test, help monitor carbonation depth, while techniques such as thermogravimetric analysis (TGA) and X-ray diffraction (XRD) have been developed to characterize the mineral phases involved. However, these approaches do not allow for an accurate or easy quantification of the mineralized CO_2.

The ANR CO_2NCRETE project builds on previous research, particularly FastCarb [2], to enhance CO_2 sequestration in recycled concrete aggregates (RCA). While FastCarb demonstrated industrial-scale feasibility, CO_2NCRETE focuses on carbonation mechanisms at particle and bulk scales. The project aims to optimize key parameters—temperature, moisture content, and CO_2 pressure—to achieve carbonation levels exceeding 90%. Improved control over these parameters, combined with precise knowledge of concrete composition, is expected to enhance the reliability of experimental results.

This still on-going study explores the quantification of bound CO_2 in RCA through cross-method analysis, comparing thermogravimetric analysis (TGA) and loss-on-ignition (LOI) methods. The interlaboratory results pave the way for standardizing a reliable and reproducible protocol, advancing the practical implementation of CO_2 sequestration in construction materials.

The goal is to establish a protocol that enables precise and reproducible evaluation of the amount of CO_2 bound in RCA, considering factors influencing the reaction, such as granular fraction, initial natural carbonation state, and the representativity of the analyzed sample.

This paper presents the results obtained from a first interlaboratory campaign.

2 Materials and Methods

2.1 Tested materials

For this study, a reference concrete mix was established. The selected formulation was designed to be representative of conventional concrete used in construction. Consequently, an XC3/XC4-class concrete was chosen, with its detailed composition presented in Table 1.

Table 1 Concrete composition.

Materials	Dosage (kg/m^3)
CEM I 52,5 N Le Teil Lafarge	330.0
Betocarb HP	50.0
Sand 0/4 Boulonnais	822.5
Gravel 4/12 Boulonnais	927.5
Masterglenium 456	0.825
Total water	208
Efficient Water	195
W/B	0.51
Density	2380

The mix comprises CEM I 52.5 N cement, a high-performance binder, and, to approximate the characteristics of a CEM II cement, a fraction of limestone was incorporated into the binder through the addition of Betocarb HP as a supplementary cementitious material. A relative high amount of cement is used to enhance the production of portlandite in the matrix.

The aggregates, consisting of 0/4 sand and 4/12 gravel from the Boulonnais region, a high-density limestone gravel, provide a well-graded granular structure conducive to mechanical stability. A superplasticizer (MasterGlenium 456) was included to enhance workability and reach de S4 rheology class. The water-to-binder ratio (W/B) was set at 0.51. The total amount of $CaCO_3$ in the composition is 760 kg/t (76%m).

A concrete volume of 60 L was produced to cast blocks and then crushed after curing time in water of 28 days. Then these RCA were sieved to achieve a controlled particle size distribution: 0/4 sand and 4/20 gravel fractions (Figure 1).

Fig. 1 Sieving process in laboratory of the concrete aggregates

2.2 Carbonation Process: Overview of the specific accelerated carbonation method

The aggregates were subjected to carbonation through a specific process optimized to maximize CO_2 capture [3]. This treatment involved exposing the RCA to a CO_2-enriched atmosphere under controlled conditions. The carbonation process was carried out at a pressure of 100 bar with a temperature of 80°C. Drying times can vary from 0 to 48 hours to assess the impact of initial moisture content on carbonation efficiency, the results presented in this paper are set for 1 hour exposition. The atmosphere consisted of pure CO_2 (100 vol% CO_2) to ensure maximum reaction potential.

Fig. 2 Illustration of the used reactor

The demonstration reactor used for the carbonation process, illustrated in Figure 2 and detailed in Figure 3, has a capacity of 20 L.

