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CO_2 uptake in cement-containing products

Background and calculation models for implementation in national greenhouse gas emission inventories

Commissioned by Cementa AB and IVL research foundation

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Preface

The climate issue is today a very important issue both globally and nationally. Many organizations and companies are actively working on climate issues and greenhouse gas emission reductions are often an important goal, as well as mapping and monitoring of greenhouse gases. At the international level, most countries report greenhouse gas emissions to the United Nations Framework Convention on Climate Change (UNFCCC). The international monitoring of net greenhouse gas emissions to the atmosphere is an important part of the mapping and monitoring of global climate efforts. The guidelines for how emission calculations are to be carried out are presented in the framework of the Intergovernmental Panel on Climate Change (IPCC) and are regulated in, for example, the document *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. In order for calculations of net greenhouse gas emissions to the atmosphere to be as accurate as possible, it is important that the guidelines and other documents are updated and improved by the IPCC such as the *2006 IPCC Guidelines for National Greenhouse Gas Inventories*.

As part of the climate work for the cement and concrete industry, the estimates of carbon dioxide emissions have been analyzed with regard to the regulations in the *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. It shows that CO_2 emissions from cement production are calculated from both the combustion of different fuels in the cement kiln and from the discharging of CO_2 from the raw materials, mainly due to various incoming carbonates. This process is usually referred to as calcination and can be exemplified by the following chemical formula showing the thermal decomposition of limestone:

$$CaCO_3 \rightarrow CaO + CO_2$$

However, the calcination reactions in cement are not chemically stable but are reversible. This means that CO_2 in air reacts with hydrated cement phases in concrete and carbonates are regenerated. This process is usually called carbonation, sometimes also referred to as recarbonation. Carbonation can take place during the lifetime of the concrete product, but also in, for example, crushed concrete as a secondary product (e.g. base course of a road or as landfilling material). This uptake of CO_2 in the concrete thus reduces the net emission of CO_2 from the raw material part. This uptake of CO_2 can be significant, which is why it is important to take this effect into account in emission calculations. The current version of the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* does not take into account the effects of carbonation. This could lead to reduced accuracy in both national and global emission calculations.

A significant amount of research is available regarding carbonation (see e.g. Appendix 2). Some CO_2 uptake models have been developed in different countries and a European standard [16] is available, with an annex on calculation of CO_2 uptake in concrete products. However, uptake models adapted to the IPCC applications are missing. This is thus the origin and background of the present study. As calculation models for CO_2 uptake in concrete are difficult and complex, an international research team has been created to capture present research and to further develop appropriate methods and calculation models for CO_2 uptake. The aim of this study was to improve the net emission estimates of climate gases by providing support for improved calculation methods. It can also be used as a guideline for the national greenhouse gas calculations and as a complement to the *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. The present report is the result of this research group's work and is intended to be used as a basis for further development work in the climate field.

The present study has been carried out by IVL Swedish Environmental Research Institute as a co-financed research project. The project is co-financed by IVL research foundation (50 %) and Cementa AB (50 %). IVL's part is part of an international project to develop methods for CO_2 uptake in concrete which has contributed to important scientific information. The results from this study will be provided to IPCC and other organizations in order to include CO_2 uptake in concrete as a part of the global CO_2 net emission calculations.

Preface to second edition

After the first edition of the report dated October 2018, the project has continued. In the subsequent project, the calculation methods have been further developed and calculation models for CO_2 uptake in concrete have been developed for both Tier 1 and Tier 2. These models are intended to be used in uptake calculations of CO_2 in concrete on a national basis for e.g. the national emissions reporting and for international reporting to the UNFCCC. The models can also, to some extent, be used for uptake calculations in specific concrete structures or groups of such structures. To communicate the knowledge about carbonation and its calculation methods, a web page has also been developed on IVL's website where information is presented and where calculation models and other information can be downloaded. The web page can be accessed at the following web address:

www.ivl.se/co2-uptake-concrete

In connection with this continued work, it has also been found appropriate to also update the existing research report that is linked to the project, where the latest information is now available. The idea is to keep both the research report and the web pages current through updating and development.

Acknowledgement

The authors of the study want to give special thanks to the technical and scientific persons who have contributed with valuable information and views to the project.

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Summary

The climate issue is today a very important issue both in an international perspective and nationally. Many organizations and companies are actively working on climate issues and greenhouse gas emission reductions are often an important goal, as well as mapping and monitoring of greenhouse gases. At the international level, most countries report greenhouse gas emissions to the United Nations Framework Convention on Climate Change (UNFCCC). The international monitoring of net greenhouse gas emissions to the atmosphere is an important part of the mapping and monitoring of global climate effects. Guidelines for national calculations of emissions and sinks of greenhouse gases are presented in the framework of the Intergovernmental Panel on Climate Change (IPCC) and are regulated in, for example, the document *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. In order for the calculations of the net greenhouse gas emissions to the atmosphere to be as accurate as possible, it is important that the guidelines and other documents are updated and improved by the IPCC such as the *2006 IPCC Guidelines for National Greenhouse Gas Inventories*.

As part of the climate work for the cement and concrete industry, the estimates of carbon dioxide emissions have been analyzed with regard to the regulations in the *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. It shows that CO_2 emissions from cement production are calculated from both the combustion of different fuels in the cement kiln and from the discharging of CO_2 from the raw materials, mainly due to various incoming carbonates. This process is usually referred to as calcination and can be exemplified by the following chemical formula showing the thermal decomposition of limestone:

$CaCO_3 \rightarrow CaO + CO_2$

However, the calcination reactions in cement are not chemically stable but are reversible. This means that CO_2 in air reacts with hydrated cement phases in the concrete and carbonates are regenerated. This process is usually called carbonation, sometimes also referred to as recarbonation. Carbonation can take place during the lifetime of the concrete product, but also in, for example, crushed concrete as a secondary product (e.g. base course of a road or as landfilling material). This uptake of CO_2 in the concrete thus reduces the net emission of CO_2 from the raw material part. This uptake of CO_2 can be significant, which is why it is important to take this effect into account in net emission/uptake calculations. The current version of the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* does not take into account the effects of carbonation as a carbon sink. This could lead to reduced accuracy in both national and global net emission calculations.

A significant amount of research is available regarding carbonation (see e.g. Appendix 2). Some CO_2 uptake models have been developed in different countries and a European standard [16] is available, with an annex on calculation of CO_2 uptake in concrete products. However, uptake models adapted to the IPCC applications are missing. This is thus the origin and background of the present study. As calculation models for CO_2 uptake in concrete are difficult and complex, an international research team has been created to capture present research and to further develop appropriate methods and calculation models for CO_2 uptake with the aim of improving net emission estimates of climate gases and providing support for improved calculation methods within the IPCC and especially the *2006 IPCC Guidelines for National Greenhouse Gas Inventories*.

The study can also be used as a guideline for the national greenhouse gas calculations. Calculation of greenhouse gas emissions and sinks for reporting to the UNFCCC is usually made by the Ministry or nationally appointed organizations in each reporting country. This organization can usually be reached via the national Ministry of Environment or the national Environmental Protection Agency (EPA). From a technical and calculation point of view and due to its complexity, it is recommended that the national CO_2 uptake calculations for concrete are performed as a cooperation between the nationally appointed calculation group and the national cement and concrete industry.

In principle, the same amount of CO_2 driven off by calcination in the cement kiln can be taken up in the concrete by carbonation. However, the amount of CO_2 that will be taken up by carbonation in reality depends on several factors. The carbonation process is a slow process that can last for many years. The time aspect is thus an important issue. The availability of CO_2 for the concrete is also crucial. The concrete must be exposed to the CO_2 in air to be able to carbonate. The transport of CO_2 molecules into the concrete is thus also an important factor as well as moisture factors. For example, if the concrete is crushed after use, the carbonation rate will increase considerably due to increased concrete surface areas.

Carbonation is thus an important aspect to take into account in climate and emission calculations for cement and concrete. Today, emissions of greenhouse gases from the different countries are reported, which in turn are used to support different climate strategies. Reporting takes place nationally to national authorities and internationally to the United Nations Framework Convention on Climate Change (UNFCCC). Both CO_2 emissions from fossil fuel combustion and emissions from the raw materials (calcination) are included. However, no consideration is given to the carbonation of concrete. This may be considered a shortcoming in these calculations, which can lead to less accurate results. A very rough estimate is that the use of concrete today accounts for about 5 % to 8 % of the world's carbon dioxide emissions. About 50 % to 60 % of the CO_2 emissions from cement production emanate from the raw materials and thus has a potential to be reabsorbed by carbonation of the concrete, partly during the use phase of the concrete products, and partly in the end-of-life and secondary use stage. This study proposes methods and models for calculating CO_2 carbonation in various cement-containing products, including mortar for rendering and cement/concrete additions such as ground granulated blast furnace slag (GGBS), fly ash, and lime filler.

Accurate model calculations of national CO_2 uptake in concrete are rather complex and involve many different factors that control the uptake. However, the calculations can also be simplified but with an increased uncertainty. Similar to the emission calculations developed for the *2006 IPCC Guidelines for National Greenhouse Gas Inventories*, three different calculations methods are identified/developed in this study, Tier 1, Tier 2 and Tier 3, in increased model complexity. According to IPCC guidelines, Tier 2 or Tier 3 methods should replace Tier 1 method for a greenhouse gas source or sink that are defined as a “key category” either on “level” or “trend”. That means that consideration should be given to categories that are of significant magnitude in later years or show a large change in magnitude over a given time series.

The calculation methods in this study are based on previous research in the area. The Tier 1 estimate is a simplified calculation method that can be used by almost all national calculation groups with a minimum of input data. The proposed Tier 1 average value is 0.23 (23 %) of the calcination emissions from the process. This includes the CO_2 uptake in existing concrete structures, in end-of-life, and secondary use. The Tier 2 method is a more complex calculation method that can be used in the national calculation groups but still with some simplifications. The

Tier 3 method opens up for the use of complex computer models for the uptake calculations that requires more knowledge and input data. Such models have been developed in a few countries on a research basis.

Abbreviations and definitions

Calcination: Is, in this case, defined as the thermal decomposition of mainly calcium carbonate ($CaCO_3$) or other carbonates under the formation of CO_2.

Carbonated concrete: Part of concrete where carbonation has occurred and colorless indication with phenolphthalein solution shows that pH has been lowered to less than about 8. Additional CO_2 uptake may have occurred in areas where pH change has not yet taken place.

Carbonated zone: Part of concrete that is carbonated.

Carbonation depth: Distance from surface to where colorless indication with phenolphthalein solution shows that pH has been lowered to less than about 8. Additional uptake of CO_2 may have occurred beyond the carbonation front, prior to pH change.

Carbonation rate: The carbonation rate depends of several factors such as the chemical reaction rate, mass transport of CO_2, humidity, temperature, porosity, CO_2 concentration in ambient air etc. For practical reasons the carbonation rate is often determined by measuring the depth of carbonation as function of time. It can then be expressed as mm/√year.

Carbonation: A chemical reaction by which CO_2 penetrates the concrete and reacts with the hydration products, forming mainly calcium carbonate.

CEM I: Is a pure Portland cement.

CEM II: Portland composite cement containing at least 65 % Portland clinker.

CEM III: Contains at least 20 % and at most 65 % Portland cement and the remaining is blast furnace slag.

Cement: Binder in concrete, and mortar and made of ground clinker, gypsum and often some added constituents such as GGBS, fly ash, silica fume, or limestone.

Clinker: Is the sintered material produced in the cement kiln when heating the raw mix to high temperature.

CO_2 uptake area: Is the area in cement containing products where CO_2 can be absorbed through carbonation.

Concrete: Construction material made mainly of cement, gravel, sand, water, and possibly of additions and admixtures.

Degree of carbonation: The amount of CO_2 uptake by carbonation in relation to maximum CO_2 uptake by carbonation. The maximum uptake of CO_2 can often be equated with the CO_2 emission from calcination that is driven off from the material. (For non-traditional raw material for clinker processing, see Chapter 2.2.) Traditionally, the degree of carbonation has been defined only within the area which has been considered carbonated and this area has been defined as the area exhibiting color change with phenolphthalein test.

DOC: Degree of carbonation.

GGBS: Ground granulated blast furnace slag.

Gt C: Gigatonne carbon.

IPCC: Intergovernmental Panel on Climate Change.

Mortar: Is a mix of cement, sand and water. It is used as bonding agent between building materials or for rendering of surfaces.

MR: Mortar used for rendering surfaces.

NIR: National Inventory Report

Portland cement: Is a common type of hydraulic cement made of mainly ground clinker and a few percent gypsum.

tonne: metric tonne = 1000 kg

UNFCCC: United Nations Framework Convention on Climate Change.

z factor: z-score percentile for normal distribution.

1 Introduction

1.1 Background

Concrete is the single most important building material in society and is used for a variety of products, such as houses, bridges, tunnels, roads, roof tiles, and other major and minor construction products, etc. These products constitute the primary use of concrete. After the lifetime of these products, the concrete is normally crushed and used as secondary products e.g. in roads or base course, or as fill material. The binder in concrete consists of cement. The most common cement type, Portland cement, is made by mixing limestone with other materials such as iron, aluminum and silicon containing minerals, often in the form of clay. It is also expected that the use of pre-calcined[1] calcium oxide sources for clinker production, beside limestone, will increase, see further Chapter 2.2. The materials are ground, mixed and burned at high temperature (1400-1450ºC) in a rotary kiln to form cement clinker. In this process, the materials sinter to form clinker. Other materials may also be present in cement manufacture such as blast furnace slag and fly ash. These materials are examples of the use of recycled materials in the manufacture.

The production of clinker requires high temperature and is therefore energy intensive. The fuels used globally are mainly coal, oil and pet coke (from oil refining), but also fuels made from residues such as waste oil, solvents, plastic and scrap tires are used. The residual products can, in this way, be treated safely and efficiently in high temperature, long residence time, and with extensive cleaning of the exhaust gases while the energy content can be used. The combusted residues can, in this way, replace and reduce the use of fossil fuels. The fossil fuels used in the cement kiln give rise to CO_2 emissions. Emissions of other greenhouse gases such as methane (CH_4) and nitrous oxide (N_2O) are formed only in small amounts since the combustion temperature is high and the combustion condition is well-controlled in the cement kilns.

In the production of cement, most of the carbon dioxide is formed partly from the combustion of the fuels needed in clinker production (cement kiln) and partly from the calcination of the limestone, e.g. according to the reaction below:

$$CaCO_3 \rightarrow CaO + CO_2$$

These calcination reactions are not permanent but reversible. This means that CO_2 is absorbed into the concrete by a process referred to as carbonation. In principle, the same amount of CO_2 driven off in the cement kiln can be taken up in the concrete by carbonation. However, the amount of CO_2 that will be taken up by carbonation in a reasonable timeframe depends on several factors. The carbonation process is a slow process that can last for many years. The time aspect is thus an important issue. The availability of CO_2 for the concrete is also crucial. The concrete must be exposed to the CO_2 in air to be able to carbonate. The transport of CO_2 molecules into the concrete is thus also an important factor. For example, if the concrete is crushed after use, the carbonation rate will increase considerably due to the increased surface area to volume ratio.

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[1] Externally calcined material i.e. CO_2 are released in another process separated from and prior to the cement/concrete production.

Carbonation is thus an important aspect to take into account in climate and emission calculations for cement and concrete. Today, emissions of greenhouse gases from different countries are reported, which in turn are used to support different climate strategies. Reporting takes place nationally to national authorities and internationally to the United Nations Framework Convention on Climate Change (UNFCCC). Guidelines for the emission calculation are developed and kept updated by the Intergovernmental Panel on Climate Change (IPCC). The current version, *2006 IPCC Guidelines for National Greenhouse Gas Inventories*, covers greenhouse gas emissions from cement and concrete processes. Both CO_2 emissions from fossil fuel combustion and emissions from the raw materials (calcination) are included. However, no consideration is given to the carbonation of concrete (although it is noted as an area for future work). This may be considered a shortcoming in these guidelines, which can lead to less accurate net greenhouse gas emission results. A very rough estimate is that the use of concrete today accounts for about 5-8 % of the world's carbon dioxide emissions from fossil fuels. About 50-60 % of the CO_2 emissions from cement production emanate from the raw materials and thus has a potential to be reabsorbed by carbonation of the concrete, partly during the use phase of the concrete products, and partly in the end-of-life and secondary use stage. We are convinced that this is an important part of the climate calculations and we therefore want to improve the calculations to better reflect the reality. This study proposes methods and models for calculating CO_2 carbonation in various cement-containing products.

1.2 Purpose and goal

The main purpose of the study is to provide input to the national and international greenhouse gas inventories by developing new calculation models for uptake of CO_2 in the cement and concrete sector. The goal is to include uptake of CO_2 by carbonation in concrete both during the lifespan of the concrete products and during their end-of-life and secondary use. Accurate measurements and good data are always important for all decision-making processes and this also applies to the climate issue. The calculation methods to be used to calculate the uptake of CO_2 in concrete have, to some extent, been based on previously performed scientific work and models, but new methodology for uptake calculations has also been proposed in this study. The study includes preparation of calculation methods with different complexity and accuracy (3 methods). In the IPCC's guidelines, such a level differentiation is often referred to as Tier 1, Tier 2 and Tier 3, which has also been used in this study. The exact definitions of the levels can vary between this study and IPCC guidelines. The method that a country will use depends on the country's ability to access statistics on cement/concrete and its use in different products. According to IPCC guidelines, the methods used should also depend on if it, in the country, will be defined as a “key category”, either on “level” or “trend”. That means that consideration should be given to categories that are of significant magnitude in later years or show a large change in magnitude over a given time series.

The uptake of CO_2 in concrete, both in primary products and in end-of-life & secondary product use, is relatively slow processes that also depend on the exposure of CO_2 from the air. The CO_2 content in air today is about 415 ppm and increases by about 1-2 ppm per year. However, almost all existing concrete takes up CO_2 continuously, while the production of cement continuously emits CO_2. This results in an annual net emission of CO_2. It is this net emission that is the focus of the calculations, although the time aspect itself also is addressed in the project. The different calculation methods relate to total CO_2 uptake over time but since they are time-generic they can also be used to develop different time series and annual uptake.

