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ORIGINAL

Carbonate quantification in co_2 removal technologies through lime carbonation: experimental comparison of analytical techniques

Cuantificación de carbonato en tecnologías de remoción de CO_2 mediante carbonatación de cal: comparación experimental de técnicas analíticas

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ABSTRACT

The increase in anthropogenic carbon dioxide emissions has driven the development of carbon removal technologies capable of reducing atmospheric CO_2 concentrations and contributing to global climate targets. Among these alternatives, direct air capture through lime carbonation represents a promising approach due to its ability to transform atmospheric CO_2 into stable calcium carbonate through chemical reactions with alkaline materials. In this context, the accurate quantification of carbonate content constitutes a fundamental element for monitoring, reporting, and verification processes associated with carbon capture and storage systems. The objective of this research was to comparatively evaluate different analytical techniques for determining calcium carbonate content in materials representative of lime carbonation DAC systems. A quantitative experimental approach was applied using synthetic samples composed of different proportions of $Ca(OH)_2$ and $CaCO_3$. The evaluated techniques included volumetric calcimetry, thermogravimetric analysis, Fourier transform infrared spectroscopy, and combustion with infrared detection. The results showed that thermogravimetric analysis and infrared combustion presented higher precision and reproducibility, while FTIR and calcimetry demonstrated advantages related to rapid analysis and lower operational costs. Furthermore, the study identified that mineralogical composition significantly influences the accuracy of analytical measurements. This research provides relevant information for the development of standardized protocols applicable to monitoring and verification systems in carbon dioxide removal technologies.

Keywords: direct air capture, lime carbonation, carbonate quantification, carbon dioxide removal

RESUMEN

El aumento de las emisiones antropogénicas de dióxido de carbono ha impulsado el desarrollo de tecnologías de remoción de carbono capaces de reducir la concentración de CO_2 atmosférico y contribuir al cumplimiento de los objetivos climáticos globales. Entre estas alternativas, la captura directa de aire mediante carbonatación de cal representa una opción prometedora debido a su capacidad para transformar CO_2 atmosférico en carbonato de calcio estable mediante reacciones químicas con materiales alcalinos. En este contexto, la cuantificación precisa del contenido de carbonato constituye un elemento fundamental para el monitoreo, reporte y verificación de los procesos de captura y almacenamiento de carbono. La presente investigación tuvo como objetivo evaluar comparativamente distintas técnicas analíticas para la determinación de carbonato de calcio en materiales representativos de sistemas lime carbonation DAC. Se aplicó un enfoque cuantitativo experimental utilizando muestras sintéticas compuestas por diferentes proporciones de $Ca(OH)_2$ y $CaCO_3$. Las técnicas evaluadas incluyeron calcimetría volumétrica, análisis termogravimétrico, espectroscopía infrarroja por transformada de Fourier y combustión con detección infrarroja. Los resultados evidenciaron que el análisis termogravimétrico y la combustión infrarroja presentaron mayor precisión y reproducibilidad, mientras que FTIR y calcimetría mostraron ventajas relacionadas con rapidez y menor costo operativo. Asimismo, se identificó que la composición mineralógica influye significativamente en la exactitud de las mediciones analíticas. El estudio aporta información relevante para el desarrollo de protocolos estandarizados aplicables a sistemas de monitoreo y verificación en tecnologías de remoción de dióxido de carbono.

Palabras clave: captura directa de aire, carbonatación de cal, cuantificación de carbonato, remoción de dióxido de carbono

INTRODUCTION

The sustained increase in anthropogenic carbon dioxide (CO_2) emissions is one of the main factors contributing to global warming and the intensification of climate change on a planetary scale. The progressive accumulation of this gas in the atmosphere has driven the need to develop strategies that complement emission reduction, as current climate scenarios indicate that conventional mitigation measures will not be sufficient to achieve international climate neutrality targets. In this context, Carbon Dioxide Removal (CDR) technologies have gained strategic importance by enabling the extraction of atmospheric CO_2 and its permanent storage through biological, chemical, or geological mechanisms (Hepburn et al., 2019; Sanz-Pérez et al., 2016).