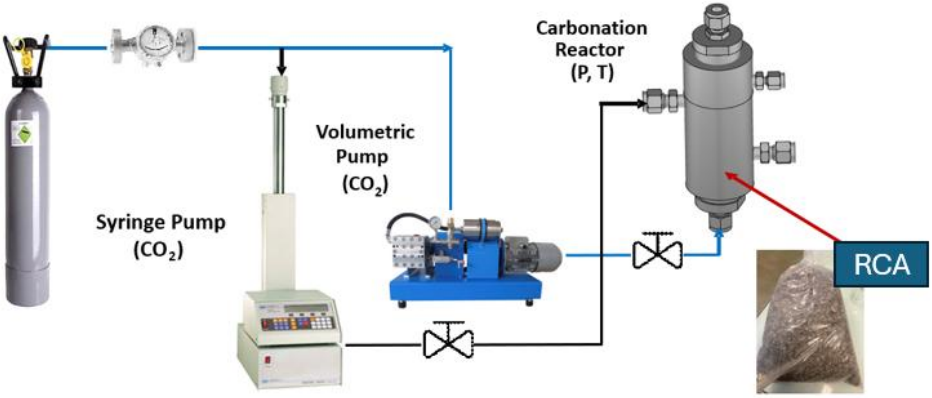

Fig. 3 Schematic presentation of the reactor

The samples are named RCA-NC before the carbonation process and RCA-C after

2.3 Cross-Method Analysis

2.3.1 Thermogravimetric and differential thermal analysis

TGA/DTA is a method used to characterize the thermal transformations of mineral phases in concrete, particularly the ones related to carbonation. TGA measures the mass variation of a small sample (100 to 200 mg) when the temperature increases at a controlled heating rate of 10°C/min under a constant nitrogen or air flow, while DTA records thermal flux variations.

Recycled concrete aggregate (RCA) samples were first dried at 80 °C for 24 hours to remove residual moisture, then cooled in a desiccator to prevent atmospheric rehydration. The material was subsequently ground using a ball mill or mortar grinder and sieved through a 200 µm mesh, ensuring uniform particle size for consistent thermal analysis. The sieved powders were stored in a sealed desiccator with a drying agent to prevent recarbonation before analysis.

The recorded variations allow to estimate the phases of the material between different temperatures. For an application to Non-carbonated and Carbonated Concrete, the mass losses between these temperatures are considered:

- 50-200 °C: Dehydration of hydrates (e.g., C-S-H).
- 450-500 °C: Decomposition of portlandite ($\Delta Ca(OH)_2$ initial mass).
- 600-900 °C: Decomposition of carbonates ($\Delta CaCO_3$ initial mass = % bound CO_2).

The mass loss between 400/450-500°C quantifies residual portlandite, while loss between 600-900 °C evaluates CO_2 capture in recycled concrete aggregates, following the equation (1) and (2).

$$\%Ca(OH)_2 = \Delta Ca(OH)_2 . \frac{M_{Ca(OH)_2}}{M_{H_2O}} \tag{1}$$

$$\%CaCO_3 = \Delta CaCO_3 . \frac{M_{CaCO_3}}{M_{CO_2}} \tag{2}$$

TGA measurements with similar conditions were carried out in 4 different labs (Lab 1 to Lab 4).

2.4 Loss-On-Ignition method, focusing on its two-step heating process (475 °C and 950 °C).

The LOI is adapted from EN-196-2:2013 (sections 4.4.1 and 5.4). This test measures mass loss of samples at controlled temperatures, adjusting specimen size to match granulometry.

The test is conducted using either a traditional furnace, where samples are periodically removed for weighing, or an instrumented furnace with an integrated balance for continuous mass measurement.

The mass of tested material, around 200 g, is higher than the one with TGA, which helps to obtain a more representative result. The heating protocol included three controlled plateaus to accurately differentiate mass losses: 415 °C plateau to removes physically bound water, a 500 °C plateau for a minimum of 4 hours, a prolonged dwell time of 4 hours ensures complete dehydration of portlandite, minimizing residual hydroxyl content and a 950 °C plateau for the decomposition of calcium carbonate.

