

Determination of the CO₂ Uptake of Construction Products Manufactured by Mineral Carbonation

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Abstract: Mineral carbonation is a technology for capturing and storing CO₂ in solid minerals. When mineral carbonation is used to produce construction materials, the quantification of the CO₂ uptake of these products is of the utmost importance, as it is used to calculate the CO₂ footprint of the product and/or carbon offset. The CO₂ uptake is generally determined by measuring the CO₂ content of a material before and after accelerated carbonation. This approach, however, does not take hydration and dehydroxylation reactions into account that may occur during carbonation, and it can therefore under- or overestimate the CO₂ uptake. Thus, a more accurate and practical method to determine CO₂ uptake, which also accounts for hydration and dehydroxylation reactions, is proposed in this paper. This method is based on analytical methods to determine the dry mass and the CO₂ content of the solid products before and after carbonation, and on the calculation of the CO₂ uptake by the following equation: CO₂ uptake (wt.%) = CO₂ carbonated (wt.%) × (weight after carbonation (g)/weight before carbonation (g) – CO₂ initial (wt.%), with CO₂ carbonated being the CO₂ content in g/100 g dried carbonated material, and CO₂ initial being the CO₂ content in g/100 g dried initial material, i.e., before carbonation. The “weight before carbonation” is the dry weight of the initial material, and the “weight after carbonation” is the product’s dry weight after carbonation. In this paper, we show that up to 44% under- or overestimation of CO₂ uptake can occur when hydration and dehydroxylation reactions are not taken into account during mineral carbonation.



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Keywords: mineral carbonation; CO₂ uptake; construction materials

1. Introduction

It is widely recognized that to avoid the worst impacts of climate change, the world needs to urgently reduce CO₂ and greenhouse gas emissions. Mineral carbonation is a technology for capturing and storing CO₂ in solid minerals. Mineral carbonation can be used to make a variety of products (chemicals, minerals, construction products, etc.). The use of mineral carbonation to produce construction materials is of particular interest, since these materials often have a significantly reduced CO₂ footprint compared to traditional construction products. The construction sector accounts for about 13% of global CO₂ emissions, and it needs to achieve complete decarbonization by 2050 [1]. Concrete and concrete-like products that incorporate CO₂ as carbonates may help in reaching complete decarbonization. It can therefore be expected that the construction industry will represent the primary market for products made by mineral carbonation.

Various initiatives and changes in legislation are being drafted to accelerate the reduction of CO₂ emissions. While in the past, the focus was mainly on geological storage, mineralization of CO₂ into products has also recently been recognized as a form of permanent storage. In the latest revision of the European Emissions Trading Scheme (‘ETS’), permanent binding of CO₂ into products (through, for example, mineral carbonation) was also included [2]. Another example in Europe is the proposed carbon removal certification scheme, in which processes based on mineral carbonation that store CO₂ in products will be qualified as “carbon removals” as long as biogenic CO₂ or CO₂ captured from the air

(DAC) is used [3]. For the enactment of mineral carbonation in the various certification schemes, it is of the utmost importance to be able to measure the CO₂ uptake of these materials accurately. The CO₂ uptake of concrete- or lime-based products during its lifecycle or CO₂ reabsorption assessment has also become an environmentally important issue. Many assessment procedures have been proposed for the calculation of CO₂ uptake, and all of these procedures have adopted a pragmatic and/or mathematical approach using various assumptions, such as the degree of cement hydration as a function of water/cement (W/C) ratio and time, the cement type, the exposure conditions during service life and in different recycling scenarios, and so on [4,5]. Typically, validation of the calculations is based on experimental results or published data on CO₂ uptake in construction products as a function of time and exposure conditions [6]. Here, too, the accurate determination of CO₂ uptake is important.

Different methods have been used in the literature to quantify CO₂ uptake. The most common method is to determine CO₂ uptake based on the CO₂ content before and after accelerated carbonation. CO₂ uptake is then calculated based on Equation (1), where CO₂ carbonated and CO₂ initial represent the CO₂ content in the dried (105 °C) material after and before carbonation, respectively [7–11]:

$$\text{CO}_2 \text{ uptake (wt.\%)} = \frac{(\text{CO}_2 \text{ carbonated (wt.\%)} - \text{CO}_2 \text{ initial (wt.\%)})}{(100 - \text{CO}_2 \text{ carbonated (wt.\%)})} \times 100 \quad (1)$$

This equation, however, may under- or overestimate the effective CO₂ uptake as it only takes into account weight changes caused by CO₂ uptake. In addition to CO₂ uptake, other reactions that may occur during carbonation may change the weight of the final product, such as dehydroxylation (loss of lattice hydroxyl ions that are released to form water molecules) and hydration reactions. Therefore, improved methods or equations are needed in order to determine the CO₂ uptake of products manufactured by mineral carbonation.