Among the various carbon removal alternatives, Direct Air Capture (DAC) is considered one of the most promising emerging technologies due to its ability to capture CO_2 directly from the atmosphere, independent of emission source locations. Unlike conventional capture systems associated with industrial processes, DAC technologies enable intervention in already distributed atmospheric carbon, generating concentrated CO_2 streams suitable for geological storage or subsequent utilization. However, large-scale implementation continues to face challenges related to energy consumption, operational costs, industrial scalability, and precise validation of the amount of carbon removed (Keith et al., 2018; McQueen et al., 2021; Erans et al., 2022).

Among the different technological configurations of DAC, processes based on alkaline mineralization have received increasing attention due to the chemical stability of the stored carbon. In particular, direct air capture via carbonation of alkaline oxides (Oxide Looping Direct Air Capture, OxL-DAC) employs calcium- or magnesium-rich materials capable of reacting with atmospheric CO_2 to form stable mineral carbonates. This mechanism replicates natural accelerated weathering processes, where alkaline minerals react with carbon dioxide to produce carbonate compounds that can remain stored over geological timescales (Gadikota et al., 2014; Kelemen et al., 2011; Sanna et al., 2014).

$$CaO + CO_2 \rightarrow CaCO_3$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Subsequently, through thermal regeneration processes, the formed carbonate can be decomposed to release concentrated CO_2 and recover the initial alkaline material, enabling the establishment of closed cycles of capture and regeneration. Calcium carbonation processes have been widely investigated due to their high theoretical capture capacity, stability of the mineralized product, and potential compatibility with existing industrial infrastructures (Fernández et al., 2012; Pan et al., 2015).

Nevertheless, the efficiency of these systems depends on factors such as reaction kinetics, ambient humidity, material surface area, CO_2 diffusion, and the degree of conversion of the alkaline sorbent. Previous research has shown that calcium-based materials may exhibit limitations associated with decreased reactivity during successive carbonation and regeneration cycles, mainly due to sintering phenomena and reduction of the reactive surface area. Therefore, it is essential to adequately characterize the chemical evolution of the material during the different stages of the DAC process (Fernández et al., 2012; Sanna et al., 2014).

A critical aspect for the commercial implementation of carbon removal technologies is the development of reliable Monitoring, Reporting, and Verification (MRV) systems. These mechanisms enable the precise determination of the amount of CO_2 effectively captured, stored, and attributed to a given technology, constituting an essential requirement for scientific validation, environmental regulation, and the future commercialization of carbon credits. In this regard, the exact quantification of carbonate generated during mineralization processes represents a fundamental parameter for establishing reliable carbon balances and ensuring process traceability (Deutz & Bardow, 2021; Erans et al., 2022).

The determination of carbonate content in alkaline materials can be performed using various analytical techniques, including volumetric calcimetry, thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), and combustion-based methods with infrared detection. Calcimetry is a widely used method to quantify carbonates by measuring the CO_2 released during an acid-carbonate reaction; however, it may present limitations related to gas losses and lower sensitivity in samples with low carbonate content.

In contrast, thermogravimetric analysis allows differentiation of dehydroxylation and thermal decomposition processes, providing simultaneous information on the presence of $Ca(OH)_2$ and $CaCO_3$ (Liu et al., 2018; Sanna et al., 2014).

FTIR spectroscopy has also been applied to identify functional groups associated with carbonate minerals through characteristic infrared absorption bands. This technique offers advantages such as speed, low sample consumption, and the possibility of non-destructive analysis; however, the simultaneous presence of different mineral phases may generate spectral interferences that affect quantitative precision. Additionally, combustion-based methods with infrared detection offer high sensitivity for determining total carbon, although they generally require specialized equipment and higher operational costs (Shi et al., 2020; Liu et al., 2018).

Despite significant advances in DAC technologies and CO_2 mineralization, there remains limited standardization of analytical procedures specifically designed for materials derived from lime carbonation processes. Many traditional methods were developed for natural matrices such as soils, sediments, or minerals with different compositions, and their performance may vary when applied to systems highly concentrated in $Ca(OH)_2$ and $CaCO_3$. This situation underscores the need for experimental comparison of different analytical methodologies under conditions representative of OxL-DAC technologies.

In this context, the present research aimed to comparatively evaluate different carbonate quantification techniques applied to the monitoring of direct air capture processes via lime carbonation. Parameters such as analytical precision, accuracy, reproducibility, operational cost, and suitability for integration into MRV systems were analyzed. The results obtained are intended to contribute to the establishment of more robust methodological procedures for the validation and scaling of advanced atmospheric carbon dioxide removal technologies through alkaline mineralization.

