Comparison of Methods for Quantifying the Carbon Content of Carbonated Wood Ash

Johanna Eichermüller*, Kilian Handke, Andreas Kappler and Harald Thorwarth

DOI: 10.1002/cite.70015

To assess mineral carbonation as a negative emission technology, the reliable quantification of the sequestered carbon is crucial. This study evaluates four methods for quantifying carbon sequestration by wood ash, through analyses of ash samples before and after lab-scale carbonation, and compares the results to the theoretical storage potential determined using the Steinour equation. Results show that CHN elemental analysis and total carbon quantification provided consistent values for total carbon content and for the amount of CO_2 sequestered. Inorganic carbon was effectively quantified using both total/inorganic carbon analysis (TC/IC) analysis and volumetric calcimetry. The findings highlight the importance of selecting analytical methods and demonstrate that oversimplified thermogravimetric analysis (TGA) can lead to misinterpretation of sequestration results.

Keywords: Carbon analysis, Carbonated wood ash, CO_2 sequestration

Received: February 03, 2025; *revised:* July 10, 2025; *accepted:* July 25, 2025

1 Introduction

Limiting man-made global warming to 1.5–2.0 °C requires net-zero emissions [1]. Since not all GHG emissions are avoidable, to achieve net zero the same amount of CO_2 must be removed from the atmosphere as is produced in the form of unavoidable residual emissions [2]. For this purpose, several carbon capture and storage (CCS) technologies are available.

Mineral carbonation is a process where CO_2 reacts with minerals that contain alkali and alkaline earth elements (especially Ca or Mg) to form stable carbonates [3–5]. The process is differentiated into natural carbonation, which occurs under natural conditions, and accelerated carbonation, i.e., a man-made process [6]. Unlike CCS pathways which involve underground storage of gaseous or liquified CO_2, mineral carbonation is a method in which CO_2 is disposed off in solid form which is considered as permanent and inherently safe [7, 8]. While CO_2 mineralization can also occur in-situ by injecting CO_2 into reactive rocks [9], there is a considerable amount of research investigating the accelerated carbonation of mineral materials in technical applications. Influencing factors on mineral carbonation such as the particle size of the mineral material and operating parameters (temperature, pressure, time, liquid/solid ratio) have been investigated in several studies [10–15].

During carbonation, various reactions take place leading to the formation of carbonates and bicarbonates (Eqs. (1)–(8)). The reaction takes place in two stages. First, the (earth) alkali oxide is converted into a hydroxide by reacting with water. This then allows the hydroxide to react with carbon dioxide. Both reactions are exothermic and exergonic ($\Delta G < 0$), this means they start spontaneously as soon as the corresponding reaction partners are available [16, 17].

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (1)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (2)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (3)$$

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O \quad (4)$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \quad (5)$$

$$K_2CO_3 + H_2O + CO_2 \rightarrow 2KHCO_3 \quad (6)$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \quad (7)$$

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3 \quad (8)$$

In addition to natural minerals, alkaline waste materials are suitable feed materials for carbonation [18]. Incineration residues are a particulary interesting source material,

[1]Johanna Eichermüller (eichermueller@hs-rottenburg.de),
[1]Kilian Handke, [2]Prof. Dr. Andreas Kappler,
[1]Prof. Dr.-Ing. Harald Thorwarth
[1]University of Applied Forest Sciences Rottenburg, Schadenweilerhof, 72108 Rottenburg am Neckar, Germany.
[2]University of Tübingen, Schnarrenbergstr. 94–96, 72076 Tübingen, Germany.

Table 1. Recent studies on determination of sequestered carbon through mineral carbonation.

Approach	Analyzed medium/ parameter	Ref.
Stoichiometric calculation: Theoretical sequestration potential derived from, e.g., the acid neutralization capacity (ANC) or the elemental composition using the Steinour equation	Solid phase (ash)	[25, 27]
Calcimetry: Volumetric determination of released CO_2 (gaseous) from carbonate material after reaction with acid (e.g., HCl)	Solid phase (ash)	[10, 25]
Thermogravimetric analysis (TGA): Gravimetric determination of sample mass loss due to heat induced decomposition of carbonate mineral (550–950 °C)	Solid phase (ash)	[17, 25, 29]
Changes in ash mineralogy or composition: Determination of inorganic carbon content or calcium carbonate phases in the sample before and after carbonation, e.g., via XRD, SEM-EDS or inorganic carbon analysis	Solid phase (ash)	[6, 13, 22, 23]
Mass balance: Calculation of molar or specific CO_2 uptake, e.g., via the ratio of CO_2 mass flow (inlet/outlet of batch carbonation reactor) or the drop of gas pressure in the carbonation reactor directly linked to CO_2 consumption in carbonation reaction	Gas flow (CO_2), pressure in reactor	[23, 26, 27]

as the carbonation process not only captures CO_2, but also partially immobilizes trace elements, thereby reducing the hazard potential of the ashes [19, 20]. There is extensive research on CO_2 sequestration with coal fly ash via direct carbonation of the bulk ash or indirect routes, where Ca is extracted from the ash to be reacted with CO_2 to form $CaCO_3$ [21]. Wood ash in particular has been investigated as raw material for CO_2 capture in several studies. Vassilev et al. [17] found high contents of alkaline and alkaline earth oxides in biomass ash that offer potential for CCS. It has been shown that wood ash is a suitable sorbent for CO_2 from flue gas after combustion [22] or fermentative biogas production [23, 24], although not all ashes are equally suitable for this process [25].

