



# Article Carbon Dioxide Uptake by Mortars and Concretes Made with Portuguese Cements

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Received: 16 December 2019; Accepted: 14 January 2020; Published: 16 January 2020



Featured Application: The Guidelines for National Greenhouse Gas Inventories, published in 2006 by the Intergovernmental Panel on Climate Change (IPCC), provides the procedure to calculate national GHGs emissions. However, it does not consider the net carbon dioxide emissions by the Portland cement clinker (released by the calcination process in the clinker fabrication minus concrete carbonation). This paper is a practical example of the net assessment to be followed.

Abstract: As the cement industry continues to address its role in the climate crisis, Portugal's cement industry has started to calculate its net CO<sub>2</sub> emissions to become an entirely carbon neutral sector. These emissions are calculated by simply subtracting the total CO<sub>2</sub> uptake due to mortar and concrete carbonation from the total CO<sub>2</sub> that is emitted during the calcination process (clinker production). However, the procedures given in the Intergovernmental Panel on Climate Change (IPCC) Guidelines for National Greenhouse Gas (GHG) Inventories to report GHG emissions do not contain any element that would grant this calculation method the status of an internationally recognized procedure. Therefore, some climate models are not accurate because they do not account for the carbon dioxide uptake due to concrete and mortar carbonation, as is evidenced in this paper. Climate models have improved since the IPCC's Fourth Assessment Report (AR4), but they can further improve by implementing carbon dioxide uptake by cement-based materials. In the present paper, a quick and easy method of evaluating net CO<sub>2</sub> emissions is utilized (simplified method) along with an advanced method. Portuguese net CO<sub>2</sub> emissions of the cement produced from 2005 to 2015 were calculated while taking carbon dioxide uptake during the service-life and end-of-life and secondary usage stages into account. Following the simplified method, 8.7 million tons of carbon dioxide were found to be uptake by mortars and concretes made with Portuguese cement over the ten-year period, in which 37.8 million tons were released due to the calcination process. In addition, an advanced method has been used to estimate the carbon dioxide uptake, which provided only slightly higher results than that of the simplified method (9.1 million tons).

**Keywords:** climate change; climate models; carbon dioxide uptake; carbonation; CO<sub>2</sub> capture and utilization; cement industry; sustainability

#### 1. Introduction

Concrete is a key, sustainable building material that was initiated by the modern society at the beginning of the 21st century. Concrete helps in the development of cities, regions and countries. Its pervasive importance is because it is possible to apply in many civil engineering and buildings uses with a relative low cost. Long-term reinforced concrete structures such as bridges, pipes, highways, and buildings demonstrate the indisputable high durability of this essential material and, therefore, its sustainability.

Cement is concrete's main constituent because is responsible for the binding of all the components, which comprise, at least, clinker and gypsum. More sustainable cements also contain different amounts of industrial wastes such as coal fly ash, ground granulated blast-furnace slag, and/or silica fume. Clinker production requires the calcination of the limestone used as raw material. This reaction produces huge amounts of carbon dioxide, which is emitted into the atmosphere. Consequently, the reduction of these carbon dioxide emissions is paramount for a better future. On the other hand, mortars and concretes suffer a well-known chemical reaction named carbonation, i.e., calcium hydroxide, where C–S–H gel, ettringite, calcium aluminates, and others react with the carbon dioxide to form calcium carbonate [1]. Thanks to this chemical reaction, it can be said that part of the carbon dioxide emitted during the calcination process is reabsorbed by cement-based materials. Consequently, hydrated cement can be considered a carbon sink (Figure 1). However, the current methodology for reporting carbon dioxide emissions referred to in the Guidelines for National Greenhouse Gas Inventories [2,3], published by the Intergovernmental Panel on Climate Change (IPCC), does not considers the carbonation process. Therefore, carbonation is not included in national inventories. The net carbon dioxide emissions (carbon dioxide released by calcination minus carbon dioxide uptake by carbonation) should be calculated by the National Inventories of Greenhouse Gas Emissions in order to have accurate data for country reporting.



Figure 1. Life cycle of CO<sub>2</sub> in the cement industry.