METHODS

Research Design

This research was conducted using a quantitative, experimental, and comparative approach to evaluate the performance of different analytical techniques for quantifying calcium carbonate ($CaCO_3$) generated during direct air capture processes via lime carbonation (lime-DAC). The study was motivated by the need to establish reliable analytical methodologies for Monitoring, Reporting, and Verification (MRV) systems, considering that precision in the quantification of mineralized carbon is essential for validating atmospheric CO_2 removal technologies (Deutz & Bardow, 2021; Erans et al., 2022).

The experimental design involved the comparison of four chemical and physicochemical analysis techniques: volumetric calcimetry, thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), and combustion with infrared detection. These methodologies were selected due to their previous application in the characterization of carbonated materials, CO_2 mineralization processes, and evaluation of alkaline materials used in carbon capture and storage technologies (Gadikota et al., 2014; Sanna et al., 2014).

Preparation and Characterization of Experimental Samples

To represent different stages of chemical conversion within a lime-DAC system, synthetic samples composed of controlled mixtures of calcium hydroxide [$Ca(OH)_2$] and calcium carbonate ($CaCO_3$) were prepared. The selection of these compounds was based on the characteristic chemical reaction of capture processes via alkaline carbonation:

The samples were prepared using analytical grade reagents and mechanically mixed until a homogeneous distribution of the components was achieved. Five levels of theoretical carbonation were established to represent progressive states of conversion of the alkaline sorbent:

Code	$Ca(OH)_2$ (%)	$CaCO_3$ (%)	Simulated process state
M1	90	10	Initial carbonation
M2	75	25	Low conversion
M3	50	50	Intermediate conversion
M4	25	75	High conversion
M5	10	90	Advanced carbonation

Subsequently, the samples were stored in airtight containers under controlled temperature and humidity conditions to prevent chemical modifications due to additional atmospheric exposure. This procedure ensured that the differences observed during the analyses were attributable exclusively to the performance of the evaluated techniques.

Analytical Techniques Evaluated

Volumetric Calcimetry

Quantification by calcimetry was performed using the acid-carbonate reaction principle, in which the $CaCO_3$ present in the sample reacts with hydrochloric acid, releasing gaseous carbon dioxide:

The volume of CO_2 released was used to indirectly calculate the carbonate content present in each sample through stoichiometric relationships. The procedure was based on standardized methodologies for the determination of mineral carbonates, considering the relationship between the mass of $CaCO_3$ and the volume of gas generated (Sanna et al., 2014).

The parameters evaluated were:

- percentage of $CaCO_3$ determined;
- relative error with respect to the theoretical value;
- time required per analysis;
- reproducibility between measurements.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was applied to determine mass variations associated with the thermal transformations of calcium hydroxide and calcium carbonate. The samples were subjected to a controlled heating program under a defined atmosphere, with continuous recording of mass loss as a function of temperature.

This process allowed the identification of two main regions:

- dehydroxylation of $Ca(OH)_2$, associated with the release of water;
- decomposition of $CaCO_3$, related to the release of CO_2.

The amount of carbonate was estimated from the mass loss corresponding to the thermal decomposition of $CaCO_3$, following procedures used in studies of mineralization and capture via calcium looping (Fernández et al., 2012; Pan et al., 2015).

The indicators analyzed were:

- percentage of $CaCO_3$ obtained;
- standard deviation;
- coefficient of variation;
- method precision.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR characterization was conducted to identify vibrational bands associated with carbonate (CO_3^{2-}) and hydroxyl (OH^-) groups. Spectra were acquired within the infrared range corresponding to the characteristic regions of calcium carbonate.

Relative quantification of $CaCO_3$ was performed by comparative analysis of spectral band intensities, considering the ratio between signals associated with carbonate and calcium hydroxide.

The parameters considered were:

- relative intensity of carbonate bands;
- correlation with theoretical $CaCO_3$ content;

- relative error;
- ability to differentiate between mineral phases.

This technique was included due to its potential application as a rapid evaluation method in operational monitoring systems for DAC technologies (Shi et al., 2020).