One method that takes into account dehydroxylation reactions is the mass gain method, which calculates the CO₂ uptake by measuring the mass of the samples before and after carbonation. Water lost during the exothermic carbonation process is collected by absorbent paper, and it is added to the mass after carbonation in Equation (2) [12–14]. Since not all vaporized water can be collected, Equation (2) provides a conservative estimate of the mass gain or CO₂ uptake [15]:

$$\text{CO}_2 \text{ uptake (\%)} = \frac{(\text{Mass}_{\text{after carb.}} + \text{H}_2\text{O}_{\text{lost}}) - \text{Mass}_{\text{before carb.}}}{\text{Mass}_{\text{before carb.}}} \times 100 \quad (2)$$

Another method that takes into account hydration or dehydroxylation reactions is the mass curve method, where the mass of the entire carbonation chamber containing the sample(s) is recorded as a function of time during the carbonation process [12,13]. The generated mass curve represents reaction kinetics. After the sample is placed in the carbonation chamber, the balance is zeroed. The CO₂ is then injected to a specified pressure, and the mass increase is recorded as a function of time. Since the pressure is maintained at a constant level by replenishing the CO₂ gas that is consumed by the sample, the increase in mass is due to the carbon uptake of the sample. At the end of the carbonation process, the pressure is released and the residual mass, *M*, is recorded. The system is calibrated by repeating the tests using a CO₂-non-reactive sample of the same volume in order to obtain a second residual mass, *m*. The mass gain or CO₂ uptake (%) of the sample is given by Equation (3) [13]. Note that the CO₂ uptake measured by this method is not influenced by any carbonates that were already present in the sample before the accelerated mineral carbonation process.

$$\text{CO}_2 \text{ uptake (\%)} = \frac{M - m}{\text{Mass}_{\text{before carbonation}}} \times 100 \quad (3)$$

The mass gain and mass curve methods work well when studying the carbonation of cement and concrete using small closed reactors fed with pure CO₂/N₂ mixtures. These methods may not be applicable when using flue gases, since such gases also contain water and other components that may react with the sample being carbonated, or when using flow through reactors. The methods are also difficult to apply in an industrial setting.

Materials that can be used as input for mineral carbonation with their key minerals are listed in Table 1. Since these materials can be rather diverse in chemistry and mineralogy, the quantification of the CO₂ uptake can be challenging. The CO₂ uptake of a material is defined as the amount of CO₂ that is taken up by the material (or gained) in the form of precipitated carbonates during the carbonation process. It is generally expressed in wt. (%), meaning (g CO₂ added during the carbonation process)/(100 g of the initial solid material).

Table 1. Selection of materials suited for mineral carbonation with the key minerals that react with CO₂ to form carbonates.

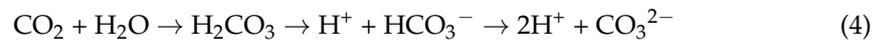
Material Type	Key Minerals	Content (%)	Reference
BOF steel slag	Ca(OH) ₂	17	[8]
	Ca ₂ SiO ₄	17	
EAF steel slag	Ca ₂ SiO ₄	12	[8]
	Bredigite (Ca ₇ Mg(SiO ₄) ₄)	11	
	Merwinite (Ca ₃ Mg(SiO ₄) ₂)	20	
	Cuspidine (Ca ₄ (Si ₂ O ₇)(F,OH) ₂)	13	
AOD steel slag	Ca ₂ SiO ₄	36	[16]
	Bredigite (Ca ₇ Mg(SiO ₄) ₄)	15	
	Merwinite (Ca ₃ Mg(SiO ₄) ₂)	20	
	Cuspidine (Ca ₄ (Si ₂ O ₇)(F,OH) ₂)	20	
Carbide slag	Ca(OH) ₂	95	[17]
Waste concrete	Ca(OH) ₂		[18]
	C-S-H (3CaO·2SiO ₂ ·3H ₂ O)		
	ettringite (Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O)		
Hydrated OPC	Ca(OH) ₂	25	[19,20]
	C-S-H (3CaO·2SiO ₂ ·3H ₂ O)	45	
	ettringite (Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O)	13	
Waste lime	CaO	90	[21]
Paper/wood ash	CaO, Ca(OH) ₂		[22]
Mine tailings	Wollastonite (CaSiO ₃)		[23]
	Olivine (Mg ₂ SiO ₄)		[24]
	Serpentine (Mg ₃ Si ₂ O ₅ (OH) ₄)		[24]