Some climate models are not accurate because they do not account for carbon dioxide uptake due to concrete and mortar carbonation. However, they can further improve the implementation of carbon dioxide uptake via cement-based materials. The need for such an improvement is based on the possibility that it could facilitate the inclusion of supplementary methodologies, not only for the sources but also for greenhouse gas (GHG) and sink effects, especially during the material's working life phase. Thus, it is a goal of the cement industry that the IPCC recognizes a method for calculating this sink due to the carbonation of cement-based materials. That is why The European Cement Association (CEMBUREAU) has promoted the creation of the concrete CO<sub>2</sub> sink project and has agreed to propose a methodology of the calculation of CO<sub>2</sub> uptake [3]. According to the simplified methodology [3], during the service life of the cement-based applications, up to 20% of the process

emissions that are related to the production of the cement can be absorbed. In addition, after the cement-based material's service-life, it is sometimes recycled as secondary material, such as aggregates, and there would therefore be an extra 3% of carbon dioxide uptake [3].

The Intergovernmental Panel on Climate Change (IPCC) recognizes the physicochemical process of carbonation for carbon removal; nevertheless, it is currently not considered in the countries' GHG emissions inventories. Consequently, the cement industry is working on developing an adequate methodology in order to allow a country to calculate the CO<sub>2</sub> removal due to concrete and mortar carbonation.

#### 2. CO<sub>2</sub> Emissions by the Cement Sector

About 65% of carbon dioxide emissions of the cement sector are due to the calcination of raw materials, mainly limestone calcination, as shown in Equation (1). The remaining 35% are emitted by the fuel combustion. Consequently, about 3% of the global anthropogenic  $CO_2$  emissions can be attributed to the calcination process of the raw materials produced in clinker kilns [4]. The calcium oxide content in a clinker is 0.65 kg CaO/kg clinker; therefore, it is necessary to extract about 1.16 kg of limestone from the earth's surface to produce 1 kg of clinker.

$$CaCO_3 \rightarrow CaO + CO_2$$
 (1)  
 $1 \text{ kg} \rightarrow 0.56 \text{ kg} + 0.44 \text{ kg}$   
 $.16 \text{ kg} \rightarrow 0.65 \text{ kg} + 0.51 \text{ kg}$ 

The largest source of the carbon dioxide emissions from the Portuguese cement industry is limestone calcination (62.4%–65.4%, 2005–2015 period). The remainder is accounted for by fuel combustion (34.6–37.6, 2005–2015 period).

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The content of CaO in clinkers amounts to 65%; then, the theoretical carbon dioxide emissions by calcination in the clinker production are 0.51 kg CO<sub>2</sub>/kg clinker. On the other hand, carbon dioxide emissions from fuel use depend on the type of fuel (petcoke, coal, fuel oil, alternative fuels, and so on).

The global cement sector indicators in 2014, published by The International Energy Agency (IEA) [5], showed that the cement sector was the second biggest industrial carbon dioxide emitter, in general, and the first biggest industrial process emitter, in particular (63% CO<sub>2</sub> process and 37% energy-related carbon dioxide). In regard to energy use, the cement sector was the second biggest industrial coal user and the third biggest industrial energy user (61% coal, 13% electricity, 13% oil, 9% gas, 3% wastes, and 2% biomass). Therefore, the cement industry could play a big role in lowering carbon dioxide emissions. Particularly, carbon intensity might be reduced in several ways, such as lowering the clinker/cement ratio, increasing energy and process efficiencies, switching to fuels with lower carbon intensities, and carbon dioxide removal. In addition, after a period of time, part of these carbon dioxide emissions is absorbed by cement-based materials when the physicochemical process known as carbonation occurs. The chemistry of carbonation has been reviewed in some papers [6–8].

Carbon dioxide emissions per ton of cement have been lowered worldwide in the last few years [9]. Nevertheless, the production of cement is growing rapidly, achieving an amount of 4.65 billion tons in 2016 (Figure 2) [10]. Asia produces 80.5% of the world's production, while Europe–CEMBUREAU only produces 5.3%.