Combustion with infrared detection

The combustion method with infrared absorption was used to determine the total carbon content in the samples. During analysis, the material was subjected to high-temperature combustion, generating CO_2, the concentration of which was quantified using infrared sensors.

The measured carbon content was subsequently converted to an equivalent $CaCO_3$ concentration using established chemical relationships.

The parameters evaluated were:

- total carbon measured;
- recovery percentage;
- analytical precision;
- processing time.

This methodology was considered as a reference due to its high sensitivity for total carbon analysis in mineral materials and industrial solids (Liu et al., 2018).

Experimental procedure

Each sample was analyzed using the four selected techniques. To ensure statistical reliability, each measurement was performed in three independent replicates, and an average value was obtained for each experimental condition.

During the experimental procedure, the following variables were controlled:

- initial composition of the samples;
- mass used for each analysis;
- temperature and humidity conditions;
- instrument calibration;
- analysis time;
- experimental repeatability.

The performance of each methodology was determined by comparing the experimental value obtained with the theoretical $CaCO_3$ content established during sample preparation.

Evaluation of analytical performance

To compare the methodologies, the following indicators were calculated:

Relative error (%)

$$Error = \frac{|\ Experimental\ value - Theoretical\ value\ |}{Theoretical\ value} \times 100$$

Analytical precision

Evaluated by the standard deviation and coefficient of variation among replicates.

Reproducibility

Determined by the variability of results obtained under equivalent experimental conditions.

Operational efficiency

Considering:

- time required per sample;
- instrumental complexity;
- approximate analysis cost;
- possibility of implementation in MRV systems.

Statistical analysis

The experimental data were processed using descriptive and inferential statistics. Measures of central tendency and dispersion were calculated, including arithmetic mean, standard deviation, and coefficient of variation.

Subsequently, a multicriteria comparison of the techniques was performed using the parameters of precision, accuracy, operational cost, and applicability for MRV systems. The results were organized in comparative tables to identify the methodology with the greatest potential for implementation in monitoring processes for direct air capture via lime carbonation.

Applicability criteria for MRV systems

Finally, each technique was evaluated considering the monitoring, reporting, and verification requirements associated with CDR technologies. The selection of the most suitable method considered not only analytical precision, but also its ability to provide repeatable, scalable measurements compatible with standardized procedures for quantification of removed CO_2.

This methodological approach enabled a comprehensive comparison of analytical techniques and the development of technical criteria for future industrial applications of lime-DAC technologies aimed at the permanent removal of atmospheric carbon dioxide.

RESULTS

The results obtained enabled a comparative evaluation of the performance of four analytical techniques applied to the quantification of calcium carbonate ($CaCO_3$) in representative materials from direct air capture processes via lime carbonation (lime carbonation Direct Air Capture, lime-DAC). The experimental evaluation was conducted across five controlled carbonation levels, allowing for analysis of each methodology's response to progressive variations in the conversion of calcium hydroxide [$Ca(OH)_2$] to calcium carbonate.

In general, the evaluated techniques exhibited an increasing trend in precision as the proportion of $CaCO_3$ in the samples increased. This behavior indicates that the chemical matrix of the material directly influenced the detection capability of each method, especially in samples with low carbonation levels where $Ca(OH)_2$ predominated. The results enabled the identification of differences associated with analytical sensitivity, measurement stability, processing time, and potential for integration into monitoring, reporting, and verification (MRV) systems.

Experimental characterization of synthetic samples

The first stage of the analysis involved verifying the initial composition of the samples prepared to represent different conversion states within the lime carbonation process. Table 1 presents the compositional distribution of the samples used and the expected values of mineralized CO_2 capture.

Table 1. Compositional characterization of the samples used to evaluate $CaCO_3$ quantification techniques

Sample code	Initial $Ca(OH)_2$ (%)	Generated $CaCO_3$ (%)	Theoretical sorbent conversion (%)	Equivalent mineralized CO_2 (g CO_2/100 g sample)	Stage represented in lime-DAC
M1	90	10	11,1	4,4	Onset of carbonation
M2	75	25	27,8	11,0	Low conversion
M3	50	50	55,6	22,0	Intermediate conversion
M4	25	75	83,3	33,0	Advanced conversion
M5	10	90	100,0	39,6	Maximum carbonation

The results demonstrated an adequate progressive representation of the mineralization process, where the decrease in $Ca(OH)_2$ was directly associated with the increase in formed $CaCO_3$. This distribution enabled evaluation of the analytical methodologies' performance under conditions similar to those observed during the initial and advanced stages of CO_2 capture using calcium-based materials.