As can be seen from Tab. 1, various studies have used different approaches and methods to determine the CO_2 captured by carbonation. This raises the question of the extent to which the different methods are comparable. As a benchmark, authors often use the theoretical sequestration potential of a material based on stoichiometric calculations [25–27]. Generally, the CO_2 uptake can be determined by quantifying the carbon (C) or carbon dioxide (CO_2) content of a material before and after carbonation [25, 28]. One group of methods used to analyze the amount of sequestered CO_2 is to quantify the carbonate phases. This can be done indirectly using volumetric [10, 25] or thermal [17, 25, 29] analysis techniques or directly using techniques such as X-ray diffraction (XRD) to quantify crystallized carbonate mineral phases [6, 13, 22, 23]. However, thermal methods that determine the amount of sequestered CO_2 based on mass loss during heating of the sample need to be considered carefully. For example, hydration and dehydroxylation reactions that may occur during wet carbonation must be taken into account in order not to over- or underestimate the actual CO_2 uptake through carbonation by incorrectly taking into account the mass of water [28]. Calcimetry, thermogravimetric analysis and methods that examine the ash composition or mineralogy before/after carbonation are all based on the analyses of the source material (untreated ash) and the carbonated ash samples. Furthermore, there are also mass balance approaches that use different parameters related to the CO_2 supply in the carbonation reactor as demonstrated by Lombardi et al. [23], Brück et al. [26], and Schnabel et al. [27].

The principles used for C or CO_2 quantification can be classified based on their mechanisms of release and quantification. Initially, CO_2 is released from the sample through different mechanisms such as acid digestion of carbonates or by heating/combustion. The released CO_2 is subsequently quantified by measuring either the volume of released gas, the change in sample mass, or by gas specific absorption columns. Tab. 2 presents an overview of the methodologies employed in this study to quantify the amount of sequestered CO_2 in wood ash. They differ in terms of the measured variable, ranging from the mass loss upon heating associated with the release of volatile components and thermal decomposition (Δm), the volume of CO_2 released as gas from carbonate mineral (ΔV), to the mass of carbon (m_C) determined in the sample. The methods can be evaluated based on various criteria, with a key consideration being the type of carbon they measure. Specifically, the total carbon content in a sample (C_{total}) can be categorized into organically bound carbon ($C_{organic}$) and inorganically bound carbon ($C_{inorganic}$). Thermal analysis methods, such as CHN elemental analysis (EA), thermogravimetric analysis (TGA), and total carbon (TC) determination quantify both organic and inorganic carbon, yielding a value for C_{total}. In contrast, methods like volumentric analysis (VA) and inorganic carbon measurement (IC) focus exclusively on the inorganically bound fraction of the total carbon within the sample.

The distinction between organic and inorganic carbon is particularly relevant when the CO_2 uptake of the sample is inferred from the total carbon content. Assuming that the total carbon content solely represents stored CO_2 is not applicable to wood ash. The presence of organically bound

Table 2. Overview and assessment of the analytical methods used for the determination of sequestered CO_2 in wood ash.

Method	Measured variable	Differentiation $C_{total}/C_{inorganic}$	Release principle	Quantification principle
TGA	Δm [g]	C_{total}	Heating/combustion	Weighing (change in sample mass)
VA	ΔV [mL]	$C_{inorganic}$	Acid digestion of carbonates	Volumetric determination of released gas
EA	m_C [mg]	C_{total}	Combustion	Non-dispersive infrared detection (NDIR)
TC	m_C [mg]	C_{total}	Combustion	Non-dispersive infrared detection (NDIR)
IC	m_C [mg]	$C_{inorganic}$	Acid digestion of carbonates	Non-dispersive iInfrared detection (NDIR)

carbon ($C_{organic}$), e.g., resulting from incomplete combustion, could artificially increase the apparent CO_2 storage capacity, leading to an overestimation. Consequently, when comparing results from different determination methods, it is vital to consider this differentiation.

If the CO_2 uptake is determined by comparing the carbon content before and after carbonation, the distinction between organic and inorganic carbon becomes less relevant. In this approach, the organic carbon, which remains unchanged during carbonation, is excluded from the assessment, ensuring a more accurate quantification of the sequestered CO_2.

This study aims at a comparison of methods to quantify the captured CO_2 in carbonated wood ash. For this purpose, the carbon and sequestrated CO_2 content in untreated (raw) wood ash and wood ash after lab-scale carbonation using 100 % CO_2 gas are analyzed with different methods. The stoichiometric CO_2 sequestration potential, which is determined using the Steinour equation, is employed as a reference. In detail, four analytical methods for determining the CO_2 bound in the carbonated ash are compared: (i) thermogravimetric analysis (TGA), (ii) volumetric analysis (VA), (iii) total/inorganic carbon analysis (TC/IC), and (iv) CHN elemental analysis (EA).

2 Material and Methods

2.1 Sample Preparation and Analysis of Raw Material

Wood ash samples were provided by the operator of a wood-fired heat and power plant with a 10-MW grate-fired furnace in Southern Germany. Samples of grate ash from the combustion chamber and of filter ash from the flue gas cleaning unit with cyclone and bag filter were provided by the operating staff.

