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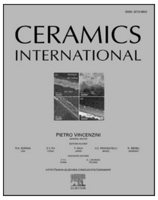

Comparing methods for determining the CO_2 content in CO_2-Sequestering materials and natural rock

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ABSTRACT

Carbon capture plays an important role in the decarbonation of the building sector. One way to capture carbon is through mineral carbonation, in which Ca and Mg compounds react with CO_2 to form stable carbonate minerals such as calcite, dolomite, magnesite and/or siderite, permanently sequestering CO_2. Various techniques are available to measure the amount of permanently bound CO_2 and quantify the carbonation potential. The suitability and accuracy of a particular method are very important, as the accurate determination of CO_2 is crucial to correctly assess the sequestration potential of different materials. This study compares the three methods: calcimetric, gravimetric and thermogravimetric analysis used for CO_2 determination in different types of ash, slag and natural rock. While the CO_2 content in natural rock is stable, the CO_2 content in slag and ash can change over time as the contained minerals gradually absorb CO_2 (by natural or accelerated carbonation) until they are fully carbonated. To avoid errors in testing the CO_2 uptake, as-received samples were first exposed to the full carbonation process and then tested. The comparison of calcimeter, thermogravimetric and gravimetric analysis of ground and sieved samples with a particle size below 125 μm shows that the results usually differ by less than 2 %. Higher deviations could be caused by non-carbonate minerals (especially in slags) that can react with hydrochloric acid during the calcimetric and gravimetric tests and/or decompose in the range where carbonates decompose, contributing to inaccurate CO_2 measurements. The measurement uncertainty was calculated for all three quantitative methods to allow a practical comparability.

1. Introduction

One major concern of the 21st century is global warming and the associated climate change caused by greenhouse gasses (GHG), whose concentration in the atmosphere is constantly increasing [1]. According to NASA, the CO_2 content in the atmosphere has increased by 110 ppm since 1958, from 317 to 427 ppm [2]. One major greenhouse gas is CO_2 which is mainly released by cement production and fossil fuel combustion, which accounts for 80–85 % of the total global energy production and is also mainly used to enable transportation [3–5]. CO_2 emissions have tripled since 1970 and the cumulative CO_2 emissions from forestry due to deforestation and changed land use (e.g. residential, commercial and recreational activities) have also increased by around 40 % [3,6]. It is therefore not surprising that ways to CO_2 capture, store and utilize (CCUS) are being sought [1]. CCUS therefore plays an important role in achieving the goals set out in the Paris Agreement to limit global warming to 1.5–2 °C, which means that greenhouse gas emissions should be reduced by at least 55 % by 2030 compared to 1990 levels [7,8]. Several initiatives have been proposed to combat rising CO_2 concentrations, some of which are based on carbon capture and utilization (CCU) and others on carbon capture and storage (CCS) [9,10].

Mineral carbonation binds CO_2 permanently and falls under CCS [9,10]. It is based on the reaction of CO_2 with materials containing metal oxides, with Ca and Mg being the most attractive metals. Various solid materials can be used to permanently bind CO_2. The most commonly used materials include silica, zeolites, alumina, amine, metal oxides, metal-organic frameworks (MOFs), polymers and various forms of carbon such as activated carbon, graphite, graphene, fullerenes, carbon nanotubes, biochar and hydro-char [11]. The products of these reactions are stable carbonate minerals such as calcite, dolomite, magnesite and

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siderite [12,13].

The degree of carbonation has been reported to decrease with increasing distance from a sample surface [14]. Carbonation also changes the microstructure by increasing the density of the surface layer, reducing the CO_2 diffusion rate [15]. Industrial residues and by-products already investigated with respect to carbonation are asbestos mine residues [16], electric arc furnace (EAF) dust, steel slag, cement kiln dust, concrete waste, coal fly ash [17], air pollution control residues [18], pulverized-fuel ash and circulating fluidized bed combustion [19], and ash transportation waters [20]. It has also been established that natural alkaline solids are less reactive and therefore less suitable for carbonation than their industrial waste counterparts [21]. Biomass ash, slag, concrete aggregates, etc. are materials with a high alkalinity and high Ca and Mg contents that have great potential to sequester carbon in the form of stable carbonate minerals that can be used later, especially in the construction industry [20,22,23].

Nielsen and Quaghebeur [4] conducted a review and made a selection of materials suitable for mineral carbonation; the most important minerals that react with CO_2 to form carbonates are stated in Table 1.

Biomass ash is produced by incinerating biomass waste including agricultural waste (AW), wood waste (WW), food waste (FW), municipal solid waste (MSW) and sewage sludge waste (SSW). Incineration reduces the waste material volume by up to 80 %, or it's mass by 70 %, but generates about 25 million tons of ash annually in the European Union which is normally landfilled [34]. Compounds in paper and wood ash suitable for accelerated carbonation are Ca and Mg rich (hydro)oxides [4]. Wood ash has been shown to have a high reactivity towards CO_2, especially the bottom ash [35,36].

The steel industry caused 7 % of the global CO_2 emissions in 2020 and this share is expected to increase in the coming years [37,38]. It produces more than 20 different co-products, including slag, dust, and process gasses [39]. The two main types of slag produced during steel production are Basic Oxygen Furnace (BOF) slag and Electric Arc Furnace (EAF) slag. Both processes require the addition of e.g. CaO and/or dolomite ($CaMg(CO_3)_2$), which combine with the silicates and other oxides in the hot metal and form the liquid slag [24]. Lime and periclase are suitable for mineral carbonation [4]. The most important minerals that react with CO_2 during mineral carbonation are lime, periclase (MgO), portlandite, dicalcium silicate (larnite in BOF steel slag and larnite, bredigite, merwinite and cuspidine in EAF steel slag) [4,40]. Carbonated steel slag can be used as a green cementitious material and a quarry filler but carbonation improves its properties, e.g. its strength [41,42].

Table 1
Selection of materials and their key minerals that are suitable for mineral carbonation (adopted from Ref. [4]).