Comparative evaluation of analytical precision

Experimental quantification revealed significant differences among the evaluated techniques. Calcimetry showed adequate performance in samples with $CaCO_3$ contents above 50%, but exhibited greater deviations under low carbonation conditions. In contrast, thermogravimetric analysis demonstrated the lowest experimental variability due to its ability to differentiate the thermal stages associated with $Ca(OH)_2$ and $CaCO_3$.

Table 2 shows that the TGA technique and combustion with infrared detection presented the lowest error values, with deviations below 1% in highly carbonated samples. In contrast, FTIR exhibited greater variations in samples with low conversion due to spectral signal overlap between alkaline mineral phases.

Operational evaluation and applicability for MRV systems

Table 2. Comparison of the quantitative performance of analytical techniques in the determination of $CaCO_3$

Analytical technique	Sample evaluated	Theoretical $CaCO_3$ (%)	Experimental $CaCO_3$ (%)	Relative error (%)	Coefficient of variation (%)	Analytical interpretation
Calcimetry	M1	10	9,2	8,0	4,6	Lower sensitivity at low carbonation
Calcimetry	M5	90	89,1	1,0	1,2	High reliability in enriched matrices
TGA	M1	10	10,4	4,0	0,8	High thermal stability
TGA	M5	90	89,7	0,3	0,4	Greater overall precision
FTIR	M1	10	11,3	13,0	5,1	Interference between $CaCO_3$/ $Ca(OH)_2$ signals
FTIR	M5	90	88,5	1,7	1,5	Good performance at high conversion
Infrared combustion	M1	10	10,1	1,0	0,7	High sensitivity for total carbon
Infrared combustion	M5	90	89,8	0,2	0,3	Maximum experimental accuracy

In addition to analytical performance, variables related to the practical implementation of each technique within monitoring systems for carbon removal technologies were evaluated. Parameters such as analysis time, relative cost, instrumental complexity, and potential for automation were considered.

The results of the multicriteria evaluation indicated that infrared combustion exhibited the best performance in terms of accuracy and processing speed, while TGA was notable for providing more comprehensive compositional information by enabling differentiation of the material's thermal transformations. Both methodologies showed greater potential for incorporation into MRV protocols aimed at quantifying CO_2 removed through mineralization.

Global analysis of experimental performance

Table 3. Multicriteria evaluation of analytical techniques for integration into MRV systems of lime-DAC

Technique	Average precision (%)	Approximate time per sample	Relative operating cost	Potential for automation	MRV capability	Main advantage	Identified limitation
Volumetric calcimetry	94,8	20–30 min	Low	Medium	Medium	Low cost and easy implementation	Lower sensitivity at low conversion
TGA	98,7	40–60 min	Medium-high	High	Very high	Simultaneous differentiation of $Ca(OH)_2$/$CaCO_3$	Higher instrumental requirement
FTIR	95,6	5–15 min	Medium	High	High	Rapid and non-destructive analysis	Spectral interferences
Infrared combustion	99,1	3–10 min	High	Very high	Very high	High sensitivity and reproducibility	Higher initial investment

The integrated comparison established that the selection of an analytical technique depends on the specific objective of the monitoring. For research applications requiring detailed characterization of the carbonation process, TGA represents a robust alternative due to its ability to simultaneously identify chemical phases present in the sample. Conversely, for industrial scenarios requiring rapid processing and continuous data generation, infrared combustion offers advantages associated with its high sensitivity and reproducibility.

Calcimetry proved to be an adequate methodology for routine low-cost assessments, although its application in advanced MRV systems could be limited by the lower precision observed in the initial stages of carbonation. Regarding FTIR, the results confirmed its usefulness as a rapid diagnostic tool, especially when combined with complementary techniques of higher accuracy.

Taken together, the experimental results demonstrated that lime-DAC systems require combined analytical strategies to ensure reliable quantification of mineralized carbon. The integration of high-precision techniques such as TGA or infrared combustion with rapid methods like FTIR could strengthen MRV protocols and improve the traceability of emerging atmospheric CO_2 removal technologies.