The ash samples were delivered in sealed plastic buckets, separated by ash type. First, impurities (coarse metal parts such as screws) were manually removed from the grate ash. For the evaluation of the results, the CO_2 capture was set in relation to the mass of the grate ash without impurities. The sample material of (1) grate ash and (2) filter ash was homogenized using a sample divider and two representative samples of each ash type were taken. One of these samples was used as a laboratory sample and the other was set aside. A part of the grate ash sample was finely ground using a jaw crusher (Funnel P-1 V2A, Fritsch, Idar-Oberstein, Germany) followed by a planetary ball mill (Pulverisette 6, Fritsch, Idar-Oberstein, Germany). Three variants were taken in the test series: (i) grate ash coarse, (ii) grate ash fine, and (iii) filter ash. During the laboratory analysis, all samples were stored in sealed plastic containers.

The elemental composition of the ash was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) in six replicates, using ground samples of grate ash and filter ash. Ash samples were prepared via aqua regia digestion according to [30]. A portion of 0.1 g (± 0.003 g) of ash was treated with 1 mL H_2O_2 (30 %, for synthesis, Roth, Karlsruhe, Germany), 4 mL HNO_3 (69 %, Rotipuran Supra, Roth, Karlsruhe, Germany), and 9 mL HCl (35 % Rotipuran Supra, Roth, Karlsruhe, Germany). The samples were digested using a microwave digestion system (Multiwave GO 3000, Anton Paar, Graz, Austria). Following digestion, the residues were diluted to a final volume of 50 mL with aqua bidest. for subsequent analysis [31, 32].

2.2 Stoichiometric CO_2 Sequestration Potential

The Steinour equation (Eq. (9)), as reported by Tominc and Ducman [25], was used to determine the stoichiometric CO_2 sequestration potential of the raw, untreated ash. The calculation was based on the CaO, MgO, K_2O, Na_2O, and SO_3 contents in the untreated ash. The values were determined based on the assumption that the measured carbonation-relevant elements are completely present as oxides in the ash.

$$CO_{2\,max}(wt\%) = 0.785 * (CaO - 0.7 * SO_3) + 1.091 * MgO + 0.935 * K_2O + 1.420 * Na_2O \quad (9)$$

2.3 Ash Carbonation Setup

The experimental setup (Fig. 1) consisted of two gas scrubber bottles connected in series and to a gas container (Plastigas, $V = 5.5$ L, Linde, Pullach, Germany) on the inlet side. A vacuum pump (ME1, Vacuubrand, Wertheim, Germany) was connected on the outlet side to generate the gas

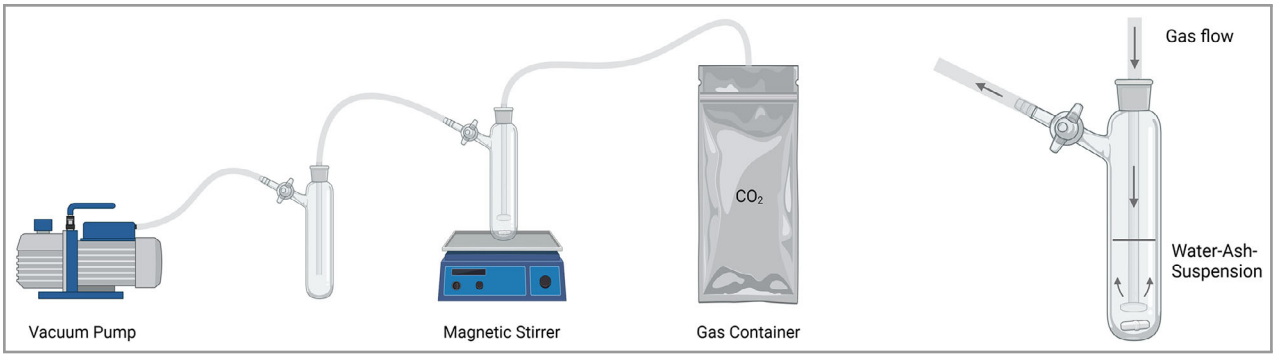


Figure 1. Experimental setup for lab-scale ash carbonation (created with BioRender.com).

flow ($V_{max} = 0.7$ m^{3}h^{-1}) through the scrubber bottles. The first scrubber bottle with a glass tube insert was used as the reaction vessel. This was placed on a magnetic stirrer (RSM-10 HS, Phoenix Instrument, Garbsen, Germany). The second scrubber bottle was employed as a collection vessel to protect the vacuum pump from contamination. The components were connected by silicone tubes ($d = 8$ mm).

At the start of the experiment, the reaction vessel was filled with 200 mL demineralized water. 40 ± 0.1 g of each ash sample (grate ash coarse, i.e., not milled; grate ash fine, i.e., milled; filter ash) was added to the vessel while stirring. The glass tube top was then inserted and the vessel sealed airtight. The gas bag filled with 100 % CO_2 (Westfalen AG, Münster, Germany) was opened and the vacuum pump switched on. The ashes were exposed to pure CO_2 for 1 min in aqueous solution. After 60 s, the vacuum pump was switched off again. The ash-water suspension was subsequently transferred to Falcon tubes and centrifuged for 8 min at 4000 rpm (Rotofix 32A, Hettich, Tuttlingen, Germany). After phase separation, the aqueous phase was discarded and the remaining sample material was placed in ceramic crucibles in which it was dried for at least 24 h at 105 °C in a drying oven (UT12, Heraeus, Hanau, Germany). After drying, it was transferred to plastic containers and sealed airtight until further analysis.