Figure 3 shows the gross carbon dioxide emissions for grey clinker; the emissions shown are the direct carbon dioxide emissions, except for the on-site electricity production and the emissions from biomass fuel. Carbon dioxide emissions due to clinker production have been reduced in the last decade, as shown in Figure 3 [9], from more than 925 kg CO<sub>2</sub>/t clinker (North America) in 2005 to 825–850 kg CO<sub>2</sub>/t clinker in 2015. In particular, it should be highlighted that Portugal has experienced a significant decrease from 855 kg CO<sub>2</sub>/t clinker in 2005 to 821 kg CO<sub>2</sub>/t clinker in 2015 (Figure 3).



Figure 2. World cement production in 2016 by region and main countries (4.65 billion tons) [10].



Figure 3. Gross carbon dioxide emissions for grey clinker from 2005 to 2015 [9].

Additionally, it should be pointed out that the European cement industry, in general, has considerably diminished its environmental impact [9,10]. There was also a slight decrease in CO<sub>2</sub> emissions in several countries in the 1990–2003 period, when considering both calcination process and fuel combustion per ton of cement, as shown in Figure 4 [11]. China, Spain, and Germany, among others, have exhibited a significant reduction of carbon dioxide emissions as consequence of their reduction of the clinker factor. That is, they followed a significant growing trend of blended cement production with an upward content of additions.

This downward trend can be confirmed looking at the development of the average value. The new climate change framework is paramount in order to maintain the current downward trend. For instance, European standardization has promoted the use of new ternary cements with the publication of the FprEN 197-1:2020 "Common cements – Part 1: Composition and essential characteristics".



**Figure 4.** CO<sub>2</sub> emissions due to the process and the combustion per ton of cement in several countries from 1990 to 2004 [11].

Five hundred million tons of carbon dioxide emissions were reported by the cement sector in 1970, and about one thousand million tons were reported in 2000. In 2010, the original value of 1970 was tripled. In the future, the use of carbon capture and storage (CCS) techniques in the cement sector will be necessary to maintain  $CO_2$  emissions at a low rate [12]. Therefore, the ultimate goal of the cement industry in regard to carbon dioxide emission levels should be about 350–400 kg  $CO_2$  per ton of cement. This objective can be achieved by increasing the addition/clinker ratio in blended cements, by using alternative fuels, by using non-carbonated raw materials, and by improving the energy efficiency.

On the other hand, the United Nations has established 17 Goals in order to implement the three legs of the sustainable development in the United Nations 2030 Agenda [13], i.e., society, environment, and economy. They are called the Sustainable Development Goals (SDGs) (Figure 5). Accordingly, the European Union has established a set of indicators to check the SDGs in Europe [14]. In particular, cement production can generate some environmental impacts, such as  $CO_2$  emissions. Nevertheless, the cement-based materials use, such as mortars and concretes, has led to the improvement of infrastructures in general, e.g., transport, water supply, and energy. Consequently, cement production plays an enormous role in human wellbeing (society) and economic development, which are two of the three legs of sustainable development.



Figure 5. Sustainable Development Goals (SDGs).

In addition, great efforts of the cement production sector in promoting sustainable development have been acknowledged (Figure 5). Cement-based materials are essential to economic growth (Goal 8), infrastructures (Goal 9), sanitation (Goal 6), sustainable cities (Goal 11) and climate action (Goal 13).

#### 3. CO<sub>2</sub> Uptake of Concrete

Carbonation is a physico-chemical process that has been extensively defined and modelled (Figure 6) in the literature [1,4,6–8]. Figure 7 summarizes the main factors that affect the carbonation uptake by mortars and concretes. These materials consist of a solid cement matrix that contains aggregates, capillary pores, and air bubbles in its interior. When one wants to calculate the amount of carbon dioxide fixed by the cement matrix, one needs to multiply the carbonation coefficient by the square root of the time ratio. Therefore, the decreasing trend of the square-root of time is well-known. This fact means that, after a period of time, the increase of carbon dioxide uptake is negligible. Given that, the carbonation uptake process involves two distinct parts: (i) maximum carbon dioxide uptake during the first twenty to fifty years and (ii) a negligible period (Figure 6). According to Figure 6, it takes between 20 and 25 years to reach 50% of carbonation and between 70 and 80 years to reach 90% of carbonation.



Figure 6. Carbonation uptake intensity (Source: elaborated by the authors).



**Figure 7.** Main factors affecting the carbonation uptake by the mortars and concretes (Source: elaborated by the authors).