DISCUSSION

The results obtained demonstrate that the selection of an appropriate analytical technique is a critical factor in ensuring the reliability of monitoring, reporting, and verification (MRV) systems associated with lime carbonation Direct Air Capture (lime-DAC) technologies. The experimental comparison showed that the evaluated methodologies exhibit different behaviors depending on the degree of conversion of $Ca(OH)_2$ to $CaCO_3$, confirming that the chemical characteristics of the analyzed matrix directly influence quantification accuracy. These results are consistent with previous studies on CO_2 mineralization, which have noted that the heterogeneity of the alkaline material and the evolution of mineral phases represent significant challenges for the quantitative validation of carbon removal processes (Gadikota et al., 2014; Sanna et al., 2014).

Volumetric calcimetry showed acceptable performance in samples with medium and high carbonate concentrations, achieving errors below 2% when the proportion of $CaCO_3$ was high. However, its lower precision in samples with low carbonation reveals a limitation related to the method's sensitivity to small amounts of CO_2 released during the acid-carbonate reaction. This behavior has been reported in research on the characterization of carbonate minerals, where it is indicated that volumetric methods may present uncertainties associated with gas losses, reaction efficiency, and experimental control. Despite these limitations, calcimetry remains relevant due to its low operational cost and ease of implementation in laboratories with limited infrastructure (Liu et al., 2018; Sanna et al., 2014).

Thermogravimetric analysis (TGA) exhibited the most stable performance among the techniques evaluated, showing low experimental deviations and high reproducibility across the entire range of concentrations analyzed. This result is related to the method's ability to identify specific thermal events associated with the dehydroxylation of $Ca(OH)_2$ and the decomposition of $CaCO_3$, allowing for more precise differentiation between the chemical phases present. Studies on calcium carbonation cycles have demonstrated that thermal characterization is a fundamental tool for evaluating sorbent conversion and understanding phenomena related to loss of reactivity, sintering, and material stability during repetitive capture and regeneration processes (Fernández et al., 2012; Pan et al., 2015).

The results obtained by TGA are particularly important in the context of lime-DAC technologies, as these systems require precise knowledge of the amount of alkaline material transformed into carbonate during atmospheric CO_2 capture. Accurate quantification of the degree of carbonation enables the establishment of reliable mass balances and determination of the actual efficiency of the removal process. In this regard, the high precision observed in this research supports the use of thermogravimetric analysis as a reference methodology for advanced characterization of materials used in carbon mineralization processes (Fernández et al., 2012; Deutz & Bardow, 2021).

Regarding Fourier-transform infrared spectroscopy (FTIR), the results indicated that this technique offers important advantages related to speed, low sample consumption, and non-destructive analysis capability. However, the decrease in precision observed in samples with low carbonation levels demonstrates that quantitative interpretation may be affected by interferences between the signals corresponding to $CaCO_3$ and $Ca(OH)_2$.

Previous research has highlighted that FTIR is an efficient tool for identifying mineral phases and functional groups associated with carbonates, although its quantitative application requires specific calibrations for each chemical matrix analyzed (Shi et al., 2020; Liu et al., 2018).

Combustion with infrared detection showed the highest overall accuracy in the study, exhibiting a high correlation between the measured carbon and the established theoretical values. This result is explained by the method's ability to directly determine the total carbon content through the complete conversion of the material into detectable CO_2. From the MRV systems perspective, this characteristic represents a significant advantage, as it enables rapid and reproducible measurements necessary for the certification of tons of CO_2 removed. Nevertheless, the main challenge identified corresponds to the cost associated with the equipment and operational requirements, which may limit its adoption in small facilities or pilot projects with budgetary constraints (McQueen et al., 2021; Erans et al., 2022).

The comprehensive comparison of the techniques demonstrated that there is no single method capable of meeting all the requirements associated with monitoring lime-DAC technologies. While TGA provides detailed information on the mineralogical transformation of the material, infrared combustion offers superior advantages in speed and sensitivity. FTIR can serve as a complementary tool for rapid assessment, and calcimetry can be used as an economical alternative for routine controls. This complementarity is consistent with research on CDR technologies, which emphasizes that validation systems require the combination of different analytical strategies to reduce uncertainties and increase the reliability of carbon balances (Hepburn et al., 2019; McQueen et al., 2021).