In order to determine the CO_2 uptake achieved, all applied analyses were carried out on sample material before and after carbonation in order to obtain a direct comparison of how the C content in the samples changed as a result of the treatment.

2.4 Analytical Methods

The C content in the ash samples was determined before and after carbonation using the methods descibed in Tab. 2: TGA, VA, EA, TC, and IC.

For the TGA, the treated samples were heated in a muffle furnace (K114, Heraeus, Hanau, Germany) in two temperature steps at 500 °C and 950 °C. The selected temperature points are based on values as reported in Vassilev et al. [17], Tominc and Ducman [25], and Jo et al. [29]. This temperature scheme is based on the principle that hydrogen carbonates and residual carbon (char) decompose below 500 °C, while between 500 °C and 950 °C, potassium, magnesium, and calcium carbonates as well as sulfides undergo thermal decomposition. Using a muffle furnace represents a simplified approach compared to the state-of-the-art method using a thermobalance and nitrogen blanketing. However, this was chosen in this study as an easily accessible and cost-efficient approach.

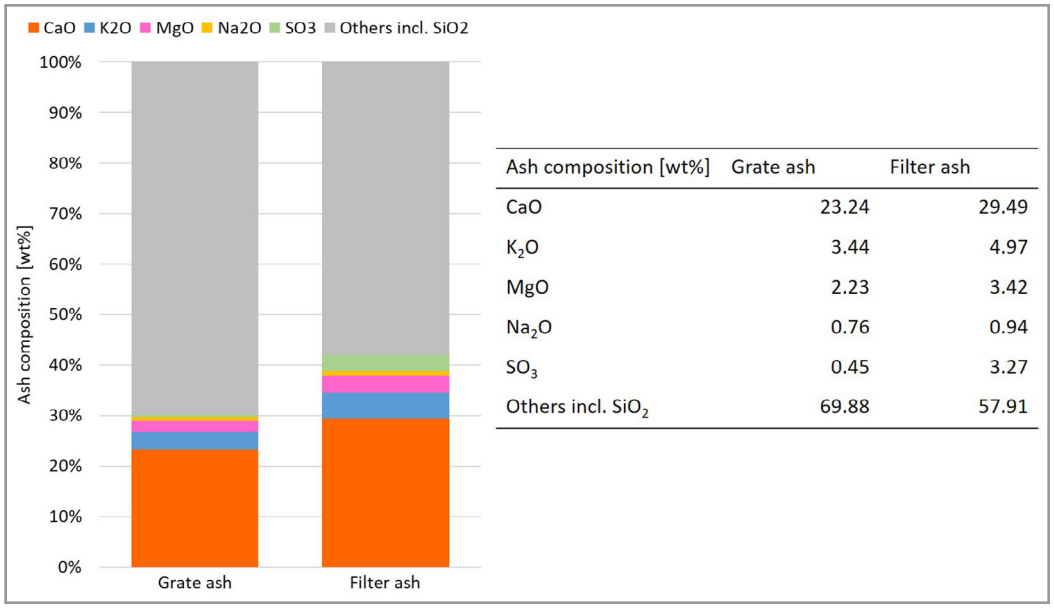
For this purpose, 1 ± 0.010 g of sample material was weighed into a ceramic crucible (CP 124S, Sartorius, Göttingen, Germany). After at least 24 h at 500 °C in the muffle furnace, the samples were transferred to a desiccator for cooling and the desiccator was evacuated. The cooled crucibles were weighed and then returned to the furnace. The procedure was repeated at a temperature of 950 °C. The C content was calculated using Eq. (10).

$$C_{total} = (m_{500\,^\circ C} - m_{950\,^\circ C})/m^*_{105\,^\circ C} 12.011/44.0098^*100[\%] \quad (10)$$

The volumetric determination of the carbonate content, also known as volumetric calcimetry [33], was carried out by means of a Scheibler device (Carl Hamm Geotechnik, Essen, Germany). The calcimeter was calibrated for each measurement campaign with 0.2 and 0.4 g pure calcium carbonate (Carl Roth, Karlsruhe, Germany). Each sample was determined in triplicate with 0.5 ± 0.010 g of sample material (CP 124S, Sartorius, Göttingen, Germany) and 7 mL of HCl (4 mol L^{-1}). Due to the large number of samples, several partial determinations were carried out.

The determination of the C content using a TC analyzer (Primacs SNC 100-IC-E, Skalar Analytical, Breda, The Netherlands) was carried out in two steps using the difference method, by measuring the total C content of the sample (TC) and then the proportion of inorganically bound C (IC). The difference between these two values corresponds to the total organic carbon (TOC, Eq. (11)).

$$C_{organic} = C_{total} - C_{inorganic} \quad (11)$$



Ash composition [wt%]	Grate ash	Filter ash
CaO	23.24	29.49
K_2O	3.44	4.97
MgO	2.23	3.42
Na_2O	0.76	0.94
SO_3	0.45	3.27
Others incl. SiO_2	69.88	57.91

Figure 2. Composition of the untreated filter ash and grate ash used as raw material for carbonation, measured by ICP-OES ($n = 6$) in weight-%.