Material Type	Key Minerals	Content of key minerals (%)	Reference
BOF steel slag	Portlandite ($Ca(OH)_2$)	17	[24]
	Larnite (Ca_2SiO_4)	17	
EAF steel slag	Larnite (Ca_2SiO_4)	11	[24]
	Bredigite ($Ca_7Mg(SiO_4)_4$)	11	
	Merwinite ($Ca_3Mg(SiO_4)_2$)	20	
	Cuspidine ($Ca_4(Si_2O_7)(F,OH)_2$)	13	
AOD steel slag	Larnite (Ca_2SiO_4)	36	[25]
	Bredigite ($Ca_7Mg(SiO_4)_4$)	15	
	Merwinite ($Ca_3Mg(SiO_4)_2$)	20	
	Cuspidine ($Ca_4(Si_2O_7)(F,OH)_2$)	20	
Carbide slag	Portlandite ($Ca(OH)_2$)	95	[26]
Paper/wood ash	Lime (CaO), Portlandite ($Ca(OH)_2$)		[27]
Waste concrete	Portlandite ($Ca(OH)_2$)		[28]
	C-S-H ($3CaO{\cdot}2SiO_2{\cdot}3H_2O$)		
	Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$		
Waste lime	Lime (CaO)	90	[29]
Hydrated OPC	Portlandite ($Ca(OH)_2$)	25	[30,31]
	C-S-H ($3CaO{\cdot}2SiO_2{\cdot}3H_2O$)	45	
	Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$	13	
Mine tailings	Wollastonite ($CaSiO_3$)		[32]
	Olivine (Mg_2SiO_4)		[33]
	Serpentine ($Mg_3Si_2O_5(OH)_4$)		[33]

In order to determine which materials are more suitable for mineral carbonation than others, it is crucial to measure how much CO_2 can be respectively captured and stored. There are some standardized test methods for determining CO_2 and carbonate (CO_3^{2-}) [4], but many other methods are also used. According to Fu et al. [43] these methods can be divided into 5 groups. The first group is based on the reaction between carbonate and hydrochloric acid where the amount of CO_2 is determined titrimetrically, gravimetrically, volumetrically or manometrically. The second group is based on determining the Ca^{2+} and Mg^{2+} ions by titration with EDTA and using inductively coupled plasma atomic emission spectrometry (ICP-OES). The third group includes measuring the inorganic carbon content with an element analyzer. The fourth includes measuring the weight loss due to the decomposition of carbonate at high temperatures via thermogravimetric analysis (TGA) and the loss on ignition (LOI) method. The last group includes methods based on correlating the carbonate content to physical parameters of the samples or on the correlation between the carbonate content based on the X-ray diffraction spectra (XRD) [43].

As CO_2 uptake will be subjected to certification in the near future, it is essential that the results are accurate and comparable. As materials that are prone to a sequestration uptake of CO_2 from the air during exposure, the results can differ significantly if samples are tested at different times, which can be challenging. To avoid this, it is more appropriate to first expose the samples to the full carbonation process and then test them. The aim of the present study is to compare different methods for CO_2 determination on different sample types. Biomass ash, slag and natural rock samples were analysed. While natural rock is stable in terms of CO_2 content, slag and biomass ash samples were also subjected to the carbonation process. The quantitative techniques used are calcimetry, gravimetric analysis and TGA. The first two are based on the quantification of CO_2 after the decomposition of carbonate in hydrochloric acid, while TGA provides the CO_2 content based on thermal decomposition. XRF and XRD analysis was used as a qualitative support for the identification of mineral phases and to clarify differences between quantitative results. For all three quantitative methods, the calculated measurement uncertainty will serve as a basis for comparison of the different methods used in practice.

2. Materials and methods

2.1. Materials

The analysed samples include seven sedimentary rocks, three slags and seven ashes, two of which were fly ashes. Fly ash A1 was produced by mainly burning beech, oak, hornbeam and poplar, while fly ash A2 was produced from the combustion of a less controlled wood mix. The ashes A3 and A4 were bottom ashes from the incineration of different types of wood. Ash A5 was mixed ash from the combustion of different wood types. The ashes A1-5 were produced by combusting wood chips. The last two ashes A6 and A7 came from a paper mill; A6 was fly ash from coal, biomass and paper sludge, whereas A7 was mixed ash from fiber paper sludge, waste wood and bark.

The slag S1 was a mineral product from steel slag processing (EOP S and refinery slag), S2 was ladle slag from steel processing and S3 was a slag of iron processing.

Seven samples of Slovene sedimentary rock of the Mesozoic age with different proportions of non-carbonate components were tested. Samples R1 and R2 were relatively pure dolomite, R3 was dolomite with organic compounds (bituminous) and the samples R4 to R7 were limestones. Sample R4 was relatively pure limestone, R6 contained a small amount of insoluble components, predominantly Fe and Al oxides and a heavy mineral fraction (i.e. Terra Rossa). Sample R6 could be characterized as a marly limestone with a considerable amount quartz and other silicates, while R7 is considered a marlstone with a dominant terrestrial component of Si oxides.

2.2. Procedure

Ashes and steel slags were subjected to the process of mineral carbonation. The samples were sieved to a particle size below 125 μm. Approximately 10 g of each sample was placed in a closed carbonation chamber with controlled conditions of 40 ± 0.5 °C, a relative humidity (RH) of 80 ± 3.2 % and 4 ± 0.1 vol% CO_2. Carbonation was monitored by initially weighing the samples, followed by weighing them after 7, 10 and 14 days in the chamber. If the difference in weight between the measurements was not more than 0.1 g, the samples were considered fully carbonated. Approximately 2 g of the sample was removed at each weighing, as carbonation was also monitored using a calcimeter.

Gravimetric analysis requires approximately 50 g of each sample to be placed in the carbonation chamber under the same conditions for up to 28 days.

2.3. Test methods

All samples were analysed using a pressure calcimeter, TGA, XRD and gravimetric analysis. For analysis, the samples were ground and sieved below 125 μm and dried at 105 °C for 24 h. They were cooled in a desiccator.

2.3.1. X-ray fluorescence analysis

Prior to chemical analysis, the samples of ash, rocks and slags were ground to pass through a 63 μm sieve. The chemical composition was then analysed using energy dispersive X-ray fluorescence spectrometry (EDXRF NexCG, Rigaku, USA) according to the Standard ASTM D4326-21 [44]. A certified reference material NIST 2690 was used to check the calibration for the determination of the ash composition. The measurements were repeated twice to ensure reproducibility of the results, and the average values were used for data analysis.