Variability in experimental protocols can impact results, primarily due to:

- Differences in sample mass.
- Variability in granular size.
- Mass loss measurement performed either inside the furnace or after removal.
- Variations in heating and temperature-holding protocols.

3 Results and discussion

3.1 TGA results on the material

Figure 4 presents an example of the results of a DTA/TG analysis performed on concrete before carbonation obtained by one of the laboratories.

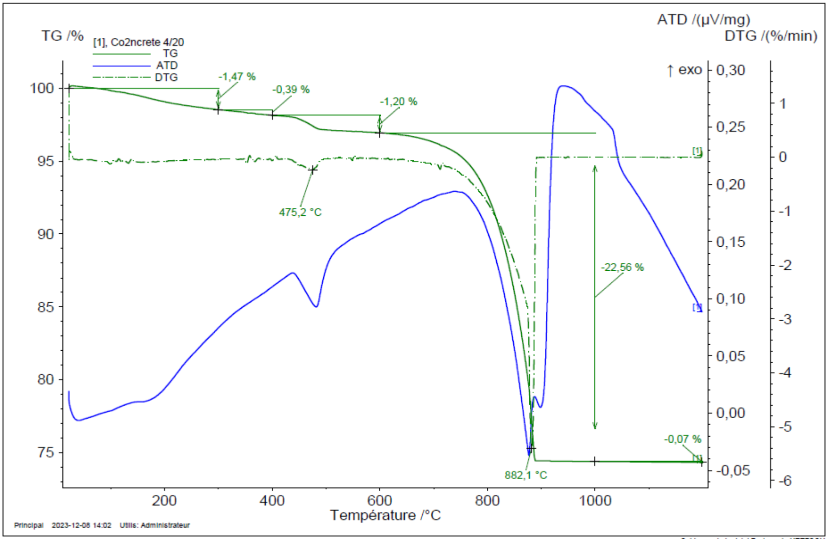

Fig. 4 DTA analysis of RCA before carbonation

The main expected thermal phases for non-carbonated concrete are clearly visible:

- Dehydration of hydrates: Between 100 and 400 °C, a small mass loss is observed, mainly corresponding to the removal of adsorbed water and the dehydration of C-S-H (calcium silicate hydrate) phases.
- Decomposition of portlandite ($Ca(OH)_2$): Around 475.2 °C, a peak is observed, corresponding to the dehydroxylation of portlandite, which is expected in non-carbonated concrete.
- Decomposition of carbonates: A significant mass loss is visible around 882.1 °C, corresponding to the decarbonation of calcium carbonate ($CaCO_3$), a typical thermal transformation of cementitious materials.

All the identified phases correspond well to the expected thermal reactions for non-carbonated concrete.

Figure 5 presents then the results of a DTA/TG analysis performed on concrete after carbonation. Some evolutions of the thermal phases for carbonated concrete are visible:

- Decomposition of portlandite ($Ca(OH)_2$): a thermal transition at 463.4 °C corresponds to the dehydroxylation of portlandite. It is noticeable that this mass loss is lower than in non-carbonated concrete, which is the result researched since carbonation reduces the amount of available portlandite.
- Decomposition of carbonates: the major mass loss around 899.9 °C corresponds to the decarbonation of calcium carbonate ($CaCO_3$). This loss is more significant than in non-carbonated concrete, further confirming the transformation of part of the portlandite into calcite due to carbonation.