In this paper, we provide an overview of the mass gain and losses that will occur during carbonation of some common minerals due to hydration or dehydroxylation reactions. We subsequently propose a novel calculation method for CO₂ uptake in construction materials based on CO₂ content, which takes into account both hydration and dehydroxylation reactions. Subsequently, an overview is given of the analytical methods and procedures that can be used to determine the CO₂ content in construction materials. Finally, the impact of this novel calculation method on the CO₂ uptake of some key minerals and materials is evaluated, and it is compared to the CO₂ uptake that is calculated by one of the most common methods applied in the literature.

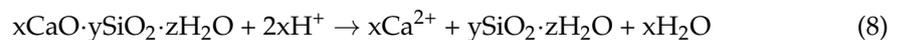
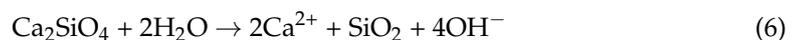
2. Results and Discussion

2.1. Mineral Carbonation

Mineral carbonation proceeds through a reaction of water containing dissolved CO₂ with alkaline materials, such as rocks, slags, concrete, etc., to precipitate solid carbonates. The dissolution of CO₂ in water and the dissociation of H₂CO₃ is described by Reaction (4):



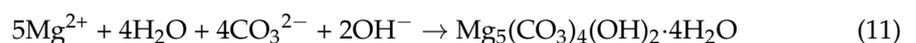
The dissolution of CO₂ is favored at a basic pH, which increases the concentration and availability of CO₃²⁻. The dissolution of Ca²⁺ or Mg²⁺ is described from several key minerals by Reactions (5)–(8):



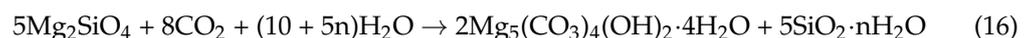
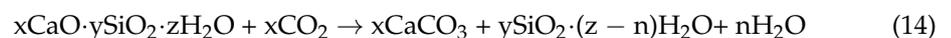
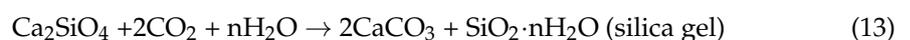
The precipitation of CaCO₃ in the presence of water is described by Reaction (9):



The precipitation of anhydrous MgCO₃ generally only occurs at high temperatures (>100 °C) because of the high energy barrier for Mg²⁺ dehydration, e.g., [25]. Instead, hydrated Mg-carbonates, such as nesquehonite or hydromagnesite, are generally formed. The precipitation of nesquehonite is described by Reaction (10), and that of hydromagnesite is described by Reaction (11):



The overall reaction of the key minerals with CO₂ is then given by Reactions (12)–(16):



The exact stoichiometric coefficients of the reactions are not always clearly defined [26], e.g., the amount of water in the (calcium modified) silica gel is unknown. From the overall Reactions (12)–(16), it is clear that the solid material gains mass during carbonation by the binding of CO₂ in solid carbonates. The material to be carbonated may, however, also lose or gain mass as a result of the dehydroxylation of hydroxides (Reaction (12)), or by the conversion of chemically bound water (solid) to free water (liquid) (Reaction (14)), or by the conversion of free water to chemically-bound water (Reactions (13), (15), and (16)).

The CO₂ uptake of a material is generally expressed as weight % (wt.%), meaning (g CO₂)/(100 g of the initial solid material). In Figure 1, a few examples are provided of the mass changes associated with the carbonation of Ca(OH)₂, Ca₂SiO₄, and Mg₂SiO₄,

respectively, which are some of the key minerals that are involved in the carbonation of industrial waste streams and natural magnesium silicate rocks (see Table 1).