2.3.2. Pressure calcimeter

The samples were analysed with a pressure calcimeter (OFITE Recording Calcimeter with DAQ, OFI Testing Equipment Inc., Houston, TX, USA, according to ASTM D 4373). In the OFITE Calcimeter, 1.0 ± 0.001 g of $CaCO_3$ reacted with 20 ± 0.01 mL of 10 % HCl in a closed reaction cell to form $CaCl_2$, CO_2 and H_2O. The pressure of the released CO_2 was measured with a manometer. The calcimeter was calibrated before the actual measurements by reacting HCl with pure $CaCO_3$ (Calcium Carbonate Precipitated, OFI Testing Equipment, Ine, CAS: 471-34-1).

2.3.3. Gravimetric analysis

The gravimetric analysis was based on the measurement of the mass change due to CO_2 emissions during the reaction of a sample in a 10 % HCl solution. The required amount of acid solution was calculated based on the sample weight and considering a 10 % excess of acid. The mixture was stirred and weighed first after 10 min and then every 5 min until a constant mass or a maximum deviation of ±0.1 g was achieved. The evaporation of the acid was also considered in the calculation, by separate acid weighting and taking into account the mass change.

2.3.4. Thermogravimetric analysis

TGA was performed for all samples using 100 μL Al_2O_3 crucibles in a TGA Q5000IR thermal analyser and TA Universal Analysis 2000 v.4.5A (both TA Instruments, New Castle, Delaware, USA). It was performed from 25 to 1000 °C using a heating rate of 10 $K\ min^{-1}$. The sample chamber was filled with N_2 at a flow rate of 25 $mL\ min^{-1}$ to prevent oxidation during the measurement.

2.3.5. X-ray diffraction

For the mineralogical analysis, the samples were sieved below a grain size of 63 μm and placed in 27 mm diameter holders. Analyses were performed by X-ray diffraction in the Bragg-Brentano setup (XRD; Empyrean X-ray Diffractometer, Cu X-ray source; PANalytical, Almelo, The Netherlands) in 0.013° steps from angles of 4–70° under clean room conditions, using the external standard corundum NIST SRM 676a. The diffraction patterns were evaluated using the PANalytical X'Pert High Score Plus diffraction software v.4.8.

2. Results and discussion

3.1. Characterization of ashes and slags

A chemical and mineralogical composition enables a first assessment of the potential suitability for sequestration. XRF analysis of the samples before the carbonation showed that the ashes mainly consisted of CaO, K_2O, MgO, Al_2O_3 and SiO_2. In particular, the samples A2, A3 and A6 showed a significantly higher CaO content, which is usually favourable for CO_2 sequestration. In contrast, the slag samples mainly consisted of CaO and MgO (except S3), Al_2O_3, Fe_2O_3 (except S2) and SiO_2. The higher CaO and MgO contents in the samples S1 and S2 imply a higher suitability of these samples for mineral carbonation than S3. It can be seen that the natural rock consists mainly of CaO and MgO, while samples R6 and R7 also contain some SiO_2. The mean values of the primary oxides measured by XRF are given in Table 2.

From mineralogical analysis it is seen that minerals which are present in ashes and are prone to carbonation are lime and portlandite (Fig. 1), while in slags the main mineral that can bind CO_2 is belite (β and γ modification) [45].

3.2. Determination of the CO_2 content in the ashes

The CO_2 content in the samples was determined by pressure calcimeter, gravimetric analysis and TGA. The results are presented in Table 3.

The $CaCO_3$ and dolomite contents were determined using the calcimeter, whereby the CO_2 content was calculated using the stoichiometric ratios stated in Eq. (1).

$$\begin{gathered} CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \\ n\,(CaCO_3) = n\,(CO_2) = 1:1 \\ 1\ mol\ of\ CaCO_3\ releases\ 44.01\ g\ of\ CO_2 \end{gathered} \qquad \text{Eq. (1)}$$

Gravimetric analyses were performed on un-sieved (>125 μm) as well as ground and sieved (<125 μm) samples. Gravimetric analysis is based on calculating the CO_2 content using the ratio between the initial and final sample mass according to Eq. (2) where m_b stands for the initial mass of the sample, acid, flask and glass stirrer, m_f denotes the mass of the flask, glass stirrer and mixture after the reaction, m_a refers to the mass of the evaporated acid and m_s stands for the initial mass of the sample.

$$w\,(CO_2) = \frac{m_b - m_f + m_a}{m_s} \times 100\% \qquad \text{Eq. (2)}$$

TGA was performed in the temperature range of the respective carbonate decomposition, meaning different temperature ranges for each sample. The temperature ranges used for CO_2 determination by TGA can vary due to the amount and type of packing of the samples in the Al_2O_3 crucibles. If the sample is pressed into the crucible or if the amount of sample analysed is larger, this can cause a thermal delay and reduce the efficiency of heat transfer within the sample, making the temperature range we use for the determination different for the same substance [46].

Table 3 shows that the CO_2 content increased in all samples exposed to the accelerated carbonation process, confirming that mineral carbonation occurred. The CO_2 content increased by up to 6 wt% in

Table 2
Chemical composition of ashes, slags and natural rocks in terms of the primary oxides (wt%), measured using XRF.

Type	Sample ID	P_2O_5	Na_2O	K_2O	CaO	MgO	Al_2O_3	TiO_2	Fe_2O_3	SiO_2	MnO	SO_3
Ash	A1	0.62	0.66	2.57	23.92	7.20	11.55	0.48	15.47	34.49	0.28	2.79
	A2	2.46	0.80	8.22	52.46	2.72	2.44	0.18	1.40	15.09	0.61	4.69
	A3	2.28	0.52	7.94	61.82	3.76	1.80	0.16	1.43	12.48	1.09	1.24
	A4	1.93	1.19	6.97	33.81	5.07	8.02	0.22	3.32	38.48	0.75	0.28
	A5	3.09	1.45	8.97	31.87	7.62	7.61	0.15	2.77	35.02	0.41	1.07
	A6	0.24	0.70	0.34	61.73	2.33	10.06	<0.10	0.54	23.76	0.00	0.32
	A7	0.24	1.51	1.23	36.63	5.22	10.85	0.72	9.99	30.02	0.14	3.46
Slag	S1	0.08	0.57	<0.10	36.77	9.68	10.95	0.32	10.03	28.19	2.72	0.72
	S2	<0.10	<0.10	<0.10	47.56	4.50	17.55	<0.10	0.90	27.33	0.08	1.90
	S3	1.12	0.96	0.39	1.25	0.92	11.61	<0.10	9.39	74.11	0.21	0.53
Natural rocks	R1	0.03	<0.10	0.11	64.30	35.05	<0.10	<0.01	0.39	0.15	0.00	0.09
	R2	0.04	<0.10	0.39	65.80	32.25	0.43	0.06	0.91	1.65	0.00	0.13
	R3	0.03	<0.10	0.19	64.30	34.85	<0.10	0.02	0.53	0.59	0.00	0.09
	R4	0.03	<0.10	0.22	95.85	3.27	<0.10	0.01	0.57	1.13	0.00	0.09
	R5	0.05	<0.10	0.16	95.75	3.36	<0.10	0.02	0.60	0.85	0.00	0.11
	R6	0.06	<0.10	1.26	49.50	24.95	4.18	0.19	5.59	13.90	0.39	0.10
	R7	0.08	<0.10	1.52	51.65	26.60	4.82	0.19	2.61	12.35	0.00	0.25