Since CO_2 uptake in cement-containing products is a measurable percentage of global CO_2 emissions, this represents a significant impact. In addition, the issue concerns several major industrial sectors. It mainly concerns the cement and concrete sector, but the construction sector and infrastructure construction sector can also be affected. For each industry sector, it is of course of great importance that data from the sector is accurate and that the sector's activities can be judged properly.

Publishing this knowledge also give new insight in how to further increase the annual CO_2 uptake.

2 Theoretic background to CO_2 uptake in cement-containing products

2.1 General description

The chemistry of cement and concrete include many different chemical reactions to achieve the specific properties of the concrete products. Different raw materials and additives are also used that can influence the chemical reactions. The focus in this study is the climate performance and behavior of different concrete products and especially the calculation of its carbon dioxide (CO_2) balance. In this chapter, we will thus present the fundamental chemical reactions of CO_2 and its corresponding flows. A more detailed description of the processes can be found in, for example reference [11].

Portland cement is made mainly of four different components; calcium, silicone, aluminum and iron. These are supplied in cement production through various raw materials such as limestone, clay, marl, silica sand, shale, etc. (the raw mix). A main raw material in cement is limestone ($CaCO_3$). In the cement kiln, the raw materials are heated up and CO_2 is driven off in the calcination reaction mainly from $CaCO_3$ according to reaction (1). In the calcination reaction, lime (CaO) and CO_2 is formed. CO_2 is released to the atmosphere in the exhaust gases from the cement kiln. CaO reacts further to form an integral part of the cement mainly as various calcium silicates, calcium aluminates, and calcium ferrites. Only a small part occurs as free CaO.

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2 \qquad (1)$$

In the manufacture of concrete, water is added to the cement to form the cement paste (hydration process). The added water will then react with different substances in the cement such as tricalcium silicates and dicalcium silicates to form hydration products such as calcium silicate hydrate (C-S-H) and also calcium hydroxide ($Ca(OH)_2$). A comprehensive presentation of cement reactions can be found in for instance [18]. The carbonation reaction is often written, for simplicity, with $Ca(OH)_2$ but CO_2 will also react with other components, such as the C-S-H.

Thus, both C-S-H gel and $Ca(OH)_2$ form a part of the cured concrete. CO_2, mainly in the atmosphere, in contact with concrete, will primarily react with $Ca(OH)_2$ in the concrete according to the principle reaction (2) but will also react with the C-S-H. These reactions represent the uptake of CO_2 in concrete, which is called carbonation.

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

CO_2 is a natural part of the atmosphere. However, the concentration of CO_2 in the atmosphere is increasing due to an extensive global use of fossil fuels. The concentration of CO_2 in the atmosphere has increased from about 280 ppm in preindustrial time to about 400 ppm today. The rate of concentration increase in the atmosphere is today about 1-2 ppm/year. An increased concentration of CO_2 in the atmosphere can, to some extent, also increase the rate of carbonation even if the contribution is small on a yearly basis.

The carbonation reaction takes place in several steps. The actual uptake and sequestration reaction is the reaction between the calcium and carbonate ions (3). This reaction takes place in water phase in the pore solution in the concrete. Water and moisture are thus important parts of carbonation.

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad (3)$$

In the alkaline pore water solution in concrete, portlandite (calcium hydroxide, $Ca(OH)_2$) can be dissolved according to reaction (4) forming calcium and hydroxide ions.

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \qquad (4)$$

CO_2 is also dissolved in the alkaline pore water solution according to reaction (5) forming carbonic acid (H_2CO_3).

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (5)$$

The protolysis of H_2CO_3 in alkaline solution proceeds in two steps, (6) and (7) forming bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions.

$$H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_2O \qquad (6)$$
$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \text{ (at high pH, in uncarbonated concrete)} \qquad (7)$$

In this way, Ca^{2+} and CO_3^{2-} are formed and can react and precipitate as limestone ($CaCO_3$) in the concrete.

An important aspect is the carbonation rate. How fast can the carbonation proceed, and which are the rate determining processes? When estimating the CO_2 uptake in the carbonated concrete one must also consider the degree of carbonation.

The *carbonation rate* depends on several factors such as the chemical reaction rate, mass transport of CO_2, humidity, temperature, porosity, CO_2 concentration in ambient air etc. The rate determining step could be crucial to the overall uptake rate. For practical reasons, the carbonation rate is often determined by measuring the depth of carbonation as a function of time. The depth is proportional to the square root of time. The carbonation rate can then be expressed as a constant in mm/√year.

The *degree of carbonation (DOC)* is defined as the amount of CO_2 taken up by carbonation in relation to the maximum CO_2 uptake in the carbonated volume of the concrete. The maximum uptake of CO_2 can often be equated with the CO_2 emission from calcination that is driven off from the material. This equality holds for the traditional clinker manufacturing process having calcium carbonate ($CaCO_3$, the main mineral in limestone) as the main calcium oxide source. The evaluation of the maximum uptake of CO_2 for non-traditional raw materials and manufacturing processes is discussed in Chapter 2.2. Traditionally, the degree of carbonation has been defined only within the area which has been considered carbonated and this area has been defined as the area exhibiting color change with a phenolphthalein test. (This test reveals where the depth within a cross section of concrete at which the pH has been reduced by carbonation to below about 9.) However, when calculating CO_2 uptake in concrete or other cement-containing products, there may be a need for a more general definition of degree of carbonation that includes all CO_2 reacted within the concrete (including that beyond the pH change region) in relation to all concrete.

In general, one can say that the chemical reactions presented above are relatively fast and cannot be considered as the rate determining step. However, there are several other factors that can slow down the carbonation rate. A common aspect for those factors is the access to, and transport of, molecules through the concrete. As carbonation proceeds, more and more $CaCO_3$ is precipitated in the concrete which can reduce the permeability of the concrete. This will reduce the access of CO_2 to the interior of the concrete, slow down the dissolution of $Ca(OH)_2$ and thus decrease the carbonation rate.

As has been mentioned, water is required for carbonation to take place. Concrete is a porous material that allows both CO_2 in air and water to penetrate into the concrete. The CO_2 gas in the pores will dissolve in the water in the pores and carbonation can start. However, if the pores are completely filled with water, the HCO_3^- or CO_3^{2-} ions have to diffuse in the water phase into the concrete. This is a much slower process and will thus slow down the carbonation rate. Obviously, there is an optimal moisture content in concrete for a maximum carbonation rate. The optimal moisture content in concrete for carbonation has been estimated to be about 60-80 % relative humidity in the concrete.

Mainly due to the formation of $CaCO_3$ in the concrete, the carbonation rate will slow down with time. Empirical experiments have shown that the carbonation rate is proportional to the square-root of time (t), $\sqrt{t}$ [11,19]. Other factors that will influence the carbonation rate are porosity of the concrete, w/c ratio, cracks in the concrete, cement type and additives, and surface treatment of the concrete products. At the end-of-life of concrete products, they are demolished and often crushed for recycling purpose. When the concrete is crushed, new surfaces are created, and most of those surfaces were previously in the interior of the concrete, with limited exposure to CO_2. This can dramatically increase the carbonation rate if access to CO_2 in air can be maintained. These smaller concrete pieces will also increase the total amount of CO_2 sequestered in an entire concrete volume. To estimate the uptake of CO_2 in concrete, it is thus important to include both the service life of the concrete products and the secondary use of the concrete after the end-of-life phase.

In the clinker manufactured in a cement kiln, there are also other compounds formed from the raw meal content that eventually can take part in the carbonation process. This has not been addressed in this study. In addition to the calcination/carbonation of the clinker from the cement kiln, there are also materials that are mixed into the cement after the cement kiln (and also mixed into concrete in concrete production). These are often called additions and can be e.g. limestone, silica fume, fly ash and ground granulated blast furnace slag (GGBS). These additions can change the carbonation rate and the reaction products of fly ash, other pozzolans, and GGBS can also take up CO_2. For a complete estimation of the CO_2 uptake it is thus important to consider both the change in carbonation rate and the effect on the total CO_2 uptake in the concrete caused by all additions. The effect on carbonation of these compounds is less known but can be taken into account in accurate uptake calculations. In the present Tier 1 and Tier 2 models, only limited effects of such uptake have been included.

2.2 Maximum uptake of CO_2 for non-traditional raw materials for clinker production

Traditionally, calcium carbonate, $CaCO_3$, has been used as the main calcium oxide source for clinker production. The CO_2 released during limestone calcination (1) can be mineralized into calcium carbonate by the carbonation reaction (2) and hence the CO_2 emissions from raw materials (also called process or calcination emissions) equal to the maximum uptake of CO_2. With the decarbonization efforts of cement industry, it is expected that the fraction of pre-calcined calcium oxide sources for clinker production will increase. In such sources, the CO_2 emissions from the materials have taken place before the material arrived at the cement kiln. Such sources comprise e.g. slags where CaO is bound in a pre-calcined glass, fines from concrete recycling where CaO is bound in cement hydrates, calcium hydroxide by-products, paper sludge incineration ash etc. Such materials do not release CO_2 upon heating, but still provide carbonatable CaO to the clinker, cement and concrete, respectively. Similarly, carbon capture technologies prevent a part of or all CO_2 emissions from being released, but do not alter the properties of clinker, including its maximum CO_2 uptake. As the CO_2 uptake is linked to the calcination, CO_2 emissions in the Simplified methodology (see Chapter 5.1), alternative raw materials and/or carbon capture technologies would lead to underestimating the actual CO_2 uptake. This problem can be overcome by using the carbonation potential based on the bulk chemical composition when calculating the full potential calcination emission. Already in 1957, Steinour [22] showed that the ultimate CO_2 uptake of a material depends in its bulk chemistry and proposed a formula.

$$CO_2^{theor} = 0.785 \times (CaO - 0.56CaCO_3 - 0.7SO_3) + 1.091 \times (MgO - 0.479MgCO_3), \qquad (8)$$

where CO_2^{theor} is the maximum theoretically achievable CO_2 uptake related to the clinker mass (kg CO_2/kg clinker) and CaO, $CaCO_3$, SO_3, MgO and $MgCO_3$ are weigh fractions of corresponding oxides and phases. Note that also other oxides such as e.g. alkalis can bind CO_2. These oxides are not included in (8) since the carbonates are soluble (alkalis) or contents are low (other).

The carbonation potential according to (8) corresponds to the calcination emissions for the traditional case based on limestone and can also be used to evaluate the maximum uptake of CO_2 of clinkers produced using the alternative raw materials or new technologies.

Since it is only the CO_2 binding potential of CaO that can be estimated with the existing methods (and not MgO), and the amounts of $CaCO_3$ and SO_3 are small, equation (8) can be abbreviated to the form it has used in the standard EN 16757.

$$CO_2 \text{ theoretic} = (M_{CO2}/M_{CaO}) \times CaO = 0.785 \times CaO$$

where
M_{CO2} is molar mass CO_2 = 44 g/mol
M_{CaO} is molar mass CaO = 56 g/mol

3 IPCC documentation of CO_2 emissions and uptake

Annual national greenhouse gas emissions and removals are reported by countries to international databases such as UNFCCC through their operations "Greenhouse Gas Inventory". The UNFCCC formulates its own activities as follows:
”The ultimate objective of the Climate Change Convention (UNFCCC) is to achieve "... stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system." Estimating the levels of greenhouse gas (GHG) emissions and removals is an important element of the efforts to achieve this objective.”

These databases can then be used to help assess the development of the climate from a global perspective and to develop global and regional climate strategies. It is therefore important that the uptake of CO_2 by carbonation in concrete and other cement-based products is included in the international emissions reporting so that accurate data on the net supply of CO_2 to the atmosphere through the use of cement and concrete are obtained.

Calculation of greenhouse gas emissions and sinks for reporting to the UNFCCC is usually made by the Ministry or nationally appointed organizations in each reporting country. This organization can usually be reached via the national Ministry of Environment or the national Environmental Protection Agency (EPA). From a technical and calculation point of view and due to its complexity, it is most likely and recommended that the national CO_2 uptake calculations for concrete are performed as a cooperation between the nationally appointed calculation group and the national cement and concrete industry. Guidelines for how calculations of the climate gases are to be made are determined by control documents developed by the IPCC. The control documents can be found on the IPCC website: https://www.ipcc-nggip.iges.or.jp/public/2006gl/

The main document that regulates emission calculations and removals is 2006 IPCC Guidelines for National Greenhouse Gas Inventories. The guideline consists of five volumes:

- Volume 1 General Guidance and Reporting
- Volume 2 Energy
- Volume 3 Industrial Processes and Product Use
- Volume 4 Agriculture, Forestry and Other Land Use
- Volume 5 Waste

The applicable emission calculations for cement production are divided into those relating to *energy production* and those relating to *industrial processes*. The emissions from a cement kiln can thus be divided into emissions from combustion (energy production) and emissions emanating from calcining the raw materials (processes) in the calcination process. The latter CO_2 emissions are classified as a process emission and regulated in Volume 3 Industrial Processes and Product Use. The CO_2 uptake in concrete is strongly related to the CO_2 emissions from the raw materials and it is thus proposed that future updates of the IPCC guidelines regulate the CO_2 uptake in the same document (Volume 3) as the process emissions. This volume of the IPCC guidelines also includes emission and uptake in product use, which is the case for CO_2 uptake in concrete products. Product use can here also include CO_2 uptake in end-of-life and secondary products i.e. for example in crushed concrete.

Volume 3 Industrial Processes and Product Use includes several industrial processes of which Chapter 2 Mineral Industry Emissions is the most appropriate for this task. CO_2 uptake can occur in several of these product systems, which is why it is important to prepare the methodology for additional industrial processes. The uptake chapter can also be separated from the emission chapters. A revised chapter structure of Volume 3, Chapter 2 can thus be as follows, with changes marked in bold:

Chapter 2 Mineral Industry Emissions **and removals**
- 2.1 Introduction
- 2.2 Cement production
- 2.3 Lime production
- 2.4 Glass production
- 2.5 Other process uses of carbonates
- **2.6 CO_2 removals**
  - **2.6.1 CO_2 uptake in cement containing products**

The present study can thus be an input to future revisions of the IPCC *Guidelines for National Greenhouse Gas Inventories*, but it can also serve as a calculation guideline for the nationally appointed emission calculation organizations as well as input to IPCC’s emission factor database (EFDB).

4 General description of CO_2 uptake models for cement-containing products

As shown in Chapter 3, the CO_2 emission model for the raw materials used in a cement kiln is presented in: *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. The calculated CO_2 emissions are based on the amount of clinker produced by a cement kiln. This amount of CO_2 driven off from the material can normally be considered as the maximum theoretical uptake of CO_2 due to carbonation of cement containing products.
In case of non-traditional raw materials, such as pre-calcined CaO sources, this will however not be the case, see Chapter 2.2.

The CO_2 uptake model will thus calculate the CO_2 uptake in different cement containing products during their service life as well as in the end-of-life processes and when used as secondary products, such as crushed concrete in a road base or as landfilling material. The emission and uptake models are illustrated in Figure 1.

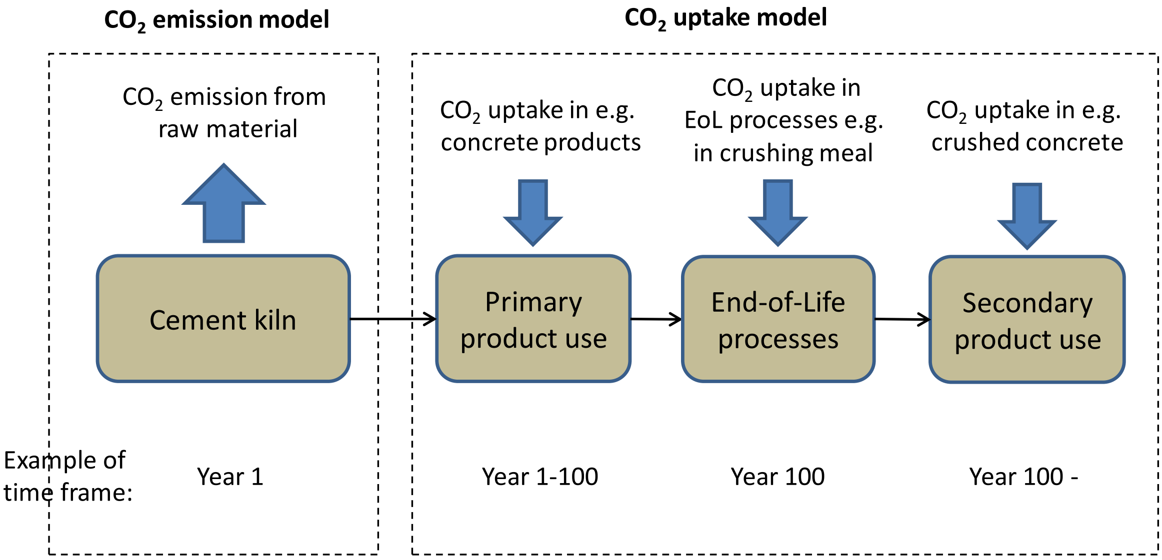

Figure 1 Schematic figure showing the CO_2 balance in cement containing products over a certain period of time.

The CO_2 uptake in concrete is a relatively slow process that takes place over many years. The first phase is uptake in e.g. concrete products or structures such as bridges, house frames, concrete tiles, concrete roads, railway sleepers, cement mortar, etc. The carbonation process takes place from the surface of the concrete when CO_2 in air diffuses into the porous concrete and reacts with $Ca(OH)_2$ and other hydrated phases to form $CaCO_3$ according to the reactions described in Chapter 2. The area of concrete surfaces or the area/volume ratio of concrete products are important factors for a CO_2 uptake model. By knowing the total yearly use of cement clinker and how much is used in different types of concrete categories (for example, in various strength classes, exposure types, and shapes and sizes of products and structures), the CO_2 uptake surface areas can be estimated. The yearly use of cement or clinker in a country can be calculated as (cement or clinker production *minus* cement or clinker exported *plus* cement or clinker imported). From the uptake surface areas, the yearly CO_2 uptake over the years can be calculated. For large concrete structures, only a smaller part of the concrete will be carbonated during its primary product use. Another factor that influences the CO_2 uptake in the concrete is the moisture content, see Chapter 2. The surface can be located in different climates, be exposed to rain or located indoors/outdoors. These factors can affect both the carbonation rate and the degree of carbonation. Also, concrete additions, such as blast furnace slag or fly ash from coal combustion, can also hydrate to produce phases that can take up CO_2, which can be important to include in the calculations.