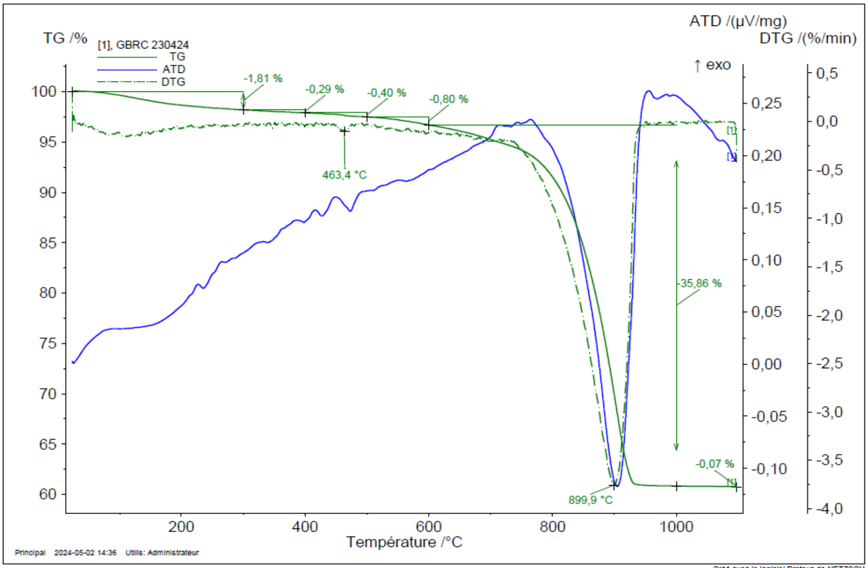

Fig. 5 DTA analysis of RCA after carbonation

These results show the relevance of performing DTA/TG analysis to observe concrete carbonation. The differences between carbonated and non-carbonated concrete are well identified, particularly through the reduction in the portlandite signature and the increase in the carbonate fraction.

However, it remains necessary to assess the accuracy and repeatability of such measurement. The study focuses then on evaluating the variability of the results across multiple samples and testing conditions to ensure the reliability of this method for systematic carbonation analysis.

3.2 Quantitative Findings

3.2.1 TGA results cross the different laboratories

The results of the tests carried in the 4 different laboratories are shown in Table 2, which highlight variability in the measurements of portlandite and $CaCO_3$ content before carbonation. Despite some discrepancies, the observed variations remain within a reasonable range, with $CaCO_3$ values fluctuating between 27.55% and 33.92% and portlandite content ranging from 5.92% to 7.40%. The associated standard deviations indicate relatively low dispersion, suggesting good reproducibility of the thermal analysis techniques (TGA) used, as illustrated in Figures 5 and 7.

These findings confirm that TGA is a generally reliable method for characterizing the mineral phases in recycled concrete aggregates before carbonation. However, the observed differences between laboratories may stem from factors such as sample preparation, experimental conditions, or intrinsic material heterogeneity.

Table 2 Results of TGA testing on non-carbonated recycled concrete aggregates (RCA-NC)

RCA-NC	ΔCa(OH)^2 (%)	%Ca(OH)^2 (%)	std %Ca(OH)^2 (%)	Δ$CaCO_3$ (%)	%$CaCO_3$ (%)	Std %$CaCO_3$ (%)
Lab1	1,46	5,92	0,75	33,92	77,08	3,91
Lab2	1,70	6,90	0,25	28,02	63,69	1,50
Lab3	1,83	7,40	0,49	27,55	62,62	0,35
Lab4	1,76	7,15	0,40	33,52	76,18	2,42
Average	1,69	6,84	0,47	30,75	69,89	2,05

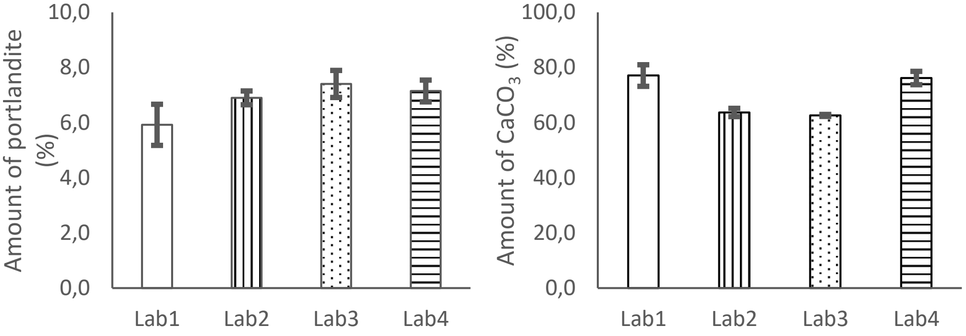

Fig. 6 and Fig. 7 Quantitative results for respectively amount of portlandite and amout of bound CO_2 (RCA-NC)

3.2.2 Results after carbonation process

The results after carbonation (RCA-C) show in Table 3 a marked decrease in the portlandite content and a significant increase in calcium carbonate (calcite) content. This confirms the efficiency of the carbonation process and the transformation of hydroxylated phases into carbonated phases.