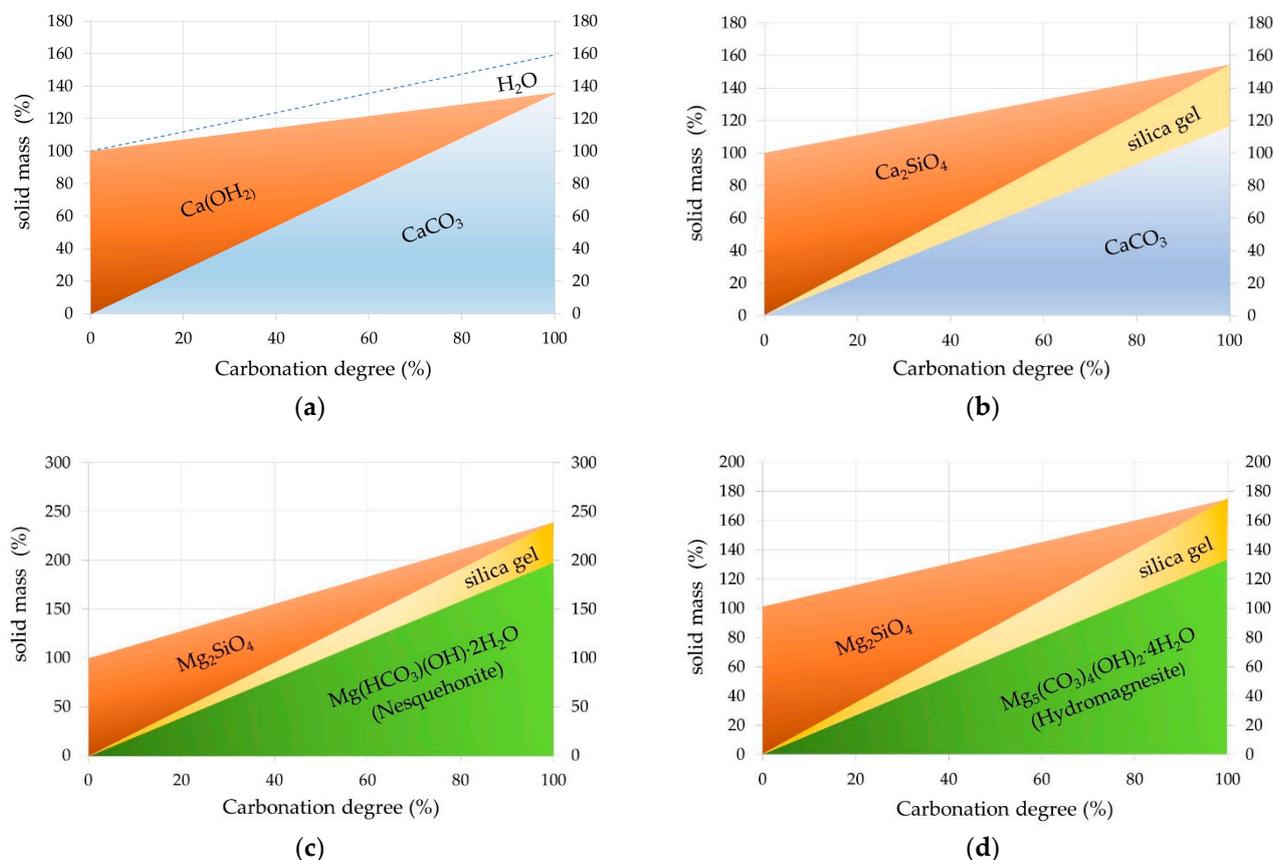


Figure 1. Weight changes of solid phases during the carbonation of $\text{Ca}(\text{OH})_2$ (a), Ca_2SiO_4 (b), and Mg_2SiO_4 (c,d).

2.2. Conversion of the Measured CO_2 Contents to a CO_2 Uptake

The determination of the CO_2 content is generally carried out on a dried sample (dried at 105°C), and therefore expresses the CO_2 content as a mass percentage of the total mass of the dried sample. The CO_2 uptake is calculated based on the CO_2 content of a material before and after accelerated carbonation. Typically, Equation (1) is used.

To calculate the CO_2 uptake more accurately, the equation should also take into account the mass change of the initial solid product that occurs during carbonation. Because processes other than CO_2 uptake may lead to weight changes during the carbonation process (e.g., crystal water can be released as free water during carbonation, or free water may become part of the crystal structure), the weight of the products before and after carbonation should be established on a dry weight basis. The conversion of CO_2 content to CO_2 uptake (in g/100 g dry, initial material) is given by Equation (17):

$$\text{CO}_2 \text{ uptake (wt.\%)} = \text{CO}_2 \text{ carb. (wt.\%)} \times \frac{\text{weight after carb. (g)}}{\text{weight before carb. (g)}} - \text{CO}_2 \text{ init. (wt.\%)} \quad (17)$$

with $\text{CO}_2 \text{ carb.}$ being the CO_2 content in g/100 g of dried carbonated material, and with $\text{CO}_2 \text{ init.}$ being the CO_2 content in g/100 g of dried initial material, i.e., before carbonation. The “weight before carbonation” is the dry weight of the initial material, and the “weight after carbonation” is the dry weight of the material after carbonation.