After the service life of a concrete structure, it will be demolished and eventually crushed into finer pieces. This will increase the specific surface area and increase the carbonation rate. The total carbonation in the entire concrete volume will also be increased when the concrete is crushed into smaller pieces. However, the use of the crushed concrete must be done in such a way that air and CO_2 are allowed to access the increased concrete and CO_2 uptake surface areas. This may require some active planning of the end-of-life/secondary use processes for concrete. The knowledge about the end-of-life/secondary use processes for concrete in different countries is lower and the uncertainties are greater. The CO_2 uptake models for secondary use are therefore relatively uncertain. However, the CO_2 uptake potential is generally large for the end-of-life/secondary use phase.

In a CO_2 uptake model, many different details can be included to improve the model performance. However, there is also a need to make simplified model calculations based on a few input data. A method to achieve this is to; only use the use of cement clinker for the model calculations. The maximum CO_2 uptake in the clinker used can be multiplied by a factor to compensate for the real uptake in both the primary use and end-of-life/secondary use phase. When using the present year's cement clinker production to calculate the uptake, one has to note that; the CO_2 uptake actually takes place in the previous year's concrete production. If the cement clinker use varies considerably over the years, this may cause model deviations that may need to be compensated for in the models. This is further discussed in Chapter 5.

5 Proposed CO_2 uptake models for cement-containing products

5.1 Overview description and strategies

This chapter presents the calculation methods for the uptake of CO_2 in cement-containing products developed in this study. The basis for the calculation methods is also presented. Three different calculation methods and levels have been developed, which have different calculation complexity and accuracy. Tier 1 represents a general but simplified calculation method for the uptake of CO_2. Tier 2 and 3 represent more accurate but complex calculation methods, which are preferred if sufficiently good input data on the use of cement in concrete applications are available. Tier 2 is a proposed advanced methodology including several aspects that will affect the annual CO_2 uptake. It is based on a simplified uptake model for the use phase and a standardized model for uptake during end-of-life and secondary use. As the uptake takes place in the standing stock of concrete structures, this method is sensitive to large variations in previous years' concrete use. Tier 3 opens up for the use of even more advanced and accurate methods and models developed in scientific projects in different countries. In a Tier 3 model, the variations in concrete use and CO_2 uptake for each year should be taken into consideration.

The annual CO_2 uptake in existing concrete structures depends on the historical use of cement. In the Tier 1 and Tier 2 methods it is therefore recommended to use the mean value of the preceding 20 years of cement/clinker consumption in the calculations.

The different calculation methods relate to an annual uptake but since they are time-generic, they can also be used to develop different time series.

5.2 Tier 1 model for CO_2 uptake - Simplified methodology

5.2.1 Proposed CO_2 uptake model for Tier 1

The present model, representing Tier 1, provides a simplified calculation method for estimating the uptake of CO_2 in existing concrete structures on a national basis. The calculations are based on the CO_2 emissions from the calcination of the corresponding amount of cement clinker used for the calculations. It can thus cover an optional period of time (e.g. annual) and different amounts of concrete. The model should be used primarily as a first estimate or in cases where resources are missing to perform more accurate calculations according to the calculation methods described for Tier 2 and Tier 3 of Chapter 5.3 and 5.4, since the uncertainty is relatively high for Tier 1 as this is a simplified calculation method. The national annual CO_2 uptake in concrete; in the use stage (existing structures), in end-of-life stage (demolition, crushing, stockpiling), and in secondary use (recycling), can be estimated according to this Simplified methodology. The uptake values are related to the estimated calcination emissions from the annual consumed clinker (produced-export+import) in the corresponding country. Note that the annual national calculated emission values from produced clinker thus should be adjusted for exports and imports of cement/clinker.

The annual CO_2 uptake in existing concrete structures depends on the historical use of cement. As values for annual consumed clinker may vary considerably, it is recommended to use the mean value of the preceding 20 years of cement/clinker consumption in the calculations.

The text of Chapter 5.2.1 to 5.2.5 presumes the use of limestone as the CaO source for clinker production. If non-traditional pre-calcined raw materials are used as a CaO source besides limestone, the uptake cannot be directly related to the calcination emissions. See Chapter 2.2 for background and Chapter 5.2.6 for calculation of CO_2 uptake.

Use stage

Two alternative calculations, A and B, for the CO_2 uptake in the use stage are given. The reason for giving two values is to give options how to handle the variation span of the calculated figures. From Chapter 5.2.3 it follows that one can present a calculated mean value (A) or a low (=Mean - St. dev.) value (B). The IPCC recommendation is to neither overestimate, nor underestimate in the calculations, which should indicate alternative A. The Tier 1 methods are associated with relatively large uncertainties in the calculated uptake figures. To reduce uncertainties, higher tier-levels methods should be used.

Alternative A:

The total uptake in the use stage can be estimated as 0.20×(the reported emission from calcination of consumed cement clinker).

If the mortar for rendering applications, in total, amount to more than 10 % but less than 30 % of the cement consumption, the uptake factor in the use stage can be estimated at 0.20 + 0.0115(MR - 10), where MR is the mortar percentage for rendering of the clinker use. If MR is below 10 % use MR=10 and if MR is above 30 % use MR=30.

Alternative B:

The total uptake in the use stage can be estimated as 0.15×(the reported emission from calcination of consumed cement clinker).

If the mortar for rendering applications, in total, amount to more than 10 % but less than 30 % of the cement consumption, the uptake factor in the use stage can be estimated at 0.15 + 0.01(MR - 10), where MR is the mortar percentage for rendering of the clinker use. If MR is below 10 % use MR=10 and if MR is above 30 % use MR=30.

End-of-life stage and secondary use

Annual uptake in the end-of-life stage and secondary use can be estimated at (0.02 + 0.01)×(the reported emission from calcination of consumed cement clinker), where the value 0.02 represents uptake for end-of-life processes and 0.01 represents uptake for secondary use.

> **Alternatively, the following estimation can be done in the end-of-life stage and the secondary use.**

- **If the annual amount of concrete being taken out of service and processed at a recycling plant is known, the CO_2 uptake in the end-of-life stage can be estimated as 10 kg CO_2/m^3 concrete.**
- **If the annual amount of crushed concrete, entering secondary use as unbound material, is known, the uptake can be estimated as 10 kg CO_2/m^3 concrete.**

The following chapters explain the background and consideration that underlie the proposed model.

5.2.2 Introduction

CO_2 uptake takes place in cement-based concrete or mortar and not in the unhydrated cement powder, but there is of course a relation between the amount of cement used and the amount of concrete produced. This relationship can be used for the design of a simplified methodology for CO_2 uptake in concrete. It can be assumed that the CO_2 uptake one year in a given region or country is related to the cement consumption in the same area. Since the cement consumption normally does not vary much in a few years perspective, it can be feasible to take the year of the reported CO_2 emission from the material as basis for the uptake. One strong motivation for this is also the fact that, due to the square root of time dependency of the uptake, the first years of carbonation and CO_2 uptake of a structure are most important. During the first 5 years, 22 % of the 100-years uptake takes place, which is about 50 % of the 20 first years of uptake. After 20 years, thus about 45 % of the CO_2 uptake has taken place. In Figure 2, a schematic figure of the square root effect on carbonation as a function of time for an object that is fully carbonated after 100 years.

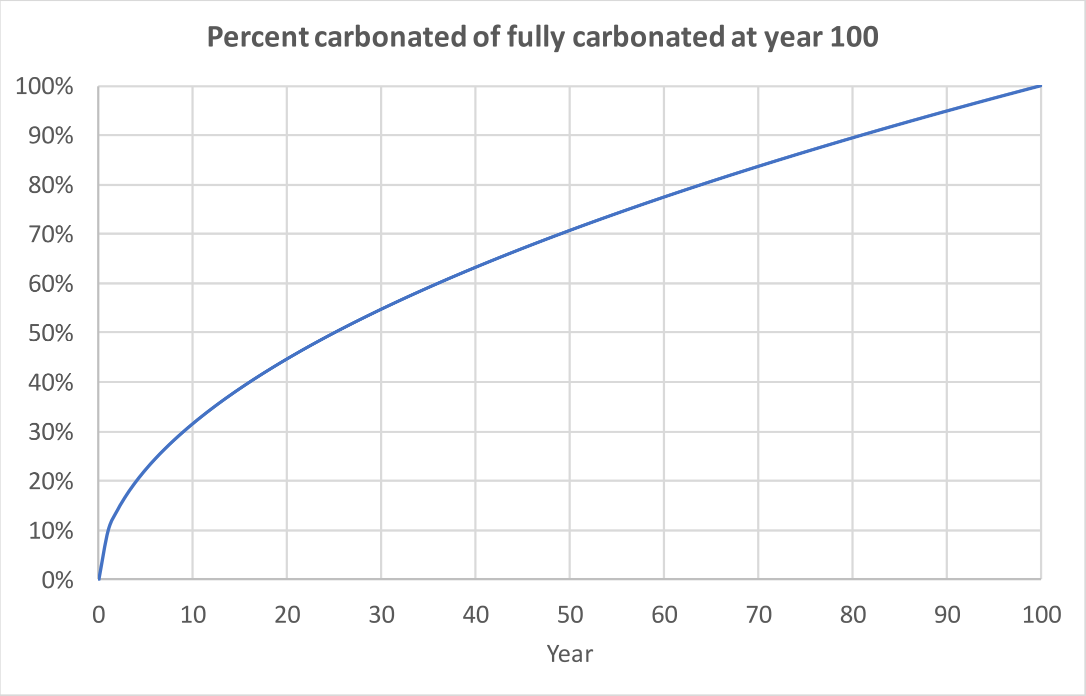

Figure 2 Schematic figure showing the square root effect of carbonation. The figure shows the carbonation percentage of an object that is fully carbonated after 100 years as a function of carbonation time.

The process-related CO_2 emission at cement production is almost solely coming from the calcination (clinker burning). This emission is annually reported country based to UNFCCC, using one of the three methods (Tier 1, 2 or 3). Independent of which of the methods is used, and since the uptake takes place in the hydrated clinker components, the annual CO_2 uptake can be estimated by multiplying the calcination emission by a factor < 1. This simple methodology (named Tier 1 according to the IPCC terminology) should, as well as the emission reporting, be possible to use for all cement production. For possible uptake in other constituents than clinker, see Chapter 5.3.8 on "Cement with additions….." below. The magnitude of this factor is crucial to establish. Below, in the chapter on the use stage, a suggestion is presented.

The main constituent of cement is normally clinker, which is formed in the cement kiln. The CO_2 emissions used in these calculations are only CO_2 that is driven off from the raw material (e.g. limestone) in the cement kiln. This is referred to as calcination in this study. The CO_2 emission from the combustion in the cement kiln and other processes is not involved in the uptake calculations.

The theoretical maximum CO_2 uptake value is mainly the same as the CO_2 emissions from calcination of the raw material. This corresponds to a factor of 1.0. Such high uptake, also referred to as 100 % degree of carbonation, can eventually be found in very well hydrated concrete pieces with good access to CO_2 and moisture and after a considerable time. In reality, a practical maximum value of 75 % is reported in the European standard EN 16757 and in other literature references, for instance [11]. This value is valid for concrete, after use phase and followed by demolishing, crushing, and secondary use. It is accordingly a value that, for the bulk of concrete, takes a long time to achieve, so in spite of the long history of use, there are probably still only small amounts of concrete that has reached this status.

The practical maximum uptake value, 75 % of the emission, can only be achieved if the production of cement had been on the present level for a long time (meaning that the addition of concrete structures each year has been approximately the same and thus formed a concrete product stock that can take up CO_2 each year) and all of the structures or their demolished and crushed residue would carbonate. With an increasing amount of cement and concrete production, it is inevitable that the uptake, taking place in earlier production, will be lower than the emission from the present production.

5.2.3 The use stage of primary product

To be able to have knowledge of the annual uptake in the existing concrete products and crushed materials, one need to perform studies and calculations based on the use of concrete. This has been done in several countries and is reported in the reference list [2,3,20,5,4,13,12,6,7,8]. An overview can be found in Annex 2, Table 6. These studies can also be the basis for the development of an Advanced methodology. The methods used in different countries are all based on the well-accepted and documented carbonation rate model of square root of time dependency [11,19]. The inventories of existing concrete structures comprise different applications, exposure, and concrete quality. The age distribution of concrete in place is estimated by cement consumption statistics over time. This makes it possible to calculate a good estimate of the annual CO_2 uptake in the existing structures.

Seven such studies are compiled in Annex 2, Table 6, "Characterization of existing models…" representing Ireland, the Netherlands, Norway, Spain, Sweden, Switzerland, and "Global". The annual CO_2 uptake, for these models, in the existing concrete structures has been found to be 16, 30, 24, 3, 27, 16, and 44 % of the corresponding calcination emissions the same year.

In the referred table and references, some values can include uptake also in end-of-life and secondary use, but these values are very small, compare Chapter 5.2.4, so the numbers are valid for, and here used, for the primary products only. Some numbers are also given as percentage of total production emissions instead of percentage of calcination emissions. Those numbers have been multiplied by 1.6 to get the uptake as percentage of calcination emissions given above.

The presented numbers on uptake in relation to calcination emissions can be used to estimate a general uptake number with the help of a statistical evaluation. Before that, some of the numbers need however explanations, comments or adjustments.

The comparably low value from the **Irish study** [5] (16 %) is said to be conservatively estimated.

The value from the **Netherlands** [20] is given in the table as 19 % of the production emissions, which multiplied with 1.6 gives 30 %. It is in the report assumed that the maximum CO_2 uptake of the slag is 0.14 kg CO_2/kg slag, corresponding to 0.14×1 440 000 = 201 600 tonne. The maximum CO_2 uptake in slag will however, as in the clinker, not be reached. If we assume that the real uptake in the slag part is 25 kg CO_2/tonne of slag (see Chapter 5.3.8 Cement with additions…) we get an uptake of 0.025×1 440 000 = 36 000 tonne. This leaves 365 000 – 36 000 = 329 000 tonne to be taken up in the clinker, corresponding to 329 000/1 318 000 = 25 %. Therefore, the clinker uptake/clinker emission is reduced from 30 to 25 %.

No adjustments are done related to the **Norwegian report** [3].

The **Spanish value** [6,7,8] of uptake related to the calcination emission is very low, only 3 %. Some reasons can be identified for the low value compared to the other studies. It is declared that the study is deliberately held on a very conservative level. The report is providing measured uptake values for laboratory samples and drilled out field samples. Uptake is estimated for a service life of 50 years for buildings and 100 years for infrastructures. The reported degree of carbonation is generally small, which for the laboratory specimens might be explained by the short time and dry testing conditions. Moreover, is it anticipated that the uptake in all interior surfaces and surfaces in contact with other materials, as well as buried concrete, is zero. The specific surface area (m^2/m^3) for the structures is also low, about 2 m^2/m^3 concrete. The large deviation from the other cement application values makes it difficult to include it in the statistical calculations below.

In a paper by C. Andrade : “Evaluation of the Degree of Carbonation in three Environments”[9], the earlier low values of degree of carbonation have been revised and updated, resulting in an uptake value increase to 10.8 – 11.2 % of the calcination emissions. However, the assumption of zero uptake in interior surfaces and buried surfaces remain, as well as a comparably low specific surface area for the interior concrete. The motive for zero uptake in interior surfaces is that these surfaces very often are coated by for instance paint or wallpaper.

From experience and established in literature, for instance [2,3,11,13] it has been shown that CO_2 uptake takes place, even if with reduced speed, also in surfaces with some kind of coating and also under ground. See also European standard CEN/EN 16757, Annex BB.

For the purpose of this report a further recalculation of the Spanish value has accordingly been done, bringing it in line with the common view of uptake in coated surfaces and surfaces underground (“normalization”).

From the Spanish report [7], Table 6 it follows that 60 % of the concrete for building structures has been classified as "not exposed". 21 % of it is located in foundations.

We now assume that the remaining 39 % "not exposed" are parts with some kind of cover, and, based on EN 16757, table BB1, that the uptake in such surfaces is reduced with the factor 0.7 (with cover/without cover). We also assume that the 21 % are under ground and that the uptake there is reduced with the factor 0.25 (in ground/½(exposed+sheltered)).

The buildings 60 % "not exposed", can now be calculated to correspond to

0.7 × 39 + 0.25 × 21 = 32.6 % of exposed.

Further the specific surface for these, so far not included, parts is anticipated to be at least 6 m^2/m^3 compared to 3 for the included building surfaces. (The Fpr CEN/TR 17310:2018 presents 8 m^2/m^3 as a typical value for buildings, including interior parts.) The value is then increased to (6/3) × 32.6 = 65 %.

This gives us for buildings 1.65 × 10.8 = 17.8 %. (10.8 % being the value according to C. Andrade's paper [9].)

From [7], Table 6 it follows that 44 % of the concrete for civil works has been classified as "not exposed". It is assumed that this concrete is under ground and, as above, that it corresponds to 0.25 × 44 = 11 % of the above ground value.

This gives for civil works 1.11 × 11.2 = 12.4 %. (11.2 being the value according to C. Andrade's paper. [9])

The relation in Spain between concrete used for buildings and for civil works is about 47/53. (Cement consumption statistics from Cembureau 2016.)

We now get for all concrete structures 0.47 × 17.8 + 0.53 × 12.4 = 14.9 %

The Spanish CO_2 uptake value used for the statistical calculation below; is accordingly 15 % of the calcination emissions.

No adjustments are done related to the **Swedish report** [2].

In the **Swiss report** [13], the degree of carbonation is set to 75 % throughout, but is later in another paper [12] changed to 50 %. An average uptake of 10 % of the total emissions, for 50 years is presented in the report. For the calcination emissions, the figure can be estimated to be 10×(1/0.63)=16 %. For 100 years, the figure can be estimated to be 16×√(100/50) = 23 %. With degree of carbonation being 50 % instead of 75 %, we get 23×(50/75) = 15 %. (According to the Annex BB of the EN 16757, the degree of carbonation varies between 40 % for indoor structures to 85 % for outdoor structures not sheltered from rain.)

The **global value** [4] of 44 % should be adjusted due to the very large amount of mortar included in the study (see also Chapter 5.2.3.1). The mortar contribution to the CO_2 uptake is about 70 % of the global study value 44 %, though the amount of cement used for this application is about 30 %. The concrete and mortar uptake figures can be calculated as follows.