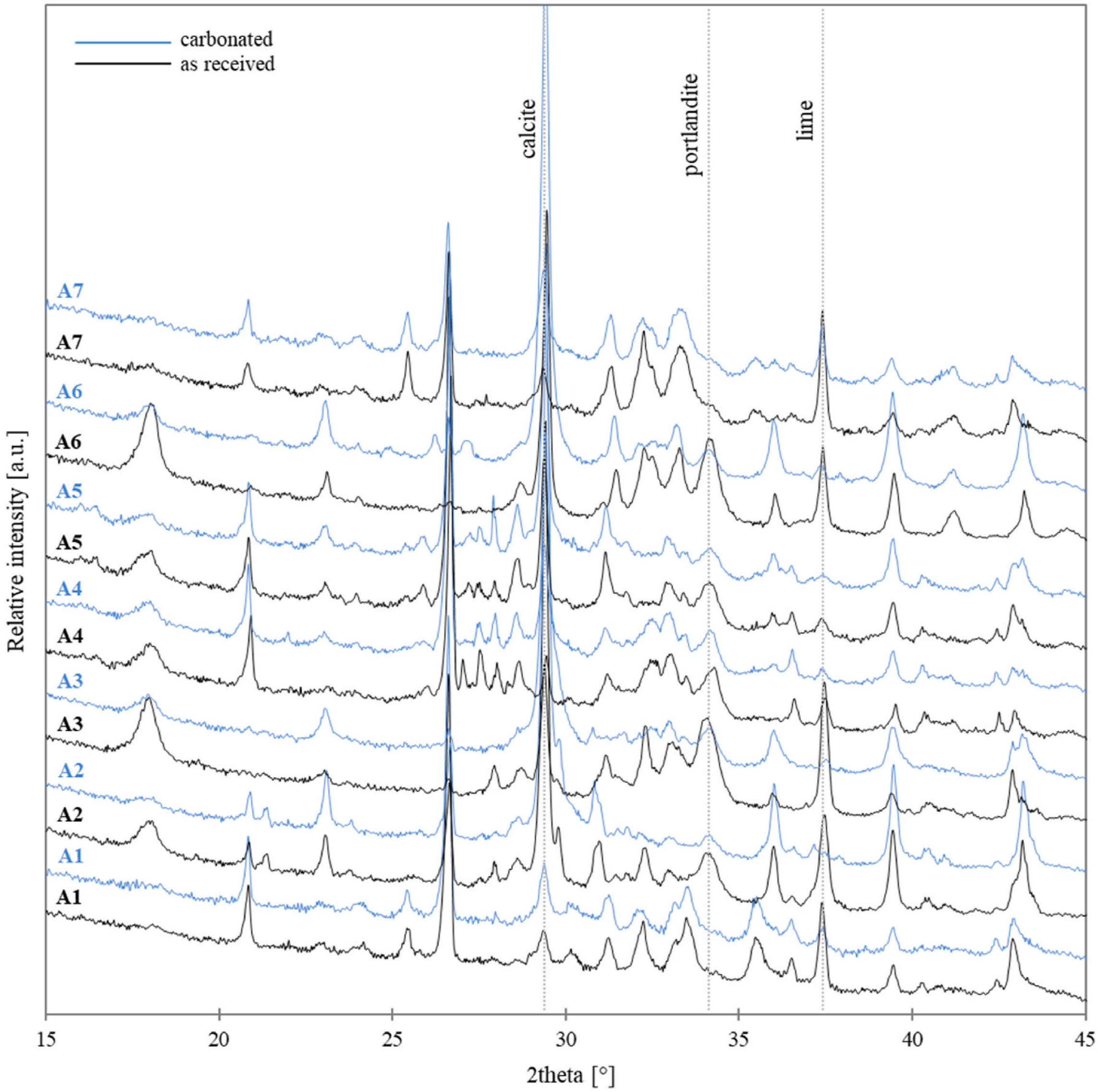


Fig. 1. XRD patterns of as received and carbonated ash samples A1-A7. The highest intensity reflections of lime (ICSD 98-007-5785), portlandite (ICSD 98-020-2221) and calcite (ICSD 98-001-8166) are highlighted.

Table 3
The CO_2 content (in wt%) in different ashes, determined with calcimeter, gravimetric analysis and TGA.

Sample ID		Calcimeter	Gravimetric analysis (<125 μm)	TGA
		CO_2(wt%)	**CO_2(wt%)**	**CO_2(wt %)**
A1	**asreceived**	2.3	3.1	3.9
	carbonated	6.4	6.8	4.8
A2	**asreceived**	14.5	13.7	17.7
	carbonated	25.4	26.2	23.6
A3	**as received**	9.2	9.4	11.4
	carbonated	22.2	23.7	21.3
A4	**asreceived**	2.3	3.0	1.4
	carbonated	6.2	6.3	5.5
A5	**asreceived**	5.0	4.2	3.2
	carbonated	9.7	10.6	8.8
A6	**asreceived**	11.4	10.0	12.9
	carbonated	26.3	27.7	25.7
A7	**asreceived**	3.0	3.3	4.7
	carbonated	7.9	9.0	7.9

samples A1, A4 and A5, while in more reactive samples A2, A3 and A6 up to 18 wt%. This variation reflects differences in the mineralogical composition and carbonation potential of each sample. It is also shown that the respective methods provide different results. The calcimetric measurements and TGA results differ by less than 2 %, except for A2 (as received) and A3 (as received). The larger difference in these two samples might be partially due to the uncertainty of the method described in subchapter 3.5. and the amount of sample used for the analysis. About 50 g of the sample was used for gravimetric analysis, 1 g for calcimetric measurement and only a few mg for TGA. Differences may also arise from the presence of portlandite, demonstrated in Fig. 2, which also undergoes carbonation, but decomposes above 350 °C [47] as shown in Fig. 3. The deductible CO_2 uptake enables to confirm whether an ash is suitable for carbon sequestration [35,48], keeping in mind that the CO_2 uptake is time dependent.