According to EN 206 [15], the exposure classes, in regard to the corrosion that is induced by carbonation where concrete-containing reinforcement or another embedded metal is exposed to air and moisture, are:

- XC1: dry or permanently wet
- XC2: wet or rarely dry
- XC3: moderate humidity
- XC4: cyclic wet and dry

On the other hand, the European standard EN 1992-1-1 (Eurocode 2) [16] deals with reinforced concrete structure design in civil engineering works and buildings. In particular, Eurocode 2 describes the minimum concrete cover for reinforcement, taking account the carbonation exposure class (XC), as shown in Table 1 [16].

**Table 1.** Environmental requirement for minimum concrete cover (mm) according to reference [16] in corrosion that is induced by carbonation.

Environmental Requirement for Minimum Concrete Cover (mm)	Structural Class					
Exposure Class: Corrosion Induced by Carbonation	<b>S1</b>	S2	<b>S</b> 3	<b>S</b> 4	<b>S</b> 5	<b>S</b> 6
XC1—dry or permanently wet	10	10	10	15	20	25
XC2—wet or rarely dry	10	15	20	25	30	35
XC3—moderate humidity	10	15	20	25	30	35
XC4—cyclic wet and dry	15	20	25	30	35	40

Based on the simplified method [3] and the advanced method, a first study for the calculation of  $CO_2$  uptake in a period of ten years (2005–2015) attributed to the Portuguese cements was carried out for this paper. Carbon dioxide emissions reported by the Portuguese cement industry and provided by the Technical Association of the Cement Industry from Portugal (ATIC) helped to estimate the percentage of reduction of  $CO_2$  emissions due to cement-based material's sink effect.

# 4. Methodology

### 4.1. Calculation of CO<sub>2</sub> Uptake of Concretes and Mortars Following the Simplified Method (Tier 1)

As mentioned in [3], the amount of carbon dioxide that can be absorbed during the service life of a product that is manufactured with cement can be calculated with a fixed conservative value by using the simplified methodology. This value could either be 15% or 20% of the CO<sub>2</sub> emissions, because the process of calcination is a long way from the maximum theoretical value of carbon dioxide that can be absorbed (around 490 kg of CO<sub>2</sub> per ton in the case of a cement without addition, CEM I). Regarding the CO<sub>2</sub> uptake of concretes and mortars during the end-of-life period, it is estimated to be 3% of the CO<sub>2</sub> emissions due to the process of calcination [3]. Equations (2) and (3) represent the general procedure to calculate the CO<sub>2</sub> uptake of cement-based materials for the service life and end-of-life stages, according to the simplified method (Tier 1). In the present study, the parameters  $\alpha$  and  $\beta$  were 0.20 and 0.03, respectively.

$$CO_2$$
 uptake (service life) =  $\alpha \times$  reported calcination emissions to the IPCC (2)

 $CO_2$  uptake (end-of-life) =  $\beta \times$  reported calcination emissions to the IPCC (3)

#### 4.2. Calculation of CO<sub>2</sub> Uptake of Concretes and Mortars Following the Advanced Method (Tier 2)

The carbon dioxide uptake by mortars and concretes that are produced with Portuguese Portland cements can be calculated according to Equation (4).

$$(CO_2)_{uptake} = C \times CO_{2,max} \times DoC \times (k_{co2} \sqrt{t/1000}) \times S/V$$
(4)

where:

(CO<sub>2</sub>)<sub>uptake</sub>: carbon dioxide content uptake, kg CO<sub>2</sub>.

C: cement manufactured, kg cement.

CO<sub>2,max</sub>: maximum carbon dioxide content able to be uptake, kg CO<sub>2</sub>/kg cement.

DoC: carbonation degree, dimensionless. In this study was 0.6576.

 $k_{co2}$ : carbonation rate, mm/year<sup>0.5</sup>.

#### t: time, years.

S/V: surface per volume ratio,  $m^2/m^3$ .