For TC analysis, 0.3 ± 0.005 g of sample material was weighed into quartz crucibles (CP 124S, Sartorius, Göttingen, Germany) and placed in the magazine of the device. The samples were heated in the combustion chamber at a previously defined temperature profile (300–1200 °C). Prior to analysis, the TC was calibrated to 0.01–30 % C content for soil samples. For the IC analysis, 0.15 ± 0.005 g of sample material was weighed into glass tubes (CP 124S, Sartorius, Göttingen, Germany) and placed in the magazine of the device after addition of 3 mL H_2O (bidest.). The samples were heated to 180 °C and treated with 20 % phosphoric acid (85 %, diluted, Carl Roth, Karlsruhe, Germany). The IC was calibrated to 0.02–12 % C content.

CHN elemental analysis (CHN 828, LECO, Mönchengladbach, Germany) was carried out according to DIN EN ISO 16948:2015-09 at a combustion chamber temperature of 950 °C. A portion of 80 ± 3 mg of sample material (CP 124S, Sartorius, Göttingen, Germany) was weighed into tin foil (Tin Foil Cups, LECO, Mönchengladbach, Germany) and pressed into closed droplets which were placed in the magazine of the instrument.

3 Results and Discussion

The composition of the ash that is used as a raw material for accelerated carbonation is crucial for carbonation efficiency. The elemental composition of the grate ash (GA) and filter ash (FA) samples is depicted in Fig. 2. The composition as found in the analyzed samples is comparable to previous results for similar ashes [34]. The calculation of the stoichiometric CO_2 storage potential ($StCO_2$) of the ash using the Steinour equation yields $StCO_2(GA) = 247$ g kg^{-1} for grate ash and $StCO_2(FA) = 310$ g kg^{-1} for filter ash. To compare the results of the stoichiometric calculation with analytical data, the values are converted from g kg^{-1} to wt %, resulting in $StCO_2(GA) = 24.7$ wt % and $StCO_2(FA) = 31.0$ wt %. Based on the stoichiometric potential, a 25 % higher CO_2 uptake can be expected for filter ash compared to grate ash.

Fig. 3 illustrates the carbon and equivalent CO_2 content of the investigated ashes before and after carbonation, measured using different techniques in comparison to the calculated stoichiometric CO_2 storage potential ($StCO_2$).

Depending on the measurement method, the carbon content prior to carbonation ($C_{before\ carbonation}$) includes unburnt organic carbon ($C_{organic}$) from the fuel and inorganic carbon ($C_{inorganic}$) that has already formed compounds either during combustion or during ash storage. Following carbonation, the carbon content $C_{after\ carbonation}$ includes the initial amount of $C_{before\ carbonation}$ as well as the additional carbon that reacted with the ash during the carbonation process C_{Uptake}. The measured C content can be converted into the equivalent mass of CO_2 (Eq. (12)).

$$CO_2[\text{wt\%}] = C[\text{wt\%}] * (44.0098\ \text{g mol}^{-1}CO_2/ 12.011\ \text{g mol}^{-1}C) \quad (12)$$

For the initially present carbon, given as CO_2 equivalent before carbonation, results range from 7–14 wt % in GA (coarse), 8–16 wt % in GA (fine), and 5–15 wt% in FA, depending on the measurement method used. Values for the sequestrated CO_2 range from an increase of 0.5–3 percentage points (wt %) in GA (coarse), 1–4.5 percentage points