Assume that the uptake factor for concrete is c and the factor for mortar is m.
The factor for concrete and mortar together is 0.44. Then
$70c + 30m = 100\times0.44$
$c/m = 30\times30/70\times70 = 0.18$ (70 % of concrete accounts for 30 % of the uptake and vice versa for mortar.)
$70\times0.18m + 30m = 44$
$m = 44/42.6 = 1.03$
$c = 0.18\times1.03 = 0.19$

The uptake factor for concrete is thus 0.19, (19 %).

(It should be noted that this calculation, with reduction of the mortar portion, shows that the high global value of 44 % is reduced to a more typical value of 19 %, which strengthen the credibility of the global study.)

After these comments, the series of numbers of CO_2 uptake related to calcination emissions to be used for the statistical evaluation are: 16, 25, 24, 27, 15, 15 and 19 %.

The statistical population of all countries´ figures of CO_2 uptake in cement-based products, related to the calcination emissions, could probably be considered approximately normally distributed. If we perform a very simple statistical analysis of the results, assuming normal distribution, we end up with a mean value of 20 % and a standard deviation of 5.1 %. The value 15 % accordingly corresponds to (Mean - 1 × St. dev.) and is a value with some safety margin.

The 95 % confidence interval based on the seven numbers equal $1.96 \times (5.1/\sqrt{7}) = 3.8$ %. The mean value could then be presented as 20 % +/- 3.8 %.

It should be noted that the statistical basis is only six country values and one global value. The base for the seven single numbers varies also for instance with statistical accuracy and with different cement types. The studies cover however a large number of structures and products.

Even if the seven studies are independent of each other, they cannot be considered as randomly selected or a statistically representative sample of an average country´s annual concrete CO_2 uptake. The true mean value could thus deviate from 20 % and the 95 % confidence interval is thus likely larger than 3.8 %.

With a mean cement consumption as basis, instead of a single year value, the accuracy of the relative uptake values presented for the different countries should be more accurate. Below, the mean cement consumption during the years 2011-2016, Table 1, is used as basis for the calculation of the relative CO_2 uptake value for five countries.

Table 1 Yearly cement consumption in ktonne [2].

Country	2011	2012	2013	2014	2015	2016	Average (μ)	Standard deviation (σ)	Coefficient of variation (σ/μ)
Ireland	1 310	1 130	1 064	1 195	1 720	1 820	1 373	319	0.23
Netherlands	5 596	5 079	3 991	4 100	4 040	4 110	4 486	681	0.15
Norway	1 874	1 943	1 993	1 967	1 960	2 060	1 966	61	0.03
Sweden	2 440	2 340	2 235	2 200	2 270	2 360	2 308	89	0.04
Switzerland	5 299	5 014	5 274	5 370	4 900	5 000	5 143	195	0.04

The so far presented numbers (based on the single year values) for the five first countries are 16, 25, 24, 27 and 15 %.

The single year values used for the calculation of these numbers are the following:

Ireland:	2000 ktonne
Netherlands	4040 ktonne
Norway:	1550 ktonne
Sweden:	2440 ktonne
Switzerland:	4553 ktonne

(The actual year lies sometimes before 2011 or has been modified in the referred country report. The single year value used for Spain is not known so no calculation has been made.)

If we chose to use the six years mean value instead, we get the following corrected numbers:

Ireland (2000/1373) × 16 = 23 %
Netherlands (4040/4486) × 25 = 23 %
Norway (1550/1966) × 24 = 19 %
Sweden (2440/2306) × 27 = 28 %
Switzerland (4553/5142) × 15 = 13 %

With these new numbers, we get, including the Spanish value 15 and the global value 19 % unchanged:

Mean value: 20.0 %
St. dev.: 5.13 %

These values are very similar to the ones we got with the single year basis.

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[2] Data from VDZ (Verein Deutscher Zementwerke e.V.). VDZ is the economic, technical and scientific association for the German cement industry.

The mean value is, as mentioned above, 20 %, (Tier 1A).

In order to estimate the annual uptake with a conservative approach, it is accordingly suggested that the annual emissions could be multiplied with the factor 0.15 to handle the variation span in the Simplified methodology (Tier 1B).

It is likely to believe that the Simplified methodology will be used in most countries, at least in the beginning of the calculation of CO_2 uptake in concrete and other cement containing products. However, due to the simplifications of the calculations used in the method, the uncertainty will be relatively high, and the accuracy of the national calculations can be poor. The uptake factor can, in reality, vary between different countries, which a general uptake factor cannot account for. Technical factors such the use of mortar can have a significant impact. However, on a global scale, the average uptake value will be reflected by the general uptake factor.

5.2.3.1 Influence of high use of mortar (from the global study)

The following indicates a method to consider a high mortar use in the cement applications. It is based on the global study [4] of the "Characterization table in annex 2, Table 6".

The mortar contribution to the CO_2 uptake is about 70 % of the global study value of 44 % carbonation, though the amount of cement used for this application is about 30 %.

The concrete and mortar uptake figures can be calculated as follows:

Assume that the uptake factor for concrete is c and the uptake factor for mortar is m.
The factor for concrete and mortar together is 0.44. Then

$70c + 30m = 100\times0.44$
$c/m = 30x30/70x70 = 0.18$ (70 % of concrete accounts for 30 % of the uptake and vice versa for mortar.)
$70\times0.18m + 30m = 44$
$m = 44/42.6 = 1.03$
$c = 0.18\times1.03 = 0.19$

The uptake factor for concrete is thus 0.19, which seems to be a reasonable value.

The uptake factor for mortar is very high, 1.0. It means that all cement used for mortar applications is totally carbonated already after one or a few years. This result is also apparent from the global report [4] as a result of thin structures (≈ 20 mm), high rate of carbonation (k = 19.6) and high degree of carbonation (average 92 %). This can be explained by a high use of mortar for rendering.

The factors 0.15 or 0.20 are suggested above to be valid for more real concrete applications, say with a mortar use of less than 10 %. If the mortar use is larger than 10 %, an adjustment factor could possibly be used. With the mortar share being 30 %, the uptake factor is 0.44. If one then assumes a linear increase of the uptake factor between a mortar content of 10 % and 30 %, we obtain:

Alternative A (Tier 1A)
With 0 – 10 % of cement use in mortar for rendering applications, the uptake factor will be 0.20.

With 10 – 30 % of cement use in mortar for rendering applications, the uptake factor will be: 0.20 + 0.0115 (MR - 10), where MR is the Mortar percentage for rendering of the clinker use. If MR is below 10 % use MR=10 and if MR is above 30 % use MR=30.

Alternative B (Tier 1B)
With 0 – 10 % of cement use in mortar for rendering applications, the uptake factor will be 0.15.

With 10 – 30 % of cement use in mortar for rendering applications, the uptake factor will be: 0.15 + 0.01 (MR - 10), where MR is the Mortar percentage for rendering of the clinker use. If MR is below 10 % use MR=10 and if MR is above 30 % use MR=30.

5.2.4 End-of-life stage and secondary use

In addition to the CO_2 uptake over the use stage of structures, there is uptake in the end-of-life stage and the secondary use, normally as crushed material. Detailed information on the amount of this material and its uptake is rare, so it is today difficult to give a reliable estimate. The percent of concrete recycling, given in some countries is unfortunately not sufficient, since it is mainly the service life at demolition, the processing of the demolished material and the applications for the crushed concrete that determines the actual uptake.

5.2.4.1 End-of-life stage (demolishing, crushing and storage)

The EN 16757, Annex BB [16] indicates a conservative value of a CO_2 uptake in the end-of-life stage (demolishing, crushing, and storage) of 5 kg CO_2/m^3 of concrete with present waste handling systems. With an average cement content of 330 kg/m^3 concrete, this corresponds to approximately 5/0.330 = 15 kg CO_2/tonne of cement or 15/490 = 3 % of a Portland cement calcination emission. The figure 5 kg CO_2/m^3 of concrete indicates a very small uptake in this stage. The potential to increase this value by applying a more advanced waste processing systems is however very large.

The **Swedish study** [2] reports that about 1.5 million tonne (625 000 m^3) of concrete is annually demolished. The annual uptake in the end-of-life stage and secondary use is presently estimated to be only 12 000 tonne and of that, about 4000 tonne of the 12 000 tonne of uptake after the use stage takes place in the end-of-life stage. This corresponds to 4 000 000/625 000 = 6.4 kg CO_2/m^3 of concrete or 6.4/0.33 = 19 kg CO_2/tonne cement, or 19/490 = 4 % of a Portland cement calcination emission.

Since the annual amount of concrete taken out of the service life is rather small compared to the annual production, 625 000/7 000 000 m^3 = 9 %, the uptake is small in relation to the annual calcination emissions, only about 0.4 %, (0.09×0.04×100) %.

The **"global" study** [4] value 44 % includes uptake in the end-of-life stage. The average exposure time is 0.4 years. The relative uptake in this stage is reported to be around 8 % (1.4/(16.1+1.4)) in concrete and around 2 % in mortar.

With about 70 % concrete and 30 % mortar we end up with a mean figure of about

0.70×0.08 + 0.30×0.02 = 0.06

Thus, about 6 % of the uptake takes place in the end-of-life stage. This corresponds to a factor 0.06×0.44 = 0.026 or 2.6 % of the annual calcination emissions. The total calcination emission being 0.55 Gt C, corresponding to (44/12)×0.55 = 2.02 Gt CO_2. The 2.6 % means an uptake in the end-of-life stage of 0.026×2.02 = 0.0525 Gt or 52.5 million tonne of CO_2. The annual amount of concrete entering the end-of-life stage is not found in the report. The uptake can therefore not be presented as kg CO_2/m^3 of concrete.

The **Norwegian study** [3] reports that the "concrete demolition rate is 10 % of the consumed concrete volume" and that 90 % of the demolished concrete "recovery rate" is available for carbonation. No figures are specified for the end-of-life stage. For a 100-years "recovery phase", a scenario is however presented, see Secondary use.

In **the Netherlands** [20], the amount of annual demolished concrete as a percentage of annual production is high, 5.1 million m^3 out of 14 million m^3, corresponding to 36 %. The Dutch study reports an uptake in the end-of-life stage of 83 000 tonne per year. The calcination emission is 1 960 0000 ton, which means that the uptake in the end-of-life stage is reported to be 83 000/1 960 000 = 4 % of the calcination emissions. Slag cement is here a considerable part of the cement consumption. The uptake per m^3 of demolished concrete is 83 000 000/5 100 000 = 16 kg CO_2/m^3 concrete.

Measurements of CO_2 uptake in crushed concrete from demolition sites and recycling plants are reported in (Kikuchi T and Kuroda Y, 2011) [10]. The presented figure of the CO_2 uptake in a couple of months is 11 kg per tonne of crushed concrete, corresponding to about 25 kg CO_2/m^3 of concrete, or to about 25/0.330 = 76 kg CO_2/tonne cement, or to 76/490 = 15 % of the calcination emissions for the cement in the crushed concrete, (Portland cement anticipated). The relation of the uptake at the end-of-life stage, to the annual total calcination emission, can be calculated if the annual recycled amount and the production can be found. The annual amount of CO_2 uptake by "recycled crusher run" is estimated at 0.37 million tonne. The annual produced amount of concrete is 500 million tonne, or about 200 million m^3. The average cement content is assumed to be 330 kg/m^3, and the calcination emission 0.480 kg CO_2 per kg cement. The emission per m^3 concrete will be 330×0.480=158 kg CO_2/m^3 concrete. The relative uptake is accordingly:
370 000/200 000 000×0.158 = 0.012 or 1.2 % of the total calcination emissions.

Considering that the concrete that is taken out of service annually is normally only a minor part of the annual production, it means that the uptake in this stage compared to the emissions is normally small. This means also that any default factor value of the calcination emissions in the Simplified methodology need to be small, (e.g. range of 0.4 – 4 %). If there, however, exists knowledge of the annual amount of concrete taken out of service (often referred to as recycled concrete), the uptake in this concrete during the end-of-life stage can be estimated to be in the range of 5 - 25 kg CO_2/m^3 of concrete.

For the Simplified methodology, it therefore seems reasonable to suggest two principal ways to report an estimated uptake value in the end-of-life stage:

If the annual amount of concrete in the end-of-life stage is known (m^3 per year), the uptake can be calculated as 10 kg CO_2/m^3 of concrete.

If the annual amount of concrete in the end-of-life stage is not known, the uptake can be calculated as 2 % of the annual calcination emissions, (factor 0.02). This also includes an anticipated minor increase of concrete to end-of-life the coming years.

Potential uptake in the end-of-life stage (demolition, crushing, and stockpiling) is very large if adequate measures are taken. The measures are storage of the crushed material in fractions and sheltered from rain in order to enhance air circulation in the piles, [17] and draft FprCEN/TR 17310, Carbonation and CO_2 uptake in concrete. See also the Advanced methodology.

5.2.4.2 Secondary use

The uptake in secondary use, mainly in various applications for crushed concrete, is probably of great importance but very few reports present reliable uptake in this case. The secondary use phase reminds a lot of the primary use phase. By crushing or other processing, new concrete surfaces for carbonation are exposed while old surfaces and volumes can continue to carbonate. Thus, similar methods as for primary concrete products can be utilized.

The **Swedish study** [2] estimates that about 8000 of the 12 000 tonne of the uptake after the use stage takes place during the "use of the mixed crushed concrete fractions", that is as secondary use. This corresponds to 8 000 000/625 000 = 12.8 kg CO_2/m^3 of concrete, or 12.8/0.33 = 39 kg CO_2/tonne cement, or (39/490)*100 = 8 % of a Portland cement calcination emission. Since 1.5 million tonne (625 000 m^3) of concrete is recycled each year and the production is about 7 000 000 m^3, the relative recycling rate is 9 %. This means that the annual uptake in the recycled concrete is less than 1 % of the annual calcination emissions, (0.09×0.08×100 = 0.72 %).

The **Norwegian study** [3] assumes a 100-years "recovery stage". The scenario is an anticipated crushed concrete particle size distribution and 10 % exposed above ground and 90 % below ground. The annual uptake is estimated to be 25 000 tonne, corresponding to 25 000/795 000 = 3 % of the annual calcination emissions. Counted as uptake related to the recovered material (1 million tonne or 400 000 m^3) the figure is 25 000 000/400 000 = 62 kg CO_2/m^3 concrete. This figure is actually the annual uptake in "recovered concrete" for 100 years, or the annual uptake 2011, assuming 100 years of 10 % recovery rate each year.

The **Dutch study** [20] doesn´t present any values for the secondary use.

The **global study** [4] claims that only 0.1 % of the initial emission is absorbed during the disposal or reuse of the concrete waste. This corresponds to about 0.001×0.49×330 = 0.16 kg CO_2/m^3 of concrete. It is uncertain however if "reuse of concrete waste" is the same as secondary use, so this very low value is, until more information is available, not taken into account.

To summarize: As in the "end-of-life stage", only a minor amount of the annually produced concrete is presently normally taken out of service and being recycled. The uptake in the secondary use applications is for this reason small compared to the emissions of the produced concrete and cement.

The default value in the Simplified methodology (without any other data than calcination emissions) must therefore be modest. Proposed is 0.01 or 1 % of the calcination emissions.

For the Simplified methodology, it therefore seems reasonable to suggest two principal ways to report an estimated uptake value in the secondary use:

If the annual amount of concrete entering the secondary use is known (m^3 per year), the uptake can be calculated as 10 kg CO_2/m^3 of concrete. This value is valid for unbound applications of crushed material.

If the annual amount of concrete entering the secondary use is not known, the uptake can be calculated as 1 % of the annual calcination emissions, (factor 0.01).

5.2.5 Summary

The annual CO_2 uptake of concrete in country or region – in the use stage (existing structures), end-of-life stage (demolition, crushing, stockpiling), and secondary use – can be estimated according to the Simplified methodology. The uptake values are related to the estimated annual calcination emissions of the consumed clinker (produced-export+import) in the same area or country. Note that the annual national calculated emission values may need to be adjusted for exports and imports of cement/clinker.

Use stage

Two alternative values, A and B, for the CO_2 uptake in the use stage are given. The reason for giving two values is to give options how to handle the variation span of the calculated figures. From Chapter 5.2.3 it follows that one can present a calculated mean value (A) or a low (Mean - St. dev.) value (B). The IPCC recommendation is to neither overestimate, nor underestimate in the calculations, which should indicate alternative A. The Tier 1 methods are associated with relatively large uncertainties in the calculated uptake figures. To reduce uncertainties, higher tier-levels methods should be used.

Alternative A:

The uptake in the use stage can be estimated as 0.20×(the reported emission from calcination of consumed cement clinker).

If the mortar for rendering applications, in total, amount to more than 10 % but less than 30 % of the cement consumption, the uptake factor in the use stage can be estimated at 0.20 + 0.0115(MR - 10), where MR is the mortar percentage for rendering of the clinker use. If MR is below 10 % use MR=10 and if MR is above 30 % use MR=30.

Alternative B:

The uptake in the use stage can be estimated as 0.15×(the reported emission from calcination of consumed cement clinker).

If the mortar for rendering applications, in total, amount to more than 10 % but less than 30 % of the cement consumption, the uptake factor in the use stage can be estimated at 0.15 + 0.01(MR - 10), where MR is the mortar percentage for rendering of the clinker use. If MR is below 10 % use MR=10 and if MR is above 30 % use MR=30.

End-of-life stage and secondary use

Annual uptake in the end-of-life stage and secondary use can be estimated at

(0.02 + 0.01)×(the reported emission from calcination of consumed cement clinker), where the value 0.02 represents uptake for end-of-life processes and 0.01 represents uptake for secondary use.

Alternatively, the following estimation can be done in the end-of-life stage and the secondary use.

- **If the annual amount of concrete being taken out of service and processed at a recycling plant is known, the CO_2 uptake in the <u>end-of-life stage</u> can be calculated to 10 kg CO_2/m^3 concrete.**
- **If the annual amount of crushed concrete, entering <u>secondary use</u> as unbound material, is known, the uptake can be calculated to 10 kg CO_2/m^3 concrete.**

Examples:

For 2 million tonne of Portland cement:
The CO_2 emission is 2 000 000×0.490 = 980 000 tonne.

Alternative A:
The CO_2 uptake in use stage, end-of-life stage and secondary use is (0.20 + 0.02 + 0.01)×980 000 = 225 400 tonne.