In Table 2, a few examples based on the reaction equations of pure minerals are listed to illustrate the difference in the calculation of CO_2 uptake with the new Equation (17) compared to the one that is currently used in the literature (1). Example 1: $\text{Ca}(\text{OH})_2 +$

$\text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ shows that 1 mol of $\text{Ca}(\text{OH})_2$ (74.095 g/mol) reacts with 1 mol CO_2 (44.009 g/mol) to precipitate 1 mol CaCO_3 (100.089 g/mol) and release 1 mol H_2O (18.015 g/mol). When starting with 100 g $\text{Ca}(\text{OH})_2$, this results in 135.1 g CaCO_3 due to the uptake of 59.4 g of CO_2 and the release of 24.3 g of H_2O . The CO_2 uptake is (59.4 g CO_2)/(100 g of the initial solid material) or 59.4 wt.%. The CO_2 content of the carbonated material that can be analyzed by an element analyzer or by TGA is, however, only 43.4 wt.%, i.e., the CO_2 content of the newly precipitated CaCO_3 , i.e., 44.009 (molecular weight of CO_2)/100.089 (molecular weight of CaCO_3) or (59.4 g CO_2)/(135 g of solid product). When calculating the CO_2 content, without taking the water loss into account, the CO_2 uptake would be 78.6% (i.e., 44.009/(100.089 – 44.009)). Note that the CO_2 uptake in Table 2 is based on simple reaction equations. These calculations are only made to illustrate that Equation (17) provides more accurate CO_2 uptake values than Equation (1), and it is the latter that is currently used in the literature.

Table 2. Examples to illustrate the effect of the changing masses on the calculated CO_2 uptake with Equation (1) that only take CO_2 mass changes into consideration. Example 1: carbonation of $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$; Example 2: carbonation of $\text{Ca}_2\text{SiO}_4 + 2\text{CO}_2 + n\text{H}_2\text{O} \rightarrow 2\text{CaCO}_3 + \text{SiO}_2 \cdot n\text{H}_2\text{O}$; Example 3: carbonation of Mg_2SiO_4 to form nesquehonite $\text{Mg}_2\text{SiO}_4 + 2\text{CO}_2 + (6 + n)\text{H}_2\text{O} \rightarrow 2\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2\text{H}_2\text{O} + \text{SiO}_2 \cdot n\text{H}_2\text{O}$; and Example 4: carbonation of Mg_2SiO_4 to form hydromagnesite $5\text{Mg}_2\text{SiO}_4 + 8\text{CO}_2 + (10 + 5n)\text{H}_2\text{O} \rightarrow 2\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O} + 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$.

Example	Initial Mass g Dry	CO_2 Gain g	H_2O Loss/Gain g	Final Mass g dry	Final CO_2 Content (%)	Calculated CO_2 Uptake (Equation (1)) (%)	Calculated CO_2 Uptake (Equation (17)) (%)	Over/Under-Estimated (%)
1	100	59.4	−24.3	135.1	44.0	78.6	59.4	+32.3
2	100	51.1	+2.0	153.1	33.4	49.3	51.1	−3.5
3	100	62.6	+76.8	239.4	26.1	35.4	62.6	−43.4
4	100	50.0	+25.6	175.7	28.5	39.8	50.0	−20.4

In Example 2, the CO_2 uptake of the complete carbonation of Ca_2SiO_4 (reaction (13)) has been calculated. The water uptake due to hydration of Ca_2SiO_4 and the formation of a hydrated silica gel or Ca-modified silica gel (when carbonation is incomplete) has been roughly estimated at 2% based on TGA results from carbonated Ca_2SiO_4 samples, e.g., [27]. Example 3 is based on the formation of nesquehonite, a magnesium hydroxy-carbonate hydrate from the carbonation of olivine (Mg_2SiO_4), i.e., reaction (15). The very high weight gain of 139.4% (62.6% due to CO_2 and 76.8% due to H_2O uptake) makes Equation (1) underestimate the CO_2 uptake by 43.4%. Nesquehonite is considered a promising solution for CO_2 storage, with potential utilization in “green” building materials [28]. Based on these examples, it is clear that hydration and dehydroxilation reactions play a very important role in the determination of the CO_2 uptake. Input materials suitable for mineral carbonation can be a combination of various minerals (Table 1) for which the impact of hydration and/or dehydroxilation reaction can differ. For metallurgical slags that contain few hydroxides and hydraulic phases, the difference between the two calculation methods will be small (normally less than 5%), especially considering that complete carbonation is very difficult to reach. For materials that mainly consist of $\text{Ca}(\text{OH})_2$, such as carbide slag or lime waste, the CO_2 -uptake calculated with Equation (1) may overestimate the CO_2 uptake by up to 32.3%. When magnesium hydroxy-carbonate hydrates are formed, such as nesquehonite, the CO_2 uptake determined by Equation (1) may be underestimated by up to 43.4%.