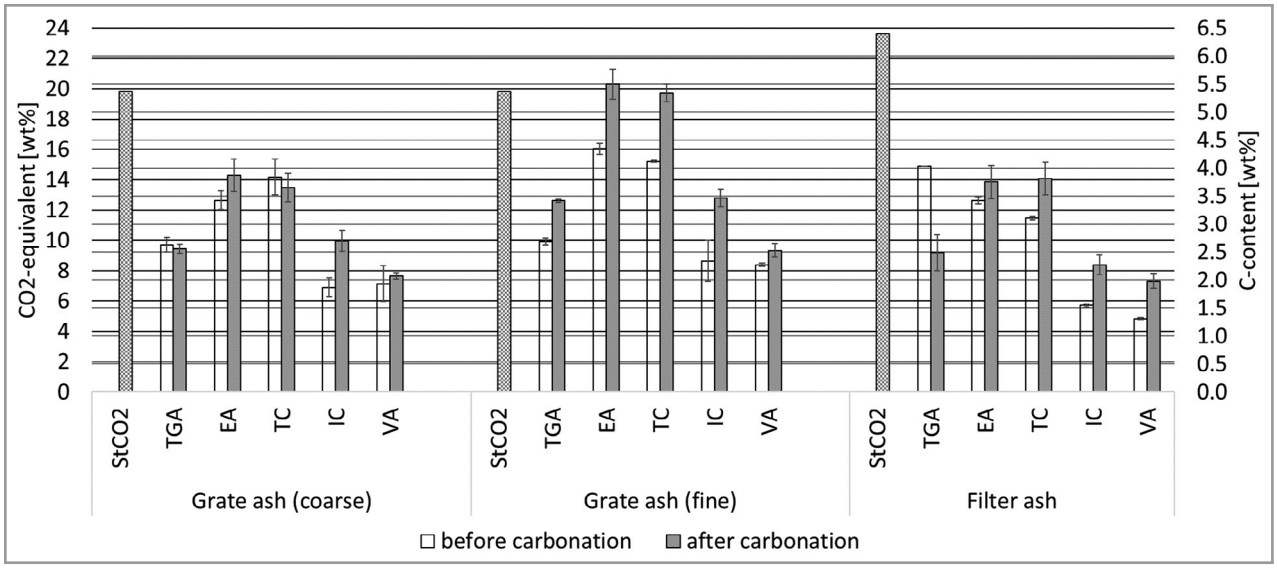


Figure 3. Mean values and standard deviation ($n = 9$) of CO_2 content (left scale) and C content (right scale) in the samples before and after carbonation analyzed via TGA, EA, TC, IC, and VA for three ash fractions in comparison to the calculated stoichiometric CO_2 storage potential ($StCO_2$).

(wt %) in GA (fine), and 1.2–2.7 percentage points (wt %) in FA, depending on the measurement method used. This results in CO_2 equivalent after carbonation ranging from 7.6–14.3 % in GA (coarse), 9.3–20.3 wt % in GA (fine), and 7.3–14 wt % in FA.

A comparison between the stoichiometric CO_2 storage potential $StCO_2$ and the CO_2 equivalent content before carbonation (based on values obtained from IC analysis) indicates the part of the sequestration potential that is already utilized. Prior to carbonation, the theoretical potential is already exploited to 28 % for GA coarse, 35 % for GA fine, and 18 % for FA. After carbonation, the share of exploited potential increases to 40 % (GA coarse), 52 % (GA fine), and 27 % (FA).

EA and TC analysis results indicate the total carbon content of the sample, while IC and VA analysis results show the inorganic carbon content. Although TGA, like EA and TC determination, is based on thermal principles, it must be interpreted differently. Unlike EA or TC, TGA does not directly quantify the carbon content. Instead, it provides a theoretical estimation, assuming that the observed mass loss during heating (Δm) is solely due to the release of CO_2. However, since Δm is the only parameter measured in TGA, it is not possible to unambiguously attribute the mass loss to the volatilization of specific compounds.

The CO_2 equivalent content calculated from TGA is consistently lower compared to the values obtained from EA and TC measurements. This discrepancy appears counterintuitive, particularly considering that TGA also accounts for mass loss due to the release of water and other volatile species within the measured temperature range. This suggests that a portion of the carbon may already be released below 500 °C, which is the starting temperature of the TGA measurement. Such early carbon release could be attributed to volatile organic carbon species or to the decomposition of carbonates with lower thermal stability. This represents a limitation of the simplified TGA method used.

EA and TC analysis provide comparable values. The VA and IC analysis also measure comparable values, whereby the IC values for bottom ash are slightly higher than those of VA. However, both values are around 1.5–2.0 % C lower than the values of EA and TC. The difference between the methods is due to the organic carbon which is still present in the ash. The thermal analyses (EA, TC, TGA) include the organic carbon, while VA and IC do not record the organic carbon content. VA and IC are based on a volumetric determination by means of an acid-base reaction, which only measures inorganically bound carbons. The distinction between organic and inorganic C content is relevant, when the CO_2 uptake of the sample is determined by measuring the total C content. The TGA for bottom ash is also in the range of IC and VA, while for fly ash it lies more between the two trends.

The TGA values cannot be clearly attributed to the TC or IC component. Theoretically, three processes take place when the ash is heated which are decisive for the loss of mass. In the lower temperature range (400–550 °C), dehydration takes place, $Ca(OH)_2$ and also some carbonates ($MgCO_3$) decompose. In the higher temperature range (up to 950 °C), $CaCO_3$ decomposes and CO_2 is released [25]. The higher temperature range may also lead to the volatization of halides or sulfur species [27]. In addition, previously unburnt carbon can be burned once the temperature is higher than when it was burned in the furnace. Therefore,

these temperature windows do not allow conclusions to be drawn with certainty about the decomposed components.

A highly simplified TGA approach using a muffle furnace was employed to evaluate whether the theoretical principles of TGA could be observed or replicated through this analytical procedure. Despite certain advantages –such as the ability to process relatively large sample masses, ease of accessibility, and cost-effectiveness – the method ultimately proved unsuitable due to its significant limitations, which outweighed its benefits. The TGA was performed manually, i.e., the samples were removed from the oven several times, cooled in the desiccator, and then weighed before being returned to the oven. This handling is a potential source of error.

In addition, manual TGA requires the selection of fixed temperature limits based on literature values at which the mass difference is determined. However, these values may vary depending on the composition of the ashes, causing the mass differences to shift. This problem could be solved by using a differential TGA (dTGA). This continuously records the temperature-dependent mass change. Mass change as a function of temperature allows conclusions to be drawn about the temperature range in which the individual phases take place [25].