Alternative B:
The CO_2 uptake in use stage, end-of-life stage and secondary use is (0.15 + 0.02 + 0.01)×980 000 = 176 400 tonne.

5.2.6 CO_2 uptake with non-traditional raw materials as CaO source beside limestone

Traditionally, calcium carbonate, $CaCO_3$, has been used as the main calcium oxide source for clinker production. The CO_2 released during limestone calcination can be mineralized into calcium carbonate by the carbonation reaction and hence, the CO_2 emissions from raw materials (also called process or calcination emissions) can be equated with the maximum uptake of CO_2.

With the decarbonization efforts of cement industry, it is expected that the fraction of pre-calcined calcium oxide sources for clinker production will increase. Such sources comprise e.g. of slags where CaO is bound in a pre-calcined glass, fines from concrete recycling where CaO is bound in cement hydrates, calcium hydroxide by-products, paper sludge incineration ash etc. Such materials do not release CO_2 upon heating, but still provide carbonatable CaO to the clinker, cement and concrete, respectively. As the CO_2 uptake is linked to the calcination CO_2 emissions in the Simplified methodology, these alternative pre-calcined raw materials would lead to underestimating the actual CO_2 uptake. This problem can be overcome by using the carbonation potential based on the bulk chemical composition.

Instead of using the calcination emission as maximum theoretical CO_2 uptake, one can use a calculation of the maximum theoretical CO_2 uptake according to the same principle as in Tier 2, here called U_{tcc}.

U_{tcc} is presented in Chapter 5.3.1.1 and 5.3.6 as being ≈ 0.49 kg CO_2/kg cement (CEM I), or ≈ 0.52 kg CO_2/kg clinker, but can be individually calculated with the following formula, which can be found for instance in the EN 16757, Annex BB.

$$U_{tcc} = (M_{CO2}/M_{CaO}) \times CaO = 0.785 \times CaO$$

where

CaO is the part of reactive CaO in the binder.
M_{CO2} is the molar mass of CO_2 = 44 g/mol
M_{CaO} is the molar mass of CaO = 56 g/mol

With limestone as raw material, a typical value for reactive CaO part is about 65 % by weight of clinker. The U_{tcc} then becomes 0.785 × 0.65 = 0.51 kg CO_2/kg clinker, which value is the same as the calcination emission. This is an approximative figure and if also CO_2 uptake in other compounds such as MgO will be taken into account, the uptake figure has to be increased to, for example, 0.52-0.54 kg CO_2/kg clinker. The calcination/carbonation figure is specific for the clinker/cement used.

With non-traditional pre-calcined CaO sources as raw material besides clinker, the same formula can be used, but with the actual reactive CaO content of the clinker.

This value of U_{tcc} = 0.785 × CaO, being the theoretical maximum of CO_2 uptake, can be used in all calculations according to Tier 1, instead of calcination emission.

5.3 Tier 2 model for annual CO_2 uptake - Advanced methodology

5.3.1 Proposed CO_2 uptake model for Tier 2

The present model, representing Tier 2, provides a more advanced calculation method for estimating the annual uptake of CO_2 in existing concrete structures on a national basis. The model should be used primarily in cases where resources are missing to perform a more accurate calculation according to the calculation methods described for Tier 3 of Chapter 5.4, yet it has the potential and knowledge to perform a more advanced and improved CO_2 uptake model than the simplified model offered in Tier 1. According to IPCC guidelines, Tier 2 and 3 should also replace Tier 1 if the uptake in the country is defined as a "key category". However, in this model, a more simplified calculation of the CO_2 uptake in existing (old) concrete structures is used compared to Tier 3 and referred to as Onward calculation method. The proposed methodology for Tier 2 is based on methodology II described below. The national annual CO_2 uptake in concrete; in the use stage (existing structures), in end-of-life stage (demolition, crushing, stockpiling), and in secondary use (recycling), can be estimated according to this methodology for Tier 2.

5.3.1.1 Primary use stage

The mean value of the preceding 20 years of cement/clinker consumption may be used together with knowledge of one year of concrete use and its distribution on different type of concrete structures. The mean value of the cement/clinker consumption should normally be easy to access and would give a better estimation of the amount of carbonating structures than only the last year's consumption especially if the cement/clinker consumption has been rapidly increasing or decreasing during later years. In the international reporting it is common to calculate the emissions/uptake for all years back to 1990. In the calculation of CO_2 uptake for year 1990, data from year 1970 thus have to be used. Thus, a relatively long uptake period is included covering most of the fluctuations in cement/clinker use for the countries. It is anticipated that the uptake during one year in existing buildings is equal to the uptake over the next (100) years in the concrete produced during the same year. For more information about this "onward" calculation method, see Chapter 5.3.3.2.1. This also means that if large variations in the use of concrete in previous years occur, e.g. if the concrete use started late in a country, the assumed uptake can deviate significantly from the assumption of the method. This can be compensated by using an average value of cement/clinker use in the country based on previous years' use (20 years or more if necessary) in the uptake calculation for a given year, instead of the present year's use of cement/clinker.

A suggested general description of the required steps in the proposed Advanced methodology II is presented below, based on parts of the Swedish study [2] above and the paper by C. Andrade [9].

- Identify typical concrete applications (frequent type of structures). Normally, at least 5 applications should be needed, corresponding to at least 65 % of the cement consumption. For instance: Bridges, residential buildings, office buildings, roof tiles, pavement, shotcrete, sleepers, and mortar. Applications outside the chosen ones are treated as the most similar of the defined ones.

Cement/clinker content, concrete quality, exposure and surface area is described for each application. Usually, the data for each application can be obtained either from knowledge of the yearly concrete volume in each application and typical concrete mixture proportions for those applications or by knowing the cement/clinker amounts and corresponding total concrete volumes for each application.

- Calculate the CO_2 uptake for each application as a function of time:

The CO_2 uptake in kg for each application during t years can be calculated as:
(The formula can be found in EN 16757, Annex BB, equation BB.7.)

$$\mathbf{CO_2\text{-uptake} = (\Sigma(k_i \times DOC_i \times A_i))\ (\sqrt{(t)}/1000) \times U_{tcc} \times C}$$

Where

CO_2-uptake is the total CO_2 uptake in kg CO_2 during t years in the application.
k_i is a constant factor for the rate of carbonation for surface i in mm/√(t).

DOC_i is the degree of carbonation for surface/volume i.

A_i is the area of surface i in m^2.

t is the number of years from start of carbonation.

U_{tcc} is the maximum theoretical uptake in kg CO_2/kg cement or clinker. The value is ≈ 0.49 for Portland cement (CEM I) and ≈ 0.52 for cement clinker.

C is cement content e.g. CEM I, otherwise clinker content in kg /m^3 of concrete.

Concrete quality, exposure and surface area for the different parts of the application are determining the content of the first brackets. If the cement/clinker content C varies between different parts of the application, the uptake must be calculated for each part and summed up.
Values of k can be found in EN 16757, Annex BB. Correction factors for k for cement with additional major constituents or concrete with mineral additions can be found in table BB.2, Table 3. Values of DOC can, for example, be found in EN 16757, Annex BB.

Table 2 Table with k-factors for calculation of depth of carbonation for different strength classes (cylinder) and exposure conditions and also degree of carbonation for different exposure conditions. This table is reproduced from Annex BB of European standard EN 16757:2017, [16].

Concrete strength	≤ 15 MPa	15-20 MPa	25-35 MPa	≥ 35 MPa	Degree of carbonation (DOC)
Parameters	**Value of k-factor, in mm/year$^{0.5}$**				Percentage
Civil engineering structures					
Exposed to rain		2.7	1.6	1.1	85
Sheltered from rain		6.6	4.4	2.7	75
In ground *		1.1	0.8	0.5	85
Buildings					
Outdoor					
Exposed to rain	5.5	2.7	1.6	1.1	85
Sheltered from rain	11	6.6	4.4	2.7	75
Indoor in dry climate ***					
With cover **	11.6	6.9	4.6	2.7	40
Without cover	16.5	9.9	6.6	3.8	40
In ground *		1.1	0.8	0.5	85

* Under groundwater level k = 0.2

** Paint or wall paper. (Under tiles, parquet and laminate k is considered to be 0.)

*** Indoor in dry climate means that the RH is normally between 45 and 65 %.

Table 3 Correction for the k-factor for cement/clinker with additional major constituents or concrete with mineral additions. This table is reproduced from Annex BB of European standard EN 16757:2017 (Table BB.2), [16].

Amount of addition (weight %)	**≤ 10**	**10 to 20**	**20 to 30**	**30 to 40**	**40 to 60**	**60 to 80**
Limestone		1.05	1.1			
Silica fume	1.05	1.1				
Fly ash		1.05		1.1		
Ground Granulated Blast Furnace Slag (GGBS)	1.05	1.1	1.15	1.2	1.25	1.3

For other cement types than Portland cement (CEM I) and concrete with mineral additions the k-factors should be increased due to higher carbonation rate according to recommendation in EN 16757, Annex BB, table BB.2. If several additions are used in the concrete, the highest of the applicable correction factors shall be used. The correction factor adjusts the carbonation rate of the specific concrete. The total CO_2 uptake will be achieved by combining this new carbonation rate with the maximum CO_2 uptake for the cement with the addition (kg CO_2/kg cement) and the degree of carbonation (DOC). However, the correct CO_2 uptake figures for additions can be difficult to obtain.

Examples of calculation of CO_2 uptake in an application can be found in EN 16757, Annex BB, example 5 and 6.

- Calculate the last 20 years mean annual cement/clinker consumption and estimate the annual concrete production and the cement/clinker distribution on the different applications.
- Calculate the CO_2 uptake for each application for 100 years. (normally)
- Calculate the sum of the annual CO_2 uptake of all concrete applications.
- The sum of the cement content in the produced concrete should always be checked against the cement production.

For mortar or very thin applications, as for instance roof tiles, where total carbonation and maximum CO_2 uptake will occur in a few years, the CO_2 uptake can be calculated as

$0.75 \times U_{tcc} \times C$ in kg CO_2/m^3.

5.3.1.2 End-of-life stage (demolishing, crushing and storage)

In the Simplified methodology, we introduced a conservative "default" value for this phase based on the present normal handling procedures of demolished and crushed concrete. These procedures include normally storage in large unsheltered piles, during a rather short period of time. Moreover, the recycling rate (the annual amount of demolished and crushed concrete in relation to the annual production) is normally low in most countries. The volumes can however be anticipated to increase in the future, as more concrete structures reach the end of their service life. It is therefore important to base CO_2 uptake calculations on the actual amounts of concrete that goes to end-of-life handling.

The following estimations for CO_2 uptake in the end-of-life stage can be given.

For normal handling procedure or recycling rate less than 5 %:
(Same as for Simplified methodology, Tier 1)

If the annual amount of concrete in the end-of-life stage is known (m^3 per year), the uptake can be calculated as 10 kg CO_2/m^3 of concrete.

If the annual amount of concrete in the end-of-life stage is not known, the uptake can be calculated as 2 % of the annual calcination emissions, (factor 0.02).

For improved handling procedure:

A preliminary suggestion is that the uptake could be set to 20 kg CO_2/m^3 of concrete if an enhanced procedure with air access in the fractions and at least 4 months storage in at least three fractions is applied. In this case, the amount of concrete need to be known.

5.3.1.3 Secondary use

Only very small amounts of concrete structures that have reached their service life, actually ends up as waste (landfill), but are used in crushed form as, or in, a new product – secondary use. It is therefore important to base the uptake calculations on the real amounts of concrete to secondary use. The CO_2 uptake in secondary use is quite similar to the uptake in primary use, so similar calculation methods could be used. However, even more factors are unknown for secondary use, so it can be difficult to create general but accurate methods. The more exact methods are often quite specific and depend on the type of secondary use (country specific) and may be treated under Tier 3 in Chapter 5.4. Here, a more general method is proposed.

Under favourable conditions for the secondary use applications, the total uptake (primary use + end-of-life + secondary use) can amount to about 75 % ([11], [16]) of the maximum theoretical potential (equal to the calcination emission), corresponding to about 110 kg CO_2/m^3 for an average concrete.

As a lowest level for secondary use, an uptake according to the Simplified method (Tier 1) can be used.

That is:
If the annual amount of concrete entering the secondary use is known (m^3 per year), the uptake can be calculated as 10 kg CO_2/m^3 of concrete. This value is valid for unbound applications of crushed material. (If the annual amount of concrete entering the secondary use is not known, the uptake can be calculated as 1 % of the annual calcination emissions, factor 0.01.)

5.3.1.4 Cement constituents and concrete additions

Different cement constituents and concrete additions are frequently used in different parts of the world, but the degree of use varies considerably between different manufacturers and countries. The materials used are also very different and their ability to bind CO_2 is also very different. The additions that are mainly used are ground granulated blast furnace slag (GGBS), fly ash, silica fume, and limestone. Relatively few data are available for the uptake of CO_2 in different additions, but some data, especially for blast furnace slag (GGBS), exist. In the first version of the Tier 2 model used here, the correction factors of the carbonation rate factor (k_i) from the standard EN 16757, Annex BB (Table 3) has been used when additions are used in the concrete. For a more accurate calculation, the maximum CO_2 uptake in the cement with addition/concrete needs to be known and used. A more detailed model for CO_2 uptake in various additions can then be made in Tier 3. In Tier 3, specific CO_2 uptake values for different additions can be obtained and used in the models.

A proposed simplified value for CO_2 uptake in GGBS has been developed as follows:
A proposed CO_2 uptake value for ground granulated blast furnace slag (GGBS) can be
25 kg CO_2/tonne GGBS, see further Chapter 5.3.8.

The following chapters explain the background and consideration that underlie the proposed model.

5.3.2 Introduction

The Advanced methodology (AM) should be used to make a better estimate of the annual CO_2 uptake than with the Simplified methodology (SM). As mentioned before, it normally gives a more accurate uptake than the simplified one, thus encouraging the extra effort.

To be able to make a good estimate of the annual CO_2 uptake, one need a good overview and knowledge of the existing concrete product stock in the country or region in question, since it is in these structures that the uptake takes place.

There is of course a correlation between the cement consumption and the concrete production. The best way to obtain a historical estimate of the concrete production is normally via the cement consumption, whose statistics are often available. For the Advanced methodology, it is essential that the sum of the cement content in the produced concrete is checked against the cement consumption. The cement consumption includes cement production as well as import and export of cement.

The basis for the Advanced methodology (as well as for the Simplified methodology) is accordingly the cement consumption. Here, we should however have knowledge of, not only the consumption of the year in question, but a historical view going at least 20 years back in order to have a reasonable picture of the volume of the concrete production and thus the concrete product stock.

In lack of data, it is in IPCC accepted to use extrapolation, expert opinion and other quantification methods.

5.3.3 The primary use stage, results from different studies

The distribution of the cement consumption on different applications, for instance infrastructure, residential buildings, and other buildings, with typical surface/volume ratio and concrete quality, should be known. It has been shown [2] that it might be sufficient to know this distribution, not every year, but on a couple of occasions. Since the CO_2 uptake takes place in concrete produced during a long time, the relative changes in cement distribution for different applications, due for instance to economic reasons, seem to even out in the long run. It is thus likely more important to have a detailed knowledge of the cement distribution on different applications and products and of their exposure and surface/volume ratio on one occasion, than a vague picture at many occasions.

The different methods listed in the table "Characterization of existing models…in Appendix 1, Table 6" have somewhat different approaches to the estimation of the annual CO_2 uptake. They are below arranged under two headlines, Advanced methodology I and II.

Two of the methods estimate the annual uptake in the existing building stock by using extensive knowledge of the historical cement use, (Advanced methodology I). These two are also the base for the later Tier 3 method.

Five of the methods estimate the annual uptake in the concrete product stock by using the assumption that the uptake during one year in concrete that was produced during the previous (100) years, which is the desired information, can be placed on an equality with the uptake the coming (100) years in concrete produced during the same year, (Advanced methodology II). This is referred to as the "Onward calculation method". The uptake in the existing concrete product stock during a specific year (the reporting year) is what is requested. This uptake can be calculated by using knowledge of the historical concrete production (100 years if possible) as in Advanced methodology I. This knowledge is, however, often not at hand and the uptake calculation is also laborious. One can instead make use of the assumption that this "true" uptake value can be estimated by the uptake the coming (100) years in concrete produced the same year (the reporting year). How accurate this estimation is depends a lot on how stable the use of concrete has been over time. See further Chapter 5.3.3.2.1.

The table below is a short survey of the six different methods.

Table 4 The table shows the different calculation principles for the different country specific CO_2 uptake models compared to Tier 1A (Mean) and Tier 1B (Mean – St. dev.).

Country/method	Advanced methodology I	Advanced methodology II	Simplified methodology Tier 1A Relative values	Simplified methodology Tier 1B Relative values
Sweden	Yes		84 %	65.5 %
Norway		Yes	112 %	88 %
The Netherlands		Yes	86 %	64 %
Ireland		Yes	125 %	94 %
Global	Yes		106 %	87 %
Switzerland		Yes	133 %	100 %
Spain		Yes	133 %	100 %

The seven methods in both Advanced methodology I and II have a similar approach when it comes to knowledge of cement distribution on different concrete applications/products. That is their relative amount, exposure, mean surface/volume ratio, concrete quality, and cement content. The CO_2 uptake of each application is calculated using k-factors and the same kind of square root of time dependency. Value of degree of carbonation may differ.

5.3.3.1 The Advanced methodology I

The Swedish method [2] uses knowledge of 100 years cement consumption and 60 years of distribution on different applications and knowledge of how concrete structures are distributed throughout the building sector to estimate the stock of concrete applications. The k-values and the degree of carbonation are very similar to the ones in EN 16757 [16]. The uptake each year is calculated as the difference between two consecutive years and is summed up for all the 7 applications/products.

Influence of uncertainties in the model

The result is obtained by using the market distribution of the concrete applications valid for the year 2010. A calculation based on actual historical statistics between 1950 and 2010 shows very similar results. The results show a dependence on the concrete quality, which is expected. If hypothetically all concrete would be of 45 MPa, the uptake would be reduced from about 300 to 170 ktonne. With 25 MPa, the uptake would increase to 470 ktonne. In practice, these extreme cases will not occur. Applying different lengths of service life (70-100 years) only results in minor changes to the uptake. The model input data, which consist of cement production and cement use in various products as well as cement types and concrete qualities, has both high availability and good reliability in most countries. The model has been designed to be robust to historical variations. The quality of the results is mainly influenced by the quality of the input data and its statistical distribution for the most recent year, compare [21].