The particle size affects the CO_2 content in the ash samples after carbonation and affects the measurements as the sample volume is much smaller with the calcimetric and especially with the thermogravimetric analysis. The values of the CO_2 content from the gravimetric analysis of sieved samples (<125 μm) differed by up to 3.2 % from the un-sieved samples (>125 μm), as is discernible in Table 4. The gravimetric results of the un-sieved samples deviate by up to 7 % from the TGA results and by up to 3.8 % from those of the calcimetric measurements. This indicates that the particle size not only has a significant influence on the carbon sequestration, but also on the reaction process and the determination of the released CO_2 [49,50]. Increasing the specific surface area of the reactant increases the probability of a reactant collision as more particles are exposed to the reaction, increasing the reaction rate [51].

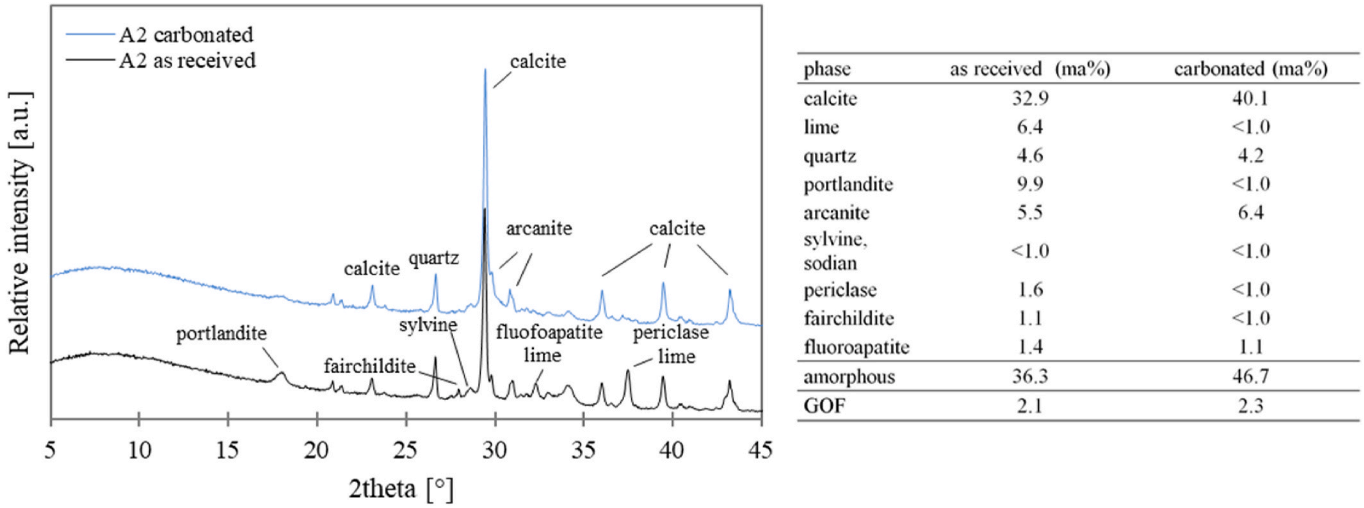
TGA and calcimetric measurements are sufficient to estimate the CO_2 content of a sample if the differences between the analytical results do not exceed 3 %. If the deviation is higher, XRD should be used to determine which phase might react with the acid and produce gaseous products which affect the pressure changes in the calcimeter, or which phase undergoes a phase transition in the temperature range used in TGA to determine the CO_2 released.

3.3. Determination of the CO_2 content in the steel slags

The results of calcimetric measurements, gravimetric analysis and TGA for the steel slags are presented in Table 5. Samples S1 and S2 showed some increase in CO_2 content after accelerated carbonation (3–6 wt%), suggesting effective carbonation in these two samples. However, sample S3 showed only a minimal change in CO_2 content (0.4–1.1 wt%). Compared to ashes, the analysed slags showed less potential for CO_2 sequestration. Apparently, not all steel slags are equally capable of binding CO_2 as some do not contain minerals that react with CO_2.

The results of the TGA and the calcimetric measurements are comparable for samples S1 and S3, as the difference is less than 0.5 %. For sample S2, the difference between the calcimetric and TGA results is 1.5 %. $CaCO_3$ thermally decomposes between 500 and 800 °C, but it is difficult to select the correct temperature range of sample S2 for determining the CO_2 content from the thermogram in Fig. 4, as the mass begins to increase starting at 700 °C [52]. In comparison, the results of the TGA, calcimetric measurements and gravimetric analysis show greater deviations for sample S1 in the as received state. This discrepancy could be due to the amount of unstable sample analysed. Despite a prior sample homogenization, the portion used for the gravimetric analysis might have contained a lower proportion of carbonates.

The XRD patterns in Fig. 5 show that the slag sample S3 contain minor amounts of portlandite as also reported for a comparable slag [4,53], while in the case of S1 and S2 these are larnite, gamma belite and merwinite. The carbonation of these slags led to the formation of calcite, vaterite and some XRD amorphous phase [45].



phase	as received (ma%)	carbonated (ma%)
calcite	32.9	40.1
lime	6.4	<1.0
quartz	4.6	4.2
portlandite	9.9	<1.0
arcanite	5.5	6.4
sylvine, sodian	<1.0	<1.0
periclase	1.6	<1.0
fairchildite	1.1	<1.0
fluoroapatite	1.4	1.1
amorphous	36.3	46.7
GOF	2.1	2.3

Fig. 2. XRD patterns of as received and carbonated sample A2. The highest intensity reflections of subsequently identified phases are highlighted. The table stated the composition evaluated using a Rietveld refinement, GOF – goodness of fit.