A relevant aspect identified in this study was the influence of the degree of carbonation on the analytical performance of the methodologies. Samples with higher $CaCO_3$ concentrations exhibited lower experimental variability, whereas those dominated by $Ca(OH)_2$ showed greater differences between techniques. This behavior confirms that the materials used in DAC systems possess characteristics distinct from the natural matrices traditionally evaluated by carbonate quantification methods. Therefore, it is necessary to develop standardized procedures specific to alkaline materials subjected to accelerated CO_2 capture and mineralization processes (Gadikota et al., 2014; Sanna et al., 2014).

From an industrial implementation perspective, the results obtained have important implications for the development of MRV protocols for carbon removal technologies. Accurate measurement of the generated $CaCO_3$ not only enables assessment of the capture process performance but also establishes reliable mechanisms for accounting for the stored carbon. This is fundamental for the future integration of DAC technologies into carbon markets, where independent validation of the amount of CO_2 removed is an essential requirement to ensure environmental transparency and credibility (Deutz & Bardow, 2021; Hepburn et al., 2019).

Finally, the findings of this research suggest that a combined strategy based on TGA and infrared combustion could provide the most suitable balance between scientific accuracy and operational applicability for lime-DAC systems. The incorporation of rapid techniques such as FTIR or cost-effective methodologies such as calcimetry would complement the main analyses and facilitate continuous monitoring schemes. Consequently, the standardization of analytical procedures adapted to lime carbonation processes represents a fundamental step to accelerate technological validation and industrial implementation of advanced solutions for permanent atmospheric carbon dioxide removal.

CONCLUSIONS

This research enabled a comparative evaluation of different analytical techniques applied to the quantification of calcium carbonate ($CaCO_3$) in representative materials from direct air capture processes via lime carbonation (lime carbonation Direct Air Capture, lime-DAC). The results demonstrated that the performance of each methodology depends directly on the chemical composition of the samples, the degree of conversion of calcium hydroxide [$Ca(OH)_2$], and the specific requirements associated with monitoring, reporting, and verification (MRV) systems for carbon dioxide removal technologies.

Thermogravimetric analysis (TGA) and combustion with infrared detection showed the best overall results due to their high precision, reproducibility, and ability to identify compositional variations with low experimental uncertainty.

The TGA technique was notable for its capacity to differentiate the thermal stages associated with $Ca(OH)_2$ and $CaCO_3$, providing detailed information on the evolution of the carbonation process, while infrared combustion demonstrated advantages related to sensitivity and speed of analysis for determining the total carbon present in the samples.

Volumetric calcimetry proved to be a viable alternative for low-cost and routine control applications, especially in materials with high carbonate content. However, its greater deviations in samples with low conversion revealed limitations for applications requiring high accuracy in the early stages of the DAC process. Similarly, FTIR spectroscopy presented advantages related to speed, low sample consumption, and non-destructive analysis, although its quantitative precision was affected by spectral interferences between mineral phases present in matrices dominated by $Ca(OH)_2$.

The results confirmed that analytical characterization of materials from lime-DAC systems requires methodologies adapted to their particular characteristics, since traditional protocols developed for soils, sediments, or natural minerals do not necessarily guarantee the same level of reliability in highly alkaline and carbonate-enriched materials. This condition highlights the importance of establishing standardized procedures specific to accelerated CO_2 mineralization technologies.

From the monitoring, reporting, and verification perspective, the research showed that the selection of analytical techniques must consider not only measurement accuracy but also factors related to operational costs, processing speed, automation, and industrial scalability. In this regard, the combination of high-precision techniques such as TGA and infrared combustion with complementary methods such as FTIR or calcimetry may constitute an appropriate strategy to strengthen the traceability and reliability of MRV systems applied to direct air capture technologies.

In general, the study provides experimental evidence for the selection of analytical methodologies aimed at validating lime carbonation processes as a technological alternative for the permanent removal of atmospheric carbon dioxide. The implementation of robust quantification protocols will improve the performance evaluation of lime-DAC systems, facilitate their integration into carbon certification schemes, and contribute to the development of scalable solutions to address the global challenge of climate change.

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CONFLICT OF INTEREST

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