This way of calculating could be characterized as an extra advanced methodology, where concern is taken to the historical cement/concrete production for 100 years, and also the distribution of cement on different applications is known under 60 years. The calculation should give a very good estimate of the annual uptake. With this methodology, it has been estimated that the CO_2 uptake in Sweden during the year of 2011 amounted to 300 000 tonne.

Comparison with Simplified methodology Tier 1A
If the Simplified methodology would be used, the result would be:
Calcination emission 455 kg CO_2/tonne cement (A mixture of CEM I and CEM II/A)
Cement consumption: 2.4 million tonne
CO_2 uptake is 0.23×0.455×2 400 000 = 251 160 tonne, corresponding to 83.7 % of the advanced methodology value.

Comparison with Simplified methodology Tier 1B
If the Simplified methodology would be used, the result would be:
Calcination emission 455 kg CO_2/tonne cement (A mixture of CEM I and CEM II/A)
Cement consumption: 2.4 million tonne
CO_2 uptake is 0.18×0.455×2 400 000 = 196 560 tonne, corresponding to 65.5 % of the advanced methodology value.

The global method [4] The data is provided for different regions (China, US, Europe and rest of the world). Degree of carbonation is set to 80 % in concrete and 92 % in average of mortar. The method uses 83 years (1930 – 2013) of cement consumption and a variety of regional information on concrete applications. The CO_2 uptake in the relation to the calcination emissions is given as a mean value for the 83 years, being 43 %, and for the year 2013, being 44 %. To be noted is the high share of cement for mortar application; 30 % is used in this application, and the uptake share is 70 %, due to the high surface/volume ratio and relatively low quality of the mortar. The uptake during the year 2013 is reported to be 0.24 Gt C, corresponding to (44/12)×0.24 = 0.88 Gt, or 880 million tonne of CO_2. This figure includes the end-of-life stage. The calcination emission during 2013 is reported to be 0.55 Gt C, corresponding to 2.02 Gt CO_2.

Comparison with Simplified methodology Tier 1A
With the suggested Simplified methodology, the uptake should have been:
(With 30 % in mortar applications.)

The uptake factor is 0.20 + 0.0115(30 - 10) + 0.02 + 0.01 = 0.20 + 0.23 + 0.02 + 0.01 = 0.46.
CO_2 uptake is 0.46×2 020 = 929 million tonne, corresponding to 929/880 = 106 % of the advanced methodology value.

Comparison with Simplified methodology Tier 1B
With the suggested Simplified methodology, the uptake should have been:
(With 30 % in mortar applications.)

The uptake factor is 0.15 + 0.01(30 - 10) + 0.02 + 0.01 = 0.15 + 0.20 + 0.02 + 0.01 = 0.38.
CO_2 uptake is 0.38×2 020 = 768 million tonne, corresponding to 768/880 = 87 % of the advanced methodology value.

5.3.3.2 The Advanced methodology II

Other methods in the country overview make use of the assumption that the uptake during one year in concrete that was produced during the previous (100) years, which is the desired information, can be placed on an equality with the uptake the coming (100) years in concrete produced during the same year. This can be characterized as "onward" calculation, which is further explained in Chapter 5.3.3.2.1.

For a 100 % identity, it is required unchanged production of cement and concrete and distribution on applications during the previous years. In practice, this unrealistic requirement can however be modified.

To be noted is that the years immediately prior to the reported year are most important for the uptake amount. This results from the square root of time dependency of the carbonation rate, which means that the concrete production of remote years becomes less important.

<u>The Norwegian method</u> [3]

The degree of carbonation is set to 70 % all over. The Norwegian report doesn´t make any calculation based on historical values of cement consumption. The output of the model is the total amount of CO_2 bound by concrete consumed in Norway in 2011, assuming an onward service life of 100 years. It is anticipated that the uptake during one year in existing buildings is equal to the uptake over the next 100 years in the concrete produced for one year. Thus, in this case, only the production of cement and concrete applications for one year need to be known.

With this method, it is estimated that the annual uptake during 2011 in Norway is 140 000 tonne in the service life and 165 000 tonne if 100 years of "recovery phase" (secondary use) is added. In total, an uptake of 305 000 tonne CO_2.

(It is however also reported that the uptake is 94 kg, resp. 111 kg CO_2/tonne cement. With the annual cement consumption being ≈ 1 800 ktonne, it means an annual uptake of 171 000, resp. 202 000 tonne. The apparent inconsistency depends on that the CO_2 uptake is calculated on basis of the actual concrete consumption, which corresponds to a "fictive" cement consumption of ≈ 1 500 ktonne.)

From the Norwegian report, it can be found that three different cements (CEM I, CEM II/A-V and CEM II/B-S) have been used. The maximum CO_2 binding 2011 (70 % of the calcination emissions) is respectively 215, 252, and 55 thousand tonne of CO_2, in total 557 000 tonne. The calcination emissions are accordingly 557 000/0.70 = 795 000 tonne.

<u>Comparison with Simplified methodology Tier 1A</u>

With the suggested Simplified methodology, we should get in the use stage:
0.20×795 000 = 159 000 tonne bound in the clinker
The GGBS amount in the CEM II/B-S (33 % GGBS) is 0.33×186 000 = 61 000 tonne.
The uptake will accordingly be 61 000×0.035 = 2135 tonne (35 kg CO_2/tonne of GGBS, compare 5.3.8, last paragraph)
Total uptake in the use stage by the simplified method is 161 135 tonne compared to 140 000 tonne with the Advanced methodology (115 %).

The End-of-life stage and secondary use would add an extra 0.03×795 000 = 23 850 tonne to the uptake, in total 185 000 compared to 165 000 with the Advanced methodology (112 %).

Comparison with Simplified methodology Tier 1B
With the suggested Simplified methodology, we should get in the use stage:
0.15×795 000 = 120 000 tonne bound in the clinker
The GGBS amount in the CEM II/B-S (33 % GGBS) is 0.33×186 000 = 61 000 tonne.
The uptake will accordingly be 61 000×0.025 = 1 500 tonne (25 kg CO_2/tonne of GGBS)
Total uptake in the use stage by the simplified method is 121 500 tonne compared to 140 000 tonne with the Advanced methodology (86 %).

The End-of-life stage and secondary use would add an extra 0.03×795 000 = 23 850 tonne to the uptake, in total 145 350 compared to 165 000 with the Advanced methodology (88 %).

The Dutch method [20]
The amount of GGBS in the different applications/products is provided. It is assumed that there is no change in the yearly concrete volume, composition, and applications. The production of cement and concrete of the year 2015 is taken as basis for the calculations. The CO_2 uptake in the use stage is 365 000 tonne. The CO_2 uptake in the "recycling stage" (end-of-life stage) is 83 000 tonne.

The "CO_2 emissions due to cement consumption" is 1 960 000 tonne. It is not quite clear, but it can be derived from the reasoning below, that this figure includes both CO_2 from calcination and fuel combustion. The cement consumption is 4 000 000 tonne and the average CO_2 emission per tonne cement is reported to be 0.49 tonne/tonne, 4 000 000×0.49=1 960 000 tonne. The slag content is said to be 36 %. If the rest is assumed to be clinker, we have a clinker consumption of 0.64×4 000 000 = 2 560 000 tonne (and a slag consumption of 0.36×4 000 000 = 1 440 000 tonne). The corresponding calcination emission can be estimated at 0.515×2 560 000 = 1 318 000 tonne CO_2. This leaves only 1 960 000 – 1 318 000 = 642 000 tonne CO_2 for the fuel part, which can be reasonable since CO_2 neutral fuels are used to a large extent[3].

Comparison with Simplified methodology Tier 1A
The Simplified methodology gives an uptake of 0.20×1 318 000 = 263 600 tonne, plus the uptake in the GGBS 0.36×4 000 000×35×0.001 = 50 400 tonne.
In total 314 000 tonne, corresponding to 86 % of the Advanced value.

Comparison with Simplified methodology Tier 1B
The Simplified methodology gives an uptake of 0.15×1 318 000 = 198 000 tonne, plus the uptake in the GGBS 0.36×4 000 000×25×0.001 = 36 000 tonne.
In total 234 000 tonne, corresponding to 64 % of the Advanced value.

The Irish method [5]
The carbonation rate for each application is calculated using a calibrated Irish formula from Silva et al. [15]. The degree of carbonation is not specified. For the year 1972, the calcination emissions are estimated to have been 780 000 tonne and the concrete produced that year is estimated to have taken up 98 000 tonne by the end of year 2013 (40 years), corresponding to 13 %. On a 100 years perspective, this should have increased to about 13√(100/40) = 20 %. The report says 16 %. The figure 16 % is used in the statistical calculation for the Simplified methodology. It also mentioned that this figure corresponds to an uptake of 75 kg CO_2/tonne cement over 100 year service life. With

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[3] Personal communication with Edwin Vermeule: A lot of secondary fuels are used in the Netherlands (> 80 %). Those fuels are, to a large extent, CO_2-neutral.

a mean cement consumption of about 2 000 ktonne, it means an annual uptake in Ireland of about 150 000 tonne.

An estimate of the cement use in Ireland over last 40 years has been done, but it is not clear if these historical year-by-year values have really been used in the calculations. The uptake during one year in the existing buildings is not explicitly reported, but if it anticipated that it is approximately equal to 100 years of uptake in one year production, the value of 16 %, or 75 kg/tonne cement, can be used.

Comparison with Simplified methodology Tier 1A
The Simplified methodology gives the uptake of 0.20 or 20 %, which in this case is more than the presented Advanced method value of 16 % (20/16 = 125 %).

Comparison with Simplified methodology Tier 1B
The Simplified methodology gives the uptake of 0.15 or 15 %, which in this case is very close (15/16 = 94 %) to the presented Advanced method value of 16 %.

The Swiss method [13, 12].
The degree of carbonation is in the report [13] set to 75 % throughout, but is later in another paper [12] changed to 50 %. As in most reports, it is anticipated that the uptake during one year in existing buildings is equal to the uptake over the next (100) years in the concrete produced for one year. An average uptake of 10 % of the total emissions, for 50 years is presented in the report. For the calcination emissions, the figure can be estimated to be 10×(1/0.63) = 16 %. For 100 years, the figure can be estimated to be $16\times\sqrt{(100/50)} = 23$ %. With a degree of carbonation being 50 % instead of 75 % we get 23×(50/75) = 15 %.
(According to the Annex BB of the EN 16757 [16] the degree of carbonation varies between 40 % for indoor structures to 85 % for outdoor structures not sheltered from rain.)

Comparison with Simplified methodology, Tier 1A
The figure 15 % is less than the Simplified methodology, Tier 1A, value, which is 20 % (20/15=133 %).

Comparison with Simplified methodology, Tier 1B
The figure 15 % is the same as the Simplified methodology, Tier 1B, value (15/15 = 100 %).

The Spanish method [6,7,8, and 9]
The Spanish results are extensively discussed and dealt with under Chapter 5.2.3, resulting in the Spanish CO_2 uptake value being 15 % of the calcination emissions.

Comparison with Simplified methodology, Tier 1A
The figure 15 % is less than the Simplified methodology, Tier 1A, value, which is 20 % (20/15=133 %).

Comparison with Simplified methodology, Tier 1B
The figure 15 % is the same as the Simplified methodology, Tier 1B, value (15/15 = 100 %).

(This assumes that the Spanish value for comparison is the one updated by the C. Andrade paper [9] and the further calculation in Chapter 5.2.3.)

5.3.3.2.1 The Onward calculation method

To simplify the uptake calculations, it can be assumed in Tier 2 that the uptake of CO_2 the present year can be equated with the uptake of CO_2 for 100 years in the current distribution of concrete products and structures, and with the current year's concrete production. In reality, this year's uptake of CO_2 takes place in today's standing concrete products and structures, in concrete produced during the last 100 years. This approximation is relatively good provided that the concrete production has been fairly stable over the years. If greater variations in concrete production have occurred, this calculation method can be improved by using a rolling average value of the use of concrete or clinker over a longer period of time.

Five of the national methods estimate the annual uptake in the concrete product stock by using this assumption.

The uptake in existing concrete product stock during a certain year (the reported year) is what is to be calculated. This can be done by using knowledge of the historical concrete production (100 years if possible) as in Advanced methodology I. This knowledge is however often not at hand and the uptake calculation is also laborious. As an alternative, one can instead make use of the assumption that this "true" uptake value can be equivalent with the uptake the coming (100) years in concrete produced the same year (the reported year). This equality can be shown to be exact valid during certain circumstances and approximate valid during practical situations.

For an exact equality, it is required that the cement or rather concrete production has been almost equal the previous years and the actual year (the reported year). This means not only the amount and type of concrete but also the use of the concrete, i.e. the applications with their exposure and surface to volume ratio. See further explanation below *).

In practice, some circumstances modify these stringent requirements. Due to the square root of time dependency of the carbonation rate, it follows that the remote years production is of less importance for the present uptake. Even if we count on 100 years of service life for concrete contributing to the CO_2 uptake, 20 years of production accounts for √20/√100=45 % of the total uptake. Therefore, the requirement on similar production of concrete and applications can be limited to the last 20 years. However, if the cement use is very different in previous years (e.g. 50 - 20 years ago), then it is recommended to use the Advanced methodology I in Tier 3.

To improve the approximation, one could use the average value of concrete production during the last 20 years (for instance estimated through cement/clinker consumption, which is generally well reported) for the onward calculation of the uptake.

The relative changes in cement distribution for different applications, due for instance to market reasons, seem to even out in the long run. It is thus normally more important to have a detailed knowledge of the cement distribution on different applications and products and of their exposure and surface/volume ratio on one occasion, than a vague picture at many occasions.

These facts accordingly make the approximation of the onward calculation methodology (Advanced Methodology II) to be an acceptable calculation method.

*) This follows from the equation for the CO_2 uptake.

$$\mathbf{CO_2\text{-uptake} = (\Sigma(k_i \times DOC_i \times A_i))\ (\sqrt{\ }(t)/1000) \times U_{tcc} \times C}$$

where all the parameters (k, DOC, A, U_{tcc} and C) are kept constant, their product being say P.

The uptake for the reported year, according to Advanced Methodology II, will, for 100 years, be P×√100.
The uptake the reported year, according to Advanced Methodology I, will for 100 years of service life be:
P×Σ(√i - √(i-1)), where i goes from 100 to 1. The result is also P×√100.
(The uptake for the reported year is the difference between this year and the year before, summarized for all the previous years: (√100 - √99) + (√99 - √98) +…. + (√2 - √1) + (√1 - √0) = √100.)

5.3.4 Discussion of "good practice" for the Advanced methodology in the Use stage

The Advanced methodology should be based on the uptake in the actual existing concrete product stock. To achieve this, we first need the historical cement use in a country or region in question. This is often not a problem, since the cement production and use are normally recorded. Moreover, it might be enough to go 20 years back, since the uptake is following a square root of time dependency. Even if we can count on 100 years of service life for concrete contributing to the CO_2-uptake, the last 20 years production of this period accounts for √20/√100 = 45 % of the total uptake the present year. The last 50 years production accounts for √50/√100 = 71 %.

Thus, what happened in the cement consumption and concrete production a long time ago is of less importance for the present uptake. Also, smaller production figures in the remote years, often make this period less important. However, when there is available statistics on cement consumption for a longer period, a more accurate estimation can be done, as in the Swedish method [2].

As we have seen in the survey above, many countries rely only on one-year figures. The difference to the Simplified methodology lies in the necessary knowledge about concrete applications, of cement distribution on different applications/products. That is their relative amount, exposure, mean surface to volume ratio, concrete quality, cement content, k-values and degree of carbonation. The rate of carbonation for each application is calculated using k-values and the square root of time dependency. The k-values given in the EN 16757, Annex BB [16] for different exposures and concrete qualities have been found to be well balanced in many studies. The important factor degree of carbonation (DOC) can also be found in the EN 16757, Annex BB for different exposures or in Table 2.

The comprehensive earlier studies by Spain [6,7,8], compiled and adjusted in the recent paper by C. Andrade [9], includes many different types of cement, two types of concrete and three exposures, compiled for the IPCC application, show that the DOC for indoor exposure is around 45 % and for outdoor exposure around 60 % for sheltered concrete and 80 % for not sheltered concrete (exposed to rain). (DOC is here expressed as the amount of CaO that has converted to $CaCO_3$ in relation to the original amount of CaO, or (which is the same) the amount of bound CO_2 in relation to the emitted CO_2 by calcination.) The Spanish figures, valid for Portland cement, are rather well in line with the ones presented in the EN 16757. The indoor is a bit higher (45 % compared to 40 %) and the outdoor is a bit lower (60 % or 80 % compared to 75 or 85 %).

5.3.5 The Advanced methodology I, based on wide historical data on cement and concrete use – an overview

Calculation method using historical data, according to, for instance, the Swedish and the Global studies [2,4], where the uptake each year is calculated as the difference between two consecutive years and is summed up for all the applications/products. Data from at least 50 years statistic of cement consumption (cement production-export+import) and knowledge of concrete use from at least three different and well-distributed years over the calculation period should be used.
This methodology is proposed to be used for “Tier 3” described in Chapter 5.4.

5.3.6 The Advanced methodology II, based on a single or few years data on cement and concrete use – an overview

The Advanced methodology II is proposed to be used for calculations at Tier 2. The mean value of at least 20 years of cement consumption may be used together with knowledge of one year of concrete use. The mean value of the cement consumption should normally be easy to access and would give a better estimation of the amount of carbonating structures than only the last year’s consumption. It is anticipated that the uptake during one year in existing buildings is equal to the uptake over the next (100) years in the concrete produced during the same year. Calculation method onwards, according to for instance the Norwegian study [3].

Both methods (AM I and II) require knowledge of cement consumption statistics and concrete production and use, but on a different level. The calculation as such is simpler with the second methodology. The result should be presented as annual amount of CO_2 uptake for a country or region.

A suggested general description of the required steps in the Advanced methodology II is presented below, based on parts of the Swedish study above and the article by C. Andrade [9]. A more comprehensive presentation is made in Chapter 5.3.1.1.