In Table 3, the same calculations were made for waste hydrated cement paste, which contains several minerals that can be carbonated. Note that it was assumed that all of the minerals that can be carbonated are fully carbonated, and that the water content in the C-S-H will be taken up by the amorphous silica that is formed during the carbonation reaction. The difference in CO_2 uptake calculated with the two equations is most likely closer to the difference that can be expected for typical construction materials.

Table 3. Examples to illustrate the difference in CO₂ uptake based on the calculation with the new Equation (17) compared to the one currently used in the literature (Equation (1)) for the carbonation of hydrated cement paste (HCP) (for the content of minerals that can be carbonated in HCP, see Table 1).

Minerals	Initial Mass g Dry	CO ₂ Gain g	H ₂ O Loss/Gain g	Final Mass g dry	Final CO ₂ Content (%)	Calculated CO ₂ Uptake (Equation (1)) (%)	Calculated CO ₂ Uptake (Equation (17)) (%)	Over/Under-Estimated (%)
Ca(OH) ₂	25	14.9	−6.1	33.8	11.0	19.7	14.9	8.0
C-S-H	45	17.3	0.0	62.3	12.5	17.3	17.3	0.0
ettringite	13	1.4	−4.3	10.1	1.8	2.0	1.4	6.4
other phases	17	0	0	17	0	0	0	0
HCP	100	33.6	−10.4	123.2	25.3	39.0	33.6	+14.4

2.3. Analysis of the CO₂ Content of a Material

Several standardized test methods are available for analysis of CO₂ or carbonate (CO₃) content of materials [29–31]. Fu et al. [32] discuss a large number of methods to analyze carbonate content in sediments. These methods can also be used to determine the CO₂ content. We only focused here on methods that are practical in an industrial context and are thus most relevant for construction materials, and there are three: (1) a method based on the reaction between carbonate and an acid, with determination of the released CO₂ by a volumetric or gravimetric method; (2) a method that measures the inorganic carbon content by an element analyzer; and (3) a method that determines the weight loss of carbonates by decomposition under high temperature conditions by thermogravimetric analysis (TGA).

2.3.1. Volumetric Determination of CO₂ (Reference Method for EN 459-2:2021)

There are several methods that are based on the dissolution of carbonates and the determination of the released CO₂ [29,31]. Reference [31] stipulates a method for the determination of carbonate content of building lime and then soils and soft rock, respectively. The CO₂ contained in these materials in the form of carbonates is released as CO₂ gas during the reaction between the sample and an acid (e.g., hydrochloric acid). In [29], quite concentrated HCl is used, and it is also heated to boiling point to assure complete reaction with the carbonates. The volume of the air/CO₂ mixture is measured as well as the air without CO₂. The latter is accomplished by adsorbing all of the CO₂ in an absorption vessel filled with potassium hydroxide solution. The difference in volume gives the volume of CO₂ in the sample, and it is used to calculate the CO₂ content of the sample. In [29], the sample mass used depends on the expected CO₂ content in the sample, and it varies between 0.1 g (expected CO₂ content > 40%) and 2 g (expected CO₂ content < 2%). In [31], 5 g of sample is used. The CO₂ content is deduced from the pressure induced by the released CO₂, and the CO₂ content is determined through a pre-calibrated curve.

2.3.2. Gravimetric Determination of CO₂

In [29], a gravimetric method is provided as an alternative to determine the CO₂ content. In this method, the sample is treated with phosphoric acid to decompose the carbonates present in the sample. The liberated CO₂ is passed through a series of absorption tubes by a CO₂ free carrier gas. The first two tubes are used to remove H₂S and H₂O. The following tubes absorb the CO₂, and their weight gain is measured to determine the released CO₂ content of the sample.