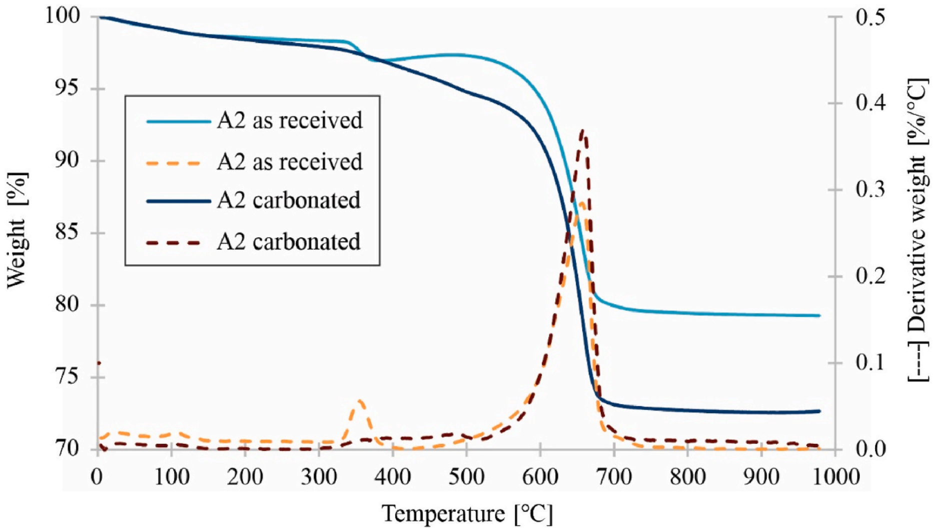


Fig. 3. TGA thermogram and DTG curve of the as received and carbonated ash sample A2.

Table 4
The influence of particle size (above and below 125 µm) on the CO_2 content in as received ashes, measured gravimetrically.

Sample ID	Gravimetry (<125 µm)	Gravimetry (>125 µm)
	CO_2(wt%)	**CO_2(wt%)**
A1	3.1	1.7
A2	13.7	10.7
A3	9.4	6.2
A4	3.0	1.6
A5	4.2	3.5
A6	10.0	7.6
A7	3.3	1.3

Table 5
CO_2 content in different steel slags, determined with calcimeter, gravimetryc analysis and TGA.

Sample ID		Calcimeter	Gravimetric analysis (<125 µm)	TGA
		CO_2(wt%)	**CO_2(wt%)**	**CO_2(wt %)**
S1	**as received**	5.4	2.7	5.4
	carbonated	8.6	9.1	8.6
S2	**as received**	1.8	1.0	0.3
	carbonated	5.1	5.3	3.6
S3	**as received**	1.9	1.1	1.6
	carbonated	1.5	2.2	1.2

3.4. Determination of the CO_2 content in natural rocks

The analysed natural rocks contain purer mineral substances than ashes or steel slags and, above all, because the carbonates are in a stable form and do not sequester CO_2 from the air. Table 6 show the CO_2 content in natural rocks for the samples with a particle size below 125 µm.

The analysed rocks mainly consist of carbonates which are consistent with the mainly sedimentary carbonate rocks common in Slovenia [54]. The CO_2 content determined using TGA differs less than 3 % from that measured using pressure calcimeter. This difference results from a measurement error of the calcimeter; the maximum theoretical CO_2 content in a sample containing only $CaCO_3$ is 44.0 %, dolomite can contain no more than 47.7 % CO_2. Nevertheless, the calcimetric results of the samples R1, R2 and R3 indicate CO_2 contents above 47.7 %. Here the TGA results are more reliable. The difference between the TGA and gravimetric results is less than 4 % and results from errors in the gravimetric analysis. The violent reaction between the sample and the acid means water vapor can escape from the reaction mixture in addition to CO_2.

3.5. Measurement uncertainty evaluation

The measurement uncertainty was determined for calcimetric measurements, TGA and gravimetric analysis. Five replicates of standard $CaCO_3$ measurements were performed with the calcimeter, TGA and gravimetric analysis, while for the XRD the minimum calcite content in samples with controlled mass of standard $CaCO_3$ in standard $MgCO_3$ that the instrument we used could detect was determined. It was found that the XRD software would only detect calcite if it was present in the sample at a concentration of at least 2 %. When analyzing a sample that we had prepared with the standard and that contained 2 % calcite, the software was unable to detect this phase in the sample. Since the composition of the sample prepared with 2 wt% standard $CaCO_3$ was known, the reference card for calcite was manually entered into the program and a Rietveld analysis was performed. If the composition of the sample is known, it is possible to determine the content of a crystalline phase, even if it is only 2 by weight. However, if the sample is unknown, it must contain more than 2 % of a particular substance for it to be detected by XRD.

The expanded uncertainty was determined to a confidence interval of 95.5 % for all three applied methods. Both type A and type B uncertainties were determined for calcimeter and TGA. The type B uncertainty for these was taken into account because the measurement results were not symmetrically distributed around the initial value but deviated in one direction. In the case of gravimetric analysis, the type B uncertainty originates from the measurement error of the balance specified by the manufacturer.

The standard deviation for type A uncertainty (s_A) represents the standard deviation of five measurement repetitions for the same type of sample by the same operator. The standard deviation for type B uncertainty (s_B) represents the absolute value of the difference between the theoretical CO_2 content for each standard and the CO_2 content that deviates the most from the theoretical value [55,56]. Using s_A, we determined the type A measurement uncertainty (u_A) using Eq. (3):

$$u_A = \frac{s_A}{\sqrt{number\ of\ mesurements}} \qquad \text{Eq. (3)}$$

s_B is used to determine the measurement uncertainty of type B (u_B)