From a methodological standpoint, these results highlight several key aspects as the effectiveness of the Carbonation Process – the near-complete disappearance of portlandite depending on the laboratory with significant increase in calcium carbonate demonstrate that the reaction has progressed, but also the interlaboratory variability – while the measured values remain close, slight differences are observed between laboratories. These variations may stem from differences in experimental conditions, as the initial drying of the sample, analytical methods, or the heterogeneous nature of the samples.

However, the relatively low dispersion of results suggests that the employed methodology is accurate, in particular for the quantification of $CaCO_3$. Optimizing analytical protocols and standardizing experimental conditions remain crucial for improving reproducibility and measurement precision.

Table 3. Results of TGA testing on carbonated recycled concrete aggregates (RCA-C)

RCA-C	$\Delta Ca(OH)^2$ (%)	$\%Ca(OH)^2$ (%)	std	$\Delta CaCO_3$ (%)	$\%CaCO_3$ (%)	std
Lab1	0.75	3.04	-	35.86	81.50	-
Lab3	0.42	1.69	0.10	35.54	80.77	1.04
LG	0.00	0.00	0.00	35.70	81.14	1.13
Average	0.39	1.58	0.05	35.70	81.13	1.09

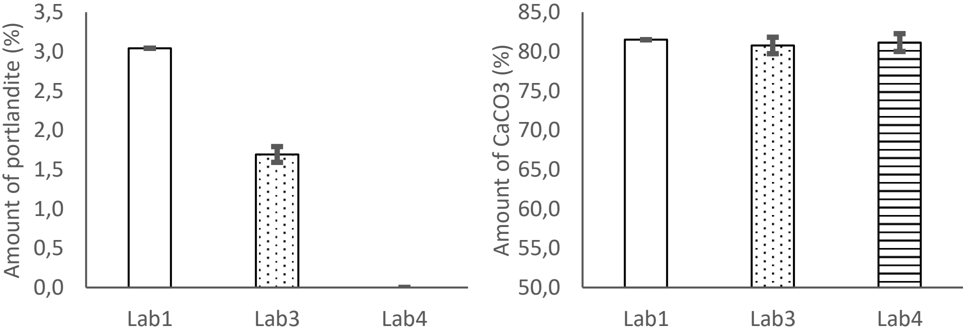

Fig. 8 and Fig. 9 Quantitative results for respectively portlandite and calcium carbonate (RCA-C)

3.3 Evaluation of carbonation and CO_2 uptake

The thermogravimetric analysis (TGA) results presented in Figure 10 indicate changes in the mineral composition of the recycled concrete aggregates before and after carbonation.

Portlandite ($Ca(OH)_2$) content: Before carbonation, the sample contained 7.03% portlandite. After carbonation, this amount decreased to 1.20%.

Calcium Carbonate ($CaCO_3$) content: Initially, the sample contained 68.08% calcium carbonate. After carbonation, this increased to 80.97%, indicating successful CO_2 mineralization. The rise in $CaCO_3$ content reflects the transformation of portlandite and potentially other cement hydrates (such as C-S-H phases) into stable carbonate phases.