#### 5. Results

#### 5.1. CO<sub>2</sub> Uptake of Concretes Manufactured with Portuguese Cements Following the Simplified Method

Table 2 shows the summary of the Portuguese domestic data for clinker annual production, total absolute gross  $CO_2$  emissions (without biomass emissions), and absolute gross process  $CO_2$  emissions from cement manufacturing plants between 2005 and 2015. The theoretical uptake has been defined as 23% of all  $CO_2$  emissions due to calcination for the service life period (20%) and the end-of-life plus secondary usage stage (2% + 1% = 3%), respectively [3]. Therefore, if a factor of 0.23 is applied to the absolute gross process  $CO_2$  emissions shown in Table 2, this factor was proposed in the IVL simplified methodology [3], the results that appear in Figure 8 can be obtained.

**Table 2.** Clinker annual production, total absolute gross  $CO_2$  emissions (without biomass emissions), and absolute gross process  $CO_2$  emissions (kilotons) from Portuguese cement manufacturing plants between 2005 and 2015.

Year	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Clinker annual production (kilotons)	7865	7777	8018	7748	6164	6484	5351	4882	5427	5968	5626
Total Absolute Gross CO <sub>2</sub> Emissions (kilotons) (without biomass emissions)	6722	6640	6811	6524	5075	5458	4455	4015	4393	4904	4621
Absolute Gross Process CO <sub>2</sub> Emissions (kilotons)	4206	4141	4256	4146	3200	3471	2825	2588	2872	3162	2978





 $CO_2$  uptake in Portuguese cement manufacturing plants has been estimated to be 8.7 million tons of  $CO_2$  during the period of 2005–2015.

### 5.2. CO<sub>2</sub> Uptake of Concretes Manufactured with Portuguese Cements Following the Advanced Method

Cement consumption and the end use of concretes from 2005 to 2015 are shown in Figure 9. The key point in this methodology is the surface per volume ratio (S/V) factor selection, which depends on the type of application. The S/V of the structural elements can be divided in several groups. The S/V ratios used in the present study were three for civil works, eight for buildings, and 20 for mortars. It was assumed that the full carbonation in mortar is achieved after 10–15 years of carbonation (year 2025). The high porosity of mortars is well-known, so their carbonation rate is much higher than that of concretes. This fact justified the assumption.



**Figure 9.** Cement consumption (solid line and left-hand scale) and end use of cement in concretes (bars and right-hand scale) from 2005 to 2015.

The carbonation rate,  $k_{co2}$  (mm/year<sup>0.5</sup>), can be calculated by applying Equation (5) to the experimental results. In the present study, the carbonation rate,  $k_{co2}$ , in concrete used in structures was estimated from the Portuguese data shown in the literature [17,18]. Figure 10 summarizes the experimental Portuguese results.

$$\mathbf{x} = \mathbf{B}\,\mathbf{\sqrt{t}}\tag{5}$$

where:

 $B = carbonation coefficient (mm/y^{0.5}).$ 

x = carbonation depth (mm).

t = time of natural carbonation (years).

The maximum stoichiometric amount of carbon dioxide that can be absorbed can be calculated by applying Equation (6), and the results of such a calculation are shown in Table 3.

$$CO_{2,max} \rightarrow (CaO_{reactive} / 100) \times binder \times (M_{CO_2} / M_{CaO})$$
 (6)

where:

 $CO_{2,max}$ : maximum amount of carbon dioxide that can be absorbed, kg  $CO_2$ /kg cement. Ca $O_{reactive}$ : kg CaO/kg binder × 100. This value is taken as 65%. Binder: Amount of cement (kg).  $M_{CO_2}$ : 44.0 g/mol.  $M_{CaO}$ : 56.1 g/mol.



**Figure 10.** Carbonation rate of Portuguese concretes made with different proportions of coal fly ash and ground granulated blast-furnace slag and (**a**) 251 kg/m<sup>3</sup> of cement, w/c = 0.65; (**b**) 342 kg/m<sup>3</sup> of cement, w/c = 0.44; and (**c**) 440 kg/m<sup>3</sup> of cement, w/c = 0.35 [17].