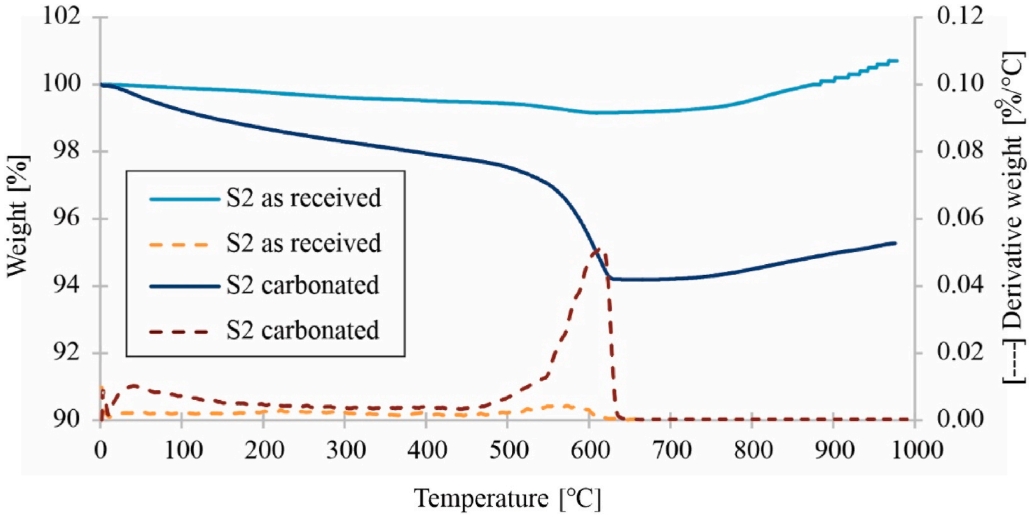


Fig. 4. TGA thermogram and DTG curve of as received and carbonated ash sample S2.

with the following Eq. (4):

$$u_B = \frac{s_B}{\sqrt{3}} \qquad \text{Eq. (4)}$$

Finally, the combined measurement uncertainty (u_C) is calculated using Eq. (5):

$$u_c = \sqrt{u_1^2 + u_2^2 + \ldots + u_i^2 + \ldots} \qquad \text{Eq. (5)}$$

to determine the expanded uncertainty of measurement for a confidence level of 95.5 %, multiplying the combined uncertainty of measurement (u_c) by a factor of 2 [55,56].

The input parameters with the greatest influence on the TGA results are the analytical balance and the temperature range used to determine the content of the specific species in the TG instrument. For the calcimetric measurements it is the pressure on the calcimeter and for gravimetric analysis it is the used balance. Table 7 shows that the measurement uncertainty for the TGA with a confidence interval of 95.5 % is only (44.0 ± 0.2)wt% of CO_2, for the calcimeter it is (44 ± 2)wt% of CO_2 and for gravimetric analysis it reaches (44.0 ± 1)wt% of CO_2.

The results presented above enable to conclude that TGA is the most reliable technique as its measurement uncertainty is only 0.2 for a confidence interval of 95.5 %. The 2nd precise method is gravimetric analysis with a measurement uncertainty of 1 % and finally the pressure calcimeter with a measurement uncertainty of 2 %. However, it is important to emphasize that calcimetric measurements can be more reliable as the precision of gravimetric analysis decisively depends on the analyst performing the measurement. Choosing of the most suitable technique for determining the CO_2 content hence depends on the desired accuracy, speed, sample quantity and available personal and financial resources. The advantage of TGA is the small sample amount required for analysis and its high precision, its disadvantage is a relatively high equipment cost. Calcimeter is much cheaper but slightly less accurate and requires a slightly larger sample amount for analysis. The cheapest technique is gravimetric analysis, but it requires a larger amount of samples, is the least accurate and most prone to human error.

4. Conclusions

Ashes and slags were subjected to a sequestration process to determine how much CO_2 they can store and, at the same time, three methods of determining CO_2 content in analysed samples were compared to confirm their suitability for accurate determination. The CO_2 sequestration potential of most of the analysed ashes was found to be higher than that of the slags.

Comparing calcimetric, thermogravimetric and gravimetric results of ground and sieved samples below 125 μm showed that the results differ by less than 2 % in most cases. Larger deviations only occurred for the gravimetric analysis of unground and un-sieved samples where the acid did not come into contact with the entire sample and therefore the particle size, confirming that the particle size plays an important role in the (gravimetric) analysis.

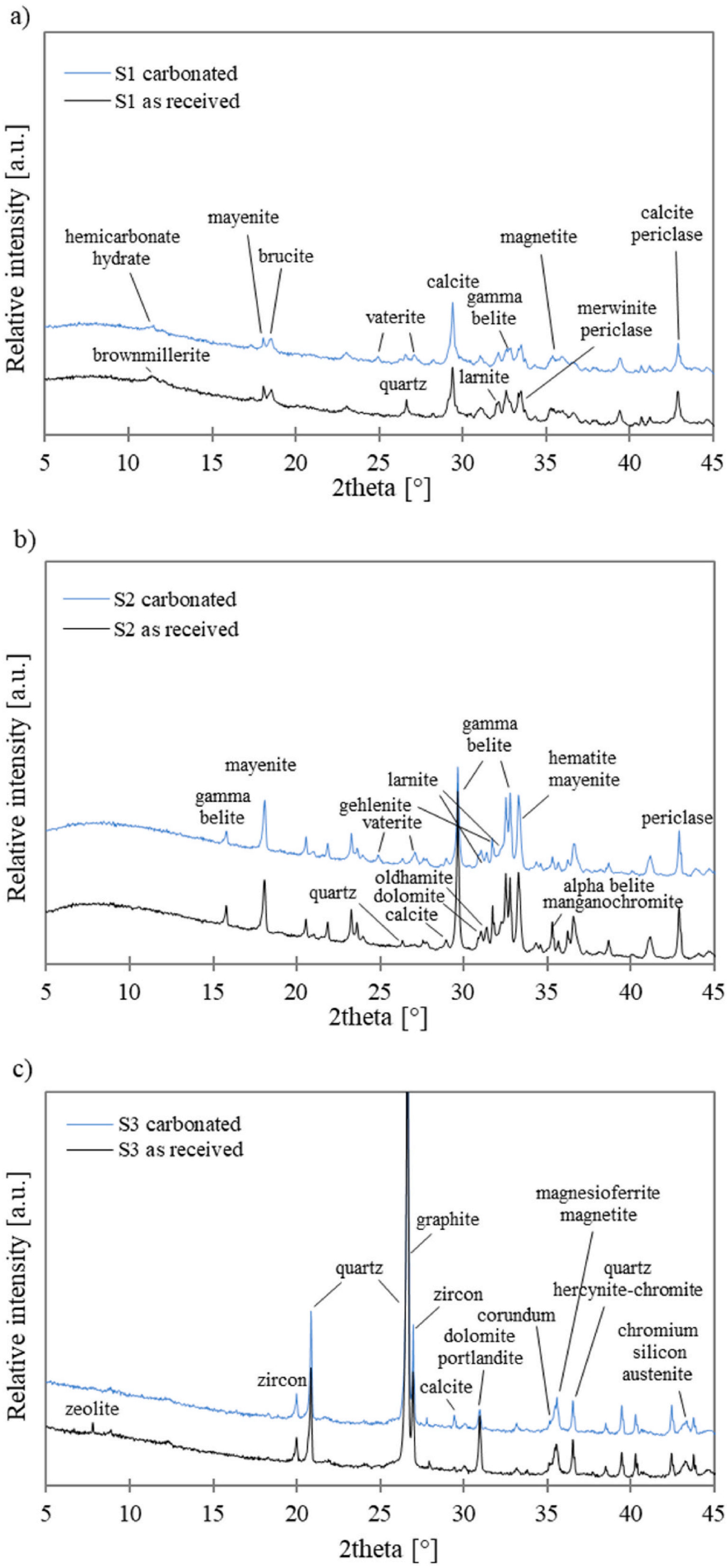
Another influencing factor is the minerals present in the samples (with the exception of carbonates), which can also react with the acid, resulting in gaseous products. The calcimeter only measures the change in pressure and not which gas is released. Deviations occur in the TGA if the peaks for carbonate decomposition and any other decomposition are not clearly separated, so that the determination of the area to be analysed in the thermogram may not be accurate enough.