4 Conclusion

This study provides a comparative assessment of four analytical methods: thermogravimetric analysis (TGA), volumetric analysis (VA), total/inorganic carbon analysis (TC/IC), and CHN elemental analysis (EA) to quantify the CO_2 equivalent carbon content in wood ash before and after lab-scale carbonation with pure CO_2. The stoichiometric CO_2 sequestration potential, calculated using the Steinour equation, served as a reference to evaluate the extent of carbonation. Results indicate that a part of the stoichiometric CO_2 storage potential was already utilized prior to lab-scale carbonation. While the stoichiometric CO_2 storage potential was found higher in filter ash than in grate ash, lab-scale carbonation was more effective with grate ash.

A key distinction among the methods lies in their measurement principles: combustion-based methods (EA, TC) provide the total carbon content, while acid digestion-based methods (IC, VA) target only the inorganic carbon fraction. EA and TC analyses yielded consistent results for total carbon, enabling reliable quantification of sequestered CO_2. Similarly, IC analysis and volumetric calcimetry provided comparable values for inorganic carbon, supporting their applicability for assessing carbonation based on carbonate formation. TGA, while also a thermal method, does not directly measure the carbon content. Instead, it estimates carbon release by attributing observed mass loss (Δm) during heating to CO_2 release. However, because other thermally unstable compounds may also contribute to Δm, and because CO_2 release can not be clearly attributed to certain temperature ranges, this approach lacks specificity and can lead to over- or underestimation of the actual CO_2 content. Thus, the simplified TGA approach employed in this study is not recommended for accurate CO_2 quantification in carbonated ash.

Overall, this study emphasizes the importance of aligning analytical techniques with the specific carbon fraction of interest, i.e., total versus inorganic, and highlights the limitations of oversimplified thermal methods like TGA. The findings contribute to a more comprehensive understanding of carbon quantification in carbonated mineral residues and support the development of standardized protocols for evaluating the CO_2 sequestration performance of wood ash and similar materials.

Acknowledgment

Open access funding enabled and organized by Projekt DEAL.

Abbreviations

CCS	carbon capture and storage
EA	CHN elemental analysis
FA	filter ash
GA	grate ash
IC	inorganic carbon analysis
$StCO_2$	CO_2 storage potential
TC/IC	total carbon analysis
TGA	thermogravimetric analysis
VA	volumetric analysis

References

[1] IPCC, Climate Change 2023: Synthesis Report. *Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change* (Eds.: H. Lee, J. Romero), Intergovernmental Panel on Climate Change (IPCC), Geneva, Switzerland **2023**.

[2] B. Erlach, S. Fuss, O. Geden, U. Glotzbach, H.-M. Henning, J. Renn, S. Rens, D. U. Sauer, S. Christoph M, I. Spiecker genannt Döhmann, C. Stemmler, C. Stephanos, J. Strefler, K. Pittel, Was sind negative Emissionen, und warum brauchen wir sie?, acatech - Deutsche Akademie der Technikwissenschaften **2022**.

[3] A. A. Olajire, *J. Pet. Sci. Eng.* **2013**, *109*, 364–392. DOI: https://doi.org/10.1016/j.petrol.2013.03.013

[4] I. S. Romão, L. M. Gando-Ferreira, M. M. V. Da Silva, R. Zevenhoven, *Miner. Eng.* **2016**, *94*, 104–114. DOI: https://doi.org/10.1016/j.mineng.2016.05.009

[5] R. Zevenhoven, J. Fagerlund, E. Nduagu, I. Romão, B. Jie, J. Highfield, *Energy Procedia* **2013**, *37*, 5945–5954. DOI: https://doi.org/10.1016/j.egypro.2013.06.521

[6] G. P. Sorrentino, A. Zanoletti, S. Ducoli, A. Zacco, P. Iora, C. M. Invernizzi, G. Di Marcoberardino, L. E. Depero, E. Bontempi, *Environ. Res.* **2023**, *217*, 114805. DOI: https://doi.org/10.1016/j.envres.2022.114805

[7] J. Fagerlund, J. Highfield, R. Zevenhoven, *RSC Adv.* **2012**, *2* (*27*), 10380. DOI: https://doi.org/10.1039/c2ra21428h

[8] W. Liu, L. Teng, S. Rohani, Z. Qin, B. Zhao, C. C. Xu, S. Ren, Q. Liu, B. Liang, *Chem. Eng. J.* **2021**, *416*, 129093. DOI: https://doi.org/10.1016/j.cej.2021.129093

[9] S. Ó. Snæbjörnsdóttir, B. Sigfússon, C. Marieni, D. Goldberg, S. R. Gislason, E. H. Oelkers, *Nat. Rev. Earth Environ.* **2020**, *1* (*2*), 90–102. DOI: https://doi.org/10.1038/s43017-019-0011-8

[10] R. Baciocchi, G. Costa, A. Polettini, R. Pomi, *Energy Procedia* **2009**, *1* (*1*), 4859–4866. DOI: https://doi.org/10.1016/j.egypro.2009.02.314

[11] R. Koch, G. Sailer, S. Paczkowski, S. Pelz, J. Poetsch, J. Müller, *Energies* **2021**, *14* (*21*), 7371. DOI: https://doi.org/10.3390/en14217371

[12] A. Polettini, R. Pomi, A. Stramazzo, *Chem. Eng. J.* **2016**, *298*, 26–35. DOI: https://doi.org/10.1016/j.cej.2016.04.015