- ➢ Identify typical concrete applications (frequent type of structures). Normally, at least 5 applications should be needed, corresponding to at least 65 % of the cement consumption. For instance: Bridges, residential buildings, office buildings, roof tiles, pavement, shotcrete, sleepers, and mortar. Applications outside the chosen ones are treated as the most similar of the defined ones.

Cement content, concrete quality, exposure and specific surface (m^2 surface/m^3 concrete) is described for each application. Especially exposure and specific surface may vary within the application.

- ➢ Calculate the CO_2 uptake for each application as a function of time:

The CO_2 uptake in kg for each application during t years can be calculated as:

(The formula can be found in EN 16757, Annex BB.)

$$\mathbf{CO_2\text{-uptake} = (\Sigma(k_i \times DOC_i \times A_i))\ (\sqrt{\ }(t)/1000) \times U_{tcc} \times C}$$

Where
CO_2-uptake is the total CO_2 uptake in kg CO_2 during t years.
k_i is a constant factor for the rate of carbonation for surface i in mm/√(t).
DOC_i is the degree of carbonation for surface/volume i.
A_i is the area of surface i in m^2.
t is the number of years from start of carbonation.
U_{tcc} is the maximum theoretical uptake in kg CO_2/kg cement or clinker. The value can be ≈ 0.49 for Portland cement (CEM I) and ≈ 0.52 for clinker.
C is cement content e.g. CEM I, otherwise clinker content in kg/m^3 of concrete.

(It is also possible to calculate an application with different U_{tcc} or C, by giving them index i and put them in the Σ – parenthesis.)

Values of k can be found in EN 16757, Annex BB. See also Table 2.
Values of DOC can be found in EN 16757, Annex BB. See also Table 2.

Examples of this kind of calculation can be found in EN 16757, Annex BB, example 5 and 6.

- Calculate the last 20 years mean annual cement/clinker consumption and estimate the annual concrete production and the distribution on the different applications.
- Calculate the CO_2 uptake for each application for 100 years. (normally)
- Calculate the sum of the annual CO_2 uptake of all concrete applications.
- The sum of the cement content in the produced concrete should always be checked against the cement production.

5.3.7 End-of-life stage and secondary use

5.3.7.1 End-of-life stage (demolishing, crushing and storage)

In the Simplified methodology, we introduced a conservative “default” value for this phase based on the present normal handling procedures of demolished and crushed concrete. These procedures include normally storage in large unsheltered piles, during a rather short period of time.

Moreover, the recycling rate (the annual amount of demolished and crushed concrete in relation to the annual production) is normally low in most countries. The volumes can however be anticipated to increase in the future, since more concrete structures reach the end of the service life. This foreseen increase should however not be speeded up for CO_2 uptake reasons. The present normal handling procedures for storage of crushed material, awaiting secondary use, are however not focused on facilitating CO_2 uptake and here; improvements can and should be implemented.

The drawback with the normal handling is the large piles of crushed material of mixed sized fractions. Although the fine fractions carbonate rapidly near the surface of the stockpile, the mixed size fractions, exposed to rain, form a rather compact material that prevents the free air circulation into the bulk of the stockpile. Measurements have shown that only up to about 0.3 m from the surface is influenced by carbonation. Changing of the handling procedures comprise commercial considerations but can be very effective when it comes to CO_2 uptake.

In [17], there is an estimate that an enhanced processing of crushed concrete, implying 1-4 months storing in five fractions, can increase the uptake in the end-of-life stage to about 20 kg CO_2/m^3 of concrete.

In the report [14], crushed concrete aggregates from waste hollow core slabs and decommissioned railway sleepers were analysed for their material characteristics. To investigate if graded crushed materials would have a better ability to absorb CO_2, the two different concrete materials used in this study were sieved and placed outdoors and sheltered from rain. The concrete was crushed and graded into three sizes; 0-4, 4-8, and 8-16 mm and placed in pallet collars with a net at the bottom. The total depth of the material was 0.4 m. After 18 months, the material was tested at four levels; 0, 0.12, 0.24, and 0.36 m from the top surface. Both the degree of carbonation and the amount of cement paste in each fraction was measured.

It was found that the grading of the crushed concrete aggregates into the three size fractions improved the CO_2 diffusion into the cement paste and increased the CO_2 uptake in the aggregates compared to the uptake of ungraded material. The main portion of the cement paste accumulated in the 0-4 mm size fraction and this fraction also experienced the highest carbonation degree; 0.45 - 0.65, but only in the outer layer. The inner layers carbonated at a lower rate, carbonation degree about 0.20, probably due to the higher gas diffusion resistance created by the finer particles. In the size fractions 4-8 and 8-16 mm, less gas diffusion resistance was experienced, and the carbonation degree was similar throughout the whole material.

From the given data on amount of cement paste and degree of carbonation of the different size fractions, it is possible to calculate the CO_2 uptake with the used storage conditions (18 months outdoors, sheltered from rain).

The cumulative grading curve of all the crushed material was not measured at the investigation but can be taken to be similar to a curve of crushed concrete presented in [17]. The following relative figures for the three fraction sizes are anticipated.

- 0 – 4 mm: 50 %
- 4 – 8 mm: 15 %
- 8 - 16 mm 35 %

In the 0 – 4 fraction, the "outer layer" constitute about 25 % (carbonation degree 0.55), and the rest about 75 % (carbonation degree 0.20). The uptake per m^3 of concrete, crushed into the three fractions, can be calculated as shown in Table 5. The total reported amount of paste in the three fractions is 378 kg/m^3, where average quality concrete has original cement paste content of about 500 kg/m^3. About 24 % (122/500) of the cement paste has been lost during the crushing and fractioning process, probably as fine dust.

Table 5 Calculated CO_2 uptake after 18 months (outdoors, sheltered from rain) in crushed concrete (1 m^3) separated into fractions, [14].

Size fraction (mm)	Relative amount	Paste		Cement* (kg)	Degree of carbonation (%)	CO_2 uptake** (kg CO_2/m^3 concrete)
		(%)	(kg)			
0 - 4 outer	0.5 × 0.25	25	75	53	55	14
0 - 4 inner	0.5 × 0.25	25	225	158	20	15
4 - 8	0.15	10	36	25	25	4
8 - 6	0.35	5	42	29	30	4
Total	**1.0**		**378**	**265**		**37**

* Paste, kg × 350/500. Cement 350 kg/m^3, Water 150 kg/m^3, w/c = 0.43 assumed (70 % of paste)

** Cement × Degree of carbonation × 0.49

From Table 5, the CO_2 uptake for the three fractions after 18 months is 37 kg/m^3 concrete. If one assumes that the uptake is proportional to the square root of time, this corresponds to about 18 kg/m^3 concrete for 4 months storage.

Some part of the hardened cement paste will separate during the crushing process as very fine particles. With suitable handling, these very fine particles will rapidly carbonate, possibly in days but up to a few weeks. If about 20 % of the cement paste is falling in this very fine fraction, and the carbonation degree is 75 %, the resulting uptake for a concrete with CEM I-cement content of 300 kg/m^3 will be an extra 0.2 × 300 × 0.49 × 0.75 = 22 kg CO_2/m^3 of concrete.
(The amount of these very fine particles is depending on crushing and sieving equipment and not yet possible to estimate accurately.)

It is important to find some way of including a future larger uptake in the end-of-life stage and to give reporting opportunities for countries with an already high rate of recycling as for instance the Netherlands and Germany. For very long storage times, years or more, and small particles in fractionized piles of low thickness, an uptake of about 75 % ([11], [16]) of the maximum theoretical potential uptake can be expected, corresponding to about 110 kg CO_2/m^3 of concrete.

The following estimations for CO_2 uptake in the end-of-life stage can be given.

<u>For normal handling procedure or recycling rate less than 5 %:</u>
(Same as for Simplified methodology, Tier 1)

If the annual amount of concrete in the end-of-life stage is known (m^3 per year), the uptake can be calculated as 10 kg CO_2/m^3 of concrete.
If the annual amount of concrete in the end-of-life stage is not known, the uptake can be calculated as 2 % of the annual calcination emissions, (factor 0.02).

<u>For improved handling procedure:</u>

A preliminary suggestion is that the uptake could be set to 20 kg CO_2/m^3 of concrete if an enhanced procedure with air access in the fractions and at least 4 months storage in at least three fractions is applied. In this case, the amount of concrete needs to be known.

The handling procedure for demolishing, crushing and storage, presented in [17], is an example of such improved procedure.

5.3.7.2 Secondary use

Only very small amounts of concrete structures that have reached their service life, actually ends up as waste (landfill), but are used in crushed form as, or in, a new product – secondary use. It is therefore important to base the uptake calculations on the real amounts of concrete to secondary use. The CO_2 uptake in secondary use is quite similar to the uptake in primary use, so similar calculation methods could be used. However, even more factors are unknown for secondary use, so it can be difficult to create general but accurate methods. The more exact methods are often quite specific and depend on the type of secondary use (country specific) and may be treated under Tier 3 in Chapter 5.4. Here, a more general method is proposed.

In the Simplified methodology, we introduced a conservative "default" value for this phase.

The annual amount of concrete presently being taken out of service and reused is, accordingly in most countries, small compared to concrete produced. The volumes can be anticipated to increase in the future, since more concrete structures reach the end of the service life.

For crushed material in secondary use, the estimation of the uptake is rather diverse, depending on the different possible applications such as

- Road base, filling material and similar unbound applications (large potential for carbonation).
- Aggregate for new concrete (limited potential for carbonation).

Uptake in these applications is also taking place in already, to some extent, carbonated material. (During the primary use and the end-of-life stage.)

The literature is rare on this subject.

Calculation of scenarios with different premises can give an estimation of reasonable uptake figures for these applications. To do this, we need however information about average carbonation status of the used crushed material, as well as carbonation rate of the new applications. This information is, so far, not available.

In [17], a theoretical discussion of a possible uptake in the secondary use is presented:

"The use phase of the crushed material is calculated to a practical CO_2 *maximum uptake. This uptake is thus reached in different time periods indicated in the comments. The use applications assume a relatively free access to air (*CO_2*). For the fractions larger than 4 mm, this can probably be achieved by using the material as filling materials in different construction applications and leaving openings in the aggregate construction for air circulation. The smaller fractions (0-4 mm) have a relatively compact structure due a large share of very fine particles. This indicates that the material should be used in thin structures. Examples of this can be top surface layers or slip control on roads. The applications for high uptake of* CO_2 *are relatively new and further development work is required. The* CO_2 *uptake is estimated for each application based on aggregate size and type of application."*

"For large aggregates, it is important to keep in mind that CO_2 is only taken up by the cement paste and not the ballast materials. Larger aggregates can thus consist of a stone covered with cement paste. Usually the stone material is stronger than the cement paste so the crushing fractures occur in the cement paste leaving a stone with a relatively thin layer of cement paste. This means that the size distribution of the ballast used in the concrete can influence the CO_2 uptake. Thus, a relatively large aggregate can show a fast carbonation. The thickness of the cement paste layer is, in this case, of significant importance."

Also in [2], the large potential of uptake in secondary use applications is emphasized.

As a lowest level for secondary use, an uptake according to the Simplified method (Tier 1) can be used.

That is:
If the annual amount of concrete entering the secondary use is known (m^3 per year), the uptake can be calculated as 10 kg CO_2/m^3 of concrete. This value is valid for unbound applications of crushed material. (If the annual amount of concrete entering the secondary use is not known, the uptake can be calculated as 1 % of the annual calcination emissions, factor 0.01.)

Under favourable conditions for the secondary use applications, the total uptake (primary use + end-of-life + secondary use) can amount to about 75 % ([11], [16]) of the maximum theoretical potential (equal to the calcination emission), corresponding to about 110 kg CO_2/m^3 for an average concrete.

5.3.8 Cement with different constituents or additions added at the concrete mixer

Different cement constituents and concrete additions are frequently used in different parts of the world, but the degree of use varies considerably between different manufacturers and countries. The materials used are also very different and their ability to bind CO_2 is also different. The additions that are mainly used are ground granulated blast furnace slag (GGBS), fly ash, silica fume, and limestone. Relatively few data are available for the uptake of CO_2 in different additions, but some data, especially for blast furnace slag, exist. It is therefore difficult to provide general recommendations for calculations of CO_2 uptake in additions, why a possibility is to include additions only when calculations are made using the Tier 3 method in Chapter 5.4. In that case, the Tier 3 method should be used when the use of additions is high in used concrete and if this affects the CO_2 uptake to a significant extent. However, the Tier 2 model might be used if reactive content of CaO could be established for the used fly ash or GGBS, and accordingly an adjusted maximum theoretical CO_2 uptake can be calculated.

To improve and simplify the uptake calculations when additions are used in concrete, a simplified CO_2 uptake calculation method for additions can be used. In the first version of the Tier 2 model used here, a correction factors of the carbonation rate factor (k_i) from the standard CEN/EN 16757, Annex BB (Table 3) can be used when additions are used in concrete, in combination with an adjusted value of the maximum theoretical CO_2 uptake (U_{tcc}, kg CO_2/kg cement) in the corresponding cement (including clinker and various additions). Note that additions to be included can be added to the cement or in the concrete production. A proposed simplified value for CO_2 uptake due to use of ground granulated blast furnace slag (GGBS) in concrete can be found below. Below is also a brief technical information about CO_2 uptake in additions that can be used for further work under Tier 3.

One has to distinguish between two effects of the additions. One is fairly well established and that is the increased rate of carbonation. Adjustment factors for the rate of carbonation compared to Portland cement (CEM I) is found for instance in the EN 16757, Annex BB [16]. For concrete of the same strength, the factors show for instance that the rate of carbonation will increase with 25 % if a binder with 40 – 60 % of GGBS is used. The rate will increase with 5 % if a binder with 10 – 20 % of fly ash is used. The increased rate of carbonation does however not mean that the total CO_2 uptake will increase. The uptake is also depending on how much of the $Ca(OH)_2$ and other compounds in the carbonated zone of the concrete that is actually converted to $CaCO_3$, (so called degree of carbonation).

GGBS, having a rather high CaO content, is the addition with the largest potential to take up CO_2. It is a latent hydraulic binder and does not need to consume $Ca(OH)_2$ from the clinker hydration to react. The fly ash and especially the silica fume contain small amounts of CaO and need the $Ca(OH)_2$ from the clinker hydration to react. Since $Ca(OH)_2$ is normally the first component of the hydrated cement to carbonate, the addition of fly ash or silica fume, can theoretically decrease the amount of CO_2 uptake, even if the rate of carbonation will increase as mentioned above.

The limestone addition is normally used in amounts less than 20 %. The increase on rate of carbonation from that addition is 10 % or less. Only minor parts of the limestone participate in the hydration, so the uptake can be assumed to take part only in the clinker reaction products.

To summarize: We have a situation with increased carbonation rate, meaning larger volume of carbonated concrete. On the other hand, a decreased amount of CO_2 bound per volume in this carbonated concrete. This fact makes it reasonable that, for the estimation of uptake in the Simplified method, (Tier 1), see Chapter 5.2.1, it is proposed that it is counted in the clinker only and the figure is based on the annual clinker calcination emission.

A solution with zero CO_2 uptake in the additions is also used in the EN 16757, Annex BB as a conservative estimation. An estimation based on clinker content only may, however, underestimate the CO_2 uptake if GGBS is used as additional constituent or addition. The problem is that there is, so far, not much knowledge of the CO_2 binding capacity of the GGBS hydration products. The attempts to estimations relate the uptake capacity to the amount of CaO, in the same way as with the clinker. The amount of CaO in GGBS is lower and varies more than in clinker.

In the **Norwegian report** [3], a calculation example is provided by which 70 % of the CaO in the GGBS can be carbonated. The amount of CaO in the GGBS is, in this case, 40 %. (The amount of CaO in the clinker is set to 65 %.) The additional uptake in the GGBS can be estimated to be 0.70×0.40/0.65 = 0.43 or 43 % of the clinker uptake. Thus, if the maximum uptake in the clinker is 515 kg/tonne, the maximum uptake in the GGBS is 0.43×515 = 221 kg CO_2/tonne. It should be emphasized that the Norwegian report does not claim that the figure 70 % for the CaO that can be carbonated is reliable. The binding capacity depends on the hydration products of the GGBS and to which extent they will carbonate under the normal partial pressure of CO_2.

We have earlier proposed that a conservative estimation is that 0.15 (0.15×515 = 77 kg CO_2/tonne clinker) of the annual calcination emissions will be taken up, (or 0.15 of the maximum uptake). If we apply the same thinking on GGBS, then 0.15×221 = 33 kg CO_2/tonne GGBS will be taken up.

Note that for concretes with GGBS, the uptake per m^3 of concrete is normally smaller than the uptake of concrete without GGBS, due to the fact that the clinker content is reduced and that GGBS take up less CO_2 per mass than clinker, (less CaO content and less "reactive" CaO).

In the **Dutch report** [20], it is anticipated that the maximum CO_2 uptake in GGBS is 140 kg CO_2/tonne GGBS. The maximum uptake in CEM I is 490 kg CO_2/tonne cement, or 515 kg CO_2/tonne clinker. A maximum CO_2 uptake of 140 kg per tonne GGBS will result in an uptake of 0.15×140 = 21 kg CO_2/tonne GGBS.

Without any more data than the values 221 and 140 kg/tonne for the maximum CO_2 uptake in the GGBS, or 33 and 21 kg/tonne for a conservative estimate of the uptake, it seems feasible to select a value of about 25 kg CO_2/tonne GGBS for the annual uptake in concrete with GGBS if the methodology in Tier 2 is used.

The value 25 kg CO_2/tonne GGBS corresponds to the maximum emission value 166 kg CO_2/tonne GGBS, which emanates from the blast furnace in the steel industry.

In line with the mean value factor 0.20 (see Chapter 5.2.3), the uptake in the GGBS can be estimated at $0.20\times166 \approx 35$ kg CO_2/tonne GGBS.