Main	Type Name	Type Notation	K <sup>1</sup>	MAC <sup>2</sup>	Factor	Factor	CO <sub>2,max</sub>
Types					(K <sub>cement</sub> /K <sub>CEM I</sub> )	(K <sub>cement</sub> /K <sub>CEM I</sub> )	kg CO <sub>2</sub> /kg Cement
CEM I	Portland cement	CEM I	95–100	0–5	95/95 = 1	1	0.49
	Portland-slag	CEM II/A-S	80-88	0–5	80/95–94/95	0.84-0.99	0.41-0.48
	cement	CEM II/B-S	65–79	0–5	65/95–79/95	0.68-0.83	0.34-0.41
	Portland-silica fume cement	CEM II/A-D	90–94	0–5	90/95–94/95	0.95–0.99	0.46-0.48
	Portland-pozzolana cement	CEM II/A-P	80-94	0–5	80/95–94/95	0.84-0.99	0.41-0.48
		CEM II/B-P	65–79	0–5	65/95–79/95	0.68-0.83	0.34-0.41
		CEM II/A-Q	80-94	0–5	80/95-94/95	0.84-0.99	0.41 - 0.48
		CEM II/B-Q	65–79	0–5	65/95–79/95	0.68-0.83	0.34-0.41
CEM II	Portland-fly ash cement	CEM II/A-V	80-94	0–5	80/95–94/95	0.84-0.99	0.41-0.48
		CEM II/B-V	65–79	0–5	65/95-79/95	0.68-0.83	0.34-0.41
		CEM II/A-W	80-94	0–5	80/95-94/95	0.84-0.99	0.41 - 0.48
		CEM II/B-W	65–79	0–5	65/95–79/95	0.68-0.83	0.34-0.41
	Portland-burnt	CEM II/A-T	80-94	0–5	80/95–94/95	0.84-0.99	0.41-0.48
	shale cement	CEM II/B-T	65–79	0–5	65/95–79/95	0.68-0.83	0.34-0.41
	Portland-limestone cement	CEM II/A-L	80-94	0–5	80/95–94/95	0.84-0.99	0.41-0.48
		CEM II/B-L	65–79	0–5	65/95–79/95	0.68-0.83	0.34-0.41
		CEM II/A-LL	80–94	0–5	80/95–94/95	0.84-0.99	0.41 - 0.48
		CEM II/B-LL	65–79	0–5	65/95–79/95	0.68-0.83	0.34-0.41
	Portland-composite	CEM II/A-M	80-88	0–5	80/95–94/95	0.84-0.99	0.41-0.48
	cement	CEM II/B-M	65–79	0–5	65/95–79/95	0.68-0.83	0.34-0.41
CEM III	Blast furnace cement	CEM III/A	35-64	0–5	35/95–64/95	0.37-0.67	0.18-0.33
		CEM III/B	20-34	0–5	20/95-34/95	0.21-0.36	0.10-0.18
		CEM III/C	5–19	0–5	5/95–19/95	0.05-0.20	0.03-0.10
CEM IV	Pozzolanic cement	CEM IV/A	65–89	0–5	65/95-89/95	0.68-0.94	0.34-0.46
		CEM IV/B	45-64	0–5	45/95-64/95	0.47-0.67	0.23-0.33
CEMV	Composite cement	CEM V/A	40-64	0–5	40/95-64/95	0.42-0.67	0.21-0.33
CEM V		CEM V/B	20-38	0–5	20/95-38/95	0.21-0.40	0.10-0.20
			0				

<sup>1</sup> Clínker; <sup>2</sup> Minor additional constituents.

By applying Equation (6) to a CEM I with 95% clinker that contains 65% CaO<sub>reactive</sub>, it can be seen that the maximum amount of carbon dioxide that can be absorbed is equal to  $CO_{2,max} = (65/100) \times 0.95 \times (44/56) = 0.49$  kg  $CO_2/kg$  CEM I. This value only applies to a cement with 95% clinker (CEM I).

As far as other cements are concerned, this value drops in proportion to clinker content. Table 3 has been prepared in order to rapidly display the maximum amount of carbon dioxide that the different EN 197-1 [19] cements can absorb.

The amount of carbon dioxide that can be absorbed, in kg of concrete or of mortar, during the service life of a material that is manufactured mainly with cement can be calculated from the input data and following the method described in Section 4.2. For the calculation, it must be noted that the carbonation follows a square root of time, and the carbonated depth is increasing each year following the equation:  $x=k\cdot\sqrt{t}$ . This means that the emissions produced in one year are incorporated into the concrete in the following years with a decreasing trend of time.