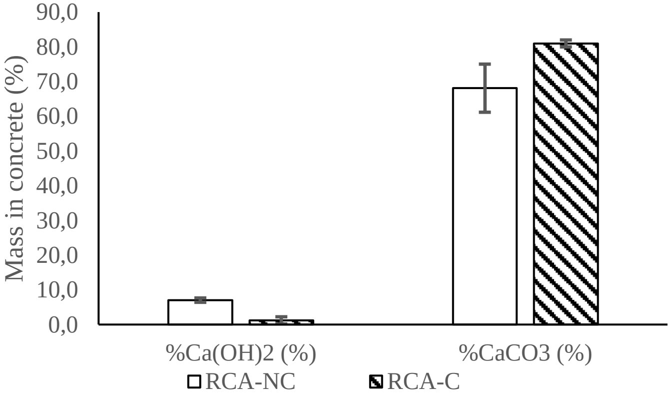

Fig. 10. Phases presence in concrete before and after carbonation process

The amount of stored CO_2 in the concrete after carbonation process is determined according to:

$$\Delta CaCO_3\,(\%)\ (\text{carbonated}) - \Delta CaCO_3\,(\%)\ (\text{initial}) = 5.67\%$$

So it can be estimated in terms of CO_2 uptake per unit mass of RCA a binding of 56.7 kg CO_2/t_{RCA} on dried material.

The estimated CO_2 uptake of 56.7 kg CO_2/t RCA obtained in this study significantly exceeds the values reported in the Fastcarb project, which reached approximately 15 kg CO_2/t_{RCA} (on the gravel) using the industrial demonstrators. This substantial increase suggests that the optimized carbonation process with the reactor employed in this study enables a more efficient CO_2 sequestration.

Additionally, an LCA analysis of the reactor process will be conducted during the project to evaluate the system's relevance and sustainability.

3.4 Consistency between portlandite consumption and calcium carbonate creation

To determine whether the increase in $CaCO_3$ content observed from TGA is consistent from a molar perspective, considering the stoichiometry of the carbonation reaction, for every mole of portlandite ($Ca(OH)_2$) consumed, one mole of calcium carbonate ($CaCO_3$) is expected to form. The molar masses of the relevant compounds are $M_{\mathrm{Ca(OH)_2}}$= 74.09 g/mol and $M_{\mathrm{CaCO_3}}$=100.09 g/mol. Thus, for each gram of $Ca(OH)_2$ reacting, approximately 1.35 g of $CaCO_3$ should be produced.

The portlandite consumption observed is 5.83%, so the expected $CaCO_3$ increase is 7.87%.

With an observed $CaCO_3$ increase of 12.89%, the increase in $CaCO_3$ exceeds the theoretical contribution from portlandite carbonation (7.87%). This suggests that additional carbonation reactions occurred, potentially involving:

- Carbonation of C-S-H (Calcium Silicate Hydrates): C-S-H phases react with CO_2 to form additional calcium carbonate, contributing to the observed excess.
- Pre-existing carbonation in the sample: Some initial carbonation may have occurred before the experiment, leading to an overestimation of the newly formed $CaCO_3$.
- Experimental uncertainties in TGA measurement: Variability in sample representativity or baseline corrections in mass loss calculations could slightly affect the quantification.

3.5 LOI results

The comparative analysis of results obtained via thermogravimetric analysis (TGA) and loss on ignition (LOI) shows in Figure 11 an overall good agreement between the two methods, with limited but noticeable discrepancies. For portlandite (%$Ca(OH)_2$), the values measured by LOI appear slightly lower than those obtained by TGA. This discrepancy may be attributed to additional mass losses during LOI analysis, particularly due to the higher temperature used in this method. Conversely, for calcite (%$CaCO_3$), the results are very similar, with LOI demonstrating slightly better reproducibility due to lower dispersion in the measured values.