[13] G. P. Sorrentino, R. Guimarães, B. Valentim, E. Bontempi, *Minerals* **2023**, *13* (*8*), 1060. DOI: https://doi.org/10.3390/min13081060

[14] M. C. Usta, C. R. Yörük, M. Uibu, T. Hain, A. Gregor, A. Trikkel, *Minerals* **2022**, *12* (*5*), 513. DOI: https://doi.org/10.3390/min12050513

[15] R. Zevenhoven, M. Slotte, J. Åbacka, J. Highfield, *Energy* **2016**, *117*, 604–611. DOI: https://doi.org/10.1016/j.energy.2016.05.066

[16] S.-Y. Pan, E. E. Chang, P.-C. Chiang, *Aerosol Air Qual. Res.* **2012**, *12* (*5*), 770–791. DOI: https://doi.org/10.4209/aaqr.2012.06.0149

[17] S. V. Vassilev, C. G. Vassileva, N. L. Petrova, *ACS omega* **2021**, *6* (*22*), 14598–14611. DOI: https://doi.org/10.1021/acsomega.1c01730

[18] H.-J. Ho, A. Iizuka, C.-H. Lee, W.-S. Chen, *Environ. Chem. Lett.* **2023**, *21* (*2*), 865–884. DOI: https://doi.org/10.1007/s10311-022-01518-6

[19] J. Chen, C. Fu, T. Mao, Y. Shen, M. Li, X. Lin, X. Li, J. Yan, *Chem. Eng. J.* **2022**, *450*, 138418. DOI: https://doi.org/10.1016/j.cej.2022.138418

[20] Z. Yao, A. K. Prabhakar, B. Cadiam Mohan, C.-H. Wang, *Waste Manage.* **2022**, *144*, 203–209. DOI: https://doi.org/10.1016/j.wasman.2022.03.033

[21] L. Jiang, L. Cheng, Y. Zhang, G. Liu, J. Sun, *Energies* **2023**, *16* (*17*), 6241. DOI: https://doi.org/10.3390/en16176241

[22] Y. Guo, C. Zhao, X. Chen, C. Li, *Appl. Energy* **2015**, *137*, 26–36. DOI: https://doi.org/10.1016/j.apenergy.2014.09.086

[23] L. Lombardi, G. Costa, R. Spagnuolo, *Environ. Sci. Pollut. Res. Int.* **2018**, *25* (*36*), 35855–35865. DOI: https://doi.org/10.1007/s11356-018-2159-z

[24] G. Sailer, J. Eichermüller, J. Poetsch, S. Paczkowski, S. Pelz, H. Oechsner, J. Müller, *Waste Manage.* **2020**, *109*, 136–148. DOI: https://doi.org/10.1016/j.wasman.2020.04.047

[25] S. Tominc, V. Ducman, *Materials* **2023**, *16* (*15*), 5284. DOI: https://doi.org/10.3390/ma16155284

[26] F. Brück, C. Fröhlich, T. Mansfeldt, H. Weigand, *Waste Manage.* **2018**, *78*, 588–594. DOI: https://doi.org/10.1016/j.wasman.2018.06.042

[27] K. Schnabel, F. Brück, S. Pohl, T. Mansfeldt, H. Weigand, *Greenhouse Gases* **2021**, *11* (*3*), 506–519. DOI: https://doi.org/10.1002/ghg.2063

[28] P. Nielsen, M. Quaghebeur, *Minerals* **2023**, *13* (*8*), 1079. DOI: https://doi.org/10.3390/min13081079

[29] H. Y. Jo, J. H. Kim, Y. J. Lee, M. Lee, S.-J. Choh, *Chem. Eng. J.* **2012**, *183*, 77–87. DOI: https://doi.org/10.1016/j.cej.2011.12.023

[30] *DIN Deutsches Institut für Normung e.V.*, Soil improvers and growing media - Extraction of aqua regia soluble elements, German version EN 13650:**2001**, Beuth Verlag GmbH, Berlin (DIN EN 13650:2002-01).

[31] DIN Deutsches Institut für Normung e.V., *Solid biofuels - Determination of major elements - Al*, Ca, Fe, Mg, P, K, Si, Na and Ti (ISO 16967:2015); German version EN ISO 16967:2015, Beuth Verlag GmbH, Berlin, 75.160.40 (DIN EN ISO 16967:2015).

[32] DIN Deutsches Institut für Normung e.V., *Solid biofuels - Determination of minor elements* (ISO 16968:2015); German version EN ISO 16968:2015, Beuth Verlag GmbH, Berlin, 75.160.40 (DIN EN ISO 16968:2015).

[33] Bodenbeschaffenheit_- Bestimmung des Carbonatgehaltes_- Volumetrisches Verfahren (ISO_10693:1995); Deutsche Fassung EN_ISO_10693:2014, DIN Media GmbH, Berlin (DIN EN ISO 10693:2014-06).

[34] J. Tejada, J. Wiedenmann, B. Gall, B. Kaiser, O. Greißl, S. Unterberger, A. Kappler, H. Thorwarth, *Fuel* **2020**, *267*, 116887. DOI: https://doi.org/10.1016/j.fuel.2019.116887