5.4 Tier 3 Annual CO_2 uptake model - Advanced user developed models

5.4.1 Introduction and background

As previously stated in this report, the calculation of CO_2 uptake in concrete and other cement-containing products is associated with difficulties. In principle, it is not possible to direct measure the uptake of CO_2 on-site in existing concrete products. Only the carbonation depth can be measured, and one is obliged to use calculation models to determine the CO_2 uptake. However, by taking samples from the structures, CO_2 uptake can be determined in laboratory. A variety of factors also affect both the total uptake and the carbonation rate. For Tier 1 and Tier 2 in Chapters 5.2 and 5.3, simplified calculation methods have been developed to make approximate calculations of the CO_2 uptake. In order to make more accurate calculations of CO_2 uptake, more advanced computer models are needed that take into account and include many of the different factors that affect the CO_2 uptake. The uptake takes place especially in the concrete surfaces on the existing concrete products in society and it is therefore important to have a good knowledge of these surfaces. This allows calculation models to be based on historical data for cement and concrete use in each country, supplemented by estimates of uptake surface areas and their characteristics and conditions.

Research on carbonation of concrete has been going on for a long time and much background information for complex computer models are already available. As already stated in previous chapters, several countries have already developed complex computer models to make accurate calculations of CO_2 uptake in each country. In Tier 3 of this chapter, we want to open up the possibility for different countries to use complex national calculation models. Unlike the calculations in Tier 1 and Tier 2, where the designated calculation resources in each country are expected to be able to perform the calculations independently, the complex computer models require collaboration with various cement and concrete researchers. One can also imagine that computer models (software) for CO_2 uptake are developed at an international level, which can then be used in other countries following a national adaptation and with national input data. The complex computer models used may, of course, undergo a normal scientific review, which is a common procedure within the IPCC.

5.4.2 Proposed CO_2 uptake model for Tier 3

For Tier 3, the design of the software (computer model) can be determined by the respective provider. However, the software must maintain high quality and be built on a scientific basis taking into account the experience in the field both nationally and internationally. The software must be objective, neutral, and calculate the CO_2 uptake values as accurately as possible with lowest possible uncertainty. Used methods and software should be transparent so that there is a possibility to conduct a scientific review of the entire system. The software must also be able to calculate the CO_2 uptake for a specific country or region, and it should also be specifically adapted to the respective geographical area. Furthermore, the software should also take into account as many as possible or most of the different aspects that affect the uptake of CO_2 in different concrete structures. Preferably, the software should also be based on the uptake of CO_2 in the actual calculated uptake areas based on historical data of annual amounts of clinker/cement or concrete used. Example of such methodology and models can be found in the peer reviewed articles [2] and [4]. Below is a list of aspects or data for CO_2 uptake in concrete or other cement-containing products that the software should be able to take into account and thus include in the model.

- Annual use of clinker/cement/concrete in the calculation region including historical data from the beginning of the time when cement began to be used. However, uptake data from primary products older than 80 years can normally be neglected as the CO_2 uptake is very slow. The use shall be calculated as (production-export+import) for the region.
- The use of additions such as blast furnace slag, fly ash, silica fume, and limestone including also specific CO_2 uptake values for each material.
- If the use of additions in concrete is substantial and has a significant impact on the CO_2 uptake, the Tier 3 method shall always be used.
- Emissions from the calcination of the materials in the cement kiln and check for the inclusion of emissions from additions for the corresponding year in the originating processes for the additions.
- Corresponding uptake areas for CO_2 in concrete structures or other cement-containing products, e.g. from the distribution in primary use for different concrete products and its area/volume ratio.
- Concrete surface environment when used in various products (porosity (w/c), temperature, indoors, outdoors, moisture, exposed to rain, underground, underwater, or surface treatment such as paint, wallpaper, asphalt/bitumen, etc.).
- Rate of carbonation including the square root of time dependence except for covered surface where a polynomial is more accurate.

- The sum of the cement content in the produced concrete should always be checked against the cement production.
- End-of-life processes for concrete or other uptake products during the calculation period including historical data. This shall include amount of concrete for demolition, type of handling (e.g. crushing, storing). How crushing into smaller fragments will increase the uptake surfaces and thereby the carbonation rate. Calculation of CO_2 uptake in the end-of-life process.
- Production of secondary products. Amount of concrete to secondary use products and its yearly CO_2 uptake, also for historical data.
- Landfill and use of remaining amounts and its CO_2 uptake. The CO_2 uptake in all end-of-life material must be included.

6 Discussion and conclusions

Climate aspects are now regarded as one of the most important environmental issues both globally and nationally. Yearly statistics on emissions of greenhouse gases (e.g. CO_2, CH_4 and N_2O) have been collected in many countries during many years and the emissions have then been compiled at a global level. Emissions of greenhouse gases have an impact on a global level. Thus, where an emission occurs is therefore of secondary importance. From the outset there was a clear focus on CO_2 from fossil fuel combustion. These emissions remain a very important contributing factor to the greenhouse effect, but recent research has shown that the cause of the greenhouse effect is considerably more complex, and several sources can contribute to the greenhouse effect. For example, CO_2 from combustion of biogenic fuels is not considered to contribute to the greenhouse effect when the growing biomass is considered to take up a corresponding amount of CO_2, but this is only applicable if a replanting occurs. In the case of e.g. deforestation, in which no biomass regrowth occurs, CO_2 emissions from combustion of such biomass can be considered equivalent to CO_2 from fossil fuels, at least as long as the deforestation exists.

The insight into the complexity of climate and climatic effects has resulted in calculation methods for emissions of climate gases that have been developed and broadened so that they now contain several different types of greenhouse gas calculations. This research study includes such a widening of the climate gas calculations by taking into account the uptake of CO_2 in concrete through carbonation. Carbonation is a process that has been known for a long time in the concrete chemistry but now has a new scope for climate gas calculations. Since concrete is not chemically stable, the concrete reacts with CO_2 in air under reformation of carbonates in the concrete. The carbonated concrete phases are chemically stable so there is no risk that the CO_2 that has been taken up will return to the atmosphere. This can only happen if the concrete is heated to a temperature where calcination can occur, i.e. about > 850 °C.

Greenhouse gas calculations made within the framework of the IPCC and UNFCCC are usually different types of emission calculations. Emissions are often relatively easy to calculate, and control measurements can usually be made, even though the amount of measurements that would have to be made can complicate the practical implementation. Simple linear calculations can often be used, using different emission factors. As regards the uptake of CO_2 through carbonation, the results of the present study show significant difficulties. Calculation of a country's annual uptake of carbon dioxide by carbonation of concrete is done by estimating the uptake in concrete surfaces on the concrete products in the country. The uptake in a concrete surface cannot be directly measured on site but must be calculated based on laboratory and field measurements from previous research. In addition, the uptake is influenced by various factors such as weather (rain and moisture), surface coatings, surfaces under water and soil, and the quality of concrete. This increases the difficulty of developing simplified but necessary methods. In this study, an attempt has been made to develop such calculation methods (Tier 1 and Tier 2). However, experience from previous estimates in the field of research shows that more advanced calculation methods are to be preferred for this type of calculations. This study opens up such calculations in Tier 3. In order for such calculations to be implemented in most countries with high quality while being cost effective, common global computer models should be developed. These models can then be used for national calculations after a local adaptation to national inputs.

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Appendix 1 – Characterization of existing CO_2 uptake models

The project has developed an overview of the various national and international models available to calculate the uptake of CO_2 in concrete. These models usually represent more advanced and complex uptake models. Table 6 below presents the different models with references and summary information about each model for comparison.

Table 6 Overview and characterization of existing models for calculation of CO_2 uptake and their background.

	Sweden	**EN 16757**	**Norway**	**Netherlands**	**Ireland**	**Switzerland**	**"Global"**	**Switzerland 2**	**Spain**
General Framework									
Published	Andersson R. et al, "Calculating CO_2-Uptake for Existing Concrete Structures during and after Service Life", 2013	Product Category Rules for Concrete and Concrete Elements, 2017	Engelsen and Justnes, "CO_2 binding by Concrete", 2014	Vermeulen E., Balans tussen emissie en opname CO_2, 2017	Fitzpatrick D. et al, "Sequestration of Carbon Dioxide by Concrete Infrastructure: A Preliminary investigation in Ireland", 2015	Nygard and Leemann, "Carbon diioxide uptake of reinforced concrete structures due to carbonation", 2012	Xi et al,"Substantial global uptake by cement carbonation",2016	Leemann, Hunkler, Widmer, "Calculation of CO_2-binding during service life of concrete", 2018	I. Galán et al, "Summary of the Study of the CO_2 Sink Effect of Cement Based Materials" 2009 I. Galan et al, "Sequestration of CO_2 by concrete carbonation" IECA Editors 2009
Number of references	23	23 in Annex BB on Carbonation	82	8	12	73	71	7	44
View	Country/society	Single product in future	Country/society	Country/society	Country/society	Product and country/society (Uptake in the total production during 50 years)	Global/society	Product (country/society)	
Perspective	Annual uptake	(PCR/EPD)	Annual uptake	Annual uptake	Annual uptake		Uptake 1930-2013		Uptake at 50 and 100 year
Base	Clinker consumption, historical 100 years	Clinker content in the product	Present cement consumption, 100 years future uptake	Cement consumption,	Clinker consumption, historical 40 years	Cement (clinker) consumption 2010	Cement consumption, historical 1930-2013, in four regions: China, US, Europe, rest of the world		Cement production
Constituents participating in the uptake	Uptake in clinker	Uptake in clinker	Uptake in CEM I, CEM II/A-V and CEM II/B-S	Uptake in CEM I (clinker) and in slag	Uptake in clinker	Uptake in clinker	Cement without specification. Cement kiln dust.	Uptake in CEM I, CEM II/A and CEM II/B	Clinker and fly ashes, limestone. Pozzolan and slags

	Sweden	EN 16757	Norway	Netherlands	Ireland	Switzerland	"Global"	Switzerland 2	Spain
FA and slag	Not taken into account	Taken into account in calculation of carbonation depth, but not for CO$_2$ uptake	Taken into account	Slag taken into account for both carbonation depth and uptake (0.14 kg CO$_2$/kg slag)	Not taken into account	Not relevant	Only clinker content accounted	Not specified	YES included
Maximum uptake value	(Degree of carb)×(emission at calcination of clinker)	(Degree of carb) ×(emission at calcination of clinker)	(Degree of carb)×(emission at calcination of clinker + 70 % of uptake in CaO of slag)	(Degree of carb)×(emission at calcination of clinker + 0,14 kg CO$_2$/kg of slag)	(Degree of carb)×(emission at calcination of clinker)	(Degree of carb)×(emission at calcination of clinker)	(Degree of carb)×(emission at calcination of clinker)		Degree of carbonation by carbonated cement
Calcination emissions (kg CO$_2$/tonne cement)	CEM I 494 (CEM II 455)	Based on actual clinker content (CaO set to 65 % of clinker)	CEM I 471, CEM II/A-V 396, CEM II/B-S 332	CEM I 490, slag 0	CEM I 479, CEM II/A 428	508 kg/tonne clinker (CEM I 483, CEM II/A 406)	"Process" emissions (calcination) 1930-2013 is 10.4 GtC	CEM I 474, CEM II/A 413, CEM II/B 357	Takes value of other works 550 kg/tonne clinker
Results									
Methods CO$_2$ uptake	300 ktonne/year 2011, (125 kg/tonne cement)		140 ktonne/year 2011 (165 including recovery phase) (70 resp. 83 kg/tonne cement	365 ktonne/year 2015 (90 kg/tonne cement). Uptake in recycling stage 83 ktonne (21 kg/tonne cement) Adjustment 75 ktonne resp. 18 kg/tonne cement)	150 ktonne/year 2011 (estimated from the value 75 kg/tonne cement)	No absolute values presented, only relative.	Global uptake 2013 is 0.24 GtC. Uptake 1930-2013 is 4.5 Gt C.1 billion tons/year 2013 (250 kg/tonne cement)	No absolute values presented, only relative	Several quantities in function of type of concrete and exposure class
Calculated as	Uptake in existing building stock, estimated with the previous 100 years cement consumption		Uptake in the 2011 production of concrete during coming 100 years	Uptake in 2015 production of concrete during coming 60 years.	Uptake in one year production of concrete during coming 100 years	Uptake in one year production of concrete during coming 50 years	Uptake in existing building stock, estimated with the previous years (1930-2013) cement consumption	Uptake in one year production of concrete during coming 100 years	Calculated as % of clinker fabrication INCLUDING THE FUEL (multiply by 1.7 the results for referring to decarbonation only
Corresponding to	17 % of production emissions year 2011		15 % of production emissions (18 % including recovery)	19 % of production (incl. import) emissions (23 % including end of life stage)	16 % of calcination emissions, corresponding to about 10 % of total.	Declared to be 10 % of the total emissions, corresponding to (1/0.63)×10 = 16 % of the calcination emissions.	Uptake 1930-2013 corresponds to 43 % of calcination emissions	17 % of calcination emissions	2.7 % of emitted CO$_2$ by decarbonation
Sensitivity	Macro calculation can be overestimated a single year but not over time						Uncertainty analysis carried out.		Surface/volume ratio was calculated for several elements and the carbonation rates were experimental values

	Sweden	EN 16757	Norway	Netherlands	Ireland	Switzerland	"Global"	Switzerland 2	Spain
Accuracy	Known method and input data based on measurements	Known method and input data based on measurements	Known method and input data based on measurements	Known method and input data based on measurements	Conservative assumptions	Reduction with a factor 1.5 according to later paper by Leemann And Hunkler, "Carbonation of concrete: assessing the CO_2-uptake, 2016.	Known method and input data based on measurements		Conservative assumptions
Carbonation theory									
Carbonation model references	Lagerblad and others. Nilsson	Lagerblad and others	Lagerblad and others. Nilsson (covered conc.)	Lagerblad and others	Silva et al (2014)	Lagerblad and others	Lagerblad and others		Various and own models
Depth of carbonation model	$d = k\,t^{\frac{1}{2}}$ Polynomial expressions for covered concrete. d = f (t2, t, t½)	$d = k\,t^{\frac{1}{2}}$	$d = k\,t^{\frac{1}{2}}$ Polynomial expressions for covered concrete. d = f (t2, t, t½)	$d = k\,t^{\frac{1}{2}}$	Formula for RH less than 70 %, modified by factors 1.0 for internal, 0.5 external sheltered and 0.3 external exposed to rain.	$d = k\,t^{\frac{1}{2}}$	$d = k\,t^{\frac{1}{2}}$		$d = k\,t^{\frac{1}{2}}$
Exposure classes	11	6	6	5	Residential 6, Civil engineering 3, Commercial 7		5		Standard: interior, outdoors sheltered and non-sheltered from rain
Strength classes	4	4	4	7	5	3 (?)	4		2 concretes and paste
Carbonation degree	50-90 %, specified for each exposure	40-85 %, specified for each exposure	70 %	40-85 %, specified for each exposure	Not specified	75 %, changed to 50 % in the paper of Leemann and Hunkler, cf "Accuracy" above.	80 % for concrete 91.5 % for mortar		Main aim of the study
Concrete data									
No. of applications (type of product)	7	Single structures/products	24	5	3	20	Depending on region, most detailed from China		Concrete elements in general
Total no of product exposures (scenarios)	33	Infinite	54	25	14	31	Depending on region, most detailed from China		3
Application surface/volume	Calculated for each application	Actual structure	Calculated for each application	Calculated for each application	Calculated for each application	Calculated for each application	Calculated for each application		Calculated with detail
"special case"	overlapping corner						Mortar and cement kiln dust		No recycling, no secondary use or mortar application
Historical use of concrete in different applications, based on statistic	60 years (100 years with less accuracy)		Not applied (use 2011 provided)	Not applied (no change in consumption during the years is assumed, 2015 is the basis)	40 years	Not applied	Depending on region, US 1997-2005, China 1996-2012, Europe (nordic countries.) 2003.		Yes, several ages were studied

	Sweden	EN 16757	Norway	Netherlands	Ireland	Switzerland	"Global"	Switzerland 2	Spain
End of calculation	See maximum uptake value	See maximum uptake value	See maximum uptake value	See maximum uptake value	See maximum uptake value	50 years, see remark below			50 years for buildings and 100 years for infrastructure
End-of-life and secondary use									
End of life processes	Demolished, crushed, stockpiled and reused as unbound material	Demolished, crushed, and stockpiled. Reuse only as additional information	Demolished, crushed, stockpiled and reused as unbound material	Demolished, crushed, stockpiled, and reused.	Only shortly treated	Demolished, crushed, stockpiled, and reused.	Demolished, crushed, and secondary use. Only small uptake		No recycling or secondary use
Demolished and crushed, % of annual production	8 %		10 %	35 % (5.1 m^3 recycled/14 m^3 produced)		Scenarios of 0, 40, 60 and 100 % recycled			no
% recycled	Existing	National provisions	10 % of annual concrete production	35 %		Scenarios of 0, 40, 60 and 100 % recycled	China 3 %, USA 60 %, Europe 61 %, ROW 25 %		no
Stored to increase uptake	Potential given	Potential given							no
Remark	Uptake during one year (2011) in existing buildings is calculated from 100 years cement statistics and 60 years concrete application statistics		Uptake during one year in existing buildings is supposed to be equal to the uptake during 100 years in one year (2011) concrete production.	Uptake during one year in existing buildings is supposed to be equal to the uptake during 60 years in one year (2015) concrete production. Concrete blocks are responsible for a significant proportion (24 %) of the CO_2 uptake.	Uptake during one year in existing buildings is supposed to be equal to the uptake during 100 years in one year concrete production. Open texture concrete blocks and roof tiles are responsible for a significant proportion of the CO_2 uptake	The uptake figure 16 % of the calcination emissions should according to the later recommendations be reduced by a factor 1.5, that is to 10.7 %. In order to be consistent with the methods in the other countries a 100 years perspective should be applied, resulting in 1.414×10.7=15 %	Uptake during 1930-2013 as well as present (2013). Uptake in mortar is significantly contributing to the large figures	This more recent but short report, present values for typical Swiss concrete house building applications	The low uptake value of 2.7 % is adjusted in a later report to 15 %. [9]

Appendix 2 – Literature overview of carbonation

Uptake of CO_2 in concrete through carbonation is not a new research field. Carbonation has been known for a long time and an extensive research exists in the field. Originally, the research was conducted to understand how carbonation affects the properties of concrete. The formation of carbonates in the concrete makes concrete stronger, but reduces the pH of the concrete, which affects the corrosion properties of the reinforcement bars. Later research on carbonation of concrete has a stronger focus on analyzing the total CO_2 balance for cement and concrete. In Appendix 2, we want to show the research width that exists in the field as a complement and a basis for the model studies that have been carried out in this study.

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