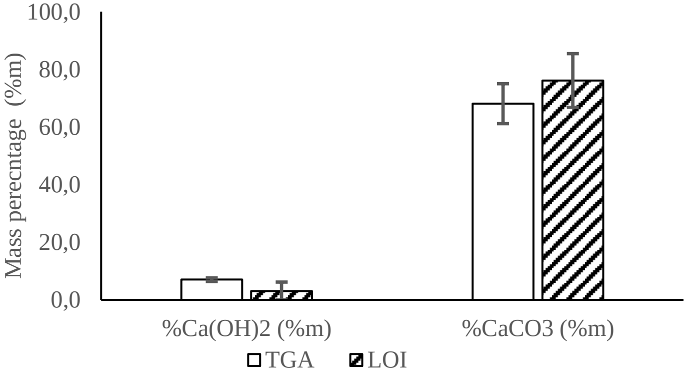

Fig. 11 LOI result on RCA-NC compared to TGA

The comparison between TGA and LOI results highlights the strengths and limitations of each method. While both techniques yield similar values for calcium carbonate content, discrepancies are observed in portlandite quantification. These differences are primarily attributed to the broader temperature intervals used in the LOI method, which limit the precision of phase identification. In LOI, the decomposition of different carbonated phases is assessed based on fixed temperature thresholds (e.g., 500°C and 950°C), potentially leading to overlapping mass losses from multiple phases and constraining interpretation. In contrast, TGA provides a continuous mass loss profile with a controlled heating rate, allowing for finer resolution in distinguishing the decomposition peaks of specific phases and enabling more precise quantification of carbonation products. This limitation in LOI interpretation may result in an underestimation of CO_2 sequestration when relying solely on this method. A combined approach using both techniques could improve the robustness of carbonation quantification by leveraging the detailed decomposition profile of TGA while benefiting from the reproducibility of LOI.

4 Conclusions

This study, conducted as part of the ANR CO_2NCRETE project, presents advancements in CO_2 sequestration via the carbonation of recycled concrete aggregates (RCA), demonstrating a marked improvement in sequestration efficiency compared to previous projects like Fastcarb by varying the carbon source and the reactor.

Pre-carbonation variability in portlandite content, ranging from 5.9% to 7.4%, was observed across interlaboratory tests, with the dispersion attributed to factors such as sample preparation, hydration differences, and instrumental sensitivity. Nevertheless, the overall consistency in calcium carbonate content suggests that the starting materials were relatively controlled.

Post-carbonation, a substantial reduction in portlandite was observed, with an increase in calcium carbonate formation. However, challenges arose due to the increased variability in portlandite content, likely caused by difficulties in detecting small residual quantities and interference from metastable calcium carbonate phases such as vaterite. These factors complicate the precise quantification of carbonation phases, which could lead to an underestimation of CO_2 sequestration if not carefully considered. Molar balance analysis reveals that, in addition to the transformation of portlandite, carbonation extended to other hydration products, notably calcium silicate hydrates (C-S-H). The significant carbonation of hydrates beyond portlandite (CH), aligns with findings from the existing literature, confirming that these phases actively contribute to CO_2 sequestration and enhance the overall carbonation potential of recycled concrete aggregates. However, distinguishing the contributions of various cementitious phases requires refined analytical techniques to ensure accurate quantification.

The CO_2 uptake of globally 55 kg CO_2/t_{RCA} achieved in this study substantially go further than the values reported by the Fastcarb project for the coarse fraction, indicating the enhanced efficiency of the optimized carbonation process employed in this work. Further analysis of the reactor process via an ACV study will assess the relevance and sustainability of the system within a broader environmental context.

Finally, the comparison between TGA and LOI methods highlights their complementary roles in carbonation analysis. While TGA provides detailed decomposition profiles and allows for more precise phase differentiation, LOI, with its broader temperature steps, tends to constrain interpretation, particularly in quantifying portlandite. This discrepancy may lead to an underestimation of CO_2 sequestration when relying solely on LOI. A combined approach utilizing both techniques could enhance the robustness and reliability of carbonation quantification, offering a more comprehensive view of the sequestration process.

The study is ongoing, with further results expected from a new concrete formulation with lower calcite content. This second phase will allow for a more refined analysis under standardized protocols, ultimately contributing to the development of a reliable protocol by the end of the project.

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