An automated carbon (TC analyzer) or element analyzer can also be used to determine the inorganic and organic CO₂ content of a sample by the combustion gravimetric method. Two representative samples (generally 0.5 to 1.0 g) are put into two individual small containers after being weighed: one for total carbon (TC) determination and the other for TOC determination. In the one for TOC analysis, carbonates are removed either by reaction with HCl or phosphoric acid, e.g., [33]. Then, both samples are combusted under O₂ at 900 °C to 1150 °C in the presence of a catalyst, which oxidizes the organic carbon

and decomposes the inorganic carbon. The CO₂ in the evolved gases is then collected in a suitable absorbent, and its mass is determined. If no organic carbon is present, the total carbon (TC) content represents the total inorganic carbon (TIC) content, and the CO₂ content in wt.% is given by Equation (18):

$$\text{CO}_2 \text{ wt.\%} = \text{TC} \times 44.01 \text{ (molar mass of CO}_2\text{)} / 12.01 \text{ (atomic mass of C)} \quad (18)$$

If organic carbon is present, an indirect method can be used, in which the TC of the sample (TC₁) is determined, and in a second sample, the TC (TC₂) content is determined after removing the carbonates. In this way, the TC and TOC are determined and the total inorganic carbon is calculated as TIC = TC – TOC, and the TIC can be recalculated to CO₂ by Equation (19):

$$\text{TIC} = (\text{TC}_1 - \text{TC}_2) \times 44.01 \text{ (molar mass of CO}_2\text{)} / 12.01 \text{ (atomic mass of C)} \quad (19)$$

TC₁ = TC is determined after the drying of the sample, and TC₂ = TC is determined after the drying of the sample and the dissolution of the carbonates with acid. Some acid treatments may not be effective in removing all carbonates, and they may therefore lead to erroneous results. This may be the case when cold dilute 10% HCl is used and the sample contains dolomite, ankerite, and/or siderite. These minerals are less soluble than calcite, and they may need a stronger acid and/or slight heating to react and release all inorganic carbon (TIC).

The thermogravimetric analysis (TGA) method determines the CO₂ content by measuring the mass loss of a sample during heating of that sample up to about 1000 °C using a TG analyzer. The heating of a sample over a temperature range allows for mass loss differentiation based on mineral form (for example, CaCO₃, MgCO₃, Ca(OH)₂, etc.). The decomposition of carbonates generally results in the release of CO₂ over the temperature range of 500–900 °C. Note that the exact temperature range depends on the nature of the carbonate minerals, with poorly crystalline and amorphous CaCO₃ decomposing between 300 and 630 °C, aragonite and vaterite decomposing between 600 and 700 °C, and crystalline calcite decomposing between 700 and 850 °C [34]. Magnesium carbonate, nesquehonite and hydromagnesite release their CO₂ between 400 and 500 °C [35,36]. Note that the decomposition of carbonates during TG analysis may be as low as 300 °C [19,27,37].

In order to verify that the mass loss is due to the decomposition of carbonates, the TG analyzer can be coupled to a mass spectrometer (MS), which enables the simultaneous analysis of the evolved gases that are emitted during the heating of the sample. The CO₂ quantity can be directly determined by the mass loss of the sample over the appropriate temperature range (e.g., 500–900 °C) as long as there is no overlap with the release of other gases, such as water from hydration products. In the case of cement samples, possible overlap with water loss from hydrated phases and materials containing mono- and hemicarbonates (where the release of CO₂ is around 400 °C (see Zajac et al. [38]) or amorphous carbonates (where the release of CO₂ is around 300 to 600 °C) makes an accurate determination of the CO₂ content of these samples difficult. A simplified method is the Loss-On-Ignition (LOI) method, which measures the weight loss between two predetermined temperatures. For carbonates, the LOI method generally uses Equation (20), e.g., [39]:

$$\text{CO}_2 \text{ wt.\%} = ((\text{wt.\% at } 500 \text{ }^\circ\text{C} - \text{wt.\% at } 900 \text{ }^\circ\text{C}) / (\text{wt.\% at } 105 \text{ }^\circ\text{C})) \times 100 \quad (20)$$

However, the results of this method have been shown to depend on factors such as sample size, exposure time, and the position of the samples in the furnace [40], and, as already been pointed out, some carbonates may release CO₂ at lower temperatures and are thus not counted in the LOI method, which only considers losses between 500 °C and 900 °C.