When analysing the measurement uncertainty, the parameters that influence the accuracy and precision of gravimetric analysis are: i) a balance error, ii) a violent reaction between the acid and the sample (in which a certain amount of water is also lost) and iii) the reaction of substances in the sample that are not carbonates but still release gas as a product. In the TGA influential parameters are the analytical balance uncertainty and the temperature range used to determine the content of CO_2, and for the calcimeter pressure measurements. The determined measurement uncertainties indicate that the most accurate and precise technique is TGA (±0.2 %), followed by gravimetric analysis (±1 %), and calcimetric measurements (±2 %).

Using a single technique is insufficient for a reliable analysis. Using calcimeter/gravimetric analysis and TGA is sufficient so long as the results do not deviate from each other by more than 3 %. If deviations exceed 3 %, quantitative XRD in the Bragg-Brentano configuration can be added (before and after carbonation) to determine which minerals in the sample that can potentially cause deviations of the measured CO_2 release.

CRediT authorship contribution statement

Nika Kavčič: Writing – original draft, Investigation, Formal analysis, Data curation. **Sara Tominc:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Lea Žibret:** Writing – review & editing, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation. **Gorazd Žibret:** Writing – review & editing, Investigation, Data curation. **Mitja Kolar:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Vilma Ducman:** Writing – review & editing, Supervision, Project



phase	as received (ma%)	carbonated (ma%)
calcite	8.4	12.0
larnite	6.5	4.3
merwinite	6.9	4.1
mayenite	1.9	1.5
periclase	6.5	4.3
gamma belite	6.3	0.7
brucite	0.1	0.9
hemicarbonate hydrate	0.7	0.6
quartz	1.0	0.7
brownmillerite	0.6	0.8
hydrocalumite	0.5	0.3
vaterite	-	4.9
amorphous	59.7	64.9
GOF	2.9	2.6

phase	as received (ma%)	carbonated (ma%)
gamma belite	29.3	25.5
larnite	24.9	21.1
mayenite	24.4	21.7
periclase	6.6	6.1
dolomite	1.0	1.1
quartz	<1.0	<1.0
calcite	<1.0	<1.0
hematite	<1.0	<1.0
manganochromite	<1.0	<1.0
oldhamite	<1.0	<1.0
vaterite	-	1.7
amorphous	9.2	19.4
GOF	2.8	2.2

phase	as received (ma%)	carbonated (ma%)
quartz	28.6	24.7
zircon	3.5	3.0
graphite	3.1	3.2
chromium silicon	<1.0	<1.0
magnetite	<1.0	<1.0
zeolite	<1.0	<1.0
magnesioferrite	<1.0	<1.0
corundum	3.1	3.1
dolomite	1.7	1.3
calcite	<1.0	<1.0
portlandite	<1.0	-
austenite	<1.0	<1.0
hercynite-chromite	1.3	<1.0
amorphous	56.3	62.0
GOF	3.7	2.8

Fig. 5. XRD patterns of as received and carbonated samples a) S1, b) S2 and c) S3. The highest intensity reflections of subsequently identified phases are highlighted. The table stated the composition evaluated using a Rietveld refinement. GOF – goodness of fit.

Table 6
The CO_2 content in as received natural rocks, determined with calcimeter, gravimetric analysis and TGA.

Sample ID	Calcimeter	Gravimetric analysis (<125 μm)	TGA
	CO_2(wt%)	CO_2(wt%)	CO_2(wt%)
R1	48.6	49.1	46.9
R2	49.1	47.2	46.3
R3	48.6	50.5	47.0
R4	44.5	46.5	43.7
R5	44.5	44.5	43.7
R6	43.0	41.3	40.6
R7	43.8	43.6	42.4

Table 7
Table stating the true CO_2 content in the sample (x), the standard deviation for type A (s_A) and type B (s_B) errors, the measurement uncertainty for type A (u_A) and B (u_B) error, the combined measurement uncertainty (u_C) and the expanded measurement uncertainty for a confidence interval of 95.5 % ($U_{95.5\ \%}$).

	x	s_A	s_B	u_A	u_B	u_C	$U_{95.5\ \%}$
TGA	44.00	0.02	0.19	0.01	0.11	0.11	0.22
Calcimeter	44.00	0.25	1.79	0.11	1.03	1.04	2.08
Gravimetric analysis	44.00	1.10	0.20	0.49	0.12	0.52	1.01

administration, Methodology, Funding acquisition, Conceptualization.

Data availability statement

The data presented in this study are openly available from the repository DiRROS: PID http://hdl.handle.net/20.500.12556/DiRROS-22772, and upon request from the first and corresponding author.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Manuscript: Comparing Methods for Determining the CO_2 Content in CO_2-Sequestering Materials and Natural Rock" Authors: Nika Kavčič, Sara Tominc, Lea Žibret, Gorazd Žibret, Mitja Kolar, and Vilma DucmanAs corresponding author I sign this declaration on behalf of all authors.Vilma Ducman.

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