The carbonation coefficients used in the present paper were taken from the Portuguese literature. Nevertheless, EN 16757 [20] contains Table BB.1 to estimate the carbonation rate,  $k_{co2}$  (mm/year<sup>0.5</sup>) exclusively on the basis of the concrete's compressive strength. It is true that there is a direct relationship between carbonation rate and concrete's compressive strength when the correlation is determined with the cement itself, the type of aggregates, additives, etc. However, when one of these factors is modified, different correlations are found [21]. Therefore, it is not possible to generalize the results compiled in Table BB.1 and to apply them to all the cements that are manufactured in Europe or for all the environments to which concrete is exposed. According to Monteiro et al., the carbonation coefficient for structural elements within the XC3 class (unpainted concrete) ranges from 3.33 to 4.20 mm/year<sup>0.5</sup> [18] and is consistent with that found in the study conducted by The Eduardo Torroja Institute of Construction Sciences - Spanish National Research Council (IETcc-CSIC) in 2010 [22]. Furthermore, the values shown in Table BB.1 (EN 16757 [20]) range from 0.50 to 16.50 mm/year<sup>0.5</sup>, i.e., they are greater than those found in actual Portuguese concretes that are manufactured in accordance with EN 206 [15]. The whole amount of carbon dioxide that can be absorbed by concretes and mortars made with Portuguese cements, consumed from 2005 to 2015, is shown in Figure 11. In addition, the growth path of carbon dioxide uptake is represented by a growing curve for each considered application (civil engineering, building and mortars). As expected, the higher the surface/volume (S/V) ratio and carbonation coefficient  $(k_{co2})$ , the higher the carbon dioxide uptake [23].



**Figure 11.** Carbon dioxide uptake (tons) considering the surface/volume (S/V) ratios of three for civil engineering works, eight for buildings, and 20 for mortars (mortars only carbonated for ten years). In addition, 3% of the absolute gross process CO<sub>2</sub> emissions due to the end-of-life stage was added to the carbon dioxide uptake reached in 2021 (green point).

The total amount of carbon dioxide that can be absorbed by concretes and mortars made with Portuguese cements, consumed from 2005 to 2015 while considering surface/volume (S/V) ratios of three for civil engineering works, eight for buildings, and 20 for mortars, is shown in Figure 11. It is assumed that the full carbonation in mortar is achieved after 10–15 years of carbonation (year 2025).

In addition, the growth path of carbon dioxide uptake is represented by a growing curve for each considered application (civil engineering, building and mortars). As expected, the higher the S/V ratio, the higher the carbon dioxide uptake.

In the present case, it can be observed that the carbon dioxide uptake during the ten years production period (2005–2015) was found to go from 5.6 to 7.4 million tons from 2050 to 2100. Consequently, the percentage of carbon dioxide uptake, considering the absolute gross process  $CO_2$  emissions, was in the range between 14.7% and 19.6% (Figure 12). Consequently, the simplified method agrees with the carbon dioxide uptake from the origin considered in the present study until the year 2100. Nevertheless, 9.1 million tons of carbon dioxide will be uptake in the year 2121 (24.2%), when 3% of the absolute gross process  $CO_2$  emissions due to the end-of-life stage is added to the carbon dioxide uptake reached in 2021.



**Figure 12.** Carbon dioxide uptake, i.e., carbon dioxide absorbed by cement-based materials consumed from 2005 to 2015 related to the absolute gross process CO<sub>2</sub> emissions (t) produced from 2005 to 2015 for surface/volume (S/V) ratios of three for civil engineering works, eight for buildings, and 20 for mortars (mortars only carbonated for ten years); 3% of the absolute gross process CO<sub>2</sub> emissions due to the end-of-life stage was added to the carbon dioxide uptake reached in 2021 (green bar).

Figure 12 shows the carbon dioxide uptake that was calculated by dividing the accumulated yearly absorption by the absolute gross process  $CO_2$  emissions; this is expressed in percentage. This figure represents the results obtained for the main applications of cement-based products (civil engineering works, buildings, and mortars). As result of the sharp decrease of the cement consumption from 2005 (8.705.000 tons) to 2010 (5.803.000 tons) and to the end of the investigation period, 2015 (2.745.000 tons), the relative uptake is lower as shown in Figure 12.