2.3.3. Comparison of Different CO₂ Determination Methods

A comparison of different methods should be conducted on samples from diverse origins, as some of the methods may work well for some samples but be less accurate when certain constituents are present in the samples. Most studies comparing methods have been carried out on natural sediments and rocks or soil samples (e.g., [32,39,41]). Li et al. [39] concluded that the automatic carbon analyzer method provided more accurate values with the lowest uncertainties in comparison to chemical methods and the LOI method. In addition, the automatic carbon analyzer can produce results in the shortest time (about 10 min). This allows for the analysis of more replicates, which will increase the precision of the results. Moreover, since the measurement is automatic, the constant presence of operators is not required.

2.3.4. Drying of Samples before Determination of the CO₂ Content

Complete drying of the samples is required to provide accurate measures of the CO₂ content of a sample. In the literature, the CO₂ content is generally measured as a weight percentage relative to the total weight of the sample dried at 105 °C [8,10,11]. This is the most commonly used method for determining the dry mass of a sample in various standards [42–45].

The dry weight (W_d) of a sample may, however, depend on the drying method, with different drying methods giving different results. The difficulty lies in the removal of all free water without affecting the chemically-bound water in the sample. This is visualized in Figure 2:

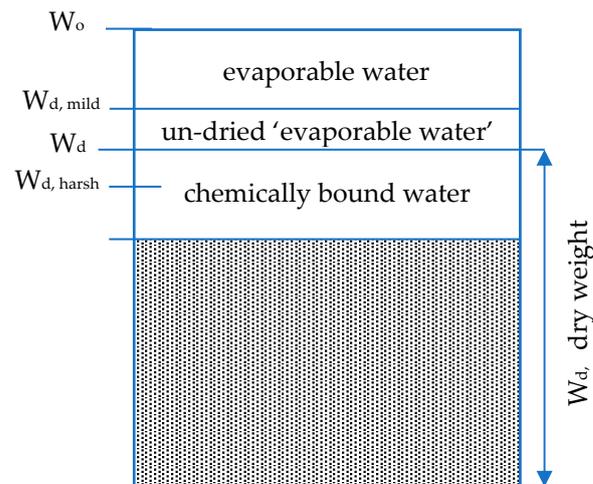


Figure 2. Effect of the drying efficiency on the estimated amount of free (unbound chemically) and chemically-bound water (Figure adapted from [46]). $W_{d, mild}$ = Dry weight after mild drying; W_d = dry weight (including bound water); $W_{d, harsh}$ = dry weight after hard drying, which may include part of the bound water.

Free water is defined as water that can be removed by drying (evaporable water). It is water that may still be present in the pores of the initial material to be carbonated, or water that is added to the material, as the carbonation reaction can only proceed in the presence of water.

Chemically-bound water is water that is chemically bound in a crystal structure (e.g., the hydration water of ettringite $(CaAl_2(SO_4)_3(OH)_{12} \cdot 26H_2O)$, or C-S-H). The removal of this water leads to changes in the crystal structure of the solid phase. This water is considered part of the solid phases contained in the sample, and it is part of the dry mass of the sample.

Dry mass, in many cases, is defined as the mass after drying at 103–105 °C until constant mass, but for some materials (e.g., hydrated cement paste), however, this may be too harsh, as hydrated cement phases may start to lose bound water at around 50 °C [47,48].

Korpa et al. [49] presented a thorough study on the effect of drying procedures on cement paste. The authors compared four drying methods: drying at 105 °C, drying over magnesium-perchlorate-hydrate, drying over dry ice (−79 °C), and freeze drying (−10 °C). In addition, drying time also influences the results. Korpa et al. [49] assumed that the correct dry mass is obtained when the mass loss during 1 day does not exceed 0.001 g per gram of the initial material. Of the methods tested, drying at 105 °C was the most harsh, leading to the lowest dry mass.

For samples reported to contain gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), drying was carried out at (40 ± 4) °C to constant mass [50].

3. Conclusions

The techniques that are used to dry and determine the CO_2 content of a sample and especially the way in which the CO_2 content of a sample is translated into a CO_2 uptake play an important role in the accurate determination of the CO_2 uptake of a material. Calculations based on the carbonation of pure minerals showed that not taking dehydroxylation and hydration reactions during carbonation into account may over- or underestimate the CO_2 uptake by up to 32.3% and 43.4%, respectively. Construction materials or waste products rich in $\text{Ca}(\text{OH})_2$ or Mg_2SiO_4 are most prone to over- or underestimation of CO_2 uptake. Taking into account the policy incentives to encourage and monetarize CO_2 storage through mineralization, it is of utmost importance to determine CO_2 uptake during mineral carbonation in a correct way.

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