Comparing the results that were obtained by applying the simplified and advanced methods, it a good agreement in general is evident. However, the advanced methods allowed for a more realistic calculation and, therefore, higher results were found when using them. As such, the 8.7 million tons found when using the simplified method became 9.1 million tons when using the advanced method proposed in the present paper. Consequently, the use of advanced methods is recommended in order to get more accurate results to be used as input data in the climate models that are developed within the IPPC's assessment report context.

Figure 13 shows the net carbon dioxide emissions by final use of the mortars, building and civil works cement consumed in Portugal from 2005 to 2015. As expected, mortars carbonated very quickly, whereas civil works concretes carbonated very slowly. Consequently, the carbon dioxide uptake performed by mortars reached about 95% in ten years. On the contrary, after one hundred years of carbonation, civil works and building concretes only reached 6.6% and 26.0%, respectively.



**Figure 13.** Net carbon dioxide emissions by final use (mortars, building and civil works). Carbon dioxide uptake from 2005 to 2021 in regard to the carbon dioxide released from 2005 to 2015 (%).

The Intergovernmental Panel on Climate Change (IPCC) is currently in its sixth assessment cycle and is developing three special reports, a methodology report on national greenhouse gas inventories and the Sixth Assessment Report (AR6). In regard to the shortcomings in the current climate models, which do not consider net carbon dioxide emissions, the lead and contributing authors as well as the review editors strongly encourage the improvement of such models by implementing the actual impact of the Portland cement sector, i.e., including the net carbon dioxide emissions by the Portland cement clinker (released by the calcination process in the clinker fabrication minus the carbon dioxide uptake by mortars and concrete carbonation).

# 6. Conclusions

The conclusions reached with this study are as follows:

- The total amount of carbon dioxide that can be absorbed by concretes and mortars made with Portuguese cements, consumed from 2005 to 2015, was found to go from 5.6 to 7.4 million tons from 2050 to 2100 when considering the surface/volume ratios of three for civil engineering works, eight for buildings, and 20 for mortars. Thus, the percentage of carbon dioxide uptake, considering the absolute gross process CO<sub>2</sub> emissions, is in the range between 14.8% and 19.6%. Consequently, the simplified method agrees with the carbon dioxide uptake from the origin considered in the present study until the year 2100. Nevertheless, 9.1 million tons of carbon dioxide will be uptake in the year 2121 (24.2%), when 3% of the absolute gross process CO<sub>2</sub> emissions due to the end-of-life stage is added to the carbon dioxide uptake reached in 2021.
- In the period of 2005–2015, CO<sub>2</sub> absorption from Portuguese cements was estimated at 8.7 million tons of CO<sub>2</sub> when using the simplified methodology and applying a factor of 0.23 (20% for service life and 3% for the end-of-life plus secondary usage stage), which is what is proposed in the IVL simplified methodology.

- Mortar's carbon dioxide uptake was about 95% in ten years. However, civil works and building concretes only reached 6.6% and 26.0% after one hundred years of carbonation, respectively.
- As expected, short carbonation periods provide a low carbon dioxide uptake. Therefore, actual service-life periods should be considered in order to assess the whole process. In addition, the great influence of the S/V ratio on carbon dioxide uptake make this a key factor in this advanced methodology
- In regard to the shortcomings in the current climate models, which do not consider the net carbon dioxide emission (released by the calcination process in the clinker fabrication minus concrete carbonation) attributed to the Portland cement clinker production, IPCC authors are strongly encouraged to improve their climate models adding the aforementioned net carbon dioxide emissions.

Author Contributions: Conceptualization, C.A. and M.Á.S.; methodology, C.A.; software, C.A.; formal analysis, C.A.; investigation, C.A. and M.Á.S.; resources, A.Z.; data curation, C.A.; writing—original draft preparation, M.Á.S.; writing—review and editing, A.Z., P.M., C.A. and M.Á.S.; visualization, A.Z. and P.M., supervision, A.Z.; project administration, A.Z.; funding acquisition, A.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Technical Association of the Cement Industry from Portugal (ATIC).

**Acknowledgments:** We would like to express our profound gratitude to the Technical Association of the Cement Industry from Portugal (ATIC) and all individuals that have kindly collaborated with us.

Conflicts of Interest: The authors declare no conflict of